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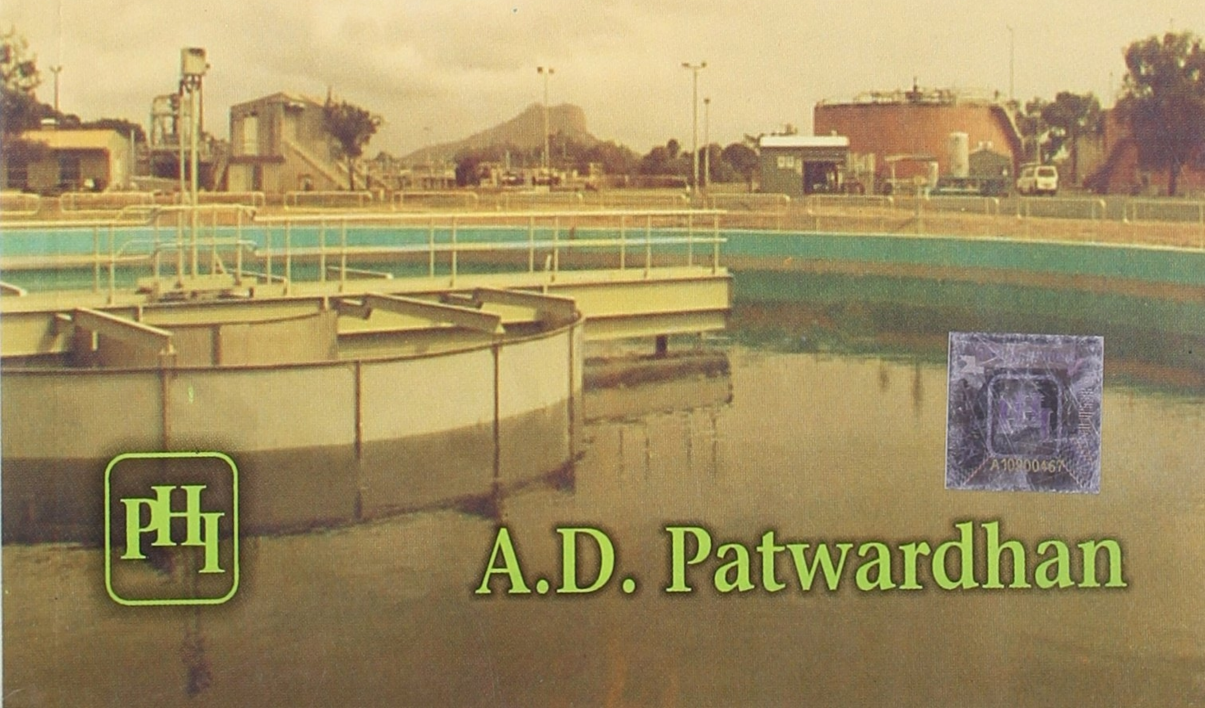
Industrial Waste Water Treatment



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INDUSTRIAL WASTE WATER TREATMENT

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This book is dedicated to
all those
who love the environment

CONTENTS

PREFACE

The idea of writing a book that would contain information about source, volume, quality, treatment, disposal, recycle, reuse and recovery of useful material from industrial waste water came to my mind during my tenure as a teaching faculty at VJTI, Mumbai. This work is designed primarily to meet the needs of undergraduate and postgraduate students of Civil, Chemical Engineering and Environmental Science and Engineering. It also offers information to consultants in Environmental Engineering and others engaged in treating industrial wastes.

Chapters 1–5 deal with the general aspects of industrial wastes, their effect on aquatic environment, unit operations and unit processes used in treating industrial wastes, sampling, analysis, characterization, conducting treatability studies. The text also provides information to enable process designers to arrive at a suitable form of treatment of waste water. Chapters 6–22 discuss the various industrial wastes, describing the manufacturing process involved. Flow diagrams are given that show the points of addition of water, power, heat, chemicals, etc.; points from where solid and liquid effluents originate and methods of treatment, reuse, recycle, and recovery of useful material from the waste water streams.

This book attempts to show the reader that it is technically possible and economically feasible to reduce and, in some cases, eliminate pollution caused by industrial waste water.

I have referred to a number of periodicals, books and conference proceedings while gathering information in this regard; I have acknowledged all of them. I thank my family members who went out of their way for showing great patience and giving encouragement while I was devoting my time in preparation of the manuscript. Special thanks are due to my friend, Professor S.K. Gajendragadkar for his help in locating useful sources of information. I am sincerely grateful to the teaching faculty at VJTI for encouraging me to complete the writing of the manuscript. Finally, my sincere thanks to all those who helped me in the preparation of the manuscript.

I would warmly welcome any constructive suggestion for improving the contents of the book.

A.D. Patwardhan

Chapter 1

TREATMENT OF INDUSTRIAL WASTE WATERS

1.1 WATER POLLUTION

Natural water is seldom chemically pure. When it rains, organic and inorganic suspended particulate matter, gases, vapours, mists, etc. in the air get dissolved in water, through which it reaches the earth's surface. In addition, water carries surface pollutants and contaminants during its flow over the ground. Water, which percolates into the ground, dissolves various salts and becomes rich in total dissolved solids. Thus, it acquires a number of impurities while in its natural state. This necessitates adequate treatment of naturally occurring water before it can be used for domestic, industrial, commercial, agricultural or recreational purposes. The extent of treatment will depend on the end use of the treated water. Use of the treated water even once adds considerably to the amount and variety of pollutants. This necessitates further treatment of the water before it can be reused, although it is not strictly necessary to have water of uniformly high quality for each of the above uses. In view of the limited availability of water for meeting our growing demands, and in the interest of protecting the environment, it is essential to think and act in terms of reducing water consumption, reusing and recycling once-used water, and minimizing the pollutional effects of waste water resulting from a variety of uses.

Domestic and industrial uses of water add a number of contaminants and pollutants to it. Contaminants are capable of causing diseases and rendering water unfit for human consumption, while pollutants are substances which impair the usefulness of water, or render it offensive to the senses of sight, taste and smell. Contamination may accompany pollution [1]. Domestic waste water contains contaminants, while industrial waste water may contain both contaminants and pollutants.

Industries use water for a variety of purposes, such as for manufacturing goods, heating, cooling, as carrier of raw material, as carrier of waste matter (which constitutes industrial waste water), as a solvent, for firefighting, for lawn sprinkling and gardening, and for use in the canteens and toilets. While only a small fraction of the supplied water is present in the end product, or is lost by evaporation, the rest is converted into industrial waste water. Indiscriminate discharge of these waste water streams into the environment can render soils 'sick', pollute the receiving bodies of water and cause air pollution by generating obnoxious gases. Treatment of these waste waters within the factory premises, or preferably their elimination at source, should be the aim of every industry. If total elimination of the waste water streams is not feasible, the least that can be done is to reduce their volume and strength, by taking one or more of the 'in-plant' measures such as reducing fresh water consumption, reusing waste water (either with or without treatment), substituting process chemicals for those which contribute to pollution, changing or modifying the manufacturing process, and following good housekeeping practices. Of course, due care must be taken to see that these steps do not adversely affect the quality of the finished product or damage the manufacturing machinery. In addition, proper disposal of residues arising out of recycling and reuse must be provided for, along with the treatment of the waste water streams, which are not to be recycled or reused.

1.2 CATEGORIES OF POLLUTANTS

Industrial wastes contain a large variety of pollutants which are categorized as follows:

1. **Inorganic pollutants.** These include alkalis, mineral acids, inorganic salts, free chlorine, ammonia, hydrogen sulphide, salts of chromium, nickel, zinc, cadmium, copper, silver, etc., anions such as phosphates, sulphates, chlorides, nitrites and nitrates, cyanides; cations such as calcium, magnesium, sodium, potassium, iron, manganese, mercury, arsenic, etc. [2].
2. **Organic pollutants.** These include high molecular weight compounds such as sugars, oils and fats, proteins, hydrocarbons, phenols, detergents, and organic acids [2]. Some of these pollutants are resistant to biodegradation and/or others are toxic to aquatic life in the receiving water. Their removal, or at least reduction to a low concentration, becomes necessary in order to be able to treat such waste water by biological means.

In addition, industrial wastes may contain *radioactive material*, which need very careful handling, treatment and disposal.

The characteristics of industrial wastes, which are combined with domestic sewage generated within the factory premises, are somewhat different from those of the industrial wastes alone, on account of dilution offered by the sewage. Further, such mixtures are easier to treat biologically because of the presence of microorganisms in the sewage. If the industrial waste is deficient in nutrients such as nitrogen and phosphorus, these elements are supplied to some extent by sewage, leading to economy in the consumption of chemicals, e.g. urea and DAP, which are commonly used for nutrient supplementation. An added benefit in such a case is that a common treatment plant can be designed for treating both, industrial wastes and sewage.

1.3 TREATMENT AND DISPOSAL OF INDUSTRIAL WASTES

The aim of the treatment is to remove pollutants from the waste water and render it fit for safe discharge to the environment. In view of the increasing demand for water, and its decreasing availability, mere 'end-of-pipe' treatment is not the answer to pollution control. Reuse, recycling and where feasible, by-product recovery must become an integral part of the treatment scheme. Experience shows that it is possible to achieve this goal without incurring heavy expenditure. In many cases, the practice of reuse, recycling and by-product recovery has resulted in not only meeting the operating costs, but also offering an attractive payback period to the industry. Some examples of successful reuse and recovery are given in the following chapters.

Methods of treating waste water can be classified as follows:

1. **Physical methods:** These include screening, sedimentation, flotation, filtration, mixing, drying, incineration, freezing, dialysis, osmosis, adsorption, gas transfer, elutriation, etc.
2. **Chemical methods:** These include pH correction, coagulation, softening, ion exchange, oxidation, reduction, disinfection.
3. **Biological methods:** These employ aerobic, facultative and anaerobic microorganisms to destroy organic matter and reduce the oxygen demand of the waste water.
4. **A combination** of the above three methods is also used to treat waste water.

Adequate treatment can also be obtained by selecting one or more of the physical, chemical and biological units and arranging them in a logical sequence, so that the effluent of one unit is suitable as influent to the next unit. Selection and sizing of the proper unit(s) is done by (a) flow measurement, sample collection and characterization of the waste water flows, (b) subjecting the waste water samples to treatability studies by employing laboratory-scale models, which may be run on a batch feed basis, semi-continuous feed basis, or continuous basis, (c) deciding which combination of unit operations and unit processes will be appropriate for the waste water under study, and (d) if necessary, running a pilot plant, which will simulate the working conditions in a full-scale plant. The size of the pilot plant may be chosen such that it can be conveniently incorporated into the full-scale plant. Industries manufacturing a variety of end products can benefit from maintaining a pilot plant, even after the full-scale plant is commissioned, in order to ensure adequate treatment of influents of varying quality. These variations in quality may occur due to change of product, raw materials, or method of production. Pilot plants can play a very important role in the case of industrial estates, in which many different industries are located together and produce waste waters of divergent quality. A common effluent treatment plant (CETP) may be the right technical solution for pollution control in such cases. Pilot plant studies help in arriving at rational design criteria for such estates, choosing the most appropriate treatment train, and avoiding costly modifications to the CETP once it goes on stream.

Disposal of treated wastes is an important step an industry has to follow in order to ensure that the delicate ecological balance of the environment is not disturbed. Disposal may be done in a receiving body of water such as a river, lake, or sea. Disposal on land is also practised, taking care to see that the soil is not adversely affected by the residual pollutants in the effluent. Where underground sewerage is available, the treated effluents may be discharged into municipal sewers, provided they meet the quality standards laid down for this mode of disposal. In addition, the quality of the industrial effluents must be such that: (i) they will not endanger the lives of the drainage maintenance crew, who may be required to enter the sewers for maintenance and repairs, (ii) the material of the sewers will not be damaged, and (iii) the effluent treatment plant, if one is provided at the end of the drainage system, will be capable of taking the hydraulic and organic loads imposed by the industrial effluents. Industries wishing to follow this mode of disposal will almost always be required to give some pretreatment to the waste water, its extent depending on: (i) the volume and strength of the waste water, and (ii) the degree of dilution offered by the sewage flowing in the drainage system.

A result of treating waste water by one or more of the above discussed means is generation of sludges, which may be organic or inorganic in nature. Sludges constitute a peculiar problem on account of their properties such as viscosity, presence of pollutants in a concentrated form, some of which can be toxic and/or hazardous or difficult to dewater and dispose of. This fact needs careful consideration while designing the waste water treatment plant. The treatment is said to be complete when the solid residues, liquid effluents and gaseous emissions are adequately treated and safely disposed of.

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Chapter 2

FLOW MEASUREMENT, CHARACTERIZATION AND TREATABILITY STUDIES OF INDUSTRIAL WASTE WATERS

The design of a waste water treatment plant begins with collecting information about the volume of waste water to be treated, its characteristics, and the degree of treatment required in order to meet specified discharge standards. Knowledge about the mode of manufacture, viz. continuous or batch is also useful. A batch process produces an effluent in the form of a slug which lasts for a short time, while a continuous process generates a waste water stream which flows continuously, although at varying rates. Based on this information, one can decide if a grab sample of the waste water would be representative of its quality, or a composite sample would be necessary. Information about the raw materials, chemicals and other ingredients used in the manufacturing process helps one to decide the physical and chemical tests to be conducted on the representative samples for characterizing the effluent. Correct interpretation of the results of the analysis of the waste water samples enables one to choose a proper treatment process.

2.1 MEASUREMENT OF FLOW

The measurement of waste water flow can be done either on the outfall channel or pipe carrying the entire waste water flow from the industry, or on the individual waste streams within the industry. The first method is useful in knowing the total flow, but cannot distinguish between the contributions of individual streams. It is useful in the case of industries that discharge a more or less uniform quality of waste water and are not likely to contain toxic pollutants, or valuable ingredients, which can be profitably recovered. Measurement of flow from individual streams helps in deciding whether some streams can be segregated, either for giving pretreatment, for recovery of by-products, or for recycling with or without treatment. Such streams, after pretreatment or recovery of by-products, can be mixed with the other effluent streams for further treatment. Measurement of flow rates should be invariably accompanied by collection of waste water samples, either as grab samples or as composite samples.

Flow measurement can be done either by measuring the cross-sectional area of the raw waste water channel and multiplying it by the velocity of flow, or by measuring the time required to fill a tank or drum of known volumetric capacity. Readings taken on a calibrated v-notch, a rectangular notch or weir built in the conveying channel can give a fairly accurate estimate of the flow rate.

2.2 COLLECTION, PRESERVATION AND CHARACTERIZATION OF SAMPLES

2.2.1 Collection of Samples

Sampling can be done as a grab sample, i.e. a sample which represents the instantaneous quality of the waste stream. Where it is known that the waste water flow rate is continuous but of varying quality, composite sampling is done. This consists of either collecting a fixed volume of sample at equal time intervals, or varying the volume of sample in proportion to the flow rate at the time of collection. In either case, the individual samples are mixed together to give one representative sample. The method of flow-proportionate sampling gives a more realistic sample than the 'fixed volume-fixed time interval' sample. The volume of sample collected should be enough to permit all physical and chemical tests to be carried out on it. The sampling period may range from 8 hours to 24 hours or even longer. Items of information, which should accompany the samples, include location of sampling point, time, day and date of sample collection, nature of sample (grab or composite), duration of sample collection (if a composite sample) and any other relevant information, which will help in the analysis.

2.2.2 Preservation of Samples

Samples collected in the field should be conveyed to the laboratory in the shortest possible time, to avoid deterioration in their quality. It is common practice to collect samples in a container surrounded by ice, so that low temperature (about 4°C) is maintained and the samples retain their original quality. Tests such as pH, temperature, colour, odour, etc. are best performed at site immediately after the samples are collected and the observations noted down. If immediate analysis of the samples is not possible, suitable preservatives should be added to them. *Chemical preservatives are to be added only when they are shown not to interfere with the examinations being made. When used, they should be added to the sample bottles initially, so that all portions of the sample are preserved as soon as they are collected* [1].

A list of preservatives, which may be used to maintain the quality of samples is given in Table 2.1.

Table 2.1 Preservatives for Waste Water Samples [2]

Parameter	Preservative	Maximum holding period
Acidity-Alkalinity	Preserve at 4°C	24 hours
Biochemical Oxygen Demand (BOD)	Preserve at 4°C	6 hours
Calcium	None required	
Chemical Oxygen Demand (COD)	2 ml/l H_2SO_4	7 days
Chloride	None required	
Colour	Preserve at 4°C	24 hours
Cyanide	NaOH to pH 10.0	24 hours
Dissolved oxygen	Determine at site	Non-holding
Fluoride	None required	
Hardness	None required	
Metals, total	5 ml/l HNO_3	6 months
Metals, dissolved	Filtrate, 3 ml/l 1:1 HNO_3	6 months
Ammonia nitrogen	40 mg/l $HgCl_2$, preserve at 4°C	7 days
Kjeldahl nitrogen	40 mg/l $HgCl_2$, preserve at 4°C	Unstable
Nitrate-nitrite nitrogen	40 mg/l $HgCl_2$, preserve at 4°C	7 days
Oil and grease	2 ml/l H_2SO_4, preserve at 4°C	24 hours
Organic carbon	2 ml/l H_2SO_4 (pH 2.0)	7 days
pH	None available	
Phenolics	1.0 g $CuSO_4$ + H_3PO_4 to pH 4.0, preserve at 4°C	24 hours
Phosphorus	40 mg/l $HgCl_2$, preserve at 4°C	7 days
Solids	None available	
Specific conductance	None required	
Sulphate	Preserve at 4°C	7 days
Sulphide	2 ml/l Na acetate	7 days
Threshold odour	Preserve at 4°C	24 hours
Turbidity	None available	

Although the table suggests a number of preservatives, the most effective preservative is maintenance of low temperature (4°C or lower).

Further, the samples should be analysed as soon as possible after collection.

2.2.3 Characterization of Samples

Characterization of the samples is the next step. The samples are analysed using physical and chemical methods. **Physical methods** include determination of temperature, colour, odour, total solids, suspended solids, settleable solids, dissolved solids, volatile solids, oil and grease. **Chemical methods** include determination of pH; acidity; alkalinity; biochemical oxygen demand (BOD); chemical oxygen demand (COD); total organic carbon (TOC); cations such as aluminium, arsenic, boron, cadmium, chlorine, chromium, copper, iron, lead, manganese, nickel, zinc; anions such as chlorides, ammoniacal nitrogen, nitrite nitrogen, nitrate nitrogen, phosphates, sulphates, sulphides, etc. In addition to these tests, the samples may have to be tested for cyanides, phenols, detergents, cellulose, hemicellulose, tannin, lignin, etc.—tests that are specific to certain industrial waste waters.

Procedures to be followed in conducting the analyses of samples should be those specified in the Standard Methods for Analysis of Water and Waste Water. It may be necessary at times to modify the analytical procedure for a certain constituent for which a standard method is not available. In such a case, the results of analysis should be presented with special mention of these modifications. The modified procedure should be subjected to a 'recovery' test, consisting of adding a known amount of the specific pollutant to the waste water sample, determining its concentration by the modified procedure and comparing the results of analysis with the original sample.

Results of analysis of the physical and chemical tests are then interpreted so that a preliminary idea of the treatment to be given to the waste water can be had. At the same time, the quality requirements of the treated effluent, as laid down by the pollution control authorities, are studied to enable the designer to narrow down the choice of unit operations and unit processes, and to decide the degree of treatment in order to meet the effluent quality standards.

Based on the results of analysis of the raw waste water samples and the quality requirements of the treated effluent, laboratory-scale experiments are then conducted. The samples are subjected to various unit operations and unit processes to find out the suitability of each for treating the waste water. Parameters such as detention time, food to microorganism ratio, surface loading, volume of sludge to be expected, its settleability, types of chemicals required and their quantities are determined, but laboratory-scale studies do not establish achieveable effluent quality or the suitability of mechanical equipment to be used in the full-scale plant.

In addition to the laboratory-scale studies, it may be necessary to run pilot plant studies, in which the actual conditions in the full-scale plant can be simulated. Pilot plants are designed to offer a certain degree of flexibility and enable collection of data which will be used in finalizing the design, the degree of automation, if any is required, the material of construction and, hence, the capital and running costs of the full-scale plant.

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Chapter 3

UNIT OPERATIONS AND UNIT PROCESSES

3.1 INTRODUCTION

The various methods used in treating industrial waste water are identical to those used in treating domestic sewage. However, the differences between the two modes of treatment arise because of (a) a very high degree of variability in the quality of industrial wastes compared to domestic sewage, (b) large variations in the flow rates of industrial wastes, and (c) the presence of hazardous and/or toxic pollutants in some industrial wastes. In terms of population equivalent, industrial waste water is usually a few times stronger than an equal volume of domestic sewage. In view of the possible presence of hazardous and/or toxic pollutants, it becomes necessary to provide adequate preliminary treatment to an industrial waste water before subjecting it to further treatment. This is achieved by employing various unit operations and unit processes.

- **Unit operations** are those in which physical forces are employed to purify waste water. Some of the important unit operations are screening, sedimentation, flotation, filtration, mixing, equalization, flow proportioning, drying, incineration, freezing, foaming, dialysis, osmosis, adsorption, gas transfer, elutriation, etc.
- **Unit processes** are those in which chemical and/or biological forces are used to purify waste water, e.g. pH correction, coagulation, oxidation, reduction, disinfection, aerobic and anaerobic biological treatment.

It is rarely adequate to apply only unit operations or only unit processes to an industrial waste water to obtain an effluent fit for discharge to the environment. Therefore, based on laboratory-scale studies and/or pilot plant studies, a proper choice of unit operations and unit processes is made, and this is arranged in a logical sequence to give an acceptable treatment scheme.

A brief description of the various unit operations and processes, and their application in industrial waste treatment is given below.

3.2 UNIT OPERATIONS

3.2.1 Screening

Screening is done to remove large suspended and floating solids from waste water in order to protect pumps, pipes and valves from clogging and damage, e.g. rags and pieces of cloth from cotton textile wastes, fine fibres from woollen mills, spent tan bark from vegetable tanning process, leather trimmings from the leather processing houses, bark from the debarking machines in the pulp and paper mills, fruit peelings and fruit rinds from fruit canning and packing industry, and, generally, in industries where good housekeeping practices are not followed. Microscreening may also be used for complete removal of suspended impurities so as to eliminate primary sedimentation.

Screens may be coarse, medium or fine, depending on the clear space between bars. Fine screens may be rotary drum type, tangential type, or vibratory type. Screens are manually or mechanically cleaned. In any case, adequate arrangement must be made to treat and dispose of the screened material.

3.2.2 Sedimentation and Flotation

Removal of finely suspended and settleable solids is done by plain sedimentation, while chemically aided sedimentation is required for removal of colloidal solids. Flotation, which may be termed ‘negative sedimentation’, is done to remove impurities, which are lighter than water and do not settle in a reasonable length of time. Like coagulants in sedimentation, flotation may be done with or without, the aid of flotation agents. Industries employing sedimentation include almost all those producing high suspended organic and inorganic solids, while flotation is particularly useful in woollen mills, slaughter houses, pulp and paper mills, oil refineries and dairies. Both sedimentation and flotation help reduce the solids load on the following treatment units. However, flotation is also used for the recovery of useful material from the waste water streams.

3.2.3 Filtration

Filtration of industrial waste water is more often practised downstream of other pretreatment processes than as a stand-alone pretreatment method. It is used during neutralization/precipitation of heavy metals and biological treatment to reduce BOD loads. It may also be used to remove lime precipitates of phosphates and as a pretreatment for waste water before it is discharged to an activated carbon column or to a dialysis or reverse osmosis unit. In reuse applications, filtration is used if the treated waste water is to be spread on land for irrigation, groundwater injection, lawn sprinkling and body-contact recreational uses [1, 2].

3.2.4 Mixing

Mixing is an important unit operation in waste water treatment. It is used for mixing of one substance with another, e.g. chlorine or sodium hypochlorite with treated waste water, liquid suspensions such as in the aeration tank of activated sludge process or sludge undergoing aerobic or anaerobic digestion; for flocculation of finely divided suspended solids with coagulants; for heat transfer as in heated digesters; and for mixing neutralizing chemicals with acidic or alkaline waste streams. Continuous, rapid mixing is achieved by providing baffles or hydraulic jumps in open channels, by fixing static mixers or venturi flumes in pipelines. Continuous mixing is achieved by pumping the tank contents and recycling a part of the pumped liquid, by using mechanical mixers, or with the help of compressed air bubbled into the liquid. Compressed air and mechanical mixers also serve the purpose of maintaining the tank contents in a fresh condition. If the waste water contains oily and greasy matter, compressed air helps float a part of this matter, which can be skimmed off. Mixing helps in giving partial treatment to waste water streams of opposite nature, e.g. mutual neutralization of acidic and alkaline effluents or partial cooling of hot streams when mixed with cold streams. Waste water streams, which are highly fluctuating in their quality and flow rates, are best handled by mixing them in equalization tanks.

3.2.5 Equalization

Equalization is used to overcome the operational problems caused by variations in quality and flow rates, to improve the performance of downstream processes, and to reduce the size and cost of downstream units of treatment. Equalization helps dilute toxic pollutants. It is also an attractive proposition for upgrading the performance of an overloaded treatment plant [2].

Equalization can be done ‘in-line’ or ‘off-line’. The former is done when equalization of plant loading is desired, while the latter is used when the downstream treatment units, especially biological units, are to be protected against shock loads due to slugs of toxic and/or organic pollutants.

The required volume of an equalization basin is determined by constructing mass flow diagram to represent the inflow and superimposing on it the rate of outflow (which would be by pumping). Two parallel lines, representing the rate of outflow, are drawn tangent to the high and low points of the mass diagram. The vertical distance between the two tangent lines represents the required volume of the equalization basin [1].

An essential requirement of an equalization basin is adequate mixing of the basin contents. This ensures a more or less uniform quality of the outflow, minimizes chances of deposition of solids in the basin and helps keep the waste water fresh.

3.2.6 Flow Proportioning

Flow proportioning is not, strictly speaking, a unit operation, but can be used in conjunction with equalization. It consists of storing a waste water stream in a tank of suitable size and discharging it into the other streams (either domestic sewage or industrial wastes), in proportion to the flow in the receiving waste water stream, so that the mixture does not exert an unduly high organic, hydraulic, toxic load on the receiving body of water or the waste water treatment plant. This method is useful in dealing with toxic wastes, or wastes having a high oxygen demand.

3.2.7 Drying and Incineration

Drying and incineration are almost exclusively used for handling waste water sludges generated during the various treatment processes. Drying is done to get rid of a large fraction of the moisture entrained with the sludge solids and to reduce its volume. This is done by spreading the sludge in a layer ranging in thickness from 20 cm to 30 cm on sand drying beds. A part of the moisture evaporates and the rest percolates through the sand and gravel layers of the drying beds. This filtrate is recycled to the plant inlet. Sludge so dried can be removed from the beds when its moisture contents are reduced to between 50% and 55%. If the space for constructing the beds is inadequate, mechanical means such as vacuum filtration, centrifugation, plate and frame presses, or belt filters are employed.

Incineration of the dried sludge is practised when the sludge contains toxic matter in concentrations which would have an adverse effect on the receiving medium such as soil. It reduces biological sludge into harmless end products such as water vapour and carbon dioxide. Incineration is preceded by heat drying so that the sludge can be burned effectively and economically. Heat drying is necessary when the sludge is to be converted into soil conditioner. Drying permits grinding of the sludge, reduction in its weight and prevention of continued biological activity. The moisture is reduced to 10% or less. Heat drying is achieved by using flash dryers, spray dryers, rotary dryers, multiple hearth dryers, or multiple effect evaporators [2]. Care must be taken to ensure that incineration does not give rise to problems of air pollution.

3.2.8 Freezing

When impure water (such as an industrial effluent) is frozen, the ice crystals formed are essentially pure water. Three steps are involved in the freezing process. First, heat is removed from the water to cool it to its freezing point. Additional heat is then removed by the vaporization of a refrigerant such as butane in direct contact with the cooled water. This causes fine crystals of ice to freeze out of the solution. When roughly half the water is frozen to ice, the ice-water slurry is transferred to another tank where the unfrozen liquid is drained off and the crystals are washed with pure water. The washed ice is transferred to another tank, where it is melted to form a pure end product [3].

3.2.9 Foaming

Foam separation is particularly useful for waste water containing foaming agents such as detergents and other surface-active pollutants. The process takes advantage of the tendency of surface-active pollutants to collect at a gas-liquid interface. A large interface is created by passing air (or gas) bubbles through the liquid. The foam becomes enriched in the pollutant and the liquid is depleted of the pollutant. The foam is subsequently collected and collapsed to produce a solute-rich liquid product [3].

3.2.10 Dialysis and Osmosis

When an electric potential is impressed across a cell containing mineralized water, cations migrate to the negative electrode and anions migrate to the positive electrode. If cation- and anion-permeable membranes are placed alternately between the electrodes, ions will concentrate in alternate compartments and become dilute in the intervening compartments. If the apparatus is arranged so that the concentrated and dilute streams flow continuously, large-scale demineralization of water can be done. Only partial demineralization is possible by this method. As the phenomenon is specific to ions, application of the process is limited to the removal of soluble ionized contaminants [3].

When solutions of two different concentrations are separated by a semi-permeable membrane, water tends to pass through the membrane from the more dilute side to the more concentrated side and produces concentration equilibrium on both the sides of the membrane. The driving force that impels this flow is related to the osmotic pressure of the system. If the pressure on the more concentrated side is deliberately increased, the flow of water through the membrane reverses, i.e. water moves from the more concentrated compartment to the less concentrated compartment. This is reverse osmosis [3]. This process can be used for the recovery of caustic soda from the spent caustic resulting from mercerizing of cloth in the cotton textile industry.

3.2.11 Adsorption

Organic contaminants in waste water, which are resistant to biodegradation and are present in dissolved state, are suitably removed by the process of adsorption. This is a surface phenomenon. It involves collection of the contaminants on a suitable interface, which can be a liquid and a gas, a solid, or another liquid. This process is used as a polishing step for improving the quality of an effluent, which has already received treatment for removal of a bulk of the contaminants. Adsorption occurs in the activated sludge process, when the dissolved and colloidal organic matter, which acts as a substrate for microorganisms, concentrates at the biomass-water interface. In the treatment of dye-bearing textile wastes, powdered activated carbon is used to adsorb the difficult-to-degrade dye molecules on the carbon along with the microorganisms. The return sludge, which contains both the carbon and the adsorbed contaminants, is aerated in a separate tank. The microorganisms in the sludge consume the dye molecules, get desorbed in the process and are returned to the aeration tank [4].

3.2.12 Gas Transfer

Gas transfer is a process by which gas is transferred from one phase to another, usually from gaseous to liquid phase. The functioning of aerobic processes such as the activated sludge process, trickling filtration, aerobic digestion of sludge depends on the availability of sufficient oxygen. Chlorine, used as a disinfectant, must be transferred from gaseous phase to liquid phase. Postaeration of treated effluents depends on gas transfer. One process for nitrogen removal consists of converting the nitrogen to ammonia and transferring the ammonia gas from water to air [2]. Industrial wastes containing volatile solvents can be conveniently treated by aeration to strip off a large fraction of the solvents, which may be recovered, thereby helping to reduce the COD of the waste water to some extent and permitting the reuse of the solvents.

3.2.13 Elutriation

Elutriation is a unit operation in which a solid, or a solid-liquid mixture is intimately mixed with a liquid for the purpose of transferring certain components to the liquid, e.g. chemical conditioning of anaerobically digested sludge before mechanical dewatering can be done by washing the digested sludge with water containing low alkalinity. Such a sludge contains a high concentration of alkalinity, which consumes a lot of conditioning chemicals. Elutriation transfers the alkalinity from the digested sludge to the wash water. The wash water is returned to the waste treatment plant. Elutriation can be done as a single stage, multistage, or countercurrent process. It is seldom used today because the finely divided solids washed out of the sludge may not be fully captured in the main waste water treatment facility [2, 5].

3.3 UNIT PROCESSES

3.3.1 pH Correction

pH correction is an almost universally used unit process required to render a waste water stream fit for further treatment in which pH value plays a vital role, e.g. ammonia removal, biological treatment, nitrification and denitrification, disinfection with chlorine, phosphorus removal and coagulation. Chemicals commonly used are sulphuric acid, hydrochloric acid, nitric acid, phosphoric acid, lime, sodium hydroxide, sodium carbonate, sodium bicarbonate, ammonium hydroxide, etc. This step in treatment requires adequate mixing between the waste stream and neutralizing chemical. As an equalization tank is provided with mixing arrangement, pH correction can be conveniently combined with equalization. Care should be taken to check whether pH correction results in increasing the suspended solids in the waste water, because some solids, which are in solution at low pH may precipitate out due to increase in pH. It is advisable to conduct laboratory-scale studies in order to choose the right type of neutralizing chemical and its optimum dose, as this has a direct bearing on the operating cost of treatment.

3.3.2 Coagulation

Coagulation is used to aid the removal of suspended solids from waste water by sedimentation. Chemicals commonly used for this purpose include alum, ferric chloride, ferrous sulphate, ferric sulphate, lime, etc. Sedimentation following coagulation results in an increase in the volume of sludge to be handled. Organic polymers are sometimes used as coagulant aids. Sludge resulting from chemical coagulation may be difficult to dewater, or difficult to biodegrade. Therefore, laboratory-scale trials should be made to select the appropriate coagulant and to provide for handling, treatment and disposal of the sludge generated by coagulation.

3.3.3 Oxidation and Reduction

Oxidation-reduction is occasionally used to remove pollutants from industrial wastes, e.g. reduction of hexavalent chromium to its trivalent form before its removal by precipitation, ozone oxidation to remove dissolved organics and cyanide during pretreatment. Alkaline chlorination is preferred to ozone treatment for destruction of cyanides [1]. Oxidation with chlorine is used for BOD reduction, odour control, as an aid to grease removal, reduction of sludge bulking in the activated sludge process, eliminating ponding and fly nuisance in trickling filtration and wet scrubbing of gas from anaerobic digestion. Chlorine is also useful in minimizing biological aftergrowths in pipelines and conduits conveying treated effluents over long distances. If a biologically treated sewage or industrial waste is to be subjected to tertiary treatment with a view to recycle it, chlorine plays a vital role in keeping down biological growths in the tertiary treatment units as well as in the recycle system.

Chlorine has been successfully used in the treatment of cyanide-bearing wastes, textile wastes, phenol-bearing wastes, oil refinery wastes, paper mill wastes, food processing wastes and tannery wastes. In these applications, chlorine acts in one or more of the following ways: (i) as an oxidizing agent, (ii) as a bleaching agent, or (iii) as a disinfectant, depending on the nature of the pollutants present in the waste water [6]. As industrial wastes are highly variable in their quality, it is necessary to determine the proper dose of oxidizing agents by conducting laboratory-scale studies.

3.3.4 Aerobic and Anaerobic Processes

Aerobic and anaerobic processes aim at converting non-settleable organic matter into settleable organic matter and to stabilize it. Purification of waste water containing biodegradable organic matter is economically done with the help of microorganisms, which may be inherently present in the waste water, or may be introduced to it in the form of domestic sewage, or in certain cases, as pure cultures of organisms for destruction of specific pollutants. Provision of proper environmental conditions to the microorganisms, such as adequate balanced food, availability of dissolved oxygen (for aerobic systems), total absence of molecular oxygen (for anaerobic systems), absence of pollutants toxic to microorganisms, correct pH value, proper temperature of waste water (depending on whether the organisms are mesophilic or thermophilic in nature), sufficient time for microorganisms to grow and complete the biochemical reactions (which result in destroying a large part of the pollutants) and the presence of inorganic cations and anions in concentrations below the toxic limits for the organisms, results in producing a satisfactory effluent.

It is apparent that almost all industrial wastes need some form of pretreatment before they can be subjected to biological treatment. This may take the form of one or more of the above-mentioned unit operations and/or unit processes, which are aimed at creating environmental conditions fit for microorganisms to work in.

Microorganisms require carbon, nitrogen, phosphorus and other elements in proper amounts, so that their metabolic activities are not hindered, e.g. the C:N:P ratio should be in the range 100:5:1–100:20:1 for aerobic treatment. Anaerobic organisms being inherently slow acting, require much less nitrogen and phosphorus compared with aerobic organisms. Inorganic ions required by most organisms, which act as micronutrients, are given in Table 3.1.

Table 3.1 Inorganic Ions Necessary for Most Organisms [2]

Substantial quantities	Trace quantities
Sodium (except for plants)	Iron
Potassium	Copper
Calcium	Manganese
Phosphate	Boron (required by plants and certain protists*)
Chloride	Molybdenum (required by plants, certain protists* and animals)
Bicarbonate	Vanadium (required by certain protists*and animals)
	Cobalt (required by certain plants, animals and protists*)
	Iodine (required by certain animals)
	Selenium (required by certain animals)

*Protists include algae, protozoa and fungi.

Dissolved oxygen is essential for truly aerobic organisms to survive. Its desirable concentration ranges between 1–2 mg/l in the activated sludge process, trickling filter process and aerated lagoons. It is maintained by mechanical or pneumatic aeration in activated sludge process and aerated lagoons. Adequate ventilation and limiting the depth of media to about 2 metres in trickling filters using stone media, along with uniform distribution of the waste water over the media, ensures proper aerobic conditions. The depth of the filter can be considerably increased with the use of plastic media, which have large voids (90% to 95%) compared with stone media (40% to 45%) and permit adequate ventilation in spite of great depths (up to 12 metres, against 2 metres for stone media). Oxygen is supplied in large quantities during daytime by the algal activity in waste stabilization ponds. Some organisms use oxygen available from nitrates in waste waters. These are anoxic organisms and are useful in the process of denitrification. Anaerobic organisms cannot tolerate even a small concentration of oxygen. Great care must, therefore, be taken when they are employed in treatment, to see that molecular oxygen has no access to the anaerobic biomass.

Toxic and inhibitory concentrations of organic and inorganic pollutants are frequently observed in industrial wastes. These can either slow down the biological process of treatment or stop it altogether if present in large concentrations. Microorganisms adapt themselves to the presence of these pollutants to some extent. A list of some of these substances, along with their threshold concentrations, is given in Table 3.2 and in Table 3.3 the list of common inhibitors of anaerobic digestion is given.

Table 3.2 Threshold Values for Aerobic Biological Treatment [7, 8]

Item	Threshold for biological treatment
pH value	6.5–8.5
Sulphides	200 mg/l
Phenols	500 mg/l (after adequate acclimatization)
Chloroform extractables (oil and grease)	50 mg/l
Hexavalent chromium	2 mg/l
Maleic acid	400 mg/l
Oxalic acid	200 mg/l
Acrylonitrile	400 mg/l
Benzoic acid	500 mg/l
Lead as Pb	1 mg/l
Nickel as nickel chloride	15 mg/l
Zinc	10 mg/l
Chlorides	8000–15,000 mg/l
Ammonia	1,600 mg/l
Dissolved salts	16,000 mg/l

Table 3.3 Some Common Inhibitors of Anaerobic Digestion [9]

Substance	Toxic threshold
Anionic detergents	900
Methylene chloride (CH_2Cl_2)	100
Chloroform ($CHCl_3$)	0.5–1.0
Carbon tetrachloride (CCl_4)	2.0–10.0
1,1,1,trichloroethane	2.25
1,1,2-trichloro-1,2,2,trifluoroethane	About 10
Monochlorobenzene	900
Orthodichlorobenzene	900
Paradichlorobenzene	1300[a]
Pentachlorophenol	1 to 2.
Cyanide	3–30[b]
Zinc	590[c]
Nickel	530[c]
Lead	1800[c]
Cadmium	1000[c]
Copper	850[c]

Note: Concentrations in mg/l for a digester fed with raw sludge with 4.5% dry solids.

[a] Concentration in sewage entering works.

[b] Initially very toxic, but bacteria acclimatize with time.

[c] Toxicity can be controlled by precipitation as non-toxic sulphide salts.

It should be noted that in waste water treatment, one rarely comes across situations where only pure cultures of microorganisms can be used to treat the waste water. This is mainly because waste water contains a large variety of organic and inorganic pollutants, which microorganisms can use as substrates. As a result, biological treatment takes place in the presence of a variety of microorganisms, all acting on specific substrates either simultaneously or sequentially. This condition can lead to either stimulation or inhibition of reactions, e.g. Table 3.4 shows the stimulatory and inhibitory concentrations of alkali and alkaline earth cations on anaerobic digestion.

Table 3.4 Stimulatory and Inhibitory Concentrations [10]

Cation	Stimulatory	Moderately inhibitory	Strongly inhibitory
Sodium	100–200	3500–5500	8000
Potassium	200–400	2500–4500	12,000
Calcium	100–200	2500–4500	8000
Magnesium	75–100	1000–1500	3000

Note:

(a) Concentrations in mg/l.

(b) Sodium and potassium—best antagonists, effective when present in stimulatory concentrations.

(c) Calcium and magnesium—Poor antagonists, add to toxicity. They become stimulatory if another antagonist is already present, i.e. 7000 mg/l of sodium and 300 mg/l of potassium decrease retardation by 80%. Add 150 mg/l of calcium and eliminate inhibition. Calcium is ineffective in the absence of potassium.

It may be mentioned here that while designing an industrial waste water treatment plant using biological process, the population of microorganisms being dealt with is a mixed culture. They act on different constituents of the waste water at different rates depending on a number of factors such as environmental conditions, presence of inhibitory or toxic substances, nature of the pollutants and their degradability, stage of growth of the organisms, their doubling time, etc. The slowest rate of degradation determines the overall rate of treatment. Adequate hydraulic retention time must, therefore, be provided in the biological reactor to ensure that 'washout' of organisms does not take place. This precaution is necessary especially at the time of startup and commissioning of the plant. The time given to the microorganisms at this stage also helps them acclimatize to the presence of various constituents of the waste water and produce a satisfactory quality of treated effluent.

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Chapter 4

STREAM POLLUTION AND SELF-PURIFICATION

The effect of discharge of waste water into natural water bodies should be considered from the following two interrelated standpoints:

- The effect of waste water on the water environment.
- The effect of the receiving water on the waste water.

The first effect considered is pollutional effect while the second effect is self-purification. These two factors are discussed in the following sections.

4.1 EFFECT ON THE WATER ENVIRONMENT

The effect of waste water on the water environment may be physical, chemical and biological.

Physical effect includes increase in turbidity and suspended solids, addition of colour, taste- and odour-producing substances, and formation of sludge banks on the beds and sides of the water bodies. Industrial wastes such as cooling waters from power stations, dyeing and printing wastes from textile industry, spent wash from alcohol distilleries, etc. raise the temperature of water in the receiving body and reduce the dissolved oxygen content in it. These conditions impart an aesthetically unacceptable appearance to the water, create an environment unsuitable for aquatic creatures such as fish, render it difficult to treat, and initiate the chain of chemical and biological effects.

Chemical effects include a drastic change in the pH value of the receiving water due to a discharge of acidic wastes such as mine drainages or alkaline wastes such as textile wastes. High chlorides render the water unacceptable as a source of drinking water, high sulphates, under favourable circumstances tend to form hydrogen sulphide and produce malodorous condition; nitrates and phosphates encourage algal and other aquatic growths; toxic and inhibitory substances either wipe out the aquatic life or severely limit its growth, and, most importantly, reduce the available dissolved oxygen in the water. The dissolved oxygen may even become zero in the presence of a slug of oxygen-demanding waste water. It takes considerable time for the receiving water to regain its original quality and re-establish the beneficial aquatic life in it. Thus, one polluter, located upstream, can create serious problems for downstream users.

Biological effects due to industrial wastes alone are not very serious because many of them do not contain pathogenic organisms that are present in domestic sewage. An exception to this is the tannery waste which contains *anthrax bacilli*. When industrial wastes are discharged in combination with domestic sewage, biological effects become significant although a large number of microorganisms in the sewage are killed by unfavourable environmental conditions in the industrial wastes. The physical and chemical effects mentioned above have an adverse effect on the aquatic biological life, e.g. turbidity and suspended solids, along with colour, cut-off penetration of sunlight into the water and reduce photosynthetic activity. Suspended solids can choke the gills of fish and kill them. Organic suspended solids settle to the bottom of the receiving body of water and in the presence of microorganisms, decompose anaerobically. The products of anaerobic decomposition gradually diffuse to the upper layers of water and add to the total oxygen demand. Anions such as chlorides, sulphates add to the total dissolved solids content of the water and interfere with the metabolic process of microorganisms. Nitrates and phosphates encourage enormous algal growth in the water.

Dead algal masses settle to the bottom and add to anaerobic conditions. Toxic and inhibitory cations such as mercury, chromium, cadmium, copper, etc. reduce the growth of microorganisms or even wipe out the microbial population, if present in high concentrations. Dissolved oxygen in the water, which is so essential to the survival of micro- and macroorganisms, is reduced and may even become zero under heavy polluting conditions. This leads to either the migration of fish populations or large-scale fish kills, which in turn add to the dead organic matter already present in the water. Toxic heavy metals and radioactive pollutants enter the biological food chain and ultimately reach the human and animal consumers. The net result of all the above effects is a drastic reduction in the usefulness of the receiving body of water.

4.2 EFFECT ON THE WASTE WATER

4.2.1 Self-Purification

4.2.1.1 Disposal into flowing water

Natural bodies of water have the ability to tackle pollution and regain their original quality in due course of time. Thus, when a polluting stream is discharged into these waters, the first step is that of dilution, the degree of dilution depending on the relative volumes of the polluting stream and receiving waters. Due to a decrease in the velocity of the polluted stream, the process of gravitational sedimentation occurs next. This may be compared with primary sedimentation in a waste water treatment plant. Pollutants such as oil and grease, which are lighter than water, float to the surface, as in an oil-water separator. Organic pollutants, which settle to the bottom, undergo anaerobic degradation, similar to the anaerobic digester, while the lighter components remain near the surface of the water and undergo aerobic decomposition. If the pollution load is light, natural aeration, which takes place continuously, provides necessary oxygen to the microorganisms in the water for oxidation of the organic matter. This is similar to aerobic treatment process in the waste treatment plant. In short, a flowing stream is similar to a waste treatment plant, but the steps of purification take place at a slow pace. In a waste water treatment plant, we create conditions similar to those in the flowing stream, but increase the rate of purification by regulating the flow rate through the plant, putting in energy from an external source and separating the stabilized end products, so that the entire process of purification takes place in a reasonable length of time.

Natural water is saturated with dissolved oxygen, or nearly so. When polluted waste water is discharged into it, microorganisms by breaking down the oxidizable organic matter use the available oxygen in the water. This results in depleting the dissolved oxygen in the water. On the other hand, atmospheric oxygen is continuously entering the water through the air-water interface, the rate of entry being a function of the difference in partial pressure of oxygen in the air and in the water. Oxygen is also produced during daytime due to photosynthetic activity of algae in the water. The exertion of biochemical oxygen demand (BOD) by microorganisms is called *deoxygenation*, while replenishment of oxygen is called *reaeration*. When the pollutant load is small, aerobic conditions prevail even in the presence of the pollutant. The interplay between deoxygenation and reaeration produces the dissolved oxygen profile, known as the *oxygen sag curve*.

The basic differential equation for the combined action of deoxygenation and reaeration states that the net rate of change of dissolved oxygen (DO) deficit (i.e. the difference between DO saturation value at the temperature of the mixture of waste water and stream water and the calculated DO of the mixture of waste water and stream water) equals the difference between (1) the rate of oxygen utilization by BOD in the absence of reaeration and (2) the rate of oxygen absorption by reaeration in the absence of BOD [1].

Expressing the rate of oxygen utilization by BOD in the absence of reaeration, the BOD equation by a first-order reaction,

$$\frac{d}{dt}(y_t) = k_1(La - y_t)$$

where y_t = BOD at time t (mg/l), k_1 = deoxygenation rate, t^{-1}, L_a = first stage ultimate BOD, (mg/l) of the mixture of waste water and stream water, and the rate of oxygen absorption by reaeration in the absence of BOD by the equation

$$\frac{d}{dt}(D_t) = -k_2 D_t$$

where D_t = DO deficit at time t (mg/l) and k_2 = reaeration rate, t^{-1}, the net effect of deoxygenation and reaeration can be written as the difference between the two above equations. The negative sign in the reaeration equation indicates that the rate of DO deficit decreases with time.

The BOD equation is written as

$$y_t = L_a \; 1 - 10^{-k_1 t}$$

The reaeration equation is written as

$$D_t = D_a . 10^{-k_2 t}$$

where D_a = DO deficit at time $t = 0$.

Thus,

$$\frac{d}{dt}(D_t) = k_1 L_a 10^{-k_1 t} - k_2 D_t$$

Integrating this equation between $t = 0$, D_a and $t = t$, D_t, we obtain

$$(D_t) = k_1 \frac{L_a}{k_2 - k_1}(10^{-k_1 t} - 10^{-k_2 t}) + D_a . 10^{-k_2 t}$$

This is the equation of the oxygen sag curve.

Figure 4.1 depicts the dissolved oxygen sag and its components, viz. deoxygenation and reaeration, with the simplifying assumption that the receiving water is being affected by only one stream of polluted liquid. In practice, this rarely happens. Analysis of an actual case is done by breaking up the stretch of the stream into individual lengths, each length spanning the point of discharge and the point of inflection.

As an engineering concept, the oxygen sag curve possesses two characteristic points: (*i*) a point of maximum deficit, or critical point, with coordinates D_c and t_c, and (*ii*) a point of inflection, or point of maximum rate of recovery, with coordinates D_i and t_i. The critical point is defined by the mathematical requirement

$$\frac{dD}{dt} = 0$$

and
$$\frac{d_2D}{dt^2} < 0$$

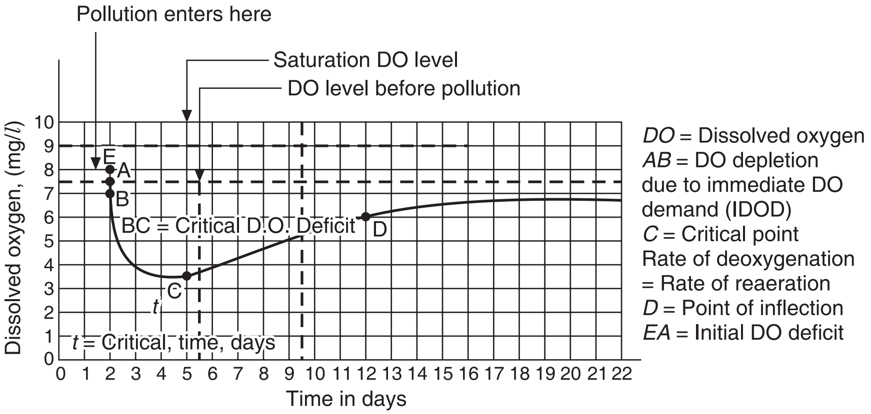

Figure 4.1 Oxygen sag curve.

Differentiation of the oxygen sag curve equation with respect to t gives the values of critical time and flow time to reach the point of inflection. It also gives the values of critical deficit and deficit at the point of inflection [1].

In addition to the phenomena of deoxygenation and reaeration, solids, which are deposited at the bottom of the receiving body of water, add to the oxygen demand (known as benthal demand) due to decomposition of organic matter in the deposited solids in the presence of microorganisms. If the receiving body is a flowing stream, the extent of this demand depends on its flow regime, e.g. when the stream flows with a low velocity, solids are deposited, while during high velocity flows, the deposited solids are scoured and flow with the water to a location where the velocity of the water is insufficient to keep them in suspension. Under quiescent conditions, gases of decomposition in the benthal deposits, mainly carbon dioxide, hydrogen sulphide and methane, bubble up in sufficient volume to lift rafts of sludge from the bottom. This can occur in streams in which the temperature of the water is high, so that microbial activity is high and the rate of decomposition is also high.

If the benthal demand is high, it is incorporated in the equation for oxygen sag curve by replacing k_1 by $k_1 + k_3$, where k_3 represents the deoxygenation rate due to decomposition in the bottom deposit. It is essential to note that the numerical values of the rates of deoxygenation, reaeration and benthal demand are temperature dependent. Therefore, whenever numerical problems on oxygen sag curve are to be solved, the resultant values of the mixture of stream water and waste water, i.e.

temperature, first stage BOD, and DO saturation value must be determined first. This should then be followed by determining the values of k_1, k_2 and k_3 at the resultant temperature. These rates are usually determined at 20°C and should be converted to their corresponding values at the resultant temperature. Formulae for these conversions are

$$k_1 \text{ at } t\ °\text{C} = k_1 \text{ at } 20°\text{C } (1.047)^{(t-20)}$$

$$k_2 \text{ at } t\ °\text{C} = k_2 \text{ at } 20°\text{C } (1.024)^{(t-20)}$$

Generally, the contribution from benthal deposits is considered to be less important than that due to deoxygenation and reaeration.

4.2.1.2 Disposal into lakes and coastal waters

The natural dispersal of waste water into lakes and coastal waters is often poor. These receiving waters are usually heavier than the waste water. So, a discharge at the surface results in the waste water overrunning the receiving water. A discharge below the surface results in the waste water surfacing like a smoke plume and on reaching the surface, fanning out radially. Because chemical diffusion is slow, natural dispersion of these waters becomes a function of wind, current and tides. Hydrographic exploration of the receiving waters will show how effective natural dispersion or dilution will be and whether water intakes, bathing beaches, shellfish layings and shore properties will be polluted. In lakes and ponds, displacement- and wind-induced currents as well as temperature and other density effects govern the degree of mixing. In the sea and its estuaries, tidal currents and the volume of the tidal prism are added variables [1]. Mathematical treatment of wind-induced mixing, dispersal by currents and disposal into tidal estuaries is given in [1].

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Chapter 5

PRETREATMENT OF INDUSTRIAL WASTES

Pretreatment involves some unit operations and unit processes, suitably combined and arranged in a logical sequence, in order to produce an effluent fit for further treatment. If the raw waste contains non-biodegradable pollutants, pretreatment is mostly given by using unit operations. If the waste has toxic and biodegradable pollutants in it, pretreatment aims at removing the former and creating conditions favourable for the microorganisms to work effectively on the latter. It is often observed that a combination of unit operations and unit processes is necessary to achieve the desired degree of pretreatment.

Unit operations frequently used are screening, sedimentation and flotation, mixing, equalization, and gas transfer. Unit processes employed include pH correction, coagulation, oxidation and reduction. A combination of the unit operations and processes is required when the above-mentioned unit processes are carried out, because they tend to convert solids in solution or colloidal state into settleable state. A detailed treatability study of the waste water reveals which of the unit operations and/or processes will be useful.

Pretreatment is also required when waste water is to be discharged into a common sewer, leading to the common effluent treatment plant, or to the municipal sewer leading to the sewage treatment plant. In the case of wastes which are very strong, the industry may be required to provide even biological treatment and produce an effluent acceptable for discharge to the common effluent treatment plant or the sewage treatment plant.

The applications of the pretreatment steps as applied to various industrial wastes are briefly described in the following sections.

5.1 UNIT OPERATIONS

Screening: This is used for the removal of floating, large-sized matter such as rags from textile industry, fine fibres of wool in woollen mills, bark and wood chips in pulp and paper industry, rubber bungs, bottles, vials, etc. in pharmaceutical industry, fruit peelings and rinds in the fruit canning industry, spent tan bark, hairs, fleshings, leather trimmings in the tanning industry, dead yeast and other solid agents used in winery and brewery, empty plastic bags, bottles and cartons in dyes and dye intermediate industry, dairies.

Sedimentation: This method is used in plain or following coagulation—in the ceramic industry, mining industry, ore beneficiation, iron and steel mills, vegetable and mineral oil refining, paper making industry, beet sugar manufacture, lubricant manufacture and engineering industry.

Flotation: This method is used in soaps and oil industry, paper industry, detergent manufacture, mining industry, lubricant manufacture.

Mixing: This is used in industries producing effluent streams with different pH values, as in chemical manufacture, regeneration and rinse waters from demineralization units, blowdown from boiler houses and cooling towers.

Equalization (in-line or off-line): This method is used in batch manufacturing processes such as pharmaceuticals, fermentation products, industries producing different effluent streams with wide fluctuations in quality, toxic chemical manufacturers, e.g. herbicides, pesticides, weedicides.

Gas transfer: This method is used in chemical manufacture using volatile solvents, waste water containing large concentrations of ammonia, pharmaceutical industry, waste water containing highly biodegradable pollutants as in the dairy industry. The purpose in this case is to reduce the chances of waste water from becoming stale or septic and creating odour nuisance. Gas transfer, in the above cases, is achieved by using compressed air, which supplies oxygen and helps to keep the waste water solids in suspension. A gas, such as ammonia, can be removed by stripping in a closed tower packed with ceramic rings.

5.2 UNIT PROCESSES

pH correction: This method is used where wastes containing high concentrations of oil and grease, with high or low pH values, high in suspended solids which can be coagulated and settled, with high biodegradable contents in addition to high or low pH, containing heavy metals which can be precipitated by adjustment of pH value.

Coagulation: This is used where all waste streams mentioned under 'pH correction' except those with high biodegradable contents are handled unless the resulting sludge with high organic content can be properly treated and disposed of.

Oxidation and reduction: This is used in wastes with chemically oxidizable pollutants, certain organic molecules which become amenable to biological treatment after oxidation, wastes containing heavy metals which can be precipitated, cyanide bearing wastes, phenol containing wastes, etc. An incidental benefit of oxidation is partial satisfaction of the oxygen demand of the waste.

Aerobic and/or anaerobic treatment: Aerobic or anaerobic treatment follows pretreatment by the above-mentioned unit operations and unit processes. Subjecting them to anaerobic process, followed by aerobic process, economically treats wastes, high in biodegradable matter. In these cases, anaerobic treatment knocks out a sizeable portion of the oxygen demand from the waste and allows aerobic treatment to be done economically, especially in terms of power consumption for mechanical methods of oxygen supply and land requirement for non-mechanical methods. An added advantage of anaerobic treatment is the availability of methane, a useful component of the result of gases formed during anaerobic degradation. The digested solids from anaerobic process can also be used as soil conditioners.

The various methods described above help 'end of the pipe' treatment of the waste water. Further, economy in treatment can be achieved by using one or more of the following measures:

1. Reduction of water consumption in the manufacturing process.
2. Reduction of the strength of waste water.
3. Modifying the manufacturing process.
4. Replacing polluting chemicals by those, which pollute less, or are non-polluting.

Some good housekeeping practices are:

1. Recycling and reusing, either with or without treatment, slightly polluted waste water streams.
2. Recovering by-products from the waste streams, where feasible.

Execution of the above measures must be done only after ensuring that they do not have an adverse effect on the quality of the finished product. It is possible to economically control pollution due to industrial wastes by following these measures.

Chapter 6

TEXTILE WASTES

This chapter deals with waste waters generated in the processing of cotton, wool, rayon, semi-synthetics, synthetics, silk and jute. Raw materials used in the manufacturing process are subjected to various physical, chemical and biological changes aimed at removing the natural impurities from the raw material, separating the cleaned portion and modifying its physical and chemical structure to get the desired end product. These natural impurities, along with the chemicals and other cleansing agents used in the process, find their way into the waste water streams and contribute to their polluting characteristics. The ease or difficulty with which these waste waters are treated depends mainly on the nature of the impurities, their concentration, their degradability and amenability to various treatment processes. Methods of disposal of the treated wastes are determined by local conditions and requirements of the pollution control authorities, in addition to the factors mentioned earlier. In general, textile industry offers good opportunities for effective treatment of its waste water, recovery of valuable chemicals and by-products from the wastes, and recycle and reuse of water used in the manufacturing process.

6.1 COTTON TEXTILE WASTES

6.1.1 Raw Material

Raw cotton, as obtained from the cotton bush, is pure cellulose, containing impurities such as waxes, gums, pectin, leaves, soil and cotton seed. It is picked from the fields, the seeds are removed by ginning, the resulting balls of cotton are pressed into bales and sent to the mills for further processing. The manufacturing process starts with the removal of loose dirt, cleaning the fibres and opening them for easy alignment. This step facilitates the operation of spinning. The cotton, thus converted into yarn, is then woven into raw cloth, known as gray goods. Impurities sticking firmly to the cotton fabric are then removed by a number of chemical processes. The fabric is then subjected to bleaching, mercerizing, dyeing and printing. Mills where gray goods are manufactured are called 'spinning and weaving' mills. Further treatment of the gray goods is done in the 'process house'. Mills, which start with raw cotton and end up with finished cloth, are known as 'composite' mills.

6.1.2 Manufacturing Process

A general manufacturing flow sheet for cotton textile fabric is shown in Fig. 6.1. Individual operations are explained in the following sections.

6.1.3 Spinning, Weaving and Sizing (or Slashing)

This is a dry process and requires the use of water only for maintaining relative humidity in the spinning and weaving section in the range 70%–75%. The cotton balls are spun into yarn and subjected to sizing (or slashing). This reduces the chances of the yarn breaking during the weaving process. The sizing agent usually used is starch, or carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA) or suitable mixture of these compounds. The agent, especially starch, is applied to the cloth in the form of a paste. The woven cloth is called 'gray goods' and is 'singed', i.e. passed quickly between two rows of burning gas flames in order to burn the 'fuzz', or tiny ends of cotton protruding from the surface of the cloth. It is then dipped into a tank containing water to prevent it from catching fire. Thereafter, it is sent to the process house for further treatment.

Waste products of spinning and weaving consist mainly of loose dirt accompanying the raw cotton and cotton dust or 'willow' dust, which is pure cellulose. The loose dirt is disposed of with other solid waste from the mill, while the cotton dust is (i) burned as fuel in the mill's boiler, or (ii) sold to outside parties as filling material in quilts. A better use of the cotton dust is to digest it with cow dung under anaerobic conditions for the production of methane gas [1, 2, 3], which can be used within the mill's canteen or for singeing operations. The cotton dust can also be composted aerobically or anaerobically to give a manure of good quality [4, 5, 6].

Another waste product in the spinning and weaving operations is the starch paste, which may be present in the waste water stream if the vessel in which the paste is prepared is washed with water. This adds considerably to the BOD of the waste water, because starch is a

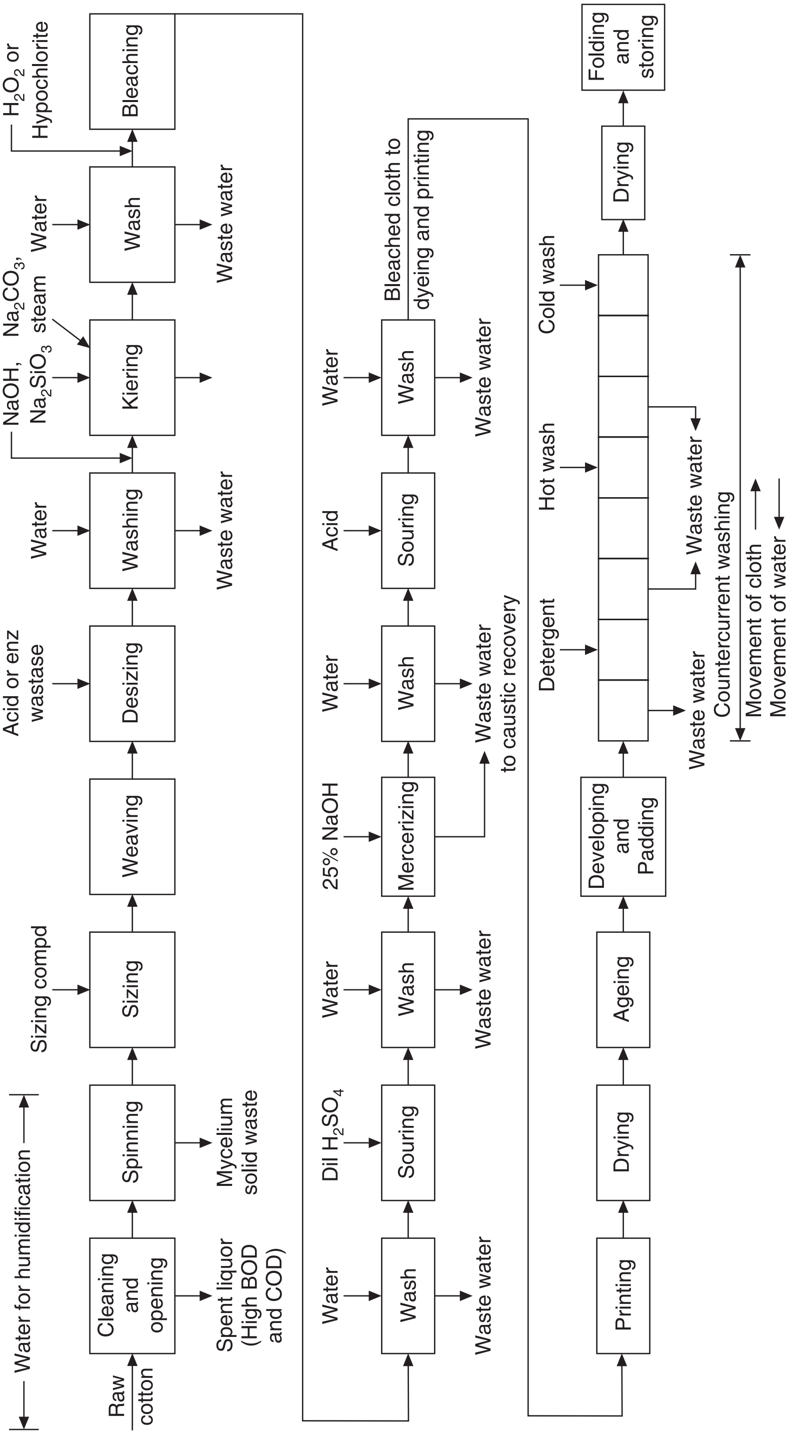


Figure 6.1 Cotton cloth manufacture in a composite mill.

biodegradable substance. This BOD load can be easily reduced by first scraping dry the vessel containing the starch paste, recovering the paste and then washing the vessel with minimum quantity of water.

6.1.4 Desizing

This is done in order to remove the excess sizing agent sticking to the cloth. The desizing compound used may be either the enzyme diastase, or a mineral acid. The cloth is washed after desizing. This is another source of waste water. Water consumption in this (and in almost all washing operations in the textile mill) can be considerably reduced by following the practice of 'countercurrent' washing, i.e. pass the cloth to be washed through a series of tanks containing water which overflows from the last tank in the series of tanks into the next tank, and so on, so that the water travels through this system in a direction opposite to that of the cloth. The cleansing power of the water is thus fully used. (See manufacturing flow sheet.)

6.1.5 Caustic Kiering (or Scouring)

This is done either under pressure or at atmospheric pressure. The kier is a tall vessel in which the gray goods are stacked. Chemicals, viz. caustic soda (NaOH), sodium carbonate (Na_2CO_3), low-BOD detergent and sodium silicate (Na_2SiO_3) are added and the cloth is subjected to high temperature by injecting steam into the kier. Waxes, gums and pectin, which are firmly sticking to the cotton fibre, are completely removed by this operation. The cloth is removed from the kier and is washed thoroughly to remove the impurities and the chemicals. The waste water from the kier has high pH, dark chocolate brown colour and a frothy appearance. This waste stream should be treated separately and then mixed with the other waste water streams for further treatment.

6.1.6 Chemicking or Bleaching

The pale yellow colour of the kiered cloth is removed by using a bleaching agent such as sodium hypochlorite (NaOCl) or hydrogen peroxide (H_2O_2), followed by water wash. This step facilitates dyeing and printing operations.

6.1.7 Souring

The bleached cloth is treated with a dilute acid and washed thoroughly to ensure complete removal of all alkaline chemicals used in the earlier manufacturing operations.

6.1.8 Mercerizing

This operation gives lustre to the cloth and increases its affinity for the dye. It consists of washing the cloth with caustic soda solution of 25%–30% strength. The caustic soda solution becomes weak with repeated use. When its strength is reduced, the spent caustic is removed from the mercerizing bath and sent to caustic recovery section, where either dialysis or multiple effect evaporation is done to separate the water from the caustic solution and build up its concentration. The recovered caustic is then 'topped up' to the required strength and is reused. The mercerized cloth is washed with jets of water. This wash water is also collected and sent to the caustic recovery section.

6.1.9 Souring

The mercerized cloth is washed first with dilute acid to remove traces of caustic soda and the salt resulting from the reaction between the caustic soda and the dilute acid is removed by a water wash. The cloth is now ready for dyeing, printing and finishing operations.

6.1.10 Dyeing and Printing

The bleached cloth is coloured with dyes of various types, and printed with various designs, depending on market demand. The wash waters from these operations are highly variable, depending on the type of dyes, dye chemicals and printing chemicals used. Dyeing and printing chemicals are designed to impart 'fast' colour and 'non-fading' designs to the cloth. As a result, waste waters produced in these sections are difficult to treat, especially from the point of view of colour removal and reduction of oxygen demand. Thorough washing of the dyed and printed cloth is done before it is dried, folded and stored.

General characteristics of waste water streams from various sections are given in Table 6.1.

Table 6.1 General Characteristics of Waste Water [7]

Chemical process	Pollutants in waste water	Nature of waste water
Desizing	Starches, fats and waxes	High BOD (about 45% of total)
Scouring (Kiering)	Caustic soda, waxes, greases, soda ash, sodium silicate, fibrous matter	Strongly alkaline, dark brown, high BOD (about 30% of total)

(Contd.)...

Table 6.1 General Characteristics of Waste Water [7] *(Contd.)*

Chemical process	Pollutants in waste water	Nature of waste water
Bleaching	Hypochlorite, chlorine, caustic soda, acids, hydrogen peroxide, sodium silicate	Alkaline, about 4% of total BOD
Mercerizing	Caustic soda	Strongly alkaline, low BOD
Dyeing	Various dyes, auxiliaries, chemicals, soap	Strongly coloured with varying hues, about 4% of total BOD
Printing	Colours, thickeners, auxiliaries	Highly coloured, about 8% of total BOD

It is apparent from the manufacturing flow sheet that almost every operation involving chemical action on the cotton is followed by water wash, which makes the cotton textile industry a water-intensive industry. It also suggests the possibility of reuse (with or without treatment), recycling and reduction in water consumption. A rough breakup of the water consumption in various operations is given in Table 6.2.

Table 6.2 Operationwise Water Consumption [8]

Item of consumption	Per cent of total
Humidification in spinning and weaving	7–13
Boiler house	10–16
Process water (wet processing and finishing)	60–80
Sanitary and miscellaneous uses	4–7

6.1.11 Reuse and Recycling

From Table 6.2, it is seen that water used for humidification is lost and cannot be recovered. Boiler blowdown may be used for floor washing, while the condensate can be fed back to the boiler. Waste water from sanitary uses can be subjected to tertiary treatment and made suitable as boiler feed water. The major consumer of water is the process house, in which wide scope for reuse, recycling and reduction of water consumption is available. Some of the steps, which can be taken, are:

1. Reducing the number of washes and using hot water for washing operations.
2. Replacing running dye bath with standing bath.
3. Using countercurrent washing method wherever feasible.

4. Observing good housekeeping practices.
5. Employing machinery which works on low material to liquor ratio.
6. Recovering exhausted dye bath contents, making up their chemical constituents to the required level and reusing them. This step saves water as well as chemicals [9].

Water from 20%–40% can be saved by using the above methods. Studies on the water consumption in the textile mills in Mumbai showed that nearly 15%–20% of the water could be reused without any treatment, while about 50% could be reused after chemical treatment and filtration [10].

6.1.12 Substitution of Chemicals

Another way to reduce pollution is substitution of low polluting chemicals for high polluting chemicals, e.g. replacing starch for sizing with CMC or PVA, replacing non-ionic detergent based on nonyl phenol ethoxylate by alfa olefin sulfonate or fatty alcohol ethoxylate in kiering, using formic acid instead of acetic acid in dyeing, employing reactive dyes in place of vat dyes and azo dyes [9]. Another interesting example is that of reducing sulphides in aniline dyeing wastes by using a mixture of molasses and other suitable chemicals [11]. An interesting paper on BOD of textile chemicals was presented by McCarthy during the proceedings of the American Association of Textile Chemists and Colorists. The paper gives an updated list of textile chemicals and expresses their BOD values as per cent rather than milligrams per litre. Multiplying the per cent figure by 10,000 does conversion to mg/l [12]. McCarthy [16] compares the BOD values of starch substitutes with BOD of starch (600–1000 mg/l), giving a range 4–16 mg/l for CMC and 375 mg/l for HPAN + Globe corn starch.

6.1.13 Modifications to Machinery

Modifying the existing machinery and/or the manufacturing process in order to reduce the generation of waste water is another way. It is observed that continuous operations require less space and use less water and chemicals than batch operations. Whenever possible, separate operations such as desizing and scouring of cotton fibres should be combined [13]. Use of suitable solvents for desizing and scouring offers a drastic reduction in water consumption, as the process requires very little water. However, complete recovery of the solvent is essential in order to avoid the problem of air pollution [14].

The printing machine is provided with a scraper blade to remove excess printing paste from the rollers. The scraped paste is collected in a trough located directly under the rollers. This paste is reused for producing combination shades. This method is particularly applicable to the printing of thin cotton cloth [9]. A drastic process modification is not to discharge the effluent at all, but to pump the process liquor to a storage tank, where it is saved to make-up the next similar bath [15].

6.1.14 Good Housekeeping Practices

Good housekeeping practices include the following:

1. Minimum use of chemicals in the process house
2. Prompt attention to leaks of water and chemicals
3. Dry-cleaning of the floor, followed by mopping the floor with a piece of wet cloth
4. Educating the workers on the importance of maintaining clean surroundings
5. Segregating strong waste streams from weak streams, providing separate conveyance system for rain water and, in general, ensuring that only the minimum amount of waste water will have to be handled at the treatment plant.

The last step is usually difficult, or in some cases, impossible to implement in existing mills, but should be given serious consideration at the design stage of a new mill. These and the other steps mentioned go a long way in reducing, and in some cases, eliminating pollution, decreasing the consumption of water and chemicals and reducing the overall cost of treating the waste water streams.

6.1.15 Characteristics and Treatment of Raw Waste Water

As previously mentioned, waste water contains natural impurities and chemicals used in the manufacturing process. The process of spinning, weaving and sizing produces negligible amount of waste water. Desizing produces a waste stream whose nature depends on the chemicals used in the process. Kiering generates waste water high in temperature, total dissolved solids, suspended solids, pH value, colour, BOD and, in general, has a frothy appearance. Waste water from bleaching section contains the unreacted bleaching agent and can be conveniently mixed with the remaining waste streams. Souring produces an effluent low in pH and can be used to partially neutralize the high alkalinity of the other waste streams. Mercerizing discharges waste water high in pH, low in suspended solids and BOD. Dyeing and printing are the two operations from which highly variable quality effluents are produced. Typical polluting loads of cotton processing wastes are given in Table 6.3 [13].

Table 6.3 Polluting Loads

Process	pH value	BOD (mg/l)	Total solids (mg/l)	BOD load (kg/ 1000 kg goods)	Total solids load (kg/ 1000 kg goods)
Desizing	—	1700–5200	16000–32,000	14.8–16.1	66–70
Kiering	10.0–13.0	680–2900	7600–17,400	1.5–17.5	19–47
Scourung	—	50–110	—	1.36–3.02	—
Bleaching	8.5–9.6	90–1700	2300–14,400	5.0–14.8	38–290
Mercerizing	5.5–9.5	45–65	600–1900	10.5–13.5	185–450
Dyeing					
Aniline black	—	40–55	600–1200	5–10	100–200
Basic	6.0–7.5	100–200	500–800	15–50	150–250
Developed	5.0–10.0	75–200	2900–8200	15–20	325–650
Direct	6.5–7.6	220–600	2200–14,000	1.3–11.7	25–250
Naphthol	5.0–10.0	15–675	4500–10,700	2–5	200–650
Sulphur	8.0–10.0	11–1800	4200–14,100	2–250	300–1200
Vat	5.0–10.0	125–1500	1700–7400	12–30	150–200

Note: Numerical figures indicate the pollution loads which the various processes generate. They can be converted into corresponding concentrations if the volume of waste water produced is known.

Chemical analysis of the waste water produced in a typical cotton textile mill is given in Table 6.4.

Table 6.4 Chemical Analysis of Composited Waste Water [17]

Item of analysis	Concentration
pH value	11.2
Suspended solids	1000
5-day 20°C BOD	1000
Chemical oxygen demand	2200
Oil and grease	Nil
Phenolphthalein alkalinity as $CaCO_3$	480
Methyl orange alkalinity as $CaCO_3$	1200
Dissolved oxygen	1.0

Note: All values except pH are in mg/l.

It is seen from Table 6.4 that the waste water is high in pH, suspended solids, BOD and COD. It is essential to treat it before discharge either to the municipal sewer, or to an inland receiving body of water, or the sea, or on land for irrigation. Fortunately, the organic pollutants in the waste water (except some of the dyes) are biodegradable. So, the waste water can be conveniently mixed with domestic sewage. As the waste is deficient in nitrogen and phosphorus, nutrient supplementation is necessary, although domestic sewage supplies a part of these elements. Process houses, which produce kier waste in large volumes may be required to treat this waste separately before mixing it with other waste water streams for further treatment. Kier waste treatment usually consists of neutralizing the high alkalinity and pH value with a suitable acid such as sulphuric acid, or passing flue gas into the waste. Coagulating the suspended solids in the waste with lime, settling overnight and discharging the supernatant from the reaction tank for mixing with the rest of the waste give further treatment. Alternatively, the waste can be subjected to aerobic biological treatment after reducing the pH to 8.5 or lower. Nutrient supplementation with urea and diammonium phosphate is necessary for successful biological treatment. In either case, the generated sludge is dewatered and disposed of on land.

As already mentioned, the pollutants in cotton textile waste water are generally biodegradable and may be suitably mixed with domestic sewage before treatment of the mixture. It is a usual practice to use activated sludge process or its modification for this purpose. Pretreatment in the form of fine screening, followed by equalization and pH correction ensures that the biological treatment is not adversely affected by fluctuations in quality and flow rates of the raw waste water.

Nemerow [18] recommends dispersed growth aeration for cotton finishing waste water. Laboratory and pilot plant studies have shown BOD reduction of 46.8% after 12 hours of aeration at reduced rate of air supply. This step had the advantage that high concentrations of sensitive sludge did not have to be handled during treatment. Biological activity during aeration produced carbon dioxide, which helped to reduce the excess alkalinity in the waste water and reduce the cost of neutralizing chemical to some extent. A BOD removal of 71% was achieved when the waste water was neutralized prior to biological treatment.

Williams and Hutto, Jr [19] experimented with aerated lagoons followed by secondary settling of textile wastes. They got a BOD removal efficiency of 75%–80% after 48 hours of aeration. Sihorwala and Reddy [20] studied the effectiveness of polyelectrolytes on the treatment of cotton textile wastes. They subjected waste water samples from two separate channels in the textile mill, one carrying waste from desizing, mercerizing and kiering while the other carrying waste from dyeing, printing and finishing operations. A mixture of the two waste streams was also studied. They found that waste water from the first stream was less amenable to coagulation than that from the second stream, while the mixture showed amenability which was between that of the two streams. Effectiveness of the treatment was assessed on the basis of colour removal, COD removal and suspended solids removal. The coagulants used were alum, ferric chloride and Catfloc-T.

6.2 WOOLLEN MILL WASTES

Woollen fibre, unlike cotton (which is a fibre of vegetable origin), is a fibre of animal origin. Wool, as removed from the sheep's back, contains considerable quantities of dirt, grass, burrs picked up during grazing, excreta, the dried perspiration of the sheep called 'suint', and the wool grease discharged from the animal's glands, which protects its skin during growth. Grease wool may contain as little as 30% fibre and 70% foreign matter, which must be removed before the fibre can be used in textile manufacture [21]. The sheep's perspiration consists largely of potash salts and water-soluble organic acids. The wool fat, or 'yolk', which is impure lanolin, is insoluble in water, but soluble in certain organic solvents [22]. For every 100 kg of finished wool, 250 kg of raw wool has to be processed. In extreme cases, raw wool may contain as little as 30% fibre, 70% foreign matter, of which 45% is grease. Contribution of wastes comes from the operations of scouring, carbonizing, dusting, bleaching, dyeing and finishing operations. The manufacturing operations are defined as follows:

1. **Grading:** The raw wool is graded according to its quality.
2. **Dusting:** Impurities are removed by mechanical means by subjecting raw wool to a dusting/opening operation, whereby the wool is opened up and is ready for the scouring process. Considerable dirt, amounting to 5%–15% of the total impurities, is removed in this step and is disposed of in a dry condition [23].
3. **Desuinting/Scouring:** Desuinting is done by washing the wool in water at a temperature 50°–55°C. Scouring with alkali, soap and soda ash follows this. This step contributes from 55% to 75% of the total BOD load and removes almost all natural and acquired impurities from the wool fibre. Water used ranges 7000 to 10,000 litres per 100 kg wool fibre [24].
4. **Drying:** Passing it through a series of driers dries the scoured wool.
5. **Carbonization:** It is a process in which hot concentrated sulphuric acid is used to convert the vegetable matter in the wool into loose, charred particles, which are mechanically crushed and then taken out of the wool in a machine called 'duster'. This step produces some solid waste but little liquid waste [24].
6. **Dyeing:** During this process, a hot dye solution is generally circulated by pumps through the wool, which is packed in a removable metal basket suspended in a kettle. Waste water generated by dyeing is highly coloured and contains many toxic substances. BOD contribution from this stream is 1%–5% of the total BOD load.
7. **Oiling:** The traditional oiling agent used is olive oil. It is mixed with water and sprayed on the wool. Oiling increases cohesion of the fibres and aids in spinning operation. The amount of oil used varies from 1% to 11% of the weight of wool. All of this oil is removed from

the woven cloth later in the finishing operation. The percentage contribution of BOD from this waste varies with the type of oil used.

8. **Spinning and weaving:** The wool fibres are spun and loosely woven into cloth.
9. **Fulling:** The loosely woven wool from the loom is shrunk into tight, closely woven cloth. There are two common methods of fulling, viz. alkali fulling and acid fulling. In alkali fulling, soap or synthetic detergent, soda ash and sequestering agents are used. In acid fulling, the fabric is impregnated with an aqueous solution of sulphuric acid, hydrogen peroxide and small amounts of metallic catalysts such as chromium, copper and cobalt. The temperature of water used ranges from 33° to 38°C. Acid fulling is always followed by alkali fulling.
10. **Washing:** The cloth is washed to remove all chemicals used in the earlier operations. Two soapings, two warm water (38°–44°C) washes and a cold rinse are given. It is estimated [24] that from 10% to 25% of the weight of the fulled cloth is composed of process chemicals, which contribute from 20% to 35% of the total BOD. Water consumed ranges between 35,000 and 85,000 litres per 100 kg of wool fabric [24].

The above operations are indicated in the process flow diagram Fig. 6.2.

Table 6.5 gives the average analysis of waste water samples collected from the second bowl of a scouring train. Numerical figures in the table are average values of 12 batches of samples.

Table 6.5 Average Chemical Analysis of Scouring Waste Water [24A]

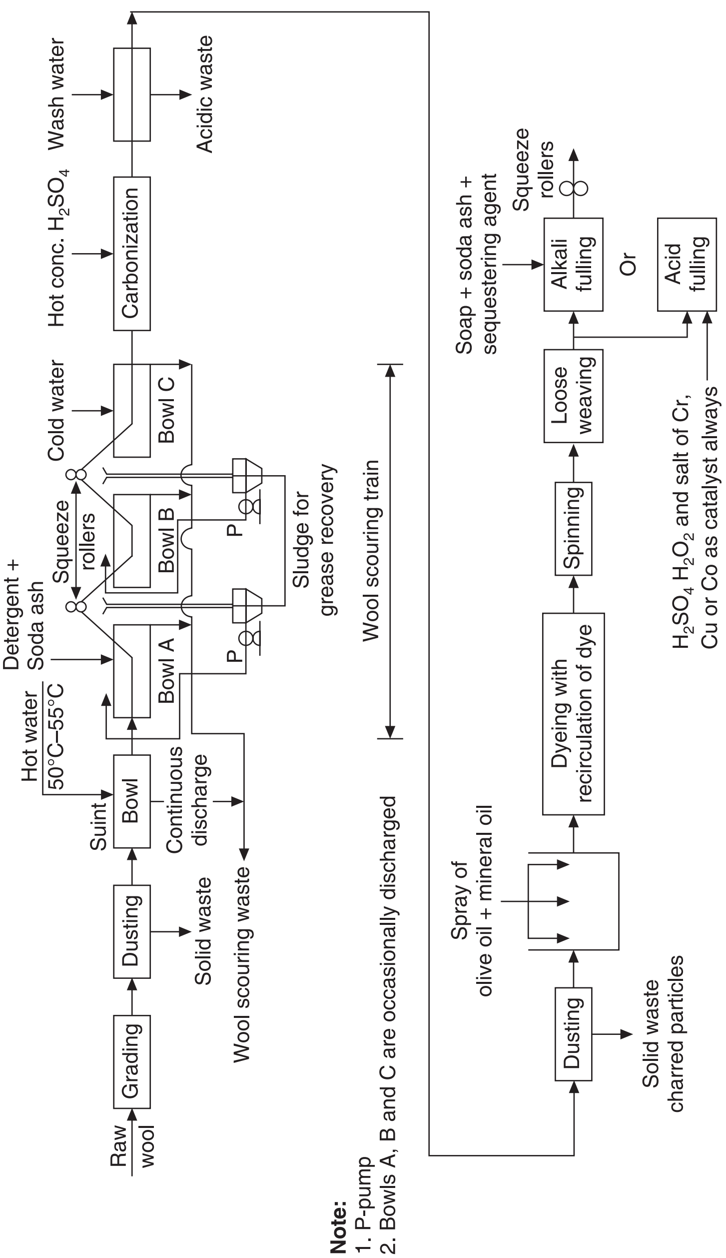
Item of analysis	Sample 1	Sample 2	Sample 3
pH value	8.1	8.2	8.5
Temperature (°C)	58	55	56
COD (mg/l)	30,000	1,24,800	1,42,600
Total solids (mg/l)	15,895	70,120	82,330
Total volatile solids (mg/l)	12,557	61,420	73,240
Volatile suspended solids (mg/l)	8060	46,065	50,960
Grease content (mg/l)	—	9980	15,240

The analysis of a mixture of all streams is given in Table 6.6 [24A].

Table 6.6 Analysis of Mixture

Item of analysis	Maximum	Minimum	Average
Total solids	69,750	11,468	31,375
Volatile solids	45,155	1850	17,345
Fixed solids	26,065	3846	14,029
5-day 20°C BOD	39,000	1800	9,608
Ether-soluble grease	—	—	11,627
pH value			9.0–9.5

Note: All values except pH are in mg/l.



Note:
1. P-pump
2. Bowls A, B and C are occasionally discharged

Figure 6.2 Manufacture of wool by detergent scouring.

The most obnoxious waste stream in woollen cloth manufacture is the wool scouring waste. It must be adequately treated, useful by-products recovered from it, the treated (or partially treated) effluent recycled to the appropriate department and the balance flow discharged to the municipal sewer (if one is available and the waste water treatment plant is designed to take the additional organic and hydraulic load).

6.2.1 Methods of Treatment of Wool Scouring Wastes

The following methods are used to treat the scouring wastes of wool.

1. Hypochlorite process
2. Acid cracking process
3. Anaerobic treatment
4. Calcium chloride plus carbon dioxide process
5. Solvent degreasing process

6.2.1.1 Hypochlorite process

Calcium hypochlorite is added to the waste to pH 7.5, the waste is settled and the scum and sludge generated are treated with sulphuric acid to pH 4.5. This mixture is maintained at 80°C and passed through plate and frame press for recovery of grease. The subnatant from settling is diluted with sewage in the ratio of 1:5 and is treated by biological means.

The volume of sludge produced is from 2% to 8% of the volume of waste treated and presents a distinct problem of disposal because it is foul smelling and it dries slowly. It can be disposed of on land after drying or can be used to fill low-lying areas after grease recovery.

6.2.1.2 Acid cracking process

The waste is settled for a short period to remove quick-settling solids. The settled waste is transferred to wooden cracking tanks, where sufficient sulphuric acid is added to neutralize the alkalinity, to precipitate the fats and to give an excess mineral acidity of about 1000 mg/l. The rest of the procedure is similar to the hypochlorite process. Grease recovery is between 50% and 60%.

6.2.1.3 Anaerobic treatment [25]

A pilot plant study was carried out, using two digesters in series, each of 1900 l capacity. The digesters were initially filled with digesting sewage sludge and sewage. Wool scouring waste was gradually added to the primary digester at the rate of 1% of the digester volume per day. Satisfactory results were obtained at the loading rate of 6%, giving a BOD reduction of 57.7% and volatile solids destruction of 48.2%. The emulsion in the waste was broken by anaerobic process. The optimum volatile acids concentration was found to be between 1200 and 1400 mg/l as HAc, while the optimum BOD loading was 0.26 kg/m^3. It was found necessary to periodically add sewage sludge to maintain good digestion.

In another experiment [26] raw wool, along with grease, was subjected to direct anaerobic digestion. It was expected that the grease would be fermented to methane and carbon dioxide. It was found that 68% of wool grease was fermented. The wool removed from the digester showed no disintegration of fibres. The concentrated liquor in the digesters could be removed for potash recovery, thus offering a simple and direct substitute for conventional wool scouring process.

Investigations [27] were done on small-scale digestion of wool scouring waste. At a conventional retention time of 20 days, the use of 100% wool waste feed resulted in 28% volatile solids destruction, with considerable amount of gas production. With a feed ratio of 2:1 (wool scouring waste to sewage sludge), the process lost efficiency rapidly and finally failed at a solids retention time of 5 days. These results were confirmed by feeding wool scouring waste (100%) to a full-scale anaerobic digester, where no significant problems were faced, although the waste contained non-ionic detergents. The supernatant from the digester had a BOD of 300 mg/l.

An anaerobic upflow filter was used to test the suitability of this process for treating wool scouring waste [27]. After several months of acclimatization, the filter was fed with 100% scouring waste. It was observed that 50%–55% destruction of COD was achieved in the bottom 30 cm of the filter, giving a COD loading rate of 2.2 kg/m^3 per day.

6.2.1.4 Calcium chloride plus carbon dioxide process

The simultaneous use of calcium chloride and carbon dioxide [28] was found to offer a simple method for treating wool scouring wastes. It was observed that 2 to 3 times the theoretical requirement of carbon dioxide had to be used for successful treatment. The mechanism of treatment was found to be that floc formation began with precipitation of calcium carbonate and calcium soaps around a nucleus of calcium chloride. The floc grew by further enmeshment of organic matter and fatty emulsions. Settling of the waste with the above chemicals resulted in sludge with solid concentration of 4–8%, which could be increased to 25% by gentle stirring. Although calcium chloride alone could treat the waste, the use of carbon dioxide reduced the dose of calcium chloride by 20–50%. This method removed 99% of volatile solids and 88% of BOD, but the remaining BOD was found to be in solution and could be treated on trickling filters using a high recirculation ratio.

6.2.1.5 Solvent degreasing process

Grease from the waste can be removed almost completely by using a solvent such as trichloroethylene, butanol, pentanol and hexanol. The solvent can be recovered by distillation [22] and grease recovered.

In addition to the above methods, the process of centrifugation is combined with scouring operation, so that grease recovery can be done simultaneously. The Wool Research Organization of New Zealand (WRONZ) has developed a process for comprehensive scour liquor handling [21]. It rationalizes the primary effluent treatment processes of floc removal, solids removal, grease recovery and flow balancing. The scour liquor is pumped through a series of bowls and side tanks, then it is passed through a parallel plate separator. The clarified liquid is degreased by a disc centrifuge. The centrate is returned to the first bowl. The overall advantages claimed for this system are: high efficiency, effluent heat recovery, continuous plant running, improved effluent discharge, reduced water consumption and efficient solids removal. Chemical treatment uses, (a) hot alum salt (aluminium sulphate or aluminium chlorohydrate) at pH 4.0–5.0, followed by polyelectrolyte addition and sedimentation, or (b) hot acid cracking with sulphuric acid, followed by lime neutralization and addition of a polyelectrolyte to obtain rapid sedimentation in a thickener. The drawbacks of both these systems are that the sludge formed is voluminous and requires large dewatering system. Further, the cost of chemicals is high compared to continuous acid cracking.

6.2.2 Biological Treatment

It is essential to remove grease from the waste water because grease interferes with oxygen transfer in aerobic biological treatment. In order to meet the stipulated standards of effluent discharges, woollen mills may have to provide from very large, highly sophisticated, nearly zero discharge evaporation plants to biological, aerobic and anaerobic, chemical and ultrafiltration plants. Among the available methods of biological treatment, the two-stage activated sludge process, either alone or in combination with anaerobic process, is commonly used. An equalization tank, provided upstream of the aeration tank, helps smoothen out the fluctuations in quality and flow rate of the waste water. If an anaerobic treatment unit is provided upstream of aerobic unit, close pH control becomes necessary.

A large mill treats a mixture of scouring waste with other waste streams from the mill by the two-stage activated sludge process. It consists of two aerobic digestion tanks, each with a hydraulic retention time from 2 to 3 days. Activated sludge is separated by secondary clarification. A COD removal of 90% is reported. The excess sludge from the secondary clarifier is thickened, dewatered by centrifugation and conditioned with lime before disposal on land [21].

Another successful process is the deep shaft aeration process. It uses to good effect the hydrostatic pressure exerted by a column of water. Air is dissolved as the liquor is forced down a 100-metre deep shaft, at the base of which the pressure is between 5 and 15 atmospheres. This results in a corresponding increase of dissolved oxygen. The process air also maintains a velocity from 1 to 2 metres per second. Reduction of COD of the waste was reported from 75 mg/l to 200 mg/l [21].

A combination of anaerobic and aerobic process was found to work better than either process alone. A plant in Siberia uses the Swedish ANAMET process of the two-stage anaerobic digestion, followed by sludge degasification, dissolved air flotation and aerobic treatment. The sludge is treated with a flocculating agent and is dewatered before final disposal. From an inlet COD of 35,000 mg/l, the treated effluent had a COD of 900 mg/l, a BOD of 50 mg/l and suspended solids of 200 mg/l. The final grease levels were less than 9 mg/l [21].

A simple scheme of treatment consists of the following:

1. A settling pit for removing settleable solids
2. A deep anaerobic pond which receives the concentrated discharges from the scouring bowls
3. An aerated lagoon with floating aerators, and
4. A large holding lagoon, which receives dilute rinses and other wastes from the mill. This lagoon also acts as an evaporation pond or holding pond for final disposal of the treated effluent on land for irrigation [29].

A woollen mill can achieve zero discharge status by providing evaporation and incineration of the scouring liquor, but the capital and operating costs are very high. In Western Europe, three such plants have been developed, two in France and one in Germany. The waste water is evaporated to 70% solids consistency and the concentrate is pyrolized at temperatures ranging 280°C–500°C in 2 of the 3 plants. A combustible oil is produced at low temperature, which is burned in a conventional boiler. At high temperature, a combustible gas is produced, which is mixed with natural gas and used for producing steam and electricity. The third plant uses a high temperature of 1200°C for incinerating the concentrated waste. Combustion products are used to generate steam [30]. The following measures reduce the strength of woollen mill wastes by replacing [3]:

1. Soap used in scouring by low-BOD detergent;
2. Soda ash by a mixture of detergent and sodium sulphate, in order to reduce high alkalinity of the waste;
3. Carding oil by mineral oils and nonionic emulsifiers; and
4. Soap used for fulling and washing after fulling with low-BOD detergents.

6.3 RAYON WASTES

Rayon, also known as ‘artificial silk’, is a form of regenerated cellulose. The idea of producing artificial silk was put forward as early as 1665. Extruding certain solutions through fine holes and producing filaments was suggested by a silk manufacturer. A patent for producing artificial silk from nitrocellulose was issued in 1883. Seven years later, another patent was taken out for cuprammonium process of producing rayon. Similarly, it was observed that alkaline cellulose reacted with carbon bisulphide to form a viscous solution, which was termed ‘viscose’. From that time onwards, the viscose process has found favour with rayon manufacturers.

The first unit for manufacturing rayon was established in India in 1935 with Japanese assistance. Today, most of the production is done using the viscose process. Rayon yarn has many uses, such as manufacture of fashion fabrics, hosiery items, knitted goods interwoven with cotton, silk, wool, linen, making ribbons, braids and tyre cord.

Manufacture of rayon consists of steps involving separation of pure cellulose from the raw material such as wood and cotton linters, converting the pure cellulose into alkaline cellulose, which is made to react with carbon bisulphide under controlled conditions to form cellulose xanthate and converting this compound into filaments by squirting it into a bath containing zinc sulphate, sodium sulphate, sulphuric acid, glucose and water. The filaments so formed are spun into yarn, bleached and/or dyed as per market demand.

Chemicals used in the manufacture of rayon include sodium hydroxide, carbon bisulphide, zinc sulphate, sodium sulphate, sulphuric acid, glucose, bleaching and dyeing agents. Various steps in manufacture are:

1. **Steeping:** Sheets of cellulose are soaked in 18% sodium hydroxide for a period from 2 to 4 hrs. at room temperature, in order to convert cellulose into alkali cellulose.
2. **Pressing:** The soaked sheets are then pressed in order to remove the extra solution of sodium hydroxide. This solution is either reused or is sent to caustic recovery plant.
3. **Shredding:** A water-jacketed shredder or a kneading machine converts the sheets into loose, bread crumb-like material in 3–4 hrs. at room temperature.
4. **Ageing or maturation:** The alkali cellulose is stored in covered bins for 2–3 days at room temperature. During this period, oxygen is absorbed and depolymerization of alkali cellulose takes place. By suitable regulation of temperature and time of ageing, a desired viscosity of the material is obtained.
5. **Churning:** At the end of the ageing period, the alkali cellulose is transferred to a tank in which carbon bisulphide is added to convert alkali cellulose into cellulose xanthate. This tank is rotated at 2–3 rpm and is maintained at 30°C, because this reaction is exothermic in nature. During churning, the cream coloured liquid changes to orange-red or brown-red colour. Time of residence in the churning tank is from 3–6 hrs.
6. **Production of viscose:** This is achieved by thoroughly mixing cellulose xanthate with a 6.5% solution of sodium hydroxide and

water. The reaction requires 3–6 hrs. to go to completion at a temperature between 15°C and 17°C.

7. **Ripening of viscose:** This is done at a temperature 15°C–20°C for 4–5 days. During this period, the viscose is filtered and deaerated to free it from fibres and air bubbles, which can interfere with the spinning process. In addition, water free from hardness is required here, because the presence of hardness-causing salts can also affect the spinning process. Filtration is done by passing viscose in upward direction through cotton wool, in order to avoid air bubbles entering the solution during filtration. The filtered viscose is stored in tanks under vacuum for at least 24 hours prior to spinning.
8. **Spinning:** Conversion of viscose into filament is done in the spinning bath, which contains a mixture of zinc sulphate, sodium sulphate, sulphuric acid, glucose and water. The viscose is squirted into the bath through a rapidly rotating, perforated disc. Contact between the viscose and the contents of the spinning bath results in the formation of rayon thread.
9. **Finishing:** The thread is wound on spools and thoroughly washed with water to remove all chemicals used in the earlier steps of manufacture. Removal of sulphur is done by the treatment of the threads with a solution of sodium sulphide heated to 45°C. The next step is to wash the threads in water. Bleaching is done with 0.05–0.1% solution of sodium hypochlorite. The last step involves drying, polishing and finishing.

A general flow diagram, showing the various steps in manufacture, is given in Fig. 6.3.

6.3.1 Sources of Waste Water

The first source of waste water is the viscose, which may be drained if it does not meet the quality requirements. This can impose a heavy load on the waste water treatment facility. The next source is the caustic recovery plant, which may use dialysis or multiple effect evaporation for recovering sodium hydroxide from the waste water generated in the process of pressing. The spinning bath produces waste water containing sodium sulphate, zinc sulphate, glucose, sulphur. Washing of the spools also produces similar type of waste. In addition, spills, leakages in pipes and conveying systems and floor washings contribute to the waste water streams. Finishing oils used for conditioning the yarn and giving it lustre also find their way into the waste water streams. Waste water from toilets and canteens in the factory premises are similar to domestic sewage.

Among the pollutants mentioned above, zinc is an important pollutant due to its toxic property and its recovery potential. But it is also observed that zinc is strongly and permanently adsorbed on silt present in the receiving stream; this can reduce the toxic effect of zinc on the aquatic

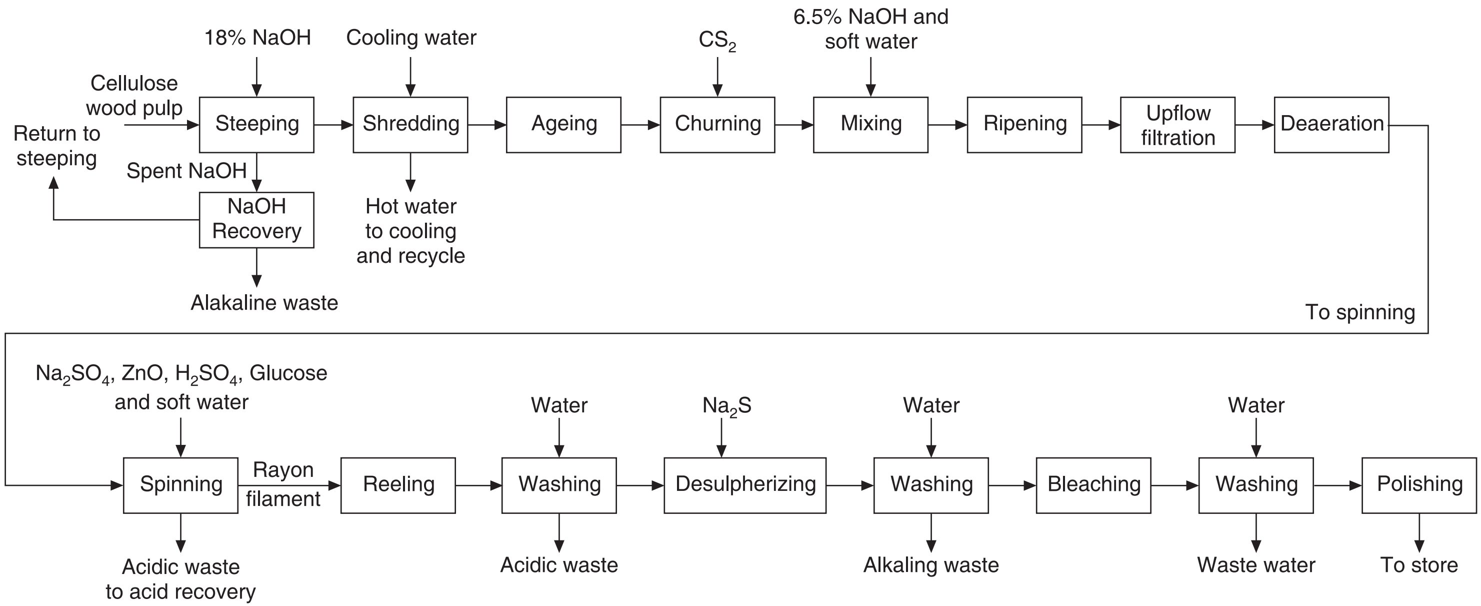


Figure 6.3 Viscose rayon manufacturing flow diagram.

organisms [32]. Another pollutant is the large quantity of fine fibres, which may be present in the waste water. They settle down to the bottom of the receiving stream and destroy bottom-feeding organisms. They can also cause fish kills by suffocating the aquatic organisms [33].

An average composition of raw waste from a rayon manufacturing plant is the following:

pH: 10.4, 5-day BOD: 700 mg/l, Suspended solids: 68 mg/l, Sulphates: 47 mg/l (after desulphurization) [33A].

Another study of the pollution of a receiving body of water near Mumbai revealed the following composition of raw waste water from a rayon mill [33]:

pH: 2.8–10.7, BOD (37°C): 60–140 mg/l, Chlorides: 30–234 mg/l, Sulphates: 40–1125 mg/l, Suspended solids: 50–150 mg/l, Total solids: 655–1600 mg/l.

6.3.2 Treatment of Waste Water

The nature of the raw waste water from a unit manufacturing rayon shows that it can be effectively treated by biological means only after it is given some form of pretreatment by physico-chemical means. An important step in pretreatment is the removal of zinc from the waste water stream. The theoretical solubility of zinc in pure water at pH 7.0 is 1.1 mg/l as hydroxide and 2.31×10^{-7} mg/l as sulphide [34]. It is precipitated as hydroxide at pH 11, but if lime is used for raising pH, concurrent precipitation of calcium sulphate can occur, especially with wastes containing high concentration of sulphates [35]. Caustic soda can also be used for this purpose.

The method of recovering precious metals by fluidized bed electrowinning is also applicable for the removal of zinc. The electrolytic cell consists of anodes of expanded mesh, while the cathodes are in the form of metal sheets. Inert beads are charged in the cell and are kept in suspension by continuous pumping of the electrolyte. The zinc gets coated on the cathode during electrolysis. After the process is completed, the deposited zinc is either peeled off or scraped from the cathode [36].

Besides being toxic to aquatic life, zinc, in concentration greater than 5 mg/l, gives an undesirable taste to drinking water. It also increases toxicity of cadmium synergistically. Its concentration in water can be reduced to a very low value by using ‘soluble sorbent clarification’, a proprietary process. It uses a specific chemical sorbent, which is soluble at low pH and insoluble at high pH. The pH of the waste water is increased to precipitate the hydroxides of dissolved metals. At the high pH, the sorbent offers additional surface area for the remaining dissolved metals to be adsorbed. The sorbent settles with the metals. It can be recovered by acidifying the sludge [34].

A modification to the manufacturing process, consisting of double steeping, helps to remove and reuse zinc [37]. Replacing harmful processed chemicals by enzymes has also been studied [38].

When the entire waste water from the mill is to be treated, all the streams, viz. acid waste, finishing waste, sulphide waste and waste stream from water treatment plant, are mixed together, resulting in a pH of about 4.5. This waste is then passed over limestone bed to raise its pH and is settled in a clarifier. The sludge generated is dewatered on drying beds and the clarified effluent is discharged to the environment, if it meets the stipulated quality standards. Further, improvement in quality can be had by removing zinc and sulphide and subjecting the waste water to biological treatment after mixing it with sewage generated within the mill's premises. Generally, nutrient supplementation is necessary to achieve the desired C:N:P ratio, although sewage is added to the waste water. Activated sludge process can remove up to 97% of the BOD from the waste water.

6.4 SYNTHETIC FIBRE WASTES

In this category are included cellulose acetate, nylon, polyester, acrylics and modacrylics. Synthetic fibres can be converted into synthetic fabric in one of the two following ways [39]:

1. Continuous filaments are used to manufacture 100% synthetic fabrics.
2. Staple yarns are used to produce fabrics that are blends of man-made fibres or man-made fibres and natural fibres.

Synthetic fibres differ from other fibres of animal and vegetable origin in absorbing little moisture. This leads to the formation of static electricity during production. This difficulty is overcome by using antistatic agents such as polyvinyl alcohol, styrene-based resins, polyalkylene glycols, gelatin, polyacrylic acid and polyvinyl acetate. They also serve as lubricants and sizing agents. They become a source of pollution when they are removed from the fabric during scouring. The manufacture of synthetic fibres can be controlled well. Therefore, natural chemical impurities are relatively absent in these fibres.

Manufacture of various fibres is briefly described in the following section.

6.4.1 Cellulose Acetate

The usual procedure consists of desizing, scour and dye bath or scour and bleach bath and two rinsings. The antistatic compounds are solubilized by diastatic or proteolytic enzymes before scouring with synthetic detergents. Dyeing is done by using disperse dyes, disperse developed dyes, acid and naphthol dyes. Disperse dyes have low solubility in water and are applied as fine dispersion. Sulphonated oil, aliphatic esters and softeners are applied to each dye at the rate of 0.02 kg per kg of fibre. The dye solution penetrates the fibre. Rinses following dyeing remove the swelling agent and the fibre contracts, trapping the dye in its body. Bleaching, if required, is done with peroxide or chlorine.

Wastes from the scour and dye baths average 50 kg BOD per 1000 kg of fabric. The volume of water required to process 1 kg of cloth averages 75 litres [39].

6.4.2 Nylon

Finishing of nylon is done by scouring with soap and soda ash, rinsing, dyeing and rinsing. Nylon fibres can be dyed by every class of dye. Unlike other synthetic fibres, nylon fibres dissolve to the extent of about 1% when processed. When nylon is used in blended fabrics, the choice of the dye depends on the other fibre. Sulphonated oils are used as dispersants in nylon dyeing. They contribute almost all the process BOD, which amounts to about 15 kg per 1000 kg of cloth dyed [39].

6.4.3 Polyester

Polyester fibre finishing is done by scouring, rinsing, dyeing and second scouring. Conventional dyeing is done from room temperature to boiling temperature, but dye carriers such as ortho-phenylphenol, biphenyl, benzyl alcohol, methyl naphthalene and chlorobenzene have to be used. When dyeing is done at room temperature, from 0.06 kg to 0.4 kg of carrier has to be used per kg of fibre. The scour waste averages 500–800 mg/l BOD, of which about 90% is contributed by the antistatic compounds used for lubrication and sizing [39].

6.4.4 Acrylics and Modacrylics

These two types differ from each other in their physical and chemical properties, but both are subjected to the same finishing techniques. They are dyed using acid dyes with cationic dyeing assistants and basic dyes with anionic dyeing assistants. The amount of carrier used ranges from 0.02 to 0.1 kg per kg of fibre dyed. Acid dye baths average 5.3 kg BOD per 1000 kg of fabric, the entire load coming from the dye carriers [39].

6.4.5 Synthetic Fibre Waste Water Treatment

As a rule, treatment of waste water from synthetic fibre manufacture should be similar to that provided for treatment of several chemicals. This is so because the raw materials used are pure compounds and contain very little impurities, which would be present in the industrial effluents. As already mentioned, nylon decomposes to a small extent and is, therefore, present in the waste water, along with process chemicals used in the manufacturing process. They contribute to the BOD in the waste water. Use of low BOD chemicals can reduce the pollution potential of these waste water to a certain extent.

The greatest pollution load is contributed by the dyeing process of polyester and acrylic fibres. In addition, odour, toxicity and high BOD are generated. But the suspended solids in the waste water are small. Therefore, it is possible to omit screens from the treatment train, which may consist of equalization, followed by chemical precipitation and biological treatment. Chemical precipitation is done to remove the toxic chemicals in the waste water before it is subjected to biological treatment. The removal efficiencies of various treatment processes are given in Table 6.7 [40].

Table 6.7 Removal Efficiencies of Various Treatment Process

Treatment method	Per cent removal efficiency of		
	BOD	Susp. Solids	T.D.S.
Screening	0–5	5–20	0
Sedimentation	5–15	15–60	0
Chemical precipitation	25–60	30–90	0–50
Trickling filter	40–85	80–90	0–30
Activated sludge	70–95	85–95	0–40
Lagoon	30–80	30–80	0–40
Aerated lagoon	50–95	50–95	0–40

Reduction of pollution due to these waste waters can be achieved if economical methods of recovering process chemicals for reuse are devised.

6.5 SILK AND JUTE MANUFACTURING WASTES

Silk occupied an important position in the textile industry in the past, till new and improved synthetic and semi-synthetic fibres such as rayon, nylon, cellulose acetate were produced. They have largely replaced silk as a fabric material.

Raw material for the production of silk yarn comes from the cocoons woven by silkworms around their bodies. These worms feed on the leaves of mulberry tree. The cocoons are plucked from the trees and subjected to boiling in soft water to separate the raw silk fibre. The dead worm and its shell form the solid waste, while the hot water, which has extracted the natural gum sericin and various soap solutions used for washing the fibre, constitute the liquid waste. The soaps are often supplemented with sodium carbonate, sodium silicate and sodium phosphate. The waste water is brown in colour, jelly-like, soapy and putrid. The average composition of the waste water is: total solids—4000 mg/l, of which 75% are volatile, BOD 900 mg/l [41].

The COD:BOD ratio ranges between 2.5 and 2.9. A composite mill in India, which manufactures silk cloth, starting from the silkworm and ending in finished goods, generates raw waste with the composition shown in Table 6.8. [43].

Table 6.8 Raw Waste Characteristics

pH value	6.0–7.0
Total suspended solids	700–800
BOD	1800–2000
COD	2800–3000
Total dissolved solids	2500
Oil and grease	Nil
Total Kjeldahl nitrogen	80–100
Ammoniacal nitrogen	Nil
Temperature	35–36°C

Note: All values except pH are in mg/l.

The above waste was treated by physico-chemical means using lime, alum and polyelectrolyte, followed by anaerobic treatment in a UASB reactor in which phosphoric acid was added to provide pH correction and supply a source of phosphorus. The UASB effluent was settled and the settled waste was treated aerobically in a fluidized aerobic biological (FAB) reactor. Tertiary treatment was provided by way of coagulation with lime, magnesium oxide, ferrous sulphate and polyelectrolyte, settling chlorination and reverse osmosis, since the treated waste water was to be recycled in the manufacturing process. If only dyeing and printing of the fabric is practised, the composition of the waste water is as follows:

pH value: 7.3
TSS (mg/l): 84
BOD5 (mg/l): 620
COD (mg/l): 1067

Treatment of the above wastes is done normally by biological means, which may be either trickling filtration or activated sludge process. In either case, nutrient supplementation is required to maintain an adequate C:N:P ratio.

Rigoni-Stern et al. [43A] treated waste water produced during printing of silk and lycra fabrics, using a single stage nitrification-denitrification scheme, followed by sand filtration and UV disinfection of the waste water. The treated effluent was used for washing and provided a saving of 30% in the consumption of fresh water.

Jute cultivation is commonly practised in West Bengal and Bangladesh, which produce nearly 90% of jute crop in the world. Retting of the harvested jute is done in water bodies. It consists of using chemical activators such as urea, ammonium sulphate, magnesium phosphate, or natural activators like banana stumps for loosening the fibres in the bark and separating them from the woody core by removal of gumlike substances. This action pollutes the water and renders it unfit for freshwater fish cultivation. Recycling of lime-treated water from such bodies allows fish yield from 600 to 800 kg per hectare against 1200 kg per hectare in the control pond [42].

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Chapter 7

DAIRY WASTES

Dairies are centres where raw milk is processed, either for immediate consumption or converted into dairy products such as whey, cheese, butter, dried milk powder and ice cream. These manufactured products may be supplied to other industries such as bakeries and candy manufacture for use as raw material in their own products. Dairies handling milk are classified as receiving, bottling, condensing, dry milk powder manufacturing, ice cream manufacturing, cheese making and butter making [1].

Waste water generated in a dairy contains highly putrescible organic constituents. This necessitates prompt and adequate treatment of the waste water before its disposal to the environment. Almost all the organic constituents of dairy waste are easily biodegradable. Hence, the waste water is amenable to biological treatment—either aerobic or anaerobic, or a combination of the two.

7.1 OPERATIONS IN A DAIRY [1]

Receiving: Raw milk is received from the fields. It is weighed and tested for its fat contents. It is stored in refrigerated containers before further processing.

Pasteurizing: This process consists of heating milk to 63°C for 30 minute and immediately refrigerating. It kills all organisms, including the pathogenic organisms, which may have entered the milk through diseased animals.

Bottling: The pasteurized milk is filled in bottles, or polyethylene sachets for distribution to the consumers. Bottling is invariably preceded by clarification and filtration.

Condensing: Pasteurized milk is heated and evaporated under vacuum. The concentrated milk is pumped through a closely set valve that breaks up fat globules. Sugar is added to the milk and the sweetened milk is filled in tin containers, packed and sent to the consumers.

Dry milk manufacture: Whole milk is preheated and centrifuged to separate the cream from the non-fat portion of the milk. The cream is pasteurized and used as ice cream mix. The non-fat portion of the milk is further heated and evaporated under vacuum to a controlled percentage of solids. The concentrated non-fat milk is then spray-dried.

Cheese making: Pasteurized milk is soured by adding a lactic acid-producing bacterial culture. The mixture is allowed to ripen under controlled temperature. The curd is then cut with knives and the excess whey is allowed to drain. Further, removal of whey is done by pressing the curd and the pressed blocks are stored under controlled temperature and humidity for the development of flavour and further ripening. It is then packaged and stored at low temperature.

Butter making: Cream to be made into butter is pasteurized and is ripened with bacterial culture. Churning at low temperature produces granules from the butterfat in the cream. Buttermilk is then drained from the churn, butter is washed, standardized for moisture and salt content and is worked further till it agglomerates into one mass. It is then packaged for distribution.

Casein making: Soured or spoiled milk is treated with mineral acid to produce casein. The casein is then precipitated. Casein is used in the manufacture of plastics, paints, resins and varnishes [2].

A general flow sheet followed in a dairy is shown in Fig. 7.1.

Milk solids consist essentially of carbohydrates, fats and proteins. Roughly the BOD of 1 kg of milk fat is 0.89 kg, 1 kg of milk proteins is 1.03 kg, and 1 kg of milk sugar is 0.69 kg. Dairy wastes are made of dilutions of whole milk and by-products. The BOD values of the products of milk are [3]:

Whole milk: 90,000–1,05,000 mg/l
Skim milk: 65,000–75,000 mg/l
Buttermilk: 55,000–65,000 mg/l
Whey: 25,000–35,000 mg/l

The manufacturing activities in a dairy are of the “batch” type, i.e. one batch of milk is processed, the equipment is drained, thoroughly cleaned and the next batch is taken for processing. As a result, the flow of waste water from a dairy comes in slugs. This fact should be taken into account in designing a waste water treatment plant to handle dairy waste water.

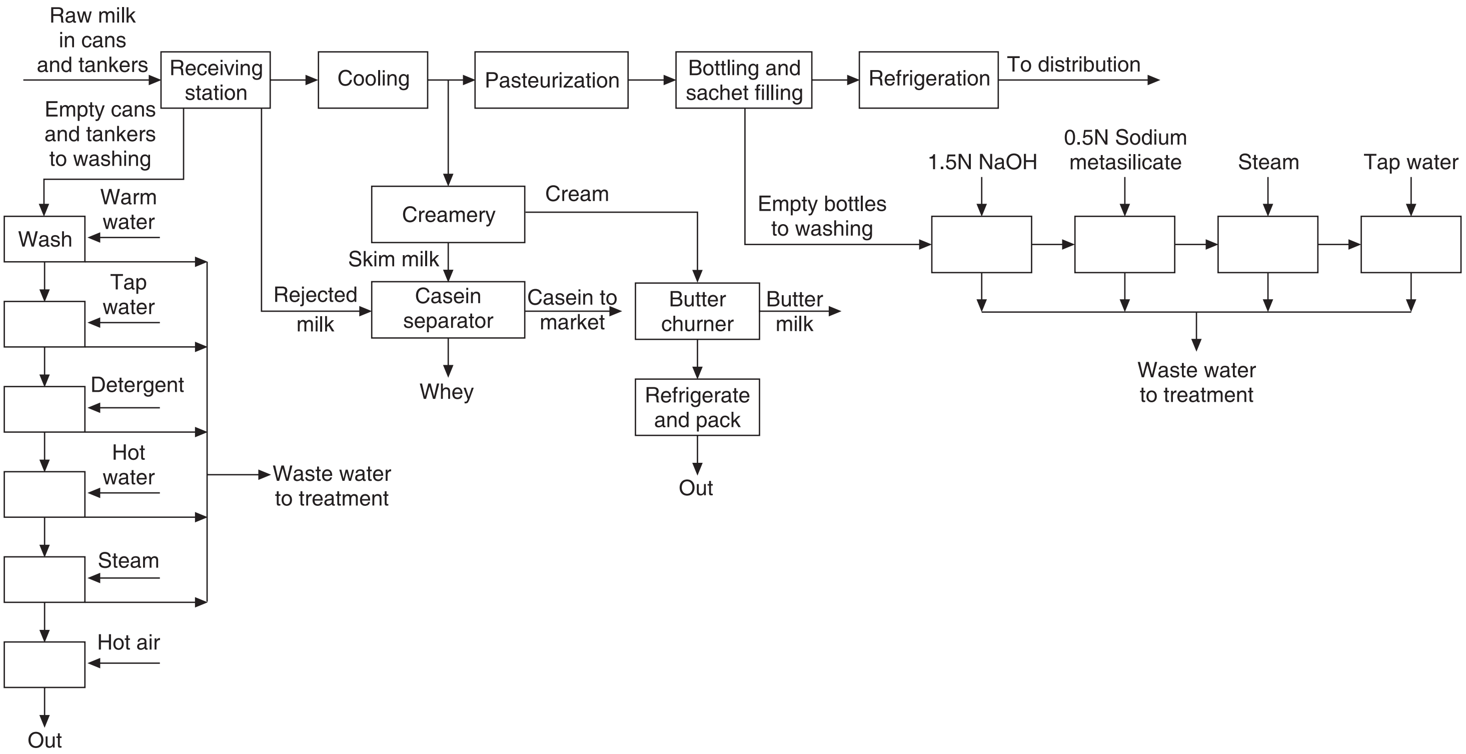

Figure 7.1 Flow diagram in a milk dairy.

The amount of water used in a dairy (and hence the volume of waste water produced) depends on its availability. However, an average value of waste water generated ranges between 4 and 8 litres per litre of milk processed. The bulk of water consumption goes towards cleaning of the equipment and floor washing. The average characteristics of dairy waste are: 5 day 20°C BOD 1200 mg/l, COD 1800 mg/l, suspended solids 600–800 mg/l, oil and grease 200–900 mg/l. The ratio of COD:BOD is favourable for applying biological methods of treatment preceded by some form of pretreatment such as flow equalization and oil and grease removal.

Biological methods of treatment include: (i) non-mechanized methods such as anaerobic ponds, aerobic oxidation ponds and combination of these two, and (ii) mechanical methods such as trickling filters, aerated lagoons and activated sludge process based on extended aeration. In large dairies, it is possible to use the anaerobic process such as anaerobic filter, or upflow anaerobic sludge blanket (UASB) process, followed by one of the non-mechanized or mechanized aerobic processes. Recently, sequencing batch reactors, aerobic as well as anaerobic, have been found to be effective in treating dairy waste waters [4].

7.2 SOURCES OF WASTE WATER

Besides the manufacturing areas and the equipment located there, a dairy also produces waste water from the operations of bottle washing, can and tanker washing, floor washing, water softening plant (if one is provided), boiler house and refrigeration plant. Chemicals and detergents used in the washing operations are also present in the waste waters. If milk is supplied in glass bottles, solid waste generated consists of broken glass pieces and aluminium foil (used to cover the mouth of the bottle). Where polyethylene bags are used in place of glass bottles, torn bags are also present in the waste water streams.

Washing of empty bottles, cans and tankers is done first with hot water, then with a chemical such as sodium metasilicate or a detergent and, finally, with steam. These are dried with hot air before they are returned to the raw milk suppliers. Essential steps in reducing the pollution load in the dairy include:

1. Allowing the cans and tankers to be emptied completely by keeping them in inverted position till almost all the milk is drained out.
2. Minimizing spillage and leakages in the bottling section.
3. Attending to leaks in pipes, valves and equipment promptly.
4. Observing good housekeeping practices.
5. Using minimum amount of water for cleaning operations.

Segregation of clean streams such as those from the boiler house and water treatment plant also helps in reducing the volume of waste water to be handled by the treatment plant. In addition, recycling of water, with or without treatment, should be practised wherever feasible.

7.3 TREATMENT OF WASTE WATER

As already mentioned, the organic impurities in dairy waste are easily biodegradable and, hence, can be conveniently subjected to biological treatment. In view of the high BOD value of the raw waste, it is possible to digest the whole waste anaerobically after reducing its oil and grease contents. Anaerobic treatment reduces the oxygen demand of the waste water by 70%–80% and results in a sizable reduction of power consumption for subsequent aerobic treatment. In addition, the gas produced by anaerobic digestion can be used as a source of energy. A dairy in Mumbai has practised this treatment for the past few years and generated enough electric power from the gas produced to meet the dairy's entire power requirement [5]. Anaerobic treatment of dairy waste is shown capable of offering usable gas within the dairy itself, with an attractive payback period of 18 months (as per 1995 figures) [6]. Satish and Gopalakrishna [7] used an anaerobic contact filter containing sand as the filtering medium for treating synthetic dairy waste. They found 90% BOD removal at a loading rate of 0.42 kg/m^3 and 73% at a loading rate of 2.2 kg/m^3. Harischandra and Saxena [8] used anaerobic digestion process for treating the waste water produced in the manufacture of cheese. A detention period of 15 days at a BOD loading rate of 2.9 kg/m^3 of digester volume gave 86% BOD reduction. The laboratory-scale digester was seeded with 20% cow dung slurry and was maintained at 37°C. The maximum gas yield was found to be 1.29 m^3/kg of volatile solids destroyed. Canovas-Diaz and Howell [9,10] studied the effect of overloading on a fixed film anaerobic downflow reactor treating cheese and whey wastes. They observed that addition of nickel in the feed greatly enhanced the treatment process, because nickel reduced the volatile acids concentration considerably. COD removal of 85% was observed at an organic loading rate of 5.5 kg COD/m^3 of reactor volume. Gas production was 2.8–3 m^3 per day. Taori et al. [11] treated waste water from an operating dairy producing pasteurized milk and butter in two upflow anaerobic pilot filters in series. The filters were fed waste water without any seed material. It took 50 days for acclimation. The mean COD loading rates for the two filters were 1.35 kg/m^3 and 1.188 kg/m^3, respectively. The COD removal was 88% at hydraulic retention times of 3.58 hours and 3.52 hours, respectively.

Dairies located in rural areas, where land is usually available, can conveniently dispose of their waste waters by spreading on land. Rajagopalan [12] has discussed at length the merits and demerits of the various systems of irrigation, viz. flood irrigation, spray irrigation and ridge and furrow irrigation. A case study for a dairy processing 300 m^3–400 m^3 of milk is also presented in the paper. Alagarasamy and

Bhalerao [13] discussed the use of aerated lagoons and oxidation ditches for the treatment of dairy wastes. They found the system rate constant for aerated lagoons as 0.274 per day for effecting 90% BOD removal at a retention time of 3.7 days. If the waste water is to be disposed of on land for irrigation, they recommend a retention time of 1.15 days. But if the treated effluent is to be discharged into a water course they prefer an oxidation ditch. These authors [14] have also presented the cost economics of treatment of dairy wastes by oxidation ponds, aerated lagoons and oxidation ditches.

While evaluating the parameters affecting anaerobic treatment of dairy wastes, Perle et al. found that it is necessary to reduce the milk fat content in the waste water to less than 100 mg/l [15]. Kolarski and Nyhuis [16] reported the performance of four sequencing batch reactors (SBRs) operating in parallel on three eight-hour cycles. They found BOD, total nitrogen and total phosphorus removals of 99%, 90% and 97%, respectively. Kaiser et al. [17] reported that a temperature-phased anaerobic biofilter treating synthetic milk waste could remove total COD by 90% at a loading of 16 kg COD/m^3 per day. Hawkes et al. [18] evaluated four pilot plant anaerobic units viz. Upflow anaerobic sludge blanket (UASB), anaerobic filter, contact filter and fluidized bed, treating ice cream wastes. They found UASB to be the least efficient at a loading rate of 2 kg COD/m^3 per day.

A full-scale aerobic sequencing batch reactor designed to treat 1000 m^3 of dairy waste water was studied by Bian et al. [19] at a COD loading rate of 1.2 kg/m^3 per day. The mean effluent concentrations were: COD 44 mg/l, BOD 10 mg/l and total suspended solids 4.6 mg/l under varying organic and hydraulic loadings. Scott and Smith [20] investigated the dual use of ceramic membrane for aeration and filtration in the aerobic treatment of ice cream waste. Influent COD and BOD concentrations of 13,330 and 6500 mg/l, respectively, were reduced by 95%. A laboratory investigation of two anaerobic sequencing batch reactors in series by Welper et al. [21] showed 95% and 90% COD and BOD reductions, respectively, when the two reactors were maintained at temperatures of 55°C and 35°C respectively, at COD loading of 22 kg/m^3 per day.

Gonzales and Stover [22] found addition of micronutrients to a dairy waste increased methane production rate significantly, while addition of cultured bacteria provided no positive benefit. Milk is often seen to turn sour during hot weather. It becomes unfit for reconditioning before its use in bottling plants and it has, therefore, to be wasted. Recovery of usable by-products from sour milk such as buttermilk, whey, casein, lactose and butter oil is an effective way of reducing pollution due to dairy wastes [2].

If dairy waste is to be treated aerobically, each kilogram of milk solids requires 1.25 kg of dissolved oxygen for its oxidation. A unit weight of milk solids produces half its weight in new cells during aerobic biological treatment. Endogenous respiration rate of these solids ranges between 0.1 and 0.2 per day at 20°C [23].

Milk waste from Siklam Mandara pasteurization plant in Alexandria, Egypt was treated in an oxidation pond. At 10 days' retention time, and a BOD loading of 246 kg/hectare per day, 80–90% BOD removals were obtained. A liquid depth of 75 cm was found to be most convenient. *Pandorina* constituted a major member of the flora, highly adaptable to dairy waste [24].

It is possible to treat dairy waste in sewage treatment plant also without reduction in the plant's performance, as experimented on a plant in the USA. Sludge digesters in this plant, designed to handle primary sludge, along with ground garbage and excess activated sludge, were fed up to 18% of the total daily load in the form of whey (containing 5.5% total solids and a BOD of 35,000 mg/l).

It showed no harmful effect on gas production [25]. In another plant, about 416 m^3 of condensed milk (dry solids 24.5% and volatile solids 94.4%) had to be discharged into the plant's ground garbage well. It was pumped to the digester in 24 hours, and showed spectacular increase in gas production in a day, which fell off gradually to its original figure in a week's time [25].

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Chapter 8

SLAUGHTERING, MEAT PACKING, POULTRY PROCESSING, FISH PROCESSING AND RENDERING WASTES

A slaughterhouse is an establishment for the killing of animals and dressing of meat. Finished products include the fresh carcass and variety of meats such as hearts, livers, kidneys and tongues. A plant, which processes fresh meat, is called a packing plant. In meat processing, fresh meat received from the slaughterhouse is chilled, trimmed and cut to produce various cuts of fresh meat and trimmings. Packing plants also produce a number of by-products such as lard and edible tallow, and material for animal feeds, glue and soap manufacture. Rendering plants process inedible scrap such as bones and trimmings [1, 2].

A general flow sheet of a slaughterhouse is tabulated here [2A]. Nearly all slaughterhouses have stockyards to hold the animals before they are slaughtered. The types of wastes produced by separate operations are tabulated [2].

Source	Waste
Stockyard	Manure
Killing floor	Blood
Dehairing	Hair and dirt
Insides removal	Paunch manure and liquor
Rendering	Press liquor
Carcass dressing	Flesh, blood, grease, manure
By-products	Grease, offal

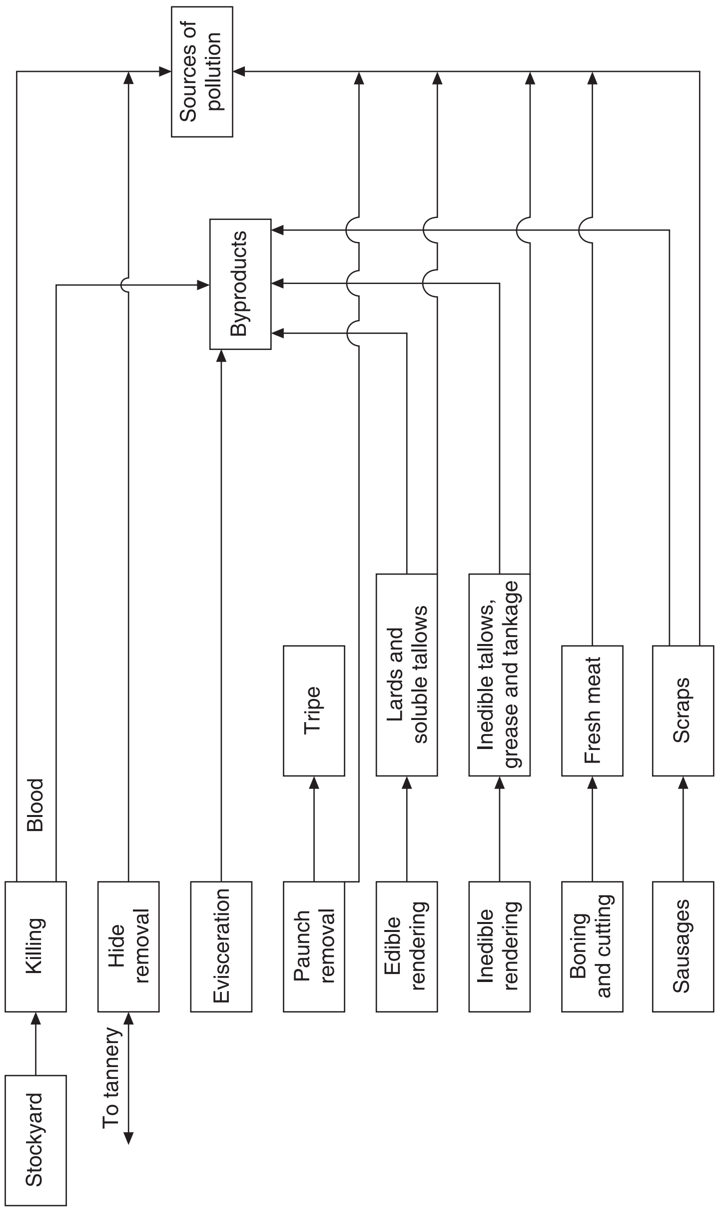

Figure 8.1 General operations in a slaughterhouse.

8.1 OPERATIONS CARRIED OUT IN SLAUGHTER-HOUSE, MEAT PACKING PLANT AND RENDERING PLANT

1. **Stockyard:** The animals are brought before midnight to be slaughtered the next day. They are not given anything to eat, in order to reduce their stomach contents. Waste water generated here consists of urine, dung, straw and wash water from washing of the vehicles, which brought the animals to the stockyard [3].
2. **Killing floor:** The animals are killed, carcasses are chilled and the blood is collected. Hides are stripped from the animals' bodies, the abdominal mass is removed and the carcasses are split into smaller pieces. The cutting process generates blood, bone dust, tissue and fat [2A].
3. **Packing plant:** Blood is collected, coagulated by heating and filtered. Various products such as sausages containing additives, like pastry, soya, spices, preservatives are made. Some packing plants recover hair and produce gelatin for sale to glue manufacturers [2].
4. **Rendering plant:** The rendering plant handles all inedible products arising out of the slaughtering and packing processes, e.g. bones, hairs, hooves, horns, hide trimmings, whole hides, grease, fat, etc. They are processed and sent to other manufacturers like tanneries, glue and gelatin makers.

8.1.1 Characteristics of Waste Water

These wastes are intermittent in flow, have high BOD, high suspended solids, are odorous and create heavy sludge deposits when discharged into water bodies. The volume and quality characteristics of the waste water vary from one plant to another and from one season to another, depending on the number and type of animals slaughtered and housekeeping practices followed. Saxena [3] surveyed 4 meat works and has given in Table 8.1 the raw waste water characteristics.

Table 8.1 Raw Waste Water Characteristics

Flow, (m^3/day)	Suspended solids	pH	BOD	Grease	Settled BOD
900	700–1000	7–8	2000	—	1200
720	900–2000	7.5–10	1900	—	1400
950	1000–3100	7–9.5	1900	—	1400
—	1500–2000	6.7–7.4	1600	1200	1000

Note: All values except flow and pH are in mg/l.

In large slaughterhouses, blood is collected and processed for feed and fertilizer. Blood has a BOD of about 1,65,000 mg/l, clots readily and decomposes rapidly. Paunch manure is segregated and disposed of separately. The quantity of paunch manure varies from 4.5 kg to 18 kg per animal [2]. It is normal practice to segregate cooling water from the slaughterhouse and meat packing plant. This practice facilitates recovery of salable by-products. Removal of grease from the waste water streams helps greatly in reducing pollution load on the downstream treatment units. Paunch manure, cutting and trimming floor wastes, hair and sludge are removed by using screens [2].

Slaughterhouses generate substantial amounts of solid wastes. If they are not handled properly, they can cause serious pollution problems. The average solid waste produced (animalwise) is given in Table 8.2 [15].

Table 8.2 Solid Waste Produced Animalwise

Animal	**kg/head**	**Quantity of solid waste** **kg/TLWK**	 **% of animal weight**
Bovine	83	275	27.5
Goat/sheep	2.5	170	17
Pig	2.3	40	4

Note: TLWK = Tonne of Live Weight Killed.

8.1.2 Treatment of Waste Water

The type of treatment depends on the size of the industry and the mode of disposal of the treated waste water. Small industries may use screening, sedimentation, filtration and chlorination. Medium and large industries may provide chemical and biological treatment in addition to screening and sedimentation. Sedimentation removes from 30% to 35% BOD and 60% to 65% suspended solids.

Chemical treatment with alum is reported to give a poorly settling floc, while ferric chloride and ferric sulphate produced better results. Chlorination of the waste water at low pH (below pH 4.2) required the least amount of chlorine [2]. A combination of ferric chloride and chlorine, used in tanks of 'Fill and Draw' type works very well for small plants [4].

Invariably preceded by physical and/or chemical treatment, biological treatment may be in the form of trickling filtration, activated sludge process, aerated lagoon or oxidation pond. Two-stage trickling filtration is reported to give 94% BOD reduction [5]. Pre-aeration and settling, followed by activated sludge aeration (with 90% return sludge to aeration tank and 10% to pre-aeration tank) has given an overall BOD reduction of 98.8% [6]. It indicates that these wastes can be successfully treated by anaerobic digestion in continuous upflow units. Loaded at the rate of 1.6 kg BOD per m^3, producing from 96% to 98% BOD removal. Gas production was about 0.05 m^3/kg. of volatile solids added. Laboratory evaluation of an anaerobic sludge blanket reactor treating beef slaughterhouse process waste has shown that granular sludge works as well as flocculent sludge at low HRT. At an HRT of 30 hours, granular sludge gave more than 70% BOD reduction [7]. Nakhla and Lugowski [8] upgraded an extended aeration system following dissolved air flotation (DAF). They converted the biological system to a biological nutrient removal system and optimized the DAF system. This resulted in considerable improvement in its performance at reduced running cost.

Malhotra and Khanna [9] presented the results of a laboratory investigation on models of aerobic pond designed on non-dimensional approach. They concluded from the study that economic treatment could be given to waste water from a small slaughterhouse in aerobic stabilization pond at an organic loading of 160 kg/ha per day with a detention time of 21 days, the BOD removal efficiency being 92%. These results were obtained for meteorological conditions at Roorkee (Lat 29°52′ N).

Saxena [10] studied the process of anaerobic denitrification of nitrified, treated slaughterhouse waste water. In a laboratory study, using an anaerobic upflow filter and methanol as a source of carbon, 95%–98.5% reduction in the nitrite and nitrate concentration was observed at loading rates of 2.64–2.8 kg nitrate nitrogen/m^3/day.

Saxena, Singhal and Hasija [11] identified 15 pathogenic fungi from the effluents of a gelatin manufacturing factory, whose effluent was being used for irrigation. Of the 15 fungi, 6 were pathogenic to man, 1 to crops and the rest, pathogenic to both man and crops. Jayangoudar et al. [12] studied the suitability of stabilization pond for giving further treatment to anaerobically treated waste water from slaughterhouse and noted that this effluent needed dilution with domestic sewage to obtain satisfactory algal growth. BOD reduction was observed to be 91.2%.

Ossein, an albimunoid material, which remains after bones are treated with dilute hydrochloric acid and are employed as raw material for the production of gelatin and glue, was subjected to coagulation with alum, lime, magnesium sulphate, ferric chloride and combinations of these [13]. Commercial alum gave suspended solids removal of 79% and COD removal of 45% at an optimum dose of 500 mg/l. Lime alone gave 76% suspended solids removal and 55% COD removal at 400 mg/l. Magnesium sulphate and ferric chloride were found to be unsuitable. Alum with lime produced sludge with good drainability.

A 630 m^3 UASB reactor, treating slaughterhouse waste, operating at an HRT of 19 hours and a COD loading of 4 kg/m^3 per day, gave a COD reduction efficiency of 85% and produced 0.9 m^3 of biogas per m^3 of waste water. The construction of the plant was preceded by studies on a pilot plant of 6.5 m^3 [14]. Kharat et al. give an overview of solid waste generation and its management in slaughterhouses. The methods described include composting, biomethanation, dry and wet rendering and incineration [15]. Meat wastes have been treated in shallow aerobic ponds 0.66 m deep at organic loading of 0.024 kg BOD/m^2/day. The waste was presettled and the BOD of settled waste water was 175 mg/l.

BOD reductions of 96% in summer and 75% in winter were observed [16]. An anaerobic pond with 6-day detention time, with a liquid depth of 4.3 m, loaded at 0.224 kg BOD/m^3/day, followed by aerobic pond with 19-day detention time and a liquid depth of 0.9 m, loaded at 0.0056 kg BOD/m^2/day gave an overall BOD reduction from 1100 mg/l to 67 mg/l [17].

A full-scale anaerobic contact process, treating meat packing waste, operated at 30–35°C, at a COD loading rate of 2.5 kg/m^3/day and an HRT of 13.5 hours, gave 90% COD removal [18]. Obayashi and Roshanravan [19] obtained 70% COD reduction from anaerobic filter loaded at 2 kg COD/m^3/day. Hanumanulu [20] conducted laboratory-scale studies on the treatment of slaughterhouse waste using anaerobic followed by aerobic process. The HRT in anaerobic digester was 5 days, while aeration time in activated sludge was 23 hours. BOD reduction of 95% was easily achieved by this combination.

8.2 POULTRY PROCESSING WASTES

Poultry processing is a specialty segment of the meat industry. Poultry plants are similar to slaughterhouses, but produce waste water different from those of the latter. Therefore, methods of treatment are somewhat different from those of slaughterhouses. This industry is generally located in rural areas, but may also be found in urban areas if a ready supply of birds is available in the near vicinity.

The sequence of processing operations is: live birds receiving, killing, bleeding, plucking, eviscerating (removal of internal organs), chilling and packing in ice or freezing for transportation. It is a good practice to receive and process poultry on the same day, without holding the live birds.

Wastes are produced in this industry from live poultry holding, killing, eviscerating and defeathering, scalding and chilling. Plant washup operations also contribute some pollution load. The major source of pollution is the waste blood, which contains feathers, dirt and some manure. Approximately 6% of the poultry body weight is blood, chickens contain enough blood to equal a 5-day BOD of 8 kg per 1000 chickens processed.

Prior to defeathering operation, the birds are immersed in hot water to relax feather follicles and to facilitate defeathering. This operation produces a continuous flow of waste water, which is high in pollution strength. Waste water flowing out of the defeathering machine and eviscerating machine is passed through a rotary or vibratory screen. The screened material is either buried or incinerated.

Grease removal from the waste water forms another important step in pretreatment. Grease content may vary between 0.5 and 1 kg per 1000 birds [21].

Visittavanich [22] gives the average characteristics of poultry processing waste water as shown in Table 8.3.

Table 8.3 Average Characteristics of Poultry Processing Waste Water

Parameter	Mean	Range
COD	2110	1260–3260
5-day BOD	1010	520–1740
TKN	150	90–200
Total solids	1940	1290–2640
Total phosphorus	14	12–17
pH	7.1	6.7–7.7

8.2.1 Treatment of Waste Water

Rusten et al. [23] have described biological pretreatment required for poultry waste water in a plant in Norway. It consists of an aerated equalization tank, followed by two moving bed biofilm reactors in series. The soluble COD removal was 90–95%. Le Roux, Lanting and Sorensen [24] reported that a full-scale treatment process for slaughterhouse wastes using approved food additives as coagulants, followed by dissolved air flotation also proved useful for poultry wastes.

A fixed growth biofiltration process, followed by an oxidation ditch was found to meet BOD and ammonia nitrogen requirements in the treated effluent [25]. Freiss [26] has given an overview of managing primary solids from poultry processing. It includes land application, composting, anaerobic treatment and rendering as alternatives. Wilson et al. [27] discussed the selection, design and startup of a sequencing batch reactor system to upgrade the effluent from a poultry processing waste water treatment plant using dissolved air flotation system. Despite some startup and operating problems, the system was able to meet the design objectives of 15 mg/l each of BOD and suspended solids in 1 year.

Richardson and Savage [28] also described the results of a waste reduction programme at a poultry rendering facility. Significant reduction in the use of water and waste load was realized from the programme.

8.3 FISH PROCESSING WASTE

Waste waters arising out of fish processing include those generated in the fishing vessels, filleting plants, fishmeal plants, fish stick plants and fish canneries. The fishing vessels discharge varying quantities of ice and a large amount of brine, mixed with fish slime, scale, blood and oil. Waste water from the filleting plant is similar to that from the fishing vessels, but contains viscera, which are separated and sent to reduction plant for processing into fishmeal or condensed fish solubles. The fishmeal plant has a waste similar to the two above-mentioned sources. Large amount of protein and small amount of carbohydrates are present in the fish stick plant waste, while waste water from fish canneries contains proteinaceous material, oil and detergents from can washing [29].

Depending on the prevalent rules and regulations, wastes from fish processing are disposed of into harbours from where the fish were landed. However, if treatment is required, it takes the form of biological process, either aerobic or anaerobic, or a combination of the two.

8.3.1 Treatment of Waste Water

Boardman et al. [30] evaluated UASB technology in both batch and continuous modes, and achieved BOD, COD and TSS removals of 87%, 83% and 83%, respectively. They observed that sodium levels of 5250 mg/l had an adverse effect on the treatment. Mendez et al. [31] used anaerobic filter for treatment in mesophilic and thermophilic temperatures. They got 64% COD removal at mesophilic temperature at a loading rate of 24 kg/m^3/day and 73% removal at thermophilic temperature at a loading rate of 9 kg/m^3. Both reactors were operated at high chlorides (8 to 19 gm/l) and sulphates (0.6 to 2.7 gm/l) resulting in high H_2S in the gas produced.

Boardman and McVeigh [32] used laboratory-scale UASB for the treatment of crab processing waste water. They achieved more than 90% BOD and COD reductions at average loading rates of 5.7 kg COD/m^3/day. Inhibition of acetate-utilizing methanogenes was found to be directly proportional to the concentration of unionized ammonia in the range of 8–155 mg/l.

Anaerobic treatment of a high salt content waste water due to hydraulic unloading of fish from ships was studied by Aspe et al. [35] Inoculum from marine sediment was found to be better than that from pig manure in starting the test reactors. Kinetic parameters were determined during the study, along with inhibitory limits of sulphates, hydrogen sulphide and sodium.

Wu et al. [34] found that gravity separation (HRT 30 min) and induced air flotation of the waste water gave oil and grease removals of 57% and 75%, respectively.

A study on the nitrification of a high-ammonia (NH_3) waste water, generated by anaerobic treatment of fish meal production waste water, indicated specific removal rates up to 1.5 gm COD/gmVSS/day and 0.25 gm N_2/gm VSS/day. At loading rates up to 0.6 gm TKN/gm VSS/day, the nitrification rate was 0.57 gm NO_X/gm VSS per day [35]. Hwang and Hansen [36] characterized trout processing wastes and investigated the potential for biological acidification. They reported that 92.9% of the COD was due to protein, which affected the formation of odd-chain organic acids under acidogenic conditions.

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Chapter 9

TANNERY WASTES

Tanning industry is one of the oldest industries in India. It involves conversion of animal hide or skin into an end product useful for making leather goods such as shoes, bags, purses, belts and clothing. Tanning of the raw hide is done either by vegetable tanning process, which yields thick, heavy duty leather, or by chrome tanning process, which gives light, thin leather. The manufacturing process starts with the removal of unwanted layers from the hide, allowing the tanning agent to penetrate the hide and convert it into a pliable material, which is finished with various colours and surface finishes.

Raw hide, taken from the dead animal's body, brings with it hair, underlain by epidermis, fatty tissue and corium ($C_{102}H_{149}N_{31}O_{38}$). It is the corium which yields leather. Corium is a semisoluble protein, which, when boiled in water, gives glue and gelatin, but when treated with tanning agents, yields leather.

9.1 MANUFACTURING PROCESS

Hides, as they are received from slaughterhouses, are usually soaked in salt solution to preserve them from microbial attack. The salt-soaked hides become very stiff when they are dried prior to transportation to the tanneries. The waste water streams produced during manufacture, can be grouped into (a) strong and intermittent streams, and (b) weak and continuous streams. A general flow sheet is given in Fig. 9.1.

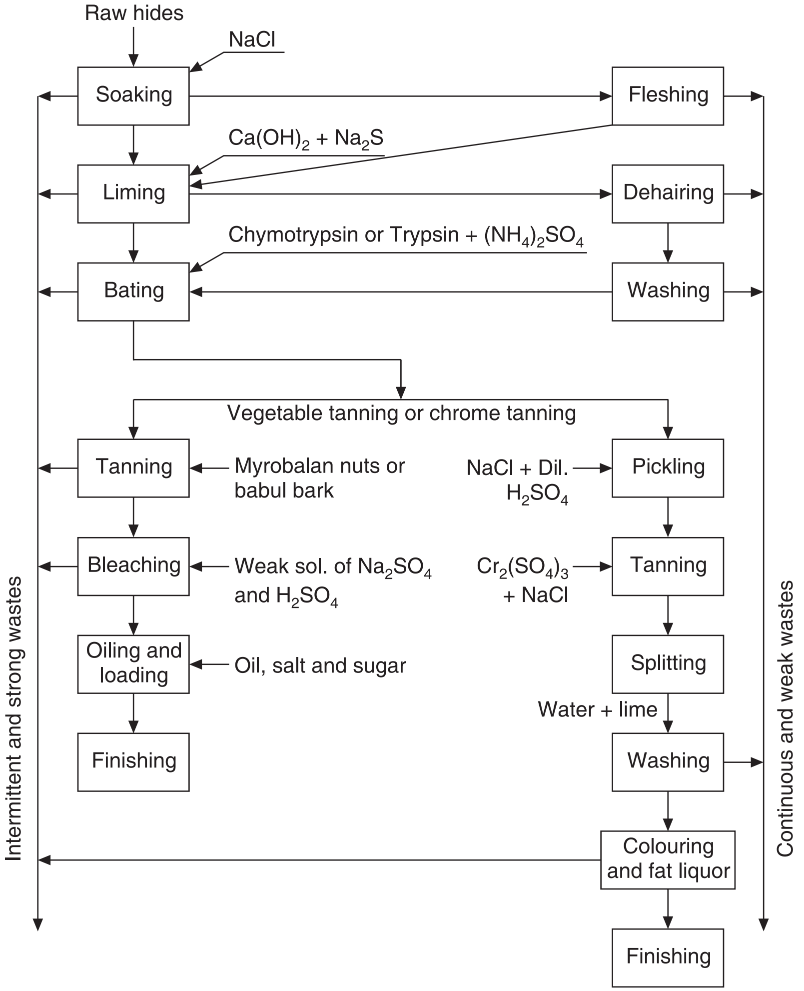

Figure 9.1 Vegetable tanning and chrome tanning.

The first step is, therefore, **soaking** the hides in water to remove the preservative salt and to remove the hides' stiff nature. Soaking may be done for 5–10 days. It produces a strong but intermittent waste water stream, because the salt-laden water is discharged occasionally. This stream contains, in addition to the salt, dirt, dung and blood and has a dark olive green colour. The next step is called **fleshing**, which removes the fatty tissue from the hides. This may be done either manually or by mechanical means. A continuous flow of water is used in this step in order to carry away the fleshings. This results in generating a continuous stream of waste water, which is quite putrescent in nature. **Liming** is the next step, in which the hides are treated with lime and an alkaline reducing agent like sodium sulphide (Na_2S). This chemical helps in the swelling process of the hide. The hair on the hides is also loosened. In the process of **unhairing**, the loosened hair is removed by mechanical or manual means. They are separated from the wash water with the help of screens. Washing of the hides also removes excess lime used earlier. An important step in preparing the hides for tanning is that of **bating**. It is done to reduce the pH, reduce the swelling, peptize the fibres and remove the protein-degradation products. Bating is generally accomplished with ammonium salts and a mixture of commercially prepared enzymes, predominantly trypsin and chymotrypsin. Bating makes the grain silky, slippery, smoother and more porous and diminishes the wrinkles on the hides [1].

The above-mentioned steps are common to both vegetable tanning and chrome tanning.

9.1.1 Vegetable Tanning

This process uses tannins obtained from tree barks of chestnut, oak, quebracho, myrobalan or wattle. Vegetable tanning is done to get both heavy leather and light leather. For producing light leather, the hides have to be split into thin layers. Vegetable tanning may be done from one week to three months. Countercurrent method of tanning is commonly used in which the hides first come in contact with weak liquors exhausted by use in other vats. These are called the ‘tail liquors’ and are the only regular discharge from the process. The hides move progressively to vats containing stronger and fresher solutions until the desired degree of tannage is obtained. In tanning heavy hides, the last vat may contain layers of solid tan bark placed between the hides [2]. When heavy leather is to be made, the tanned hides are subjected to bleaching for the removal of excess tannin and the resulting colour to some extent. Bleaching is done with the help of weak solution of soda ash, weak solution of sulphuric acid and a final rinse with water. The quantities of chemicals used are 0.75 kg of soda ash and 2 kg of sulphuric acid per 100 kg of hide [2].

Heavy leather is then subjected to finishing operations such as treatment with oils to give flexibility and addition of salts and sugar to add weight. The leather may then be rolled, polished, and given artificial grain.

Light leather, after splitting, is subjected to thorough washing and dyeing. The desired degree of flexibility is achieved by ‘fat liquoring’, in which the dyed leather is treated with water emulsions of various oils. The exhausted solutions from these operations are discharged frequently and contribute to the general waste a group of coloured solutions and oily emulsions, which are not present in a tannery producing heavy leathers.

9.1.2 Chrome Tanning

The process of chrome tanning is of a shorter duration than vegetable tanning and produces a more resistant leather. After bating, the hides are subjected to pickling, a process in which sodium chloride (5%–8% strength) and sulphuric acid (0.75% strength) are used. The reaction is allowed to continue for 10–16 hours. Tanning is done by charging the hides in drums containing basic chromium sulphate and sodium chloride. The latter promotes penetration of the chromium salt into the hides. Towards the end of the tanning period, sodium carbonate or some other alkali is added to the drums to promote combination of the tanning material with the hides [2]. The tanned hides are then thoroughly washed with water and neutralized with lime. They are then subjected to colouring, fat liquoring and finishing.

There are a few special tanning processes aimed at producing white garments, chamois leather, etc. in which sheepskin is the raw hide. These skins may be tanned using chrome tanning chemical or alum or even vegetable tanning agents.

The operations of soaking, fleshing, liming and unhairing are carried out in the **beam house**, bating and washing of hides is done in the **scrub house**, while tanning, bleaching, fat liquoring and finishing is done in the **tan yard**. Washing, liming, bating, tanning, bleaching and dyeing produce strong but intermittent wastes, while fleshing, unhairing and washing to remove excess lime and excess tannin produce weak but continuous waste streams.

Solid wastes generated per tonne of raw hide processed are given in Table 9.1. [3]

Table 9.1 Solid Wastes from Raw Hide Processing

Solid waste	Generation kg
Salt from shaking of raw hides	75–90
Salt from solar evaporation pans	200–225
Hair	100–125
Raw trimmings	50–60
Lime sludge	50–70
Fleshings	100–125
Wet blue trimmings	25–40
Chrome splitting	55–75
Chrome shavings	80–100
Buffing dust	50–75
Dyed trimmings	30–60
Sludge (35% dry solids basis)	300–400

This above waste matter has commercial value, in that the salt can be recovered and reused, hair are used for making plaster binders, raw trimmings can be converted into glue and gelatin, or are useful for making leather boards, lime sludge is useful for correcting acidic soils, fleshings are used as poultry feed, chrome sludge can be converted into bricks and spent vegetable tan bark is used as fuel [3].

Water consumption in litres per kg of raw hide processed in various states of India is [3]

Punjab: 100.
Tamil Nadu: 35–40
Uttar Pradesh: 40
West Bengal: 50

A ‘tannery equation’ developed after a survey of about 500 tanneries in India is [3]

1 kg hide/skin + 50 kg water + 0.5 kg chemicals = 0.3 kg leather + 50 kg effluent + 1.2 kg solid waste.

9.2 DISPOSAL OF WASTE WATER

Waste water produced per tonne of hide processed ranges between 35 and 40 m^3. Tannery waste water may be disposed of on land for irrigation, into municipal sewers or into the sea (if the tannery is located near the sea). But these wastes have very high total dissolved solids because of the use of salt as preservative. The TDS may be as high as 20,000 mg/l. Therefore, the raw hides are dusted before soaking to remove the dried salt. Further, soaking is done in a series of tanks and water from the first tank, which has the highest concentration of salt in it, is stored in evaporation ponds and the dried salt is disposed of with other predustings. This step reduces TDS considerably, but not low enough to meet irrigation water standards. If the waste water is treated after this step, it can be used for

1. Aquaculture, in which a large amount of protein material in the form of fish is produced in a small area. The high organic content of the waste water helps in increasing the yield of fish.
2. High-rate transpiration system, in which plants like bamboo, neem and shishum, with high transpiration capacity are planted in specially designed fields with wide ridges and furrows. Such a system permits the disposal of from 250 to 450 m^3 of waste water per hectare per day without the risk of polluting groundwater, because all the applied water is used up.
3. Cultivation of grass in constructed wetland systems. Disposal into the sea can also be done, taking care to see that the waste water will not return to the shore during high tide.

If the raw wastes are disposed of in streams, they exert a high oxygen demand, impart colour, give undesirable taste and odour to the receiving water, form sludge deposits at the bottom of the stream, destroy fish food and cause chromium toxicity to fish. Bathers in such streams are also exposed to *anthrax bacilli* [4].

When discharged on land, they adversely affect the soil productivity because of the high sodium absorption ratio. Some complex organics such as tannin, are also inhibitory to plants. Discharge of raw wastes into municipal sewers results in the deposit of calcium carbonate, formed by reaction between lime and carbon dioxide. Hair, which are present in the waste water, act as binding agents and form a thick mortar, which chokes the sewer. Concrete sewers can also suffer from corrosion due to the presence of hydrogen sulphide [4]. It is possible to safely dispose of raw tannery waste into municipal sewer if the flows of waste and sewage are in the ratio of 10:100. But screening and settling are necessary before discharge to the municipal sewers.

Pollution due to these wastes can be reduced at source by taking the following measures:

Reduce water consumption by (a) good housekeeping, (b) segregation of cleaner streams for direct reuse without treatment, e.g. wash water after bating, pickling, neutralization and dyeing can be used for washing after soaking and liming and for floor washing, (c) adoption of batch washing instead of continuous washing, (d) treating individual streams and recycling them in the same process (taking care to see that such reuse does not adversely affect the quality of finished goods) [4]. Change process chemicals for reducing pollution load: (a) replace lime and sodium sulphide by suitable enzymes, by oxidation process, by use of diethylamine or caustic soda in place of lime, (b) replace pentachlorophenol, a suspected carcinogen by 2-thiocyanomethyl thiobenzothiazole (TCNTB) as recommended by Central Leather Research Institute (CLRI), Chennai, and (c) use solvent degreasing in place of conventional degreasing chemicals [4].

9.3 CHARACTERISTICS OF WASTE WATER

Tannery wastes have high BOD, COD, total solids and are usually alkaline in nature. They have an unpleasant odour. The organic matter in the raw waste does not putrefy quickly if stored for a short period, due to high pH, but emits obnoxious smell when the pH is lowered. An average composition of combined wastes (including wash waters) in a typical Indian tannery is given in Table 9.2 [5].

Table 9.2 Average Composition of Combined Wastes in Tannery

Item	Combined waste	Hourly maximum
Average flows (m^3/day)	1310	2240
pH	8.9	12.3
Alkalinity as $CaCO_3$, (mg/l)	260	700
Chlorides, as Cl (mg/l)	4280	10,600
Total solids (mg/l)	10,505	23,410
Suspended solids (mg/l)	1080	3310
OOD (mg/l)	3700	6675
BOD (mg/l)	1725	4000

The waste load contributed by the combined operations of leather processing per tonne of hides processed is given in Table 9.3 [3]:

Table 9.3 Waste Load of Leather Processing

Parameter	Pollution load (kg)
Biochemical oxygen demand	70
Chemical oxygen demand	180
Chlorides, as Cl	270
Total dissolved solids	600
Suspended solids	100
Sulphides, as S	4
Total chromium (as basic chromium sulphate)	30

The characteristics of spent vegetable tan liquor are given in Table 9.4 [6] and in Table 9.5, the characteristics of spent chrome tan liquor [7].

Table 9.4 The Characteristics of Spent Vegetable Tan Liquor in a Typical Indian Tannery

Item	Range (mg/l) Minimum	Maximum	Average (mg/l) except pH
pH	4	6.5	5.4
Total solids (mg/l)	17,240	63,156	30,000
Suspended	1008	4968	2578
Volatile	7170	55,488	22,000
Ash (mg/l)	7668	10,070	8000
5-day 20°C BOD	10,660	24,000	15,000
COD (mg/l)	23,712	55,000	30,000
Total nitrogen (mg/l)	217	500	319
Tannin (mg/l)	6800	12,000	10,000
Reaction rate, K_1	0.067	0.15	—

Table 9.5 Characteristics of Spent Chrome Tan Liquor

Item	Value
pH	3.4
Alkalinity, as $CaCO_3$	zero
Acidity, as $CaCO_3$	5260
Chlorides,	7200
Total solids (mg/l)	9250
Suspended solids	1160
Chemical oxygen demand	1800
Sulphate, as SO_4	3600
Chromium, as Cr^{3+}	5125

Note: All values except pH are expressed in mg/l.

9.4 TREATMENT OF WASTE WATER

Preliminary and primary treatment consists of (i) screening to remove hair, and (ii) settling, plain or chemically aided, to remove lime and other settleable solids from the waste water. These two steps are necessary, irrespective of the method of disposal or further treatment. Plain sedimentation for 24 hours gives a BOD removal of 40%–50% and suspended solids removal of 80%–90% [2]. However, Sutherland [8] could secure suspended solids reduction of 69% by plain settling for 2 hours. The settling tanks may be of 'fill and draw' type or continuous type. Sludge removal is done manually or by mechanical means. The sludge dewaters easily in 6–8 days in winter and 4–6 days in summer. This sludge was found to have better fertilizer property than cow dung [9]. Where chemical precipitation is used, better BOD and suspended solids removals are obtained.

Chemical coagulants used are alum, ferric chloride and lime, while pH correction, when necessary, is done with sulphuric acid or carbon dioxide from flue gas. The waste water can be effectively treated by coagulation with alum, pH correction with sulphuric acid and mixing with compressed air to give 93% suspended solids reduction and 57% BOD reduction. Treatment with alum for a mixture of soaking effluent + screened lime effluent + bating effluent + pickling effluent + spent vegetable tanning effluent in proportion of 4:4:4:3:1 gives 57% BOD removal and 61% total solids removal. If ferric chloride is dosed at the rate of 200–500 mg/l, a high degree of clarification, with complete removal of sulphides is achieved. The resulting sludge is incinerated after dewatering. An elaborate form of treatment consists of mixing intermittent effluents, bubbling flue gas through the mixture till pH reaches 6.4–6.7, adding lime to pH 8.3 and settling for 3 hours. The supernatant is treated with 400 mg/l of ferric chloride and after settling, removal of BOD, colour and total solids is observed to be 80%, 98% and 50%, respectively [10, 11, 12, 13].

Biological treatment by trickling filters requires pretreatment of spent tan liquor with lime, settling for 24 hours, treating the clarified waste water with 140 mg/l of ferrous sulphate and then spreading the waste water on trickling filter using coke as a medium. The hydraulic loading rate varies from 2.1 to 3.4 million litres per hectare per day. Effluent from the trickling filter is then passed through sand beds with a hydraulic loading of 3.3–4.8 million litres per hectare per day. The filtered effluent has a BOD between 30 and 80 mg/l [14].

A trickling filter fed with 60% tannery waste and 40% sewage, after removing caustic alkalinity and subjected to organic loading rate of 12,800–14,700 kg BOD per hectare per day, achieves 88–90% BOD removal with a recirculation ratio of 2:1 or 3:1 [15]. Study on the use of activated sludge process for treating tannery waste was conducted by Chakrabarty et al. [15]. The raw waste from a vegetable tannery was composited and settled. Its analysis was: pH 6.2–9.0, alkalinity

780–1800 mg/l, chlorides 1075–11,500 mg/l, suspended solids 500–1900 mg/l, volatile suspended solids 140–700 mg/l, BOD 1200–3100 mg/l, total nitrogen 50–650 mg/l, phosphate 0.5–11.5 mg/l, tannin 300–800 mg/l. The above waste was mixed with sewage in the ratio of 30:70 and was aerated. Steady state was reached in 30 days. At a BOD load of 0.5 kg/kg sludge, BOD removal efficiency was found to be 95%, at an aeration period of 6 hours. The efficiency dropped to 90% and 80% when the BOD load was increased to 0.7 kg and 1 kg, respectively. There was a drastic fall in efficiency when the BOD loading rate was increased to 1.2 kg/kg sludge. It was also observed that the activated sludge settled rapidly and removed about 50% colour. The average oxygen requirement was found to be 98.6 mg/gm volatile solids in the sludge.

In view of the high oxygen demand of vegetable tan liquor, it is possible to subject it to anaerobic treatment for knocking out a sizeable portion of the oxygen demand. This step enables economic design of aerobic treatment of the whole waste following anaerobic treatment. Chakrabarty and Trivedi [6] conducted laboratory-scale experiments on spent vegetable tan liquor and found that the waste could be anaerobically digested at 37°C at volatile solids loading rate of 0.69 kg/m^3 digester volume/day, corresponding to a hydraulic detention time of 32 days. The digestion yielded about 0.85 m^3 of gas per kg of volatile matter added. The average BOD of the liquor was 15,000 mg/l, which was reduced to 500 mg/l after digestion. The process was found to fail at an organic loading rate of 1.48 kg/m^3/day, corresponding to a hydraulic detention time of 27 days.

Laboratory and pilot plant studies were conducted by van Groenestijn et al. [16] on composite tannery waste water from beam house and wet finishing to assess the suitability of single-stage and two-stage anaerobic process, using the Upflow Anaerobic Sludge Blanket (UASB) reactor. The study showed that anaerobic process could be successfully used for treating the above wastes. Segregation of chrome tanning waste and pickling liquor was found necessary. Pilot plant studies at Kanpur indicated a total COD removal efficiency of 60% at loading rates of 3.5–6 kg COD/m^3/day [17].

Chen et al. [18] obtained 80% and 55% COD removal efficiencies at loading rates of 6–20 kg/m^3 in an anaerobic fluidized bed reactor from a waste which was pretreated by chemical coagulation and flocculation. The pretreatment probably removed a large fraction of the slowly degradable protein and permitted high COD loading rates.

A pilot plant of 10 m^3 capacity, for treating a mixture of tannery waste and domestic sewage was constructed and studied at Kanpur [19]. It consisted of screens, equalization tank of 40 m^3 capacity and UASB reactor. The unit was started with domestic sewage sludge and after 2 months a mixture of 10% tannery waste and 90% sewage was fed. At the end of the stabilization period, the UASB was receiving 100% tannery waste (from which pickle waste and chrome liquor were excluded). At a hydraulic retention time of 12–16 hours, the unit was able to reduce suspended solids by 70%, BOD by 60% and COD by 70%. Gas with a methane content of 80% was produced at the rate of 0.40–0.72 m^3 per kg COD destroyed.

Govindan [19] conducted laboratory-scale studies on the treatment of a mixture of tannery wastes and domestic sewage in waste stabilization pond in ratios ranging from 1:1 to 1:6. It was observed that the percentage BOD and COD reductions ranged from 64 to 93 and 60 to 89, respectively, at a hydraulic retention time of 18 days. Good algal growth was also observed in the ponds.

Tannery wastes are known to contain high concentrations of sulphates and sulphides, which can adversely affect methane generation in anaerobic treatment process and add considerably to the cost of aerobic treatment which follows anaerobic process. Therefore, with a view to minimize these problems, Ravindranath et al. [20] conducted laboratory and pilot-scale studies for treating tannery wastes anaerobically in a UASB reactor. The purpose of the study was also to reduce COD, recover sulphur and produce biogas. It was observed that 70% of the total COD was removed, along with recovery of 90% of the sulphur compounds. The recovered sulphur could be used for manufacture of sulphuric acid. The sulphur recovery system also helped to clean the biogas.

It is known that nearly 90% of the tannin is absorbed in the hide during vegetable tanning process, while only 60–65% chromium compounds are absorbed in the hide in chrome tanning, the rest finding their way into the effluent. In view of the toxic property of chromium and in the interest of economy, it is essential to recover and recycle chromium from chrome tanning wastes. Chromium can be recovered in one of the following three ways:

1. Direct reuse of spent liquor for the next batch. The drawback of this method is accumulation of salts and other impurities due to repeated use, which has an adverse effect on the tanning process.
2. Indirect reuse in which chromium is precipitated from the spent liquor with an alkali and the precipitate is dissolved in sulphuric acid to get back chromium sulphate. This is an efficient method and the recycled chromium does not adversely affect the tanning process.
3. Separating chromium compounds from the spent liquor by electrodialysis and membrane separation. Although the chrome liquor is cleaner than that produced by direct method, it is very costly.

Keeping this in view, Rajamani et al. [21] developed a system for recovery of chromium from the tannery waste, using magnesium oxide and sulphuric acid. Spent chrome liquor was segregated, screened and collected in a tank. A calculated quantity of magnesium oxide was added to the waste and stirred till pH rose to 8.0. The precipitate, chromium hydroxide settled in the tank in two hours to form a compact sludge. Supernatant from the tank was removed and sulphuric acid was added to the sludge to dissolve it and to form basic chromium sulphate. The effect of recycling of recovered chromium on the quality of tanned leather was also studied. It was found to meet all quality standards. The payback period for the entire recovery plant was found to be less than three years.

Other studies for chromium recovery/removal included adsorption of hexavalent chromium on spent myrobalan nuts, a waste product of vegetable tanning. It was observed in this study that 1 gm of spent nut removed 97% of hexavalent chromium from initial concentration of 5 mg/l at an optimum pH of 2.5 [22]. The economics of recovery of chromium from chrome tanning effluent was studied by Siddiqui et al. [23].

They compared the suitability of magnesium oxide and sodium hydroxide for precipitating chromium. Other factors studied to find the efficiency of removal included temperature, alkali dose and initial chromium concentration. They observed that magnesium oxide was more effective than sodium hydroxide, reaction with chromium was independent of temperature when magnesium oxide was used. MgO produced a better settling sludge and the payback period for a tannery processing 500 hides per day would be about 2 years.

Verma and Shukla [24] used electrolytic separation of chromium from chrome tannery waste water. They found that chromium reduction was directly proportional to the initial chromium concentration.

Prasad and Unni Nayar [25] characterized spent chrome tan liquor from various tanneries and subjected them to treatment with lime, sodium bicarbonate and magnesium oxide for recovery of chromium. They found that magnesium oxide gave the best results. Reduction of BOD and COD of 85% and 90%, respectively, were obtained. The recovered chromium liquor was exhausted in chrome tanning trials only to the extent of 45% against 65–70% for basic chromium sulphate. Therefore, chemicals, viz. adipic acid, oxalic acid and pthalic acid, were added to the recovered chrome supernatant, which resulted in increase of exhaustion from 45% to 64%.

Singaram [26] used fast-growing aquatic weeds to absorb chromium from tannery wastes. Water hyacinth, pseudo water hyacinth and Lemna were exposed to various dilutions of the waste for seven days and were then analysed for chromium in their foliage and their roots. Water hyacinth accumulated the maximum chromium, followed by Lemna and pseudo water hyacinth.

In another study involving the waste management of chrome tanning process, Mazumdar and Chaudhari [27] found that of the COD produced by liming and unhairing processes, 38% was contributed by input chemicals, mainly as sulphur radicals. Deliming and bating contributed 20.9 kg COD, of which 11.46 kg was inorganic, and also as sulphur radicals. They recommend segregation of the above waste streams, settling, sulphur removal and then removal of biodegradable organic matter. After recovery of chromium from the spent tan liquor, the rest of the waste streams could be mixed together for further treatment.

Tanneries are almost always located in clusters. Therefore, it should be possible to provide a common effluent treatment plant (CETP) for them, in order to overcome the problem of pollution due to them. Such a plant was provided for 14 tanneries in Bangalore, where the daily effluent produced was 1000 m^3. Treatment consisted of grit removal, equalization, lime dosing, primary settling, acid dosing, activated sludge process and sludge dewatering on drying beds. The treated effluent was fit for discharge to the municipal sewer, where it mixed with 20,000 m^3/day of domestic sewage. This mixture was successfully treated in the sewage treatment plant at the end of the outfall sewer [28].

The State of Tamil Nadu, which has a large number of tanneries, had 30 CETPs, of which 9 were in operation, 9 were under construction and 12 were proposed in 2000 AD. Sivacoumar, Kothandaraman and Biswas [29] studied one of these plants, which was receiving 2500 m^3/day of effluent from 87 tanneries. The effluent was pretreated by settling, screening and solar evaporation of soak liquor and pickle liquor in individual tanneries. The CETP consisted of screens, equalization tank, chemical treatment with lime, alum and polyelectrolyte, primary settling, activated sludge process, sludge dewatering on drying beds and sand filtration. The plant was found to be underloaded. So, the performance was improved by conducting laboratory-scale studies and modifying the full-scale treatment as indicated by these studies. The treated effluent had a BOD of 30 mg/l and COD of 144 mg/l.

A pilot reverse osmosis (RO) plant of 20,000 litres/day capacity was installed in a tannery at Ranipet, India to assess the suitability of using this process for recovery of water from secondary and tertiary treated tannery effluent. The tertiary treatment consisted of pressure sand filtration, photochemical oxidation, softening and cartridge filtration. The recovered water, which met drinking water quality standard, was used in important wet finishing and fat liquoring operations. Reject from the RO unit was partly sent to evaporation pond and partly recirculated in the treatment system [30].

Sludge produced in a tannery comes from soaking, liming and vegetable tanning, especially if tanning is done in pits filled with crushed barks and nuts. It is also generated in screen chambers, grit chambers, manholes, presettling tanks, chemical dosing tanks and clarifiers in effluent treatment plants. Final disposal of sludge from all these sources poses a serious problem. Rajamani et al. [31] suggest that pilot studies may be conducted for disposal by (i) incineration, (ii) use as fertilizer, (iii) use in brick making, and (iv) anaerobic digestion.

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Chapter 10

SUGAR MILL WASTES

Production of sugar from sugar cane is a seasonal operation, depending on the availability of sugar cane, which lasts from October to May. Sugar can also be produced from beet, the production activity being limited to about 100 days in a year. As a result of its seasonal nature, sugar industry presents peculiar problems for pollution control.

10.1 PRODUCTION FROM SUGAR CANE

Cane, cut from the fields, is washed in water, cut into small pieces and crushed to extract the raw juice. This operation produces a solid waste in the form of bagasse, which is a raw material for paper making. The juice is then heated to 102°C, its pH is adjusted between 7.6 and 7.8 with lime and it is settled in multitray clarifiers to remove suspended solids and unreacted lime from the juice. The sludge thus produced is called 'lime mud'. It is dewatered on vacuum filters and the filtrate is recycled. The dewatered lime mud is disposed of. The clarified juice is treated with sulphur dioxide to remove its pale yellow colour. Double carbonation may also be done. The juice is then heated further to remove moisture from it and is then passed through vacuum pans and crystallizers for further removal of moisture and to encourage crystallization. Moisture content of the juice at inlet to the crystallizer is about 46%. Centrifugation of the juice separates the crystals from the remaining moisture. This liquid is called 'molasses' and is the raw material for production of alcohol. The sugar crystals sticking to the wall of the centrifuge are scraped off, sieved, graded and packed in bags. A general manufacturing flow sheet is given in Fig. 10.1.

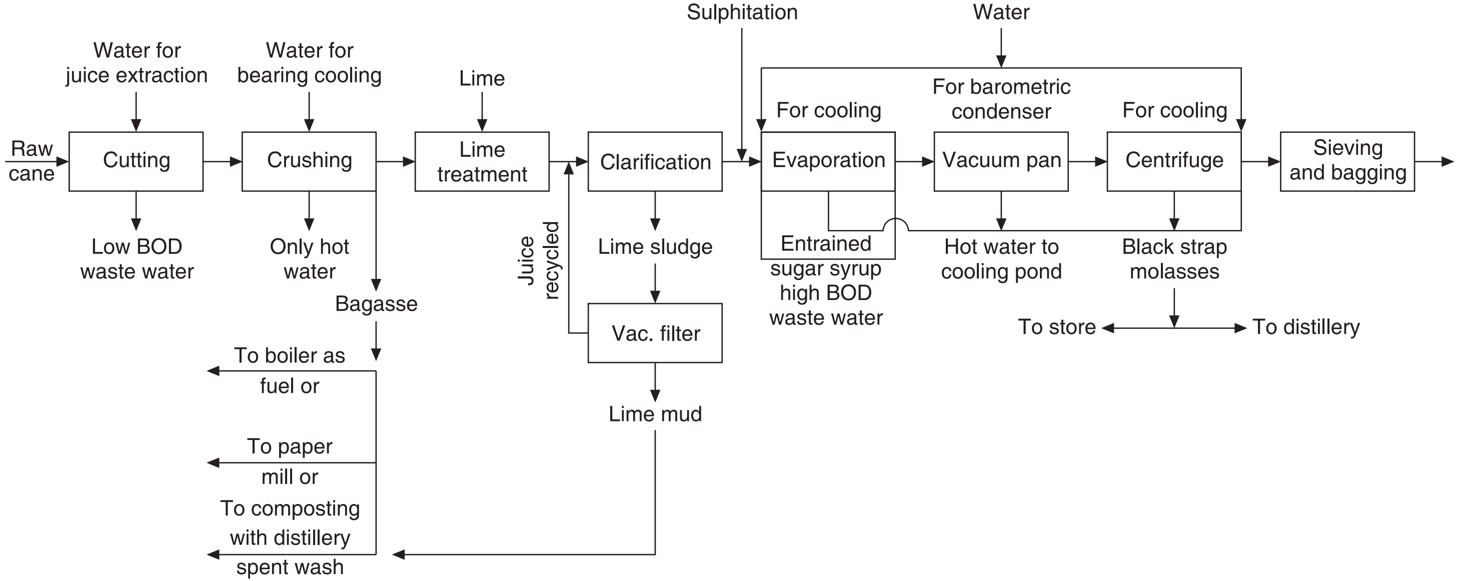

Figure 10.1 Cane sugar manufacturing flow diagram.

The operation of washing and crushing cane is done in the 'mill house', while the remaining operations are done in the boiling house. A rough breakup of water consumption per day per tonne cane crushed in various operations in the mill is the following:

- Mill house: 730 litres
- Boiling house and floor wash: 230 litres
- Filter cloth wash: 360 litres
- Condenser and cooling: 1640 litres.

  Sapkal and Gunjal [1] have surveyed 8 sugar mills in Maharashtra and measured the waste water flows from them, ranging from 945 m^3/day to 2389 m^3/day, depending on their crushing capacity.

Verma et al. [2] in a survey of 25 factories in western Uttar Pradesh, with a crushing capacity from 900 tonnes to 3600 tonnes per day, estimated water consumption ranging from 10,600 m^3/day to 38,700 m^3/day, or 10.6 m^3/tonne of cane crushed. A survey of four typical Khandsari sugar units in South India by Rao et al. [3] showed water consumption from 6.6 m^3/day to 11.6 m^3/day, or 44 litres to 78 litres/tonne of cane crushed. These are small-scale units and work for 4–5 months in a year, from December to April. The sugar produced is incompletely refined and has, therefore, a brownish white colour.

10.1.1 Characteristics of Waste Water

The characteristics of waste water streams produced from various operations are given in Table 10.1 [4].

The characteristics of combined waste water from the sugar mill are tabulated here [4].

Parameter	Range of value
Temperature, (°C)	30–40
pH	4.6–6.0
Dissolved solids	1000–1200
Suspended solids	250–300
Oil and grease	5–10
COD	2000–3000
BOD	1000–1500

Note: All values except pH and temperature are in mg/l.

10.1.2 Disposal of Waste Water

Sugar mills are almost always located in rural areas, where the raw material is easily available. Therefore, disposal of the raw waste water may be done on land for irrigation. Direct disposal into nallas or streams in the vicinity of the mill leads to stagnation and generation of obnoxious

Table 10.1 Characteristics of Waste Water Streams from Various Operations

Source	Temperature	pH	Dissolved solids	Suspended solids	Oil and grease	COD	BOD
Mill house	25–30	5.0–5.5	350–400	500–550	30–50	1000–1500	700–1000
Boiler blowdown	85–90	5.8–6.0	450–500	50–100	–	500–550	30–40
Boiling house	40–60	4.5–5.0	400–450	400–600	5–10	2000–3000	1500–2000
Excess condensate	60–70	6.0–6.2	80–1000	5–10	–	250–300	100–150
Sulphur house	30–35	–	–	–	–	–	–
Lime house	25–30	9.0–10.0	1400–1500	3500–4000	4–6	200–250	100–150
Rotary filter wash	25–35	6.2–6.8	2000–3000	2600–4200	–	1200–3000	1000–2500
Floor and boiler washing	–	7.0–7.2	2200–2500	2100–2300	–	1000–2400	800–2000

Note: All values except pH are in mg/l and temperature in °C.

smell. The waste water also becomes black in colour. The characteristics of the waste water show that it can pollute the land as well as groundwater. Further, the COD:BOD ratio is favourable for subjecting the waste water to biological treatment. Hence, it is proper to consider this form of treatment, keeping in mind that this is a seasonal industry, and the treatment units will get raw waste water for a limited period of time. Choice of the treatment method has to be made accordingly.

10.1.3 Treatment of Waste Water

10.1.3.1 Plain settling

In laboratory columns, plain settling of waste water was studied by Rajgopal and Bhargava [5]. Data collected from the column settling tests were used to develop families of curves between overall per cent removals versus overflow rate and detention time. Based on these curves, an equation relating overall removal, initial suspended solids concentration and overflow rate was offered for the design of primary settling tank with initial suspended solids concentration up to 450 mg/l. In order to account for turbulence, inlet and outlet conditions and other factors, which can affect settling process in actual practice, they also recommended that the calculated overflow rate be divided by a factor ranging from 1.25 to 1.75 and detention time multiplied by a factor from 1.5 to 2.0.

10.1.3.2 Anaerobic digestion

Anaerobic digestion of the waste water was studied by Sinha and Thakur [6]. They used laboratory scale digesters maintained at 36°C. Hydraulic retention times of 6 days, 3 days and 2 days were tried out at different organic loading rates. They observed that BOD removal efficiency ranged between 88.8% and 95.8%, volatile fatty acids never exceeded 1400 mg/l (as acetic acid) and a sudden increase of volatile acids by 200–300 mg/l in 24 hours resulted in a ‘stuck’ digester. The maximum BOD loading rate was 15.58 kg/m^3.

A pilot scale study was conducted for two years by Ramjeawon et al [7] using a 1 m^3 capacity UASB reactor. They concluded that UASB reactor offers a viable solution for handling sugar mill waste water. At a retention time of 6 hours and an average temperature of 26°C, a loading rate of 12.5 kg COD/m^3 per day gave 90% destruction of influent COD and methane production of 0.2 m^3 per kg COD destroyed. The calorific value of the gas was 15–20 MJ/m^3. But the influent required nutrient supplementation; alkali addition at the rate of 0.6 g per gram of influent COD accounted for nearly 70% of the annual running cost.

Farooqi et al. [8] characterized granular sludge developed on cane sugar mill waste and studied the effect of temperature on methanogenic activity, yield coefficient of methanogens, effect of unfed storage of granular sludge at room temperature on its methanogenic activity and physical characteristics of the sludge. They found that the granular sludge retained 50% of its methanogenic activity even after 100 days of storage. This factor is important for sugar industry, which is a seasonal industry. Further, the sludge was found to readily adapt to distillery waste and slaughterhouse wastes.

Manjunath et al. [9] conducted continuous flow experiments at 30°C in a laboratory scale UASB reactor loaded up to 13 kg COD/m^3/day and a sludge loading of 1.25 kg VSS/m^3/day. Corresponding hydraulic loading was 6 m^3/m^3/day. Gas production up to 5 m^3/day was obtained. It contained 70–75% methane. The seed sludge used came from a drugs and pharmaceutical industry effluent treatment plant. Radwan and Ramanujam [10] operated a modified rotating biological contactor (RBC) with four compartments and fed it with synthetic sugar cane waste water to study the biokinetic coefficients based on Kornegay and Hudson model. They got COD removal efficiencies up to 97% for COD inputs ranging from 1087 mg/l to 3257 mg/l. Sinha and Sinha [11] studied the effect of the presence of water hyacinth in the oxidation pond treatment of a mixture of anaerobically digested sugar mill effluent and effluent from a septic tank. They observed that water hyacinth could thrive well in this mixture and in addition, enhanced the rate of biological oxidation. It also coagulated turbidity from the waste water and removed the colour present in the waste water.

10.1.3.3 Treatment in lagoons

Mostly anaerobic treatment in lagoons is widely practised in the sugar industry. Aerobic lagooning is possible only if the organic load is limited to 60 kg/ha/day [4]. As the waste has a high BOD, anaerobic treatment to knock out a bulk of the oxygen demand, followed by aerobic (or facultative) pond system can produce a satisfactory quality effluent. This waste is high in carbohydrates but low in nitrogen and phosphorus. Hence, continuous nutrient supplementation, either with chemicals or with domestic sewage is necessary. This offers the advantage of maintaining continuity of sewage treatment even during the non-crushing season. Further, anaerobic organisms in these lagoons can be reactivated even after a long period of starvation. Bhaskaran and Chakrabarty [12] studied a combination of anaerobic–aerobic pond pilot system. They found BOD reduction in anaerobic pond from 1600 mg/l to 550 mg/l in 7 days, at a loading rate of 0.23 kg/m^3/day. This was followed by an oxidation pond, loaded at 316 kg BOD/ha/day, which produced an effluent with a BOD ranging from 34 mg/l to 180 mg/l for a retention time of 13 days. When the retention period was reduced to 7 days and loading was changed to 325 kg/ha/day, the effluent BOD ranged between 41 mg/l and 118 mg/l. Gupta [13] reports a BOD removal of 40–59% in anaerobic pond loaded at 0.08–0.56 kg BOD/m^3/day.

Batch treatment of sugar mill wastes was successfully demonstrated in Australia [14]. Shallow ponds 1 m deep were operated in a batch mode. They became anaerobic for the first 3 weeks, during which time 70–90% BOD was removed. The combined effect of wind action and shallow depth of the ponds turned them into aerobic ponds. They gave an effluent BOD of less than 30 mg/l after a further retention period of 3–5 weeks. Rao et al. [3] treated composite waste water with a BOD of 25,000 mg/l from a khandsari sugar mill by plain settling, followed by a two-stage anaerobic lagoon and an aerobic lagoon. The effluent had a BOD of 30 mg/l.

10.1.3.4 Activated sludge process

It has not been preferred, mainly because of the seasonal nature of the industry. It is adopted where land is not available for constructing ponds. Most full-scale plants treating about 5000 m^3/day operate at MLSS of 2000–4000 mg/l. Annual startup may take about 5 weeks to develop MLSS of 2000 mg/l with molasses and sewage. A major problem with the activated sludge is bulking, which results in poor settling and rapid loss of biomass from the secondary clarifier. One or more of the following factors may be responsible for bulking, viz. nutrient imbalance, low pH, low DO in the aeration tank, high organic loading, greater than 0.7 kg BOD/kg MLSS/day. A BOD:N:P ratio from 100:2.5:0.5 to 100:5:1 was recommended by Miller [15]. Other applications of activated sludge process were described by McNeil et al. [16], Bruijn [17], Bathgate et al. [18], Simpson and Hemens [19] and consisted essentially of two-stage aeration or combination of activated sludge process, followed by extended aeration, or anaerobic lagoon, followed by aerobic treatment.

10.1.3.5 Trickling filtration

On a large-scale trickling filtration has not been favoured because of long induction period, high recirculation rates for high strength wastes and the risk of blockages [4]. Early experiments [17, 20, 21, 22] demonstrated BOD reductions from 70% to 90%. Media used were stone or plastic material. Two-stage filtration was done. The recirculation ratio varied from 1.8 to 4. Huang et al. [23] reported the use of rotating biological contactor for treating sugar mill effluent, with more than 80% COD removals. Saravanane et al. [24] studied the viability of biogas generation from a mixture of press mud and domestic sewage. The optimum concentration of total solids in a mixture of sewage and press mud was found to be 5%. At this concentration, 80 m^3 of gas was produced per tonne, against 65 m^3 per tonne when only press mud was digested. The maximum COD removal efficiency was found to be 70%, with biogas yield of 0.65 m^3 per kg COD. Nitrogen content in the digested sludge was found to be 2.32%. Hence, it could be used as a fertilizer.

10.1.3.6 Solid wastes

The two solid wastes generated in the manufacture of sugar are: (i) bagasse and (ii) press mud. Bagasse is produced during the crushing operation. It has a calorific value of about 1920 Kcal/kg and is mainly used as a fuel in the factory's boiler. It can also be used as a raw material in paper making [4]. Agrawal [25] has suggested extraction of furfural from bagasse, followed by production of single cell protein (SCP) without appreciably reducing its calorific value, so that it can be used either as fuel or as raw material in paper making. Press mud contains all non-sucrose impurities along with $CaCO_3$ precipitate and sulphate. Press mud from double sulphitation contains valuable nutrients like nitrogen, phosphorus, potassium, etc. and is, therefore, used as a fertilizer. Press mud from double carbonation is used as a landfill [4].

10.2 PRODUCTION FROM BEET

Beets are dug up from the fields either mechanically or manually and conveyed to the factory through an open channel, called 'flume', in which water flows continuously. The fruits roll along the bottom of the flume and get partially washed. The flume ends in a screen, where the fruits are retained, while the water is collected, treated by settling, filtration and disinfection before return to the head end of the flume. The washed beets are passed over a picking table, where the spoiled beets and foreign material are removed and disposed of as animal feed. The washed beets are weighed, sliced into long, narrow V-shaped pieces called 'cossettes' and conveyed to diffusers for extraction of sugar. Factories may operate on what is known as 'Straight House' in which sugar is extracted from the cossettes till a thick, heavy molasses is obtained, or on 'Steffens House' for further extraction of sugar. The raw juice from the diffusers is heated and discharged into the first carbonation tank where it is treated with milk of lime and carbon dioxide. The precipitate is filtered or settled and the filtrate is carbonated a second time, again filtered and then treated with sulphur dioxide gas with further filtration. The sludge and material retained on the filters is called 'lime cake'. It is diluted and discharged as slurry.

The juice is concentrated in multiple effect evaporators, filtered and sugar recovered by evaporation in vacuum pans until the desired crystal size is obtained. The sugar crystals are separated by centrifugation. The residue, 'beet molasses' is either sold or further treated for recovery of sugar by the 'Steffens Process'. This process consists of diluting the molasses to a specific concentration and treating with lime to produce insoluble calcium saccharate, which is removed from the liquor by filtration and introduced into the raw sugar liquor at the main purification step of the normal extraction process, where the sugar is recovered by treating with carbon dioxide [26]. A general manufacturing flow sheet is given in Fig. 10.2.

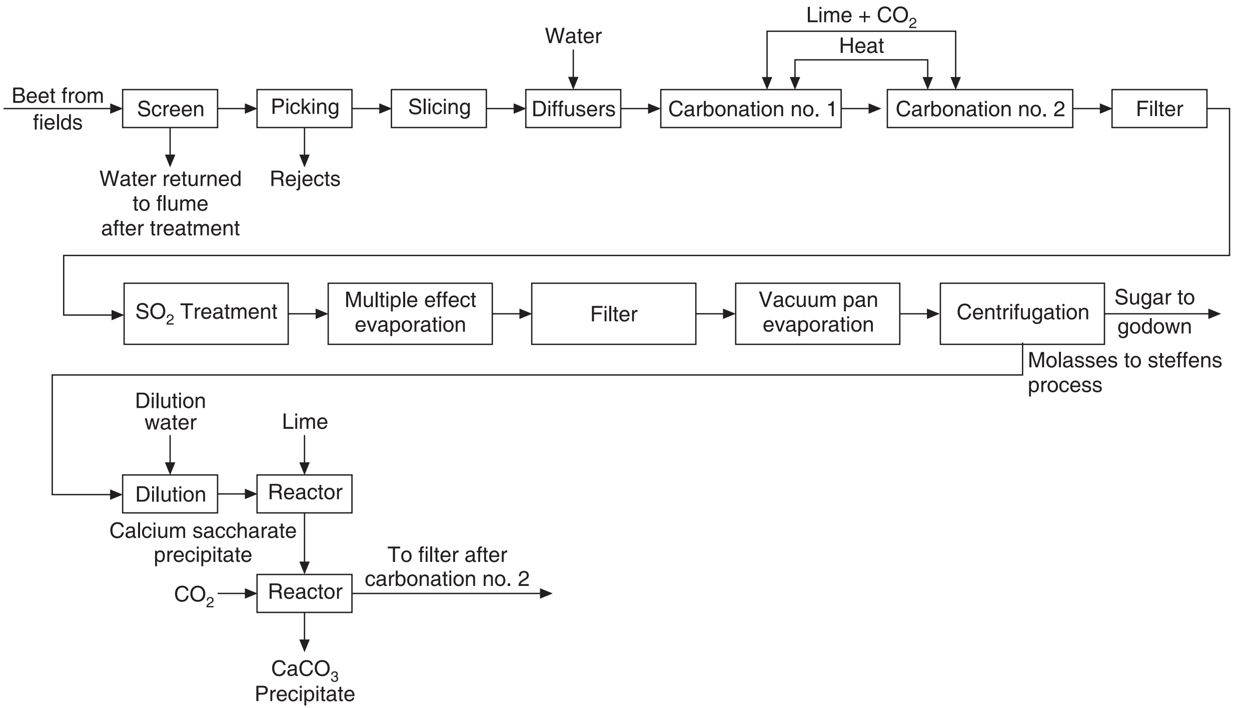

Figure 10.2 Beet sugar manufacturing flow sheet.

Sugar beet juice can also be treated with ion exchangers for the removal of non-sugars from second carbonation before evaporation and crystallization. This increases sugar yield, produces less molasses which are treated further by ion exchange and are converted into an edible product [26].

10.2.1 Characteristics of Waste Water

This is a seasonal industry; so the values given in Table 10.2 are those which occur during 3–4 months of operation and are not annual averages [27].

Table 10.2 Characteristics of Waste Water Generated in Sugar Production

Waste Stream	5-day BOD (mg/l)	Suspended solids (mg/l)
Flume water	210	800–4300
Pulp screen water	910	1020
Pulp press water	1710	420
Pulp silo drainage	7000	270
Lime cake slurry	8600	1,20,000
Barometric condenser water	40	–
Steffen waste	10500	100–700

10.2.2 Waste Water Disposal

The method most commonly used is that of lagooning, in which the waste water generated through the period of production is stored in shallow lagoons. Care is taken to avoid stagnation of the waste water, which can lead to odour nuisance. Storage is continued after the production is over and the waste water with a relatively low BOD is discharged under controlled conditions into the receiving body of water, depending on its flowrate. Where large tracts of land are not available, it is necessary to reduce the generation of waste water, reuse and/or recycle waste water, either with or without treatment and seek ways of recovering by-products from the waste streams. Flume water is recycled after treatment. Continuous diffusion process for extraction of sugar can eliminate pulp screen water and pulp press water. Lime cake can be returned to the farmland to correct acid pH conditions, or can be burnt in special equipment so that it can be used in the step of purification. The Steffen waste, which is a filtrate, contains 2–3% solids. It contains a basic chemical for the production of monosodium glutamate [27].

Treatment of the waste water in contact anaerobic systems was reported by Fuchs [28]. The process was selected because of the high calcium content of the waste water. It provided COD removals of more than 93%.

Habets et al. [29] documented the startup of an internally circulated anaerobic reactor for treating waste water from the production of sugar and inuline, a food structure enhancer. The feed to the reactor had a COD of 7900 mg/l and chlorides of 4200 mg/l. After seeding with granular sludge from another reactor, the reactor was able to take a loading of 26.5 kg COD/m^3/day with removals of 65%–80%.

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[The asterisk (*), wherever given, indicates that original article was not referred to.]

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Chapter 11

PULP AND PAPER MILL WASTES

The manufacture of paper from pulp is a water-intensive industry. It involves: (a) conversion of raw material into pulp by digestion with various chemicals, and (b) conversion of pulp into paper. A mill which carries out these two functions under the same roof, is called *an integrated mill*. Raw material used in this industry is mainly cellulose, which is obtained from wood, rags, old paper, hemp, wheat and rice stalks, bamboo, esparto grass, bagasse, etc. Besides cellulose, these raw materials also contain hemicellulose, lignin, wood sugars, etc. The process of pulping separates cellulose from these components, which is then converted into paper. Depending on the end product required, the raw material is changed, e.g. wood and bagasse are used for making low and medium grade paper, newsprint is used for making high quality paper, while rags are used for producing fine writing paper.

On the basis of the nature of the raw material, different pulping processes are used, viz. (a) mechanical pulping, (b) semichemical pulping, (c) sulphate pulping, (d) sulphite pulping, (e) chemi-mechanical pulping. Chemicals used in the pulping process are sodium hydroxide, sodium sulphate, calcium bisulphite and sodium sulphite. The yield of pulp depends mainly on the raw material, as shown below in Table 11.1.

Table 11.1 Yield of Pulp from Different Sources

Raw Material	Yield (%)
Rags	70–80%
Esparto grass	40–45%
Straw	40–50%
Wood (using sulphite process)	40–50%
Waste paper, waste fibres, bagging	70–90%
Bamboo	40%
Jute	50%
Bagasse	50%

The BOD contributed by various pulping processes is the following:

- Mechanical pulping: 60–100 kg/tonne of pulp
- Semichemical pulping: 100–200 kg/tonne of pulp
- Chemical pulping: 200–250 kg/tonne of pulp

A chemical pulping process for agricultural residues such as bagasse, straw, etc. was used by Ketkar, Khanolkar and Pudumjee [1], in which a mixture of water and ethanol under pressure was used to separate lignin from the raw material. Advantages claimed include: (a) higher yield of pulp with pure lignin as by-product, (b) recovery of ethanol, (c) reduced colour in the effluent, and (d) availability of recovered lignin for conversion into value-added products.

11.1 MANUFACTURING PROCESS

The raw material (especially wooden logs) is subjected to soaking, debarking and chipping before digestion. Soaking loosens the bark and removes the sap from the wood. The loosened bark is removed by mechanical means. The logs are then chopped into small pieces and are digested by one of the above-mentioned methods, e.g. chemical pulping. The chemicals used are sodium sulphide, sodium hydroxide and sodium carbonate. The period of digestion varies from 2 to 5 hours at 170°C and a pressure of 8–9 kg/cm^2. Cellulose is separated from the digested pulp by blowing it in a 'blow pit'. The waste water produced here is black liquor. It is an obnoxious waste and contains unreacted chemicals and other impurities from the wood. But it offers scope for recovery of valuable chemicals.

The digested pulp, which is predominantly cellulosic in nature, is washed with water. This step produces brown stock wash water. The pulp is then screened to remove knots and uncooked wood. This pulp has a pale yellow colour, due to the presence of lignin and hemicellulose, which is bleached with chlorine or chlorine dioxide, sodium hydroxide or calcium hypochlorite, to produce white pulp. This pulp is sent to the paper mill for the production of paper. The volume of waste water generated depends on the nature of raw material and ranges from 150 to 500 m^3/tonne of dry pulp produced.

Deinking wastes are produced when pulp is recovered from old printed paper. The main source of waste water is the pulp washing machine. The quantity of waste water and its quality depends on the grade and quality of the paper handled, the degree and type of treatment given to it, and the efficiency of the washing machine. Deinking treatment results in producing high concentration of dissolved organic matter, besides coating chemicals, fillers and fibre debris. Removal of sizing material and fillers from the pulp results in shrinkage from 20% to 40% between the paper and the deinked pulp.

The process of paper making consists of passing the bleached pulp through a beater, where it is given a uniform consistency; fillers (as required by the final product) such as alum, clay, calcium carbonate, barium sulphate, titanium dioxide, wax emulsion and colour are added. The pulp is then passed through a machine called *Jordan*, in which the fibres are cut to appropriate size. It is then spread over travelling wire screens known as *Fourdrinier*, over which a continuous shower of water is sent in order to align the fibres. The fibres form a mat over the wire screen. This is paper. The spray of water also helps remove small-sized cellulose fibres. The waste water, which collects under the wire screens, is known as white water. It is passed through a 'save-all', which separates the fibres by settling, and clarifies the white water for reuse. The clarified water is chlorinated to prevent formation of black spots on the paper. The save-alls are of wire screen type, settling type, flotation type or filtration type, using diatomaceous earth as the filtering medium. The fibres are recycled to the beater. The wet paper is then passed through a series of squeeze rollers covered with felt from outside and heated by steam from inside. The dried paper is then wound into rolls and sent to storage. A general flow sheet of the manufacturing process is shown in Fig. 11.1.

11.2 POLLUTIONAL EFFECTS

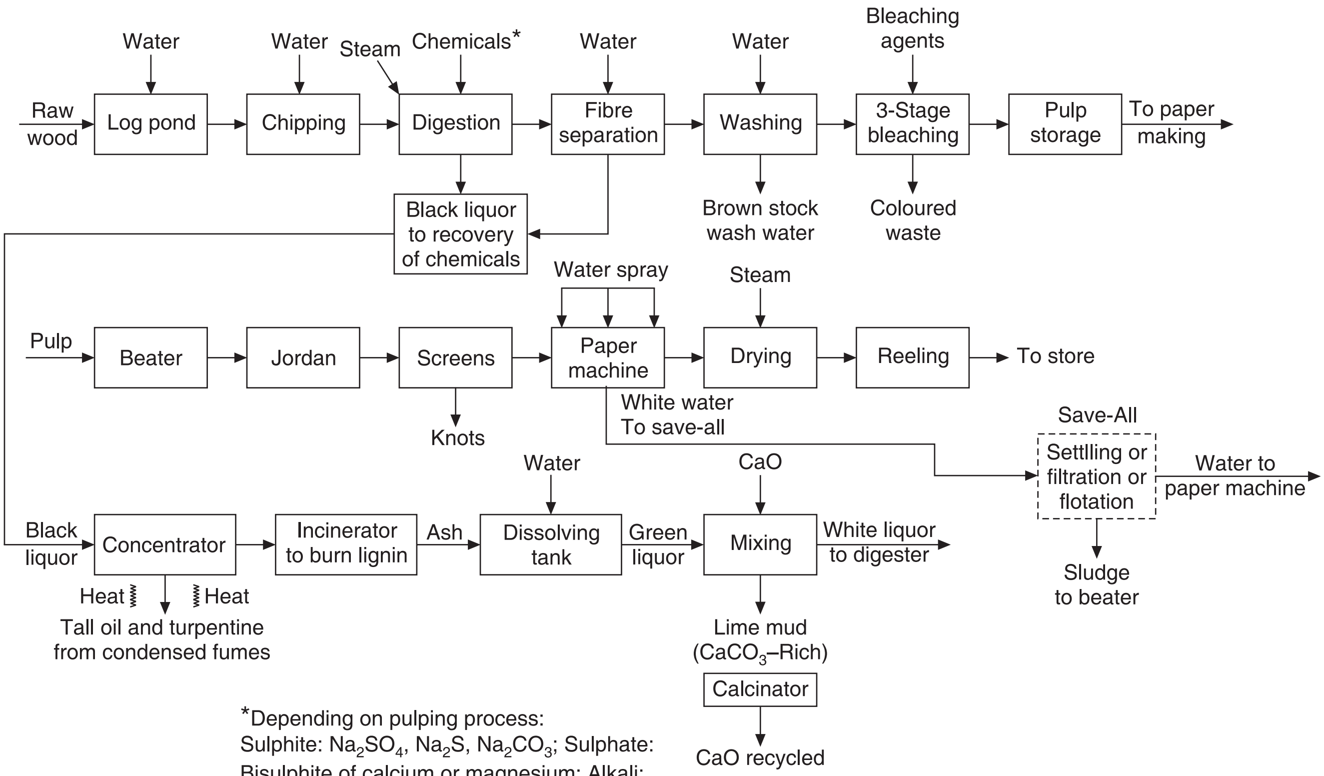
The pollutional effects of discharging raw waste water from a paper mill are:

1. Oxygen depletion in the receiving body of water
2. Presence of undesirable colour, odour and taste in the water
3. Reduced photosynthesis
4. Formation of blanket of suspended solids settling at the bottom of the receiving body of water
5. The death of fish
6. Toxicity added to the aquatic life due to the formation of mercaptans, pentachlorophenol, sodium pentachlorophenate, etc.

11.3 CHARACTERISTICS OF RAW WASTE WATER

The waste water is usually alkaline in nature, has high suspended solids, high total solids, high COD and relatively low BOD. The approximate analysis of waste water from a typical pulp and paper mill is the following:

- pH value: 8.0–9.0
- Total solids: 1500–2500 mg/l
- Suspended solids: 600–1500 mg/l
- COD: 300–2500 mg/l
- 5-day 20°C BOD: 150–1000 mg/l



*Depending on pulping process:
Sulphite: Na_2SO_4, Na_2S, Na_2CO_3; Sulphate:
Bisulphite of calcium or magnesium; Alkali:
NaOH or $Ca(OH)_2$

Figure 11.1(a) Paper manufacturing in an integrated mill.

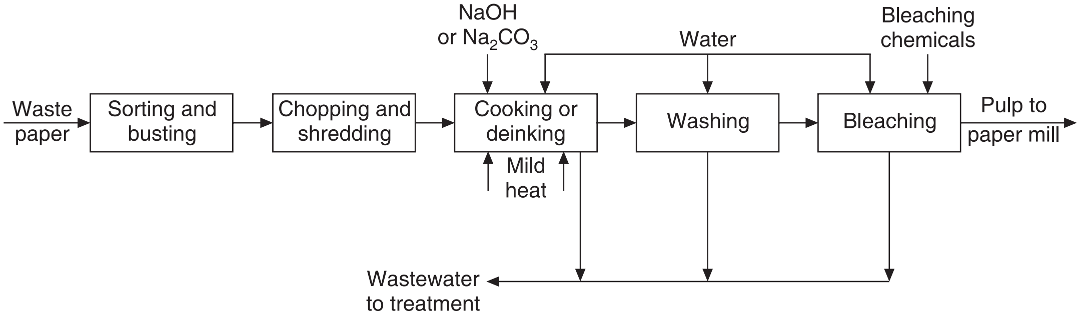


Figure 11.1(b) Reclaimed paper process.

Dhaneshwar et al. [13] studied four paper mills, two of which employed the kraft process, one used the sulphite process, and one manufactured tissue paper. Their study showed that the sulphite process produced the strongest waste, while the soda process generated the weakest waste. As already mentioned, paper making industry is a water-intensive industry. Therefore, every attempt is made to reuse, recycle and recover water and chemicals used in the manufacturing process. Steps in the manufacturing process where reuse and/or recycling is possible are:

1. Soaking and debarking; marginal treatment such as settling and chlorination may be necessary before reuse, because repeated use of the water leads to accumulation of total dissolved solids and of organic matter, which leads to microbial growth.
2. Paper making: white water is settled, filtered, chlorinated and reused in the showers of the Fourdrinier. It can also be used for diluting the bleached pulp before it is spread over the Fourdrinier. The settled fibres are added to the pulp.
3. Steam used in drying the paper is condensed and reused.

Besides saving water, there is great scope for recovering valuable chemicals from the waste water streams, especially the black liquor. Each pulping process uses different chemicals, e.g. the sulphate (also called ‘Kraft’) process uses sodium sulphate, sodium hydroxide and sodium carbonate. Sodium sulphate is converted to sodium sulphide during pulping. The black liquor from this process is concentrated by heating. The vapours are condensed to yield tall oil and turpentine. The concentrated liquor is treated with sodium sulphate and the mixture is incinerated. This destroys the dissolved organic residues from the liquor and generates heat. The residue, known as smelt, is dissolved in water to form ‘green liquor’. Quick lime (CaO) is used to causticize the green liquor and is settled to yield ‘white liquor’, which is returned to the digester to convert wood chips into pulp. The settled sludge contains calcium carbonate ($CaCO_3$), which is calcined to give calcium oxide and carbon dioxide. The calcium oxide is reused to causticize green liquor.

In the sulphite process, chemicals used are either calcium bisulphite $Ca(HSO_3)_2$ or magnesium bisulphite $Mg(HSO_3)_2$ and sulphur. Chemical recovery is not possible if calcium bisulphite is used, but with magnesium bisulphite, the chemicals are recovered by burning the concentrated liquor to get magnesium oxide (MgO). It is slaked to give magnesium hydroxide $Mg(OH)_2$, which is treated with sulphur dioxide (SO_2) to give magnesium bisulphite. If sulphite liquor is produced on sodium base or ammonium base, it can be fermented to produce Torula yeast and alcohol. When subjected to pyrolysis, it gives phenols. Addition of lime yields Vanillin. Further, direct recovery of acetic and formic acids, dimethyl sulphoxide and lignosulphonates is also possible. However, some toxic substances such as dimethyl sulphide, methyl mercaptans are also produced during the recovery processes.

11.4 TREATMENT OF WASTE WATER

Waste water from pulp and paper mills can be subjected to physical, chemical, and biological methods, or combinations of the above, depending on the nature of the waste water and the quality requirements of the treated effluent, before disposal into the environment. An important requirement in the treatment process is that of colour removal. Various methods have been adopted for this.

11.4.1 Methods of Colour Removal

The colouring bodies in pulp and paper mill wastes come from wood extractives, lignin and its degradation products, formed by the reaction of chlorine with lignin. Conventional activated sludge process removes about 1/3rd of the colour in the waste by adsorption on the sludge, rather than by biological action. Use of coagulants such as alum, ferric chloride and chemicals such as lime and magnesium sulphate removes colour but results in the formation of voluminous sludge.

Mittal and Mehrotra [2] studied the use of alum and clay for colour removal from combined waste water of kraft pulp making and paper making waste water. They observed 95% colour removal and sludge with improved settling property as shown by reduction of the sludge volume index from 474 to 120 ml/g. They also observed that lowering pH lowered the optimum alum dose. Maximum colour removal was observed at pH 5.2. Ramteke et al. [3] used pyrolized char from paper mill sludge and found 37.5%–75% colour removal from a 1% solution of black liquor at carbon doses varying from 40 g/l to 100 g/l. During investigations on the use of paper mill waste water for irrigation, Deshmukh and Deshpande [4] observed that the percolates from the field had no colour and no lignin. They attributed this to the base exchange capacity of the soil containing calcium and other multivalent salts. They used calcium sulphate to provide calcium ions and found that no appreciable reduction of lignin (and hence of colour) could be obtained at $CaSO_4$ dose of less than 1000 mg/l. With initial lignin concentration of 1000 mg/l and $CaSO_4$ dose varying from 1000 to 2500 mg/l, lignin removal efficiency ranged between 63.4% and 80%, respectively. At initial $CaSO_4$ concentration of 2500 mg/l and lignin varying from 300 mg/l to 5000 mg/l, the colour removal ranged between 67.2% and 88.1%. Upadhyaya and Singh [5] studied the use of various chemical coagulating agents and chlorine for removal of colour from waste water generated in a hardwood kraft paper mill. The waste water came from pulp mill, brown stock wash water, waste water discharged from alkaline extraction stage of bleach plant and combined effluent from all areas of the mill. They found that a combination of alum, calcium hypochlorite and ferrous sulphate in the presence of chlorine water was most effective and gave colour, BOD and COD removals of 97%, 71% and 64%, respectively. Pawels and Bhole [6] tried various anionic, cationic and non-ionic polyelectrolytes in combination with alum, aluminium chloride, ferric chloride and magnesium chloride on a Kraft paper mill waste water to study their removal efficiencies of colour, COD and suspended solids. Aluminium chloride alone could remove 59.4% colour. Alum (300 mg/l) with Magnafloc 155, an anionic polyelectrolyte (0.05 mg/l) reduced suspended solids, COD and colour by 91.6%, 97% and 66.7%, respectively. The nonionic polyelectrolyte EA 1533 gave maximum colour removal (93.3%) at a dose of 0.3 mg/l with 300 mg/l of alum. In another study involving the use of polyelectrolytes with coagulants for colour removal, Rohella et al. [7] collected waste water samples from a pulp and paper mill using sabai grass and recycled waste paper as raw material. During preliminary studies, they electrolyzed the sample for 60 minutes and found 97.5% colour removal and only 67.6% turbidity removal. Alum, used alone in doses from 10 to 20 mg/l reduced turbidity by 23.14% but showed no colour removal. So cationic polyelectrolytes were used with alum (20 mg/l). Polyelectrolyte Rishlyte 80 L, at a dose of 0.2 ml/l gave 96.26%, 55.65% and 82.58% reductions of turbidity, COD and colour, respectively, while there was practically no significant improvement with the addition of 20 mg/l of alum. They concluded, therefore, that alum addition was not required.

Prasad and Gupta [8] used two white-rot fungi, *Phanerocheate chrysosporium* MTCC-787 and *Trametes versicolor* MTCC-138 to study colour removal from a paper mill using eucalyptus as the main raw material. Basic nutrients such as carbon and nitrogen had to be added to the fungal culture, because the fungi cannot use lignin as a source of carbon. In the presence of these nutrients, colour removal was seen to be 93.8% [9]. A bagasse-based paper mill effluent was used to study colour removal by the white rot fungus *Trametes versicolor* [9]. Effluent supplemented with ammonium nitrate and glucose, but no fungus, showed 40% colour removal. The maximum colour removal was found to be 60% on the fourth day of the culture inoculated with the fungus after addition of 0.175% ammonium nitrate and 1% glucose substrate. Peralta Zamora et al. [10] immobilized the enzyme horseradish peroxidase on Amberlite IRA-400 ion exchange resin, which showed maximum efficiency of colour removal and degradation of phenolic species from kraft mill effluent, pulp bleaching effluent and black liquor. Colour removal from UV-irradiated effluent was better than from non-irradiated effluent, suggesting that photo-enzymatic colour removal would be useful for industrial application. These researchers also found that effluents from textile manufacture and kraft pulp mills were decolourized by ultraviolet radiation in the presence of free titanium dioxide, free zinc oxide or zinc oxide supported on silica gel. Duran et al. [11] found total colour removal from kraft mill effluent after 2 hours of UV irradiation in the presence of zinc oxide. When zinc oxide was immobilized on sand, the rate of colour removal doubled. A combined photochemical biobleaching process halved the time required for 50% biological colour removal after 10 minutes of irradiation.

An ink removing technique, developed at the University of Florida, successfully removes inks, pigments and dyes from newsprint, glossy magazines, even tissue and increases the amount of recycled paper which plants can use to produce more paper [11A].

11.4.2 Biological Treatment

Among the different methods of biological waste water treatment are activated sludge process and its modifications, trickling filtration, anaerobic treatment and its modifications, waste stabilization ponds, etc. In a study of treatability of strawboard waste, Srinivasan [12] found that satisfactory results could be obtained by subjecting the waste water to 14 days of bacterial-fungal treatment, followed by 6 days of algal-bacterial symbiotic treatment. The above work was extended to pilot plant study by Srinivasan, Jayangoudar and Kothandaraman [13]. They found that a selected inoculum was required to bring about 90% BOD reduction. The BOD loading applied was 169 kg/ha/day. The BOD of the effluent was found to be 80 mg/l. Verma et al. [14] studied the presence and concentration of various algal species growing in the effluent from a paper mill over a period of time covering summer, monsoon and winter. They found that in spite of the presence of phenolic substances (15 ± 0.86 mg/l) in the waste water, 26 species belonging to 14 genera were present.

Valsamma, Anto and Joseph [15] assessed the viability of water weeds *Azolla pinnata* and *Lemna minor* and the chlorophycean alga *Scenedesmus bijugatus* in paper mill effluents. They observed that the algae could be grown on clear effluent with addition of nitrogen and phosphorus. Reduction of BOD and COD of the effluent from 90 and 1000 mg/l to 18 and 400 mg/l, respectively, was also observed. Water weeds did not require nutrient supplementation for growth and for reduction of BOD and COD.

In general, *waste stabilization ponds* have found limited application in the treatment of paper mill waste water, mainly because of the colour, which interferes with photosynthesis and the difficulty in degrading the cellulose molecule under aerobic conditions. Even when the waste water is settled before pond treatment, satisfactory quality of effluent is obtained only with a detention time of 20–30 days.

Aerated lagoons are quite commonly used for treatment of total mill waste water. Mechanical aerators are used for aeration. Nutrient supplementation with nitrogen and phosphorus compounds is essential. Sewage may also be used to supply nitrogen and phosphorus, thereby reducing to some extent the requirement of chemical compounds for nutrient supplementation. Resin acids present in the waste water cause foaming, which severely reduces oxygen transfer. Proper spacing of aerators, addition of antifoaming agents or spraying a jet of water to break up the foam are some of the remedial measures against foaming. Design criteria for aerated lagoons used are: organic load 0.04–0.06 kg/m^3/day, detention time 5–10 days, depth 4–5 metres, C:N:P::100:1.5:0.3. As these wastes contain a large amount of suspended solids, it is advisable to provide primary settling before biological treatment to ensure satisfactory removal of settleable solids [16].

Sastry, Alagarsamy and Kothandaraman [17] studied the characteristics and treatment of combined waste water from a pulp and paper mill and concluded from laboratory scale studies that plain settling of composite and paper machine waste reduced BOD and suspended solids by 30–42% and 74–76.7%, respectively. Addition of lime or lime sludge even up to 1000 mg/l did not improve the quality of the settled effluent in terms of colour removal. However, the combined waste was amenable to anaerobic and aerobic lagooning treatment after nutrient supplementation (BOD:N:P::100:2:0.5). Srinivasan and Manuel [18] found that settled waste from strawboard making mill could be treated by activated sludge process, when it was diluted with sewage in a ratio of 2 parts waste to 1 part sewage. BOD removal efficiency increased when ammonium nitrate or ammonium phosphate was added as nutrient supplement.

A high capacity reactor system, developed in Germany, consists of a steel tank with a height to diameter ratio of 6:1, inside which there is an open-ended draft tube into which air is introduced. This produces high turbulence. The air is dispersed into small bubbles and reduces the size of bacterial agglomerates, thereby increasing their surface area. This enables the biomass to withstand shock loads and sudden changes in pH. Advantages claimed for this process are: reduction in capital and operating costs, reduction in production of excess sludge by 60%, less footprint area and nitrification even at low temperatures [19].

Rajakumari and Murugesan [20] studied the application of UASB reactor to the treatment of pulp and paper mill wastes. They observed that organic loading rate and volatile suspended solids were the most significant factors which interfere with treatment efficiency. Production of biogas was strongly influenced by increase in organic loading rate. Addition of nutrient to the feed enriched and supported the flocculent bed, which in turn was reflected in increased treatment efficiency. Biological degradation of lignin from pulp mill black liquor was studied by Woodward et al. [21]. They acclimated the organisms from a river water receiving lignin-bearing waste water and produced a heterogeneous bacterial culture which could effectively degrade lignin. The acclimated activated sludge reduced COD by 80%, lignin by 90% (initial lignin 1000 mg/l) and colour by 98%. The mechanism of removal was biosorptive in nature.

A case study of anaerobic-aerobic treatment of pulp mill effluents was presented by Deshpande et al. [22]. The mill, with a 30 TPD bleached bagasse pulping capacity, produced 2000–2200 m^3 of black liquor daily.

This was digested anaerobically in two 6200 m^3 capacity mild steel digesters with a retention time of 50 hours. At a COD loading rate of 5 kg/m^3/day, BOD and COD removals of 90% and 70%, respectively, were observed. Gas production was 12,000–14,000 m^3/day with 75% methane. Energy from the biogas, which was used in the boilers, reduced LSHS oil consumption by 3 to 4 tonnes daily. Effluent from the digesters was treated in an activated sludge system. The overall BOD and COD removal of the system was 98% and 85%, respectively.

Anaerobic digestion of cooker liquor from strawboard mills was studied by Srinivasan and Dixit [23]. They found that the laboratory-scale digester could be loaded up to 0.03 g of volatile matter/l of digester volume/day and gave a gas yield of 0.59 l/g of volatile matter added. Addition of feed had to be continuous and regular, otherwise the performance of the digester was adversely affected. Volatile matter destruction was found to be 90%.

Rudraiah et al. [24] used an anaerobic rotating biological contactor to treat waste water from a waste paper-based pulp and paper mill. The investigators also tried to determine the gas kinetics, based on various models. They found that the substrate removal efficiency ranged between 76.5% at COD loading rate of 6 kg/m^3/day and 96.5% at 0.3 kg/m^3/day. Optimum conditions were found to be: influent pH–6.9 to 7.0, Temperature–32 to 35°C, HRT–1 day, rotational speed–10 RPM and organic loading rate–1.45 kg COD/m^3/day.

Mall and Upadhyay [25] studied the possibilities of using solid wastes generated during the making of pulp and paper. They have suggested (a) reburning of lime sludge after desilication, (b) use of fly ash in cement manufacture, (c) use of lime sludge, fly ash and effluent sludge as soil conditioner, (d) use of bamboo and wood dust for making fire bricks for energy generation. Prakash and Chandra [26] tried the use of lime mud and alum for colour removal from paper mill waste in place of clay and alum. They observed that the volume of sludge produced was less with the former combination than with the latter. Moreover, the lime mud-alum combination produced sludge with better drainability. Recycling of paper mill cellulosic waste by the production of single cell protein (SCP) was suggested by Sandhya and Joshi [27]. They found that cellulosic waste from small paper mills contains about 67% cellulose and 31–35% inorganics. This waste could be converted into sugar, alcohol or SCP, or could be used as a source of carbon in biodegradation of lignin.

Chakravarti et al. [28] have shown that secondary sludge from waste treatment plant of a paper mill can be profitably used for rearing of fish-fry, both in the laboratory and in the field. Growth and mortality of the fish reared, thus, were comparable with those reared in the conventional way of induced manuring and feeding. Paice et al. [29] subjected effluent from a mechanical pulp mill containing sulphites to activated sludge treatment. They found that sulphites up to 500 mg/l were handled by the activated sludge without ill effects. Better than

90% removal of BOD and resin and fatty acids was achieved at an aeration period of 24 hours. Bhatia et al. [30] modified an existing aerated stabilization basin to handle increased load, due to the addition of a deink mill to the existing thermomechanical pulp mill, by fine bubble membrane technology and added a secondary clarifier. Automatic cycling of air to individual air headers in on-off sequence ensured optimum mixing and aeration. Villenevieue and Tremblay [31] carried out definition studies to construct conventional secondary treatment systems for four Canadian white paper mills. They concluded that sequencing batch reactor was the appropriate method. It also reduced cost by 30%. Marshall et al. [32] discussed the criteria for selection and performance of a fixed film submerged biological contactor (SBC) and a fluidized bed biological system under pilot plant conditions. They found that the SBC was able to take wide variations in load and strength of the waste water.

11.5 DISPOSAL OF WASTE WATER

It is a common practice to dispose of treated effluent from a paper mill on land for irrigation, where adequate land is available for such disposal. BOD loadings are usually limited to 225 kg/ha/day, pH should be between 6.0 and 9.0 and the sodium adsorption ratio (SAR) should be less than 8. Contamination of groundwater was observed in a few cases, where pulping liquors were applied to highly porous sandy soil. Therefore, evaluation of soil type, direction of ground water movement, and location of existing wells in the area to be irrigated must be done before such application [33].

The physico-chemical and biological characteristics of a paper mill were studied by Suriyanarayanan, Jayakumar and Balasubramanian [34]. They concluded that although there were increases in the pH value, nitrogen and phosphorus contents and sodium, calcium and magnesium concentrations (because of the addition of salts of these elements during manufacture) in the treated effluent, it was fit for use as irrigation water.

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Chapter 12

FERMENTATION INDUSTRY WASTES

Fermentation industry produces antibiotics, alcoholic beverages, industrial alcohol, yeast, etc. Different raw materials are subjected to the process of fermentation to yield the above end products. As a result, the waste waters generated contain the undergraded raw material, chemicals used to support fermentation, biological agents used in the process, and so on. A number of useful by-products can be obtained from the residues of fermentation.

12.1 PHARMACEUTICAL INDUSTRY

Products of this industry may be classified as:

- Chemical—antihistaminics or hypnotics
- Antibiotics—narrow spectrum or broad spectrum
- Biologicals—vaccines or sera
- Animal—hormones or extracts
- Vegetable—fluid extracts

Forms in which the above products are used are tablets, pills, capsules, elixirs, extracts, tinctures, emulsions, suspensions, solutions, lotions, syrups, mixtures, sprays, ointments, etc. Some units in the pharmaceutical industry produce bulk drugs, while others make formulations. Still others are engaged in receiving various ingredients of a drug and mixing them in proper amounts to give the final product. All the units have a ‘filling and packing’ section, which produces a large amount of solid wastes such as paper cartons, bottles, ampoules, rubber stoppers. A unit having Quality Control laboratory has usually an animal house attached to it. Dead animals and other solid wastes from this section need to be handled carefully and disposed of effectively.

12.1.1 Manufacturing Process

Pharmaceutical industry produces medicinals both by fermentation and by organic synthesis. Industries based on fermentation process produce vitamins (particularly B_2, B_{12} and C), various antibiotics, organic acids, enzymes, etc. Antibiotics and vitamins are synthesized by fungi or bacteria in large, stirred tanks from a fairly complex nutrient solution of organic matter and minerals. Raw materials such as corn steep liquor, distiller's solubles, soyabean meal, fish or whole solubles are used to provide nitrogen and growth factors, while energy is supplied by various sugars and starch. Industries which only formulate the drugs and use standard methods of mixing, pelletizing, capsulating and packing, use raw materials such as sugar, corn syrups, lactose, calcium, gelatin, talc, diatomaceous earth, alcohols, wines, glycerine, aspirin and other vitamins and antibiotics [1, 2].

The manufacturing operations include seed production, fermentation to increase the biomass, production of the desired metabolite, filtration of the biomass, pH adjustment, removal of colour from the fermented broth, extraction of the end products with solvents or on suitable resin columns, evaporation, filtration and drying. In addition to the solid wastes mentioned above, mycelium, filter aids, liver pulp and dust from the tabletting section are produced during manufacture. Liquid wastes generated are classified as: (a) process wastes consisting mainly of used chemicals, spent fermentation broth, washings and contaminated batches, (b) the sanitary wastes, and (c) cooling water. A manufacturing flow sheet is given in Fig. 12.1.

Average chemical composition of the process wastes produced in the manufacture of penicillin is tabulated [3] see also Fig. 12.2.

Colour	**Colourless**
Odour	Fruity
pH value	6.3
5-day 37°C BOD	1490
Free ammonia nitrogen	5
Albuminoid nitrogen	13
Organic nitrogen	18
Phosphates	72
Sulphates	50
Chlorides	90
Total solids	1900
Suspended solids	420
Volatile solids	880

Note: All values except pH are expressed in mg/l.

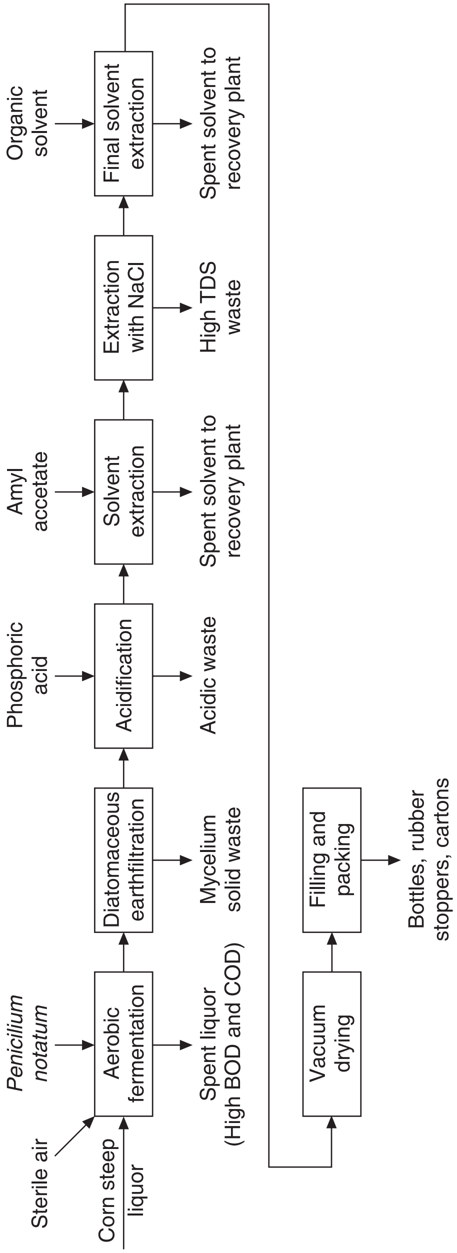

Figure 12.1 Penicillin manufacturing flow diagram.

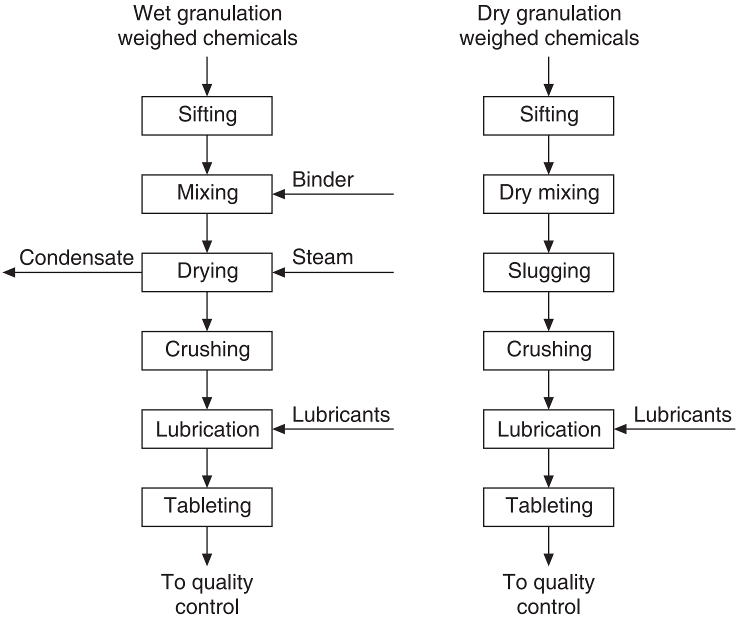

Figure 12.2 Pharmaceutical industry-tableting.

The above figures, especially BOD, can reach very high values, if excess of solvents such as amyl acetate or acetone are discharged into the waste water streams.

Average chemical composition of the process wastes produced in the manufacture of streptomycin is tabulated here [3].

Colour	**Pale yellow**
Odour	Septic
pH	6.2
5-day 37°C BOD	1794
Free ammoniacal nitrogen	2.6
Albuminoid nitrogen	28.4
Organic nitrogen	29.1
Phosphates	65
Sulphates	52
Chlorides	104
Total solids	3594
Suspended solids	1750
Total volatile solids	1446

Note: All values except pH are expressed in mg/l.

Synthetic drugs manufacturing plants produce effluents which can be classified as:

1. Highly acidic, with pH less than or equal to 1.0
2. Combined waste waters from all manufacturing blocks, except those from intermediates
3. The floor washings from all blocks
4. Sewage from the toilet blocks

In addition, the effluents contain varying concentrations of heavy metals such as copper, chromium, zinc, nickel and mercury [4].

The synthetic drugs plants use a number of organic and inorganic chemicals and produce a variety of drugs in different sections of the plant. The volume and composition of liquid wastes vary from one plant to another and one product to another. So, a ‘typical’ plant cannot be considered in this industry [5].

12.1.2 Recovery of Solids

A noteworthy feature of pharmaceutical wastes is the possibility of solids recovery from the spent broth, which is achieved by evaporation of the broth. Although the suspended solids in the waste remain nearly constant after evaporation, there is a distinct reduction in volatile solids, nitrogen, sulphur, reducing sugars and BOD, as seen from Table 12.1 [6].

Table 12.1 Recovery of Solids

Item of analysis	Concentration (mg/l) Before	After	Removal(%)
5-day 20°C BOD	4030	2110	47.6
Total solids	12,400	4300	63.3
Volatile solids	7150	1630	77.2
Suspended solids	1390	1170	15.8
Total nitrogen	400	95	76.2
Total sulphur	429	82	80.8
Reducing sugars	943	187	80.1
Ammoniacal nitrogen	131	70	46.5

A process patented by Eli Lilly and Co. reduces pollution at source by passing the spent broth through a reverse osmosis (RO) unit. Clarified and filtered spent broth is contacted with the semipermeable membrane until 80–90% of the broth penetrates the membrane and the concentration of the antibiotic increases five to tenfold. The waste water recovered thus has low BOD and COD. It is recycled through an RO element and reused as process water[2].

Production of penicillin involves cultivation of the mold *Penicillium-notatum-chrysogenum* under submerged aerobic conditions. To recover the drug, the mold mycelium is separated by filtration and the penicillin is adsorbed or extracted from the filtrate. The BOD of the wet penicillium mycelium cake from the filter is reported to be from 40,000 to 70,000 mg/l. Composition of the dried mycelium cake is tabulated here.

Ingredient	%
Moisture	8
Protein (6.25X T.N.)	32
Fat	7
Minerals	20
Crude fibre	7
Nitrogen-free extract	26
Micrograms/Gram	
Choline	3700
Thiamine	6
Riboflavin	37
Pantothenic acid	64
Niacin	7
Biotin	5
Pyridoxine	13
B_{12}	0.02

The mycelium and filtrate are found to be rich in pantothenic acid and can supply riboflavin and certain unidentified growth factors to chicks [7].

12.1.3 Treatment of Waste Water

Methods of treatment include physical, chemical and biological or a combination of the three. An essential step before biological treatment is to recover solvents from the waste water and separation of mycelium. The recovered solvents can be reused, while mycelium is used as chicken feed, since it contains essential growth factors in addition to pantothenic acid and riboflavin as already mentioned.

An established flow sheet includes screening, grit removal, oil and grease removal (optional), equalization, adjusting pH between 7.0 and 8.0, two-stage trickling filtration and final clarification. The treated effluent is fit for discharge to municipal sewers. High rates of recirculation, ranging from 7:1 to 15:1 are required. The filter medium supports a thick, gelatinous biological growth, which may not slough easily. This can lead to ponding and a reduction in BOD removal [8].

Two-stage trickling filtration can treat the wastes effectively with the following combinations:

- Process waste plus sewage (50:50) plus nutrients
- Sewage plus process waste plus spent broth (85 plus 11.5 plus 3.5)
- Sewage plus spent broth (90 plus 10)

Addition of chlorination and sand filtration of the effluent from trickling filter can give up to 99.3% BOD reduction [6].

Activated sludge process and its modifications have been effectively used in treating pharmaceutical waste water. Deshmukh, Gadgil and Subramanyam [9] conducted laboratory-scale studies on effluent streams from a synthetic drugs manufacturing plant. The streams selected were: (a) wastes from all manufacturing sections, except those from intermediates, and (b) floor washings. Batch treatment of a 1:1 mixture of the two streams was successful at a loading rate of 0.2 kg BOD/kg MLVSS/day. Complete mixed activated sludge process produced an effluent of less than 100 mg/l BOD at a loading rate of 0.26 kg BOD/kg MLVSS/day. Ghosal and Bhowmik [10] developed a method of treating drug manufacturing waste water containing up to 125 mg/l of phenols. They carried out the study in three phases, viz. (i) survival of developed biomass under varying influent quality, (ii) viability of the biomass in the presence of pharmaceutical waste containing phenols, and (iii) continuous monitoring of the effectiveness of the biomass in the real system. The full-scale plant consisted of primary clarification, equalization-cum neutralization, activated sludge process and filtration through a carbon bed. The treated effluent had a BOD of 24–30 mg/l, COD of 180–230 mg/l and phenol content between 0.6 and 1.0 mg/l. A study involving bio-augmentation with acclimatized cells from an off-line reactor to an upflow anaerobic fluidized bed system was conducted by Saravanane, Murthy and Krishnaiah [11]. The raw waste with COD ranging from 14,000 to 18,000 mg/l could not be consistently treated in a conventional mode of operation. But addition of 30–73.2 g of acclimated cells from an off-line reactor every 2 days helped in giving 88.5% COD removal.

Yeole, Gadre and Ranade [12] treated waste water generated in the production of liver and beef extract by employing anaerobic treatment followed by aerobic treatment. At a loading rate of 0.7 kg COD/m^3/day, anaerobic treatment removed 89% COD and 91% BOD but the effluent still had 1200 mg/l BOD and 2300 mg/l COD. Settling of the effluent followed by activated sludge process produced an effluent with 50 mg/l BOD and 290 mg/l COD. Electrochemical oxidation of pharmaceutical waste using cast iron electrode was done in a batch study by Deshpande et al. [13]. They observed 72% COD removal in 2 hours of electrolysis and suggest that pharmaceutical wastes could be effectively pretreated by anodic oxidation.

Sachs et al. [14] studied the performance of anaerobic filter for removal of COD from waste water generated in synthetic drugs manufacture. At an organic load of 0.56 kg COD/m^3/day, and a waste strength of 2000 mg/l, the filter removed consistently 70–80% COD and 94% BOD. Temperature was maintained at 37 °C and hydraulic retention time was 36 hours. Colour removal was also better than that from the existing aerobic system. At the same retention time, the filter could remove only 18% COD and 25% BOD when the organic load was increased threefold. Waste water produced from the manufacture of ayurvedic medicines was treated in pilot anaerobic filters in series by Naphade et al. [15]. The factory used medicinal plants, herbs, their skins, roots, etc. for extracting medicines from them and produced an effluent of 6 m^3/day with a BOD of 35,000 mg/l, COD ranging from 58,200 to 61,200 mg/l and pH between 4.2 and 4.6. The pilot filters were acclimated to the waste water in 60 days, by using raw sewage first, and then gradually increasing the waste water feed. The pH of the influent was adjusted between 7.0 and 8.0 with lime. The hydraulic retention time was 6 hours. Effluent from the second filter was treated with lime and polyacrylamide. Considerable reduction in BOD, COD and colour was observed. Pyridine, commonly used as a solvent in the manufacture of many drugs, is present in waste waters of pharmaceutical industry. Pyridine compounds are hazardous in nature and persist for a long time in the environment, as they are poor substrates for indigenous microorganisms. Therefore, a laboratory-scale study was carried out to determine whether pyridine could be degraded by *Bacillus* consortia in an upflow aerobic fixed film reactor (UAFFR) [16]. Pharmaceutical waste containing 4200 mg/l pyridine was collected from an industry manufacturing cephalexin, a broad spectrum antibiotic. It was passed through the reactor packed with polyurethane foam. The characteristics of the waste water were as given in Table 12.2.

Table 12.2 Waste Waters from Manufacture of Cephalexin

Parameter	Value
pH	7.6
Electrical conductivity (EC)	6.8 mS/cm
Total dissolved solids	46,500
Total volatile solids	10,000
BOD	3,100
COD	9,405
Total organic carbon (TOC)	9,800
Chlorides	9,430
Sulphates	2,000
Total Kjeldahl nitrogen	9,900
Phosphates	Below detectable limits
Pyridine	4,200

Note: All values, except pH and electrical conductivity are expressed in mg/l.

It was observed that 82% pyridine removal was possible at an organic loading of 0.5 kg TOC/m^3/day at a hydraulic retention time of 8 hours. A small bulk drug manufacturing industry in South India generating about 45 m^3 of waste water per day, had the composition as given in Table 12.3.

Table 12.3 Characteristics of Waste Water from Drug Manufacturing Industry

Parameter	Sample 1	Sample 2
pH	3.6	3.4
Acidity as $CaCO_3$	35	50
COD	2,19,520	3,20,000
BOD	1,20,000	1,30,000
Suspended solids	2000	1200
Nitrogen, as N	5700	4880
Phosphorus, as P	1300	1200

Note: All values except pH are expressed in mg/l.

Treatment suggested for rendering this waste water fit for discharge to a lake was as follows:

Equalization for 5 days; preaeration for 6 hours; neutralization with NaOH and settling for 3 hours; anaerobic lagooning for 60 days; secondary anaerobic lagooning for 40 days; extended aeration for 5 days with MLSS of 4000 mg/l and loading of 0.15 kg/kg BOD [17].

Another bulk drug manufacturer produced waste water containing predominantly inorganic salts such as sodium sulphate, aluminium chloride and basic chromium sulphate in addition to organic pollutants. An important step in waste water treatment was segregation of waste streams bearing inorganic salts and their recovery. This was followed by equalization, coagulation with aluminium chloride and settling, mixing the settled waste water with sewage and sullage from the plant and giving biological treatment in an aerated lagoon of 5 days' detention time. The treated effluent was further treated with activated carbon for removal of colour-causing organics. The effluent was discharged into the sea [17].

Kothari, Shah and Patel [18] studied the effect of using fermenter exhaust air on the performance of activated sludge process, treating waste water from the industry producing antibiotics and chemicals. A comparison was made between quality of treated effluents produced by aeration with normal air and with fermenter exhaust air. It was observed that there was no difference in the quality of the two effluents, except that effluent from aeration with normal air showed 4% better BOD removal. A precaution to be taken was that steam used for sterilizing the fermenter should not be allowed to enter the aeration basin because of its high temperature. They also observed that 75% of the power consumed in the effluent treatment plant was for aeration. This cost could be saved by replacing normal air with fermenter exhaust air.

Control of bad odours from the sludge (consisting of primary sludge + aerobically digested secondary excess sludge) was achieved by a pharmaceuticals company in the U.S.A. The volume of waste water produced was about 7 million litres/day. The amount of hydrogen peroxide required to control odours was about 91 metric tonnes per year [19].

12.2 DISTILLERIES

The beverage alcoholic industry uses different grains, malted barley and molasses as raw material. On the other hand, the industrial alcohol industry uses molasses as raw material. Cane or beet molasses is used in the production of rum, while whisky and brandy are produced from grain starch. Wineries use fruit juice, particularly grape juice, as raw material [20,21]. Distillery waste water, known as spent wash, slop, vinnasse, dunder, etc. constitutes one of the most obnoxious wastes. It has a high BOD, COD, dissolved solids and low pH, but it is amenable to biological treatment. It can be profitably subjected to anaerobic treatment to get gas (which has fuel value), followed by aerobic treatment, in order to meet discharge standards.

Molasses, generated during the manufacture of sugar from cane or beet, is a waste product containing sugar, which can no longer be extracted economically. It is, therefore, used in the manufacture of industrial alcohol. According to the data of All India Distillers' Association, about 1.6 million kilolitres of alcohol are produced per year by 309 distilleries in India [22]. The manufacturing process involves dilution of the molasses with water to 12–20% sugar, acidification with sulphuric acid, fermentation with the help of yeast, *Saccharomyces cerevisiae* under controlled conditions of pH and temperature, and nutrient supplementation with nitrogen and phosphorus. Fermentation is done for a period ranging from 12 to 60 hours, at a temperature of 30°C, at the end of which the ethanol concentration is between 7 and 10%. The fermenter produces yeast sludge with about 30% solids, which is separated either for recirculation or used for its food value. The dilute ethanol is then subjected to azeotropic distillation in a two-or three-stage distillation train to give a final concentration of 95%. The first column of the train removes the bulk of water and other constituents from the ethanol and is the principal component of spent wash [21]. The other waste water streams come from fermenter washing, floor washing, cooling water, etc. It takes from 3 to 10 kg of molasses to produce 1 litre of alcohol and produces 10 to 15 litres of spent wash. The total volume of waste water per litre of alcohol produced ranges from 60 to 100 litres. Cooling and condenser waters are generally 6 times the volume of spent wash and are generally not polluted, as they are used in surface condensers. A general manufacturing flow sheet is given in Fig. 12.3.

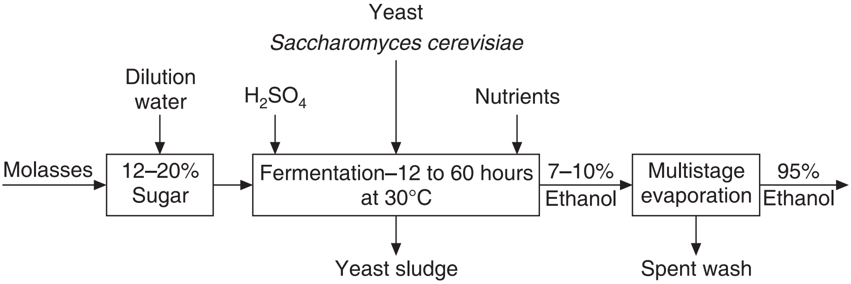

Figure 12.3 Ethanol manufacturing flow sheet

Characteristics of molasses distillery waste water are given in Table 12.4 [12].

Table 12.4 Characteristics of Waste Water in Molasses Distillery

Parameter	Range	Average
COD	15–176	77.7
pH	3.5–5.7	4.2
Temperature, °C	80–105	94
Total solids	21–140	78.5
Suspended solids	1–13	5.1
Dissolved solids	25–110	56.9
5-day BOD	7–95	35.7
Ash	16–40	28.9
Volatile fatty acids	0.7–5.5	2.18
Reducing sugars	14–45	26.5
Total nitrogen	0.6–8.9	1.79
Ammoniacal nitrogen	0.04–0.89	0.26
Organic nitrogen	0.6–8.7	1.94
Sodium (Na_2O)	0.13–2.51	1.04
Potassium (K_2O)	4.8–22.59	10.73
Calcium (CaO)	1.26–6.7	3.52
Magnesium (MgO)	0.66–2.35	1.63
Phosphorus (P^{5+})	0.026–0.326	0.168
Silicate (SiO_2)	–	1.51
Chloride (Cl^-)	0.68–7.39	3.79
Sulphate (SO_4^{2-})	1.56–6.6	4.36
Total iron (Fe^{2+})	0.001–0.12	0.69
Copper (Cu^{2+})	0.004–0.03	0.014
Zinc (Zn^{2+})	0.027–0.225	

Note: The above values, except pH and temperature, are expressed in grams/litre.

In view of the highly polluting nature of spent wash, it is essential to adopt measures such as recycling, using in irrigation, evaporation and incineration, production of biomass/biochemicals and production of food supplements [2] before subjecting the waste water to treatment. Recycle of spent wash reduces the volume of waste water to be treated. If the distillery is associated with a sugar mill, the spent wash can be used as a portion of cane wash water. It can also be used as dilution water of molasses before fermentation [2]. Spent wash, diluted 20 times, can be safely used for irrigation of sugar cane. At this dilution, it provides sodium equivalent to 200 kg/hectare. The degree of dilution will depend on the composition of the spent wash, nature of soil, inorganic salts and their concentration in the spent wash, etc.

Evaporation of spent wash is done to produce animal feed or fertilizer. If it is incinerated after evaporation, potash can be recovered from the ash. If the distillery is associated with a sugar factory, recovery of potash after evaporation and incineration would appear to be economical, as the sugar factory can supply the steam required for potash recovery plant [22, 23]. The use of spent wash for production of fodder yeast helps reduce the reducing sugars, and, hence, the BOD of the waste water. *Candida utilis* and *Candida tropicalis* have been successfully grown on spent wash. Some distilleries recover dry yeast powder from spent wash mixtures [24].

Dried stillage can be used as fodder feed. Bhaskaran [25] reported that sludge from aeration of distillery waste contains about 800 micrograms of vitamin B_{12} per kg of dried sludge and can be used as a supplementary animal or poultry feed. Boruff [26] has reported on the commercial production of Riboflavin and other B-vitamins and antibiotics from stillage. It is possible to completely recover grains in the form of dried solids for use as cattle feed. The slops are screened to remove the grains, which are treated further to form dried solids. They have a special value in dairy and poultry feeds on account of their proteins, vitamins and fat contents [27]. Effects of discharge of raw spent wash on land or into water are:

1. *On land:* Pollution of groundwater, charring of vegetation and crops, accumulation of salts and increase in electrical conductivity of soil.
2. *Into water:* Lowering pH of receiving water, increase in organic load, depletion of dissolved oxygen, large-scale fish kills, bad odours and discoloration of water.

12.2.1 Treatment of Waste Water

Among the various methods, physico-chemical methods were found to be much less effective than biological methods. Sedimentation, plain or aided by coagulants, was not effective. In fact, it led to anaerobic conditions and odour nuisance. However, Duval [28] has successfully pretreated wine distillery waste by centrifugation, autoflocculation and settling. The settled sludge was found to be suitable as animal feed.

Kato et al. [29] used reverse osmosis of distillery waste and recycled it to the corn mashing stage, resulting in increasing the alcohol yield by 5.8%. Rembowski et al. [30] used reverse osmosis on stillage from beet molasses with a BOD of 10,000 mg/l. The permeate had a BOD of 600 mg/l which was used as molasses dilutent. The reject had 15% dissolved solids. After evaporation, they were found suitable as fodder additive. Dubey [31] reported that stillage could be treated by electro-flocculation with the addition of 6.5% sodium chloride to a waste with a pH from 3.8 to 7.0 and a temperature from 49–82°C.

The characteristics of spent wash are such that it is amenable to biological treatment since the COD:BOD ratio and BOD:N:P ratio are favourable. High BOD of the waste water indicates that it is economical to treat the waste water first by anaerobic means, followed by aerobic means. Anaerobic treatment has the obvious advantages of requiring less power, producing small amount of excess sludge and producing a gas with good fuel value. The high BOD of spent wash requires that anaerobic treatment must be followed by aerobic treatment in order to meet the stipulated quality standards. Anaerobic treatment may be given using fixed-film bioreactors or non-attached biomass reactors. It may or may not be necessary to raise the pH value and lower the temperature of the waste water. Considerable work has been done on treating the waste water by anaerobic means. Parthasarthy et al. [32] conducted laboratory-scale treatment of waste water from a distillery attached to a sugar mill. The composition of the waste water was: pH 3.2–4.4, total solids 9–11% with 75% volatile solids, BOD 26,000–50,000 mg/l, COD 50,000–1,15,000 mg/l, total nitrogen 1,200–1,500 mg/l, chlorides 10,150–11,300 mg/l, phosphates 80–100 mg/l, temperature 75°C. The waste could be digested anaerobically at retention times of 12 days and 8 days at BOD loading rates of 11kg/m^3/day and 6.12 kg/m^3/day, respectively. Gas production was 124 m^3/kg BOD destroyed and contained 60% methane. They suggested recirculation of the gas produced in order to supply CO_2 in the initial stages of operation.

Waste water from a distillery producing rectified spirit was treated in a pilot anaerobic lagoon by Rao [33]. The waste water had a BOD between 35,000 and 45,000 mg/l, pH between 4.0 and 5.4, temperature 90–100 °C, volatile solids were about 75% of total solids. Cow dung was used as seed material. Stable conditions were established in 60 days. At an organic loading of 0.6 kg BOD/m^3/day, BOD and volatile solids reductions were 90–95% and 78%, respectively. Volatile acids as high as 21,800 mg/l were recorded in the lagoon, but the pH remained above 6.75 and no ill effect was observed on the performance of the lagoon.

Treatment of distillery waste was done by Gadre and Godbole [34] in laboratory-scale upflow anaerobic filters. They observed that no pH correction was required to the influent, as indicated by satisfactory gas production and COD reduction. At hydraulic retention times of 30, 20 and 15 days and COD loading from 2.05 to 6.81 kg/m^3/day, COD removal ranged between 55% and 77%. The methane content in the gas varied from 60–72%. Vaidyanathan, Meenambal and Gokuldas [35] also used laboratory-scale two-stage upflow anaerobic filters to determine biokinetic coefficients for distillery wastes. They started the reactors with 25% seed and 75% waste water after adjusting the pH to 7.0. BOD loading rate for the two stages was maintained at 0.84 kg/m^3/day and 0.195 kg/m^3/day, respectively. A summary of the coefficients for the two stages is tabulated here.

Particulars	**Stage I**	**Stage II**
Sludge production coefficient (y)	0.065	0.203
Decay coefficient, day^{-1}, k_d	0.0014	0.0014
Substrate removal coefficient, mg/l (k_s)	5396	3998
BOD removal rate, day^{-1} (k)	0.11	0.08

The overall BOD removal was 92.85% and COD removal was 81.73%. The BOD removal efficiency was seen to increase with increasing sludge mean cell residence time (MCRT). Manihar [36] used two separate reactors for acidification and methane generation from spent wash. The acidification reactor of 20 litre capacity was constantly stirred and was operated at a maximum hydraulic retention time of 2.5 days, while the methane reactor of 100 litre capacity was filled with random PVC rings with a void volume of 97% and was provided with recirculation rate varying from 15 to 25 times the inflow. The maximum COD loading rate achieved was 25 kg/m^3/day at a COD removal efficiency of 60–70%. The biogas generated varied between 25 and 45 m^3/m^3 of spent wash and had methane content of 60–70%. This corresponds to 0.40 m^3/kg COD destroyed.

Manihar [37] has also studied the economics of treating spent wash in two reactors in series, viz. biological conditioning and control reactor (BCCR) and methane upflow reactor (MUR). The distillery produced 2080 m^3 of waste water per day. Each of the two reactors had a parallel plate separator on its effluent end. Sludge from each parallel plate separator was recycled to its corresponding anaerobic reactor. The raw waste had a BOD of 43,825 mg/l and COD of 110,400 mg/l. Daily gas production was 71,600 Nm^3 with a coal equivalent of 78 MT/day. Ranade et al. [38] isolated 36 anaerobic bacterial species from spent wash digesting slurry. They also studied the effect of sulphides on methanogenic bacteria and found that all of them (10 numbers) tolerated 1 gm/l of sulphide but were inhibited at 2 gm/l. A total of 10 sulphate-reducing bacteria were obtained from the methanogenic reactor wherein the sulphate concentration was 1.2 gm/l. Eight of the ten isolated species were inhibited at 6 gm/l sulphate, while two were inhibited at 10 gm/l. The authors have expressed the possibility of better control over the digestion process, if adequate knowledge of the number and types of microorganisms, pH value of the digesting mass and volatile fatty acids (VFA) content is available to the operator.

A hybrid reactor, combining the features of a UASB reactor and anaerobic contactor, was developed at Daurala Sugar Works, Meerut, India. The reactor is provided with phase separation to optimize acid formation and methane generation. The acid phase reactor has a working volume of 1050 m^3 and provides a retention time of 34–36 hours. COD loading is 48–50 kg/m^3/day. It is provided with recirculation system. The methane phase reactor, with a working volume of 7700 m^3, provides a retention time of 9–10 days. At a COD load of 9–11 kg/m^3/day, it produces 3.1 m^3 of gas/m^3 of reactor volume. The reactor also has recirculation system. The entire unit is constructed in mild steel and is reported to be working well since its commissioning in 1992 [39, 40].

Seenappa, Jagannath Rao and Kale [41] have reported successful disposal of distillery waste sludge along with press mud cake, water hyacinth, silveroak litter and cow dung. They used the earthworm *Eudrilus eugeniae* to decompose the organic matter in the above mixture. They observed that from 45% to 65% of the supplied organic matter was recovered as compost with 10% moisture and 10–15% of unfed material.

Laboratory-scale studies were conducted by Ilyas et al. [23] for treating spent wash in anaerobic filters. Raw waste was collected from a molasses-based distillery at Anupshahar, U.P. India. PVC pipe pieces were used as filter medium. The initial startup was done using a mixture of cow dung slurry and rumen waste slurry after straining it through cheese cloth. The reactors were fed spent wash, diluted with tap water in one reactor and with the treated effluent in the other. It was observed that pH correction was not required to the raw waste because of the degradation of proteinaceous matter in the waste, reduction of sulphates to sulphides and alkalinity present in the dilution water. Datar et al. [42] described a technique of making the anaerobic biomass stick to the tower packs in anaerobic fixed film fixed bed (UAFFB) reactor by introducing aerobic biomass into these reactors, because such biomass has the ability to produce slime layer to which the anaerobic mass can attach itself. Diluted spent wash was used as feed to the reactor. It was observed that the above technique reduced the acclimatization period to 24 days, even when the COD loading rate was 5.95 kg/m^3 reactor volume/day. The thickness of the anaerobic film was found to be as large as 1.5 mm. At a hydraulic retention time of 5 days and influent COD of 35,000 mg/l, gas production was 0.436 m^3/gm COD reduced/day.

Berchmans and Vijayavalli [43] studied the effect of electro-oxidation on BOD, COD, pH, dissolved solids, etc. of a distillery waste. They found complete removal of BOD and colour, but the pH of the treated waste water was 1.3, indicating acid build-up during treatment. Patil and Kapadnis [44] used hydrogen peroxide, calcium oxide and soil bacteria to remove BOD and colour from distillery waste. They found that the dark brown colour due to meladoinin pigment in the waste water could be effectively removed by hydrogen peroxide-calcium oxide, while the lemon yellow colour formed after hydrogen peroxide-calcium oxide treatment could be removed by hydrogen peroxide-bacteria treatment.

Laboratory-scale studies were conducted by Godbole, Zende and Dhamankar [45] for treating spent wash with water hyacinth. The waste water was diluted from 1% to 20%. Plants placed in 1% and 2% diluted waste water grew, while others either stopped growing or wilted. The uptake of potassium, calcium and phosphorus by the plants was observed. It was found that potassium uptake was the highest. COD reduction was about 42%. Repin and Skvortsov [46] recommend anaerobic and aerobic treatment of spent wash, followed by physico-chemical method for colour removal. The anaerobic treatment consists of anaerobic digestion, followed by clarification and storage in an anaerobic lagoon. Aerobic treatment is done in two stages. They recommend both pneumatic and surface aeration in the aeration tanks, in order to match the oxygen demand with supply. They claim a power saving of up to 40% with this arrangement. Secondary clarifiers in each stage are provided with parallel plate separators. Colour removal can be done either by chemical coagulation and settling, or by ozonation, or by carbon adsorption, or membrane filtration.

Rao, Ranade and Gadgil [47] have described details of converting spent wash into compost by using aerobic method of composting. They conducted laboratory-scale experiments, using spent wash and press mud from sugar mills, to determine mixing ratio, operating parameters, final compost quality, pollution potential and effect of applying the compost on soil quality and crop yield. They found that bagasse could replace press mud for the process of composting. After using this compost for six years, it was found that about 4–6 tonnes of compost is required per hectare of land for sugar cultivation. The crop yield was increased by 10–15%. There was no ill effect on the soil where the compost was used.

Gokarn, Oswal and Sankpal [48] studied the use of *Moringa oleifera* (drumstick) seeds for removing colour from distillery spent wash previously treated by anaerobic and aerobic means. They found that the seed acts as coagulant as well as coagulant aid and also promotes colour removal by activated carbon. Another attempt at colour removal by electrochemical means was done on laboratory scale by Sankpal, Dongare and Gokarn [49]. They used distillery effluent first treated anaerobically and aerobically, followed by chemical treatment to get a COD value between 3000 and 4000 mg/l. However, the waste water subjected to electrochemical treatment had a COD of 6500 mg/l. At a current density of 50 mA/cm^2, it took 5 minutes for colour to change from dark brown to colourless, COD from 6500 to 145 mg/l, BOD from 1200 to 38 mg/l and total dissolved solids from 13.5 to 6.2 gm/l. Ferric chloride and aluminium sulphate were found to accelerate the process of colour removal.

Nimbalkar et al. [50] treated spent wash from a continuous fermentation-based distillery in a laboratory-scale two-phase anaerobic digester system. Dilution or neutralization of the raw waste was not done. At a COD loading rate of 7.2–7.6 kg/m^3/day, 2 days HRT in the acidogenic phase and 16 days' HRT in the methanogenic phase, 76% COD reduction and 60–80% volatile fatty acids reduction was obtained.

Studies on aerobic cultivation of yeast on spent wash were done by Sharma et al. [51] in order to reduce BOD and get yeast as a by-product. A pure culture of *Saccharomyces cerevisiae* was adapted to the spent wash. It was possible to adapt the culture to 100% waste water without addition of nutrients. The optimum pH was 5.0–5.5 and optimum inoculum dose between 85 and 100 mg of dry yeast/70 ml of the waste. Total sugar (which is responsible for BOD in the waste) and BOD reductions were observed to be 60% and 57.5%, respectively.

In order to improve the overall waste water management practice, Gulati [52] suggests evaporation and drying processes for spent wash. The system consists of subjecting the spent wash to multiple effect evaporation after biomethanation. Evaporation is done till the total solids in the waste water reach 40%. The resultant slurry is passed through a spray dryer where it is converted into fine powder. The condensate is recycled for irrigation while the dried powder is mixed with coal and used as fuel. The condensate can also be used as make-up water to cooling tower, or as molasses dilution water. The fine powder can be used as manure on account of its high mineral content. When used as a fuel, the ash contains over 20% potassium as K_2O. No pollution is added to the environment by this process and it becomes, in effect, a ‘zero discharge’ process. Such a plant was supplied to M/s Ugar Sugar Works, Ugar Khurd in 2002 AD. and is reported to be working satisfactorily since then.

Mahajani and Dhale [53] used wet air oxidation to treat distillery spent wash, after it was subjected to biomethanation. The aim was not only to reduce the COD of the effluent but also to produce acetic acid as a value-added product. Experiments were done in the range of 180–210°C and oxygen partial pressure between 0.69 MPa and 1.38 MPa. Cobalt sulphate was used as a catalyst in the reactions. It was seen that the colour destruction was 95% and COD reduction was 65%. In addition acetic acid was formed, which could be recovered by conventional method of extraction. Colour removal and simultaneous COD reduction from spent wash was tried by Ramteke, Wate and Moghe [54] with the help of pyrochar prepared from waste sludge of paper mills. Its performance was compared with that of commercially available activated carbon. It was observed that the pyrochar could remove colour and COD caused by organic matter as well as by the colouring matter, while the commercially available activated carbon removed only colour and COD associated with colour. Weiland and Wulfert [55] conducted pilot plant studies to assess the performance of different types of porous plastic packings used in treating slops from ethanol fermentation by the upflow anaerobic filters. They used three different packings with nearly equal voids but widely varying unit surface areas. They concluded that the reactor performance was influenced more by the shape and size of the support media rather than by unit surface area. High COD removals of 95% could be achieved at COD loading of 10 $kg/m^3/day$.

12.3 BREWERIES

Breweries make beer from grains like barley in two stages:

1. Preparation of malt from the grain, in which the grains are steeped to remove colour. They are then made to sprout under aerobic conditions. The grain is then dried, sprouts are screened and the grain is transported to the brewing section.
2. The malt is treated with hot water which turns it into 'wort' and the starch in it is converted into sugar by boiling with hops. Hops contain resins which dissolve in the wort and contribute the typical bitter taste to the beer. The resins also act as preservatives against the growth of bacteria. The wort is then filtered and cooled. The filtrate is inoculated with a suspension of yeast, which ferments the sugar to alcohol. At the end of the fermentation, the yeast and malt residue is filtered and the beer is carbonated before packing [20, 35]. Liquid wastes originate in the malt house as well as in the brewery. Malt house waste contains high concentration of dissolved organic solids and low suspended solids. This waste is usually alkaline in nature. The brewery produces waste in the form of fermentation residue, which is usually acidic in nature. In addition, wastes from floor and equipment washing, yeast preparation, cooling water are also produced. Composition of malt house and brewery wastes is given in Table 12.5 [21].

Table 12.5 Composition of Malt House and Brewery Wastes

Item	Malt house waste	Brewery waste
pH	6.9–9.5	4.0–7.0
BOD	20–204	70–3000
Total solids	428–700	272–2724
Suspended solids	22–339	16–516
Total nitrogen	14–56	7–42

Note: All values except pH are expressed in mg/l.

12.3.1 Treatment of Waste Water

Brewery wastes are less strong than spent wash from distilleries and can, therefore, be subjected to aerobic treatment in the form of two-stage activated sludge process or trickling filtration. The BOD removal of 90–94% can be achieved. If adequate land is available, the waste may be neutralized and used for broad irrigation [2].

Ince et al. [57] used a pilot-scale, cross-flow, ultrafiltration membrane, anaerobic reactor system to study microbial changes during startup and steady state conditions, when treating brewery waste. They achieved 97% COD removal efficiency at a COD loading of 28.5 kg/m^3/day.

A survey was conducted by Mino [58] to identify filamentous microorganisms in activated sludge plants. A Gram-positive, Neisser-negative filament resembling both *Microthrix spp.* and *Nostocoida limicola* was predominant in the plant treating brewery waste. Anderson et al. [59] investigated the microbial kinetics of a cross-flow, ultrafiltration membrane, anaerobic reactor system treating brewery waste water at four different MLVSS values ranging from 10–15 to 40–50 g/l. Values obtained were:

Maximum specific growth rate: 0.022 day^{-1}
Growth yield: 0.038 gm VSS/gm COD
Decay coefficient-0.0037 day^{-1}
Half saturation coefficient: 390 mg COD/l.

Pilot and full-scale data were presented by Horng et al. [60] for treatment of a brewery waste with COD of 10,000 mg/l in a UASB reactor, followed by submerged, aerobic, fixed film reactor. Pilot tests showed COD removals of 93% for the UASB loaded at 8.9 kg/m^3/day and 64% for the aerobic system, loaded at 0.8 kg COD/m^3/day. Leal et al. [61] subjected an anaerobic, upflow filter to treatment of brewery waste of 8000 mg/l COD under mesophilic conditions. They obtained 96% COD removal after a six month startup period. The average gas produced was 7.1 m^3/day with 80–95% methane. Cronin and Lo [62] examined UASB reactor performance in terms of treatment efficiency and methane production under different hydraulic retention times and organic loading rates. They found that as the COD loading rate increased with time, the influence of the amount of seed material used became pronounced and that a period of at least two weeks was required to prevent delays in the startup when activated sludge was used as seed material.

12.4 WINERIES

In the production of wine, ripe, clean grapes are pressed to give ‘must’, containing juice, skins, seeds and pulp. Red table wines are made by direct fermentation of the must, while white wines are made by removing suspended solids or ‘pomace’ and then fermenting the juice. Dessert wines are made, after partial fermentation, by mixing with neutral brandy, which arrests fermentative activity.

12.4.1 Treatment of Waste Water

Three different types of wastes are generated at a winery, viz. (a) pomace, (b) waste from fermenting, decanting, blending and bottling of the wines, and (c) waste coming from brandy plant which may be compared with de-alcoholized stillage of molasses alcohol distilling plant. The residues from fermentation, called 'lees' are available for distillation to brandy. Brandy can be made from wine, from 'lees' or from pomace. Pomace, as dumped from the presses, contains 30–40% water and on this basis, forms about 12% of the weight of grapes pressed. Potassium tartarate, a useful chemical, can be recovered from lees, pomace and stillage. Stillage is the least readily disposable of all winery wastes. Intermittent irrigation of sandy soils with stillage offers an effective solution. Rate of application is about 800 m^3/ha/week. Stillage can also be treated with lime and then settled. The clarified waste, diluted 50%, can be effectively applied to trickling filtration and treated [63,64].

Fumi et al. [65] examined treatment of winery waste by activated sludge process, using a modular, multistage system and found COD removal of 98% for an influent COD ranging from 2000 mg/l to 9000 mg/l. The plant could withstand large variations in temperature and hydraulic and COD loading rates. Physical and chemical methods have also been used for treating winery wastes. Salame et al. [66] developed a regenerable filter aid for wine clarification during wine production which reduces the problem of disposal of diatomaceous earth. Medialdea et al. [67] used potassium permanganate at the rate of 200 kg/tonne in a mixing tank, where the redox potential was monitored and lowered the COD to 1000 mg/l, i.e. by 68%. Coma et al. [68] used chitosane as a flocculant for pretreatment and reduced suspended solids by 98% and COD by 40%. Noilet et al. [69] investigated the use of microfiltration and reverse osmosis with and without coagulation to reduce the COD of winery effluent.

Several biological methods have been developed for treatment of winery wastes. Rochard et al. [70] considered that the time required for sufficient purification in aerated storage tanks would be 3–8 weeks. Using aeration tanks in series, Canler et al. [71] found that with some storage of the raw waste, it was possible to achieve 96–98% BOD removal efficiency at a loading rate of 0.12 kg/kg VSS/day. Houbron et al. [72] used a sequencing batch reactor to treat waste with a COD ranging from 2000mg/l to 5000 mg/l, and achieved removals of 97.5% for BOD, 93–96.3% for COD, 50% for TKN and 88% for total phosphorus. The effluent COD was 240–280 mg/l. Orditz et al. [73] used sand filters to further purify aerobically treated waste water to achieve COD reduction from 1493 to 50 mg/l, BOD from 939 to 6 mg/l, NH_4 from 11.5 to 0.6 mg/l, TKN from 35.6 to 2.3 mg/l and total phosphorus from 18.0 to 8.8 mg/l at hydraulic load of 50 mm/day. Racault et al. [74] evaluated a two-stage high rate and a low-rate activated sludge system and obtained 97–98% COD removal at a HRT of 10–15 days. Sludge was produced at the rate of 0.32–0.43 mg/mg COD removed. Muller [75] treated the waste in a UASB reactor and got better than 90% BOD and COD removal efficiencies at loading rates of 941–13,600 mg COD/l. In another study, Torrijos and Moletta [76] evaluated the performance of a 330 m^3 covered lagoon with suspended fishing nets for microbial growth to take place on them. From an average COD load of 18,000 mg/l, the system achieved 95.3% removal.

Maunoir et al. [77] evaluated a multiple component system consisting of a clarifier-digestion tank, an upflow anaerobic biological filter followed by a downward aerobic filter. The system achieved 85% TSS and 60% COD removal in spite of loadings 4.5 times the designed values. Lefebvre et al. [78] found that inserting a yeast buffering tank in a multicomponent treatment process reduced overloading on the activated sludge system. The yeast adapted readily to the variation of sludge load, which could be eventually removed by co-flocculation and settling.

12.5 RECOVERY OF BY-PRODUCTS

It is possible to recover useful products from distilleries, breweries and wineries. Tartaric acid is present in grapes and is obtained from tartar, a by-product of winery. Tartar consists largely of potassium acid tartarate, which is insoluble in alcohol and separates as precipitate as the alcohol concentration increases during fermentation [79]. Pomace, produced during the manufacture of wine, contains about 4–6% tartarate. Stillage from brandy production contains from 0.2–0.7% tartaric acid. Tartarates can be separated by chemical precipitation or by ion exchange [26]. Using electromembrane technique, Audinos et al. [80] recovered 80% of tartaric deposits in wine production tanks. Chaussier et al. [8] combined centrifugation with ultrafiltration to recover the colloidal tannic and phenolic fraction of winery lees. They estimated that at a winery producing 20,000 hectolitres/year, it would be possible to recover 200–700 kg of polyphenols/year and 40–170 kg of colloidal matter. Yu et al. [82] used brewery malt waste as a source of carbon to increase rates of microbial synthesis of packaging bioplastics.

During fermentation, there is about a fourfold increase in the weight of yeast cells. After saving a small fraction for subsequent batches, the balance is disposed of as wet feed. Yeast deposited in fermenters and storage vats is concentrated by centrifugation or filtration and is drum dried or spray dried. The dry product is an excellent source of protein and vitamins and is commonly used as feed supplement. Its composition is tabulated here [26].

Crude protein (%)	40–45
Crude fat (%)	0.7–1.5
Nitrogen-free extract (%)	40
Fibre (%)	5–6
Ash (%)	6–7
Thiamine (Microgram/gram)	90–120
Riboflavin (Microgram/gram)	60–80
Niacin (Microgram/gram)	120–240

Food or pharmaceutical yeast is prepared from surplus yeast by washing and removing the bitter character, which is derived from the hops and the metabolites of the yeast. Yeast sludge from distilleries contains degradation product of the dead yeast and organic debris from the malts such as proteins, fats, vitamins and carbohydrates. Spent wash from a distillery contains all the above nutrients and unfermented sugars, amino acids, caramels, ammonium phosphate, etc. Yeast powder of pharmaceutical grade can be obtained from a mixture of yeast sludge and spent wash. Spent wash is first screened, evaporated and dried and is called the dried distiller's solubles (DDS), which can be used as animal feed, or can be incinerated to recover potash. The resulting ash is purified by leaching with water, filtration and acidifying with sulphuric acid. Vacuum evaporation and crystallization gives chlorides and sulphates of potassium. About 3.85 tonnes of potash or 5.75 tonnes of potassium chloride and 1.27 tonnes of potassium sulphate can be produced from about 320 tonnes of spent wash [20].

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Chapter 13

THE ENGINEERING INDUSTRY

This chapter discusses mining of coal, ores (ferrous and non-ferrous), extraction of metals from the ores, problems of pollution due to these activities and solutions to the problems.

13.1 THE MINING OF COAL

Coal is one fuel which is considered useful whenever thermal energy is required on a large scale. Geologically, coal is an organic rock having a structure of layers, which vary greatly in thickness, lustre and texture. It is removed from the earth either by tunnelling if the coal seams are deep, or by open cast mining when the seams are near the surface. The extracted coal requires processing for the removal of rocks and other mineral impurities, followed by sizing or screening. There are three main varieties of coal, viz. anthracite, bituminous and lignite [1, 2].

Wastes from coal mining may be classified as: **solid**—including earth, rock and shale and a certain amount of waste coal; **liquid**—including surplus water which flows out of the mine and acid mine drainage water, which is formed due to reaction between the pyrite (FeS_2) in the soil, moisture and oxygen; **gaseous**—consisting of methane, carbon monoxide and carbon dioxide. The solid wastes do not cause serious pollution, but can catch fire spontaneously due to the presence of sufficient combustible coal and organic matter; gaseous wastes can form an explosive mixture with air and must be adequately vented. The acid mine drainage must be neutralized before disposal. The operation of crushing and washing the coal results in the presence of fine coal particles in the wash water [2]. These particles are settled before the waste water is discharged into the environment or recycled into the mining operation. (See flow sheet in Fig. 13.1.)

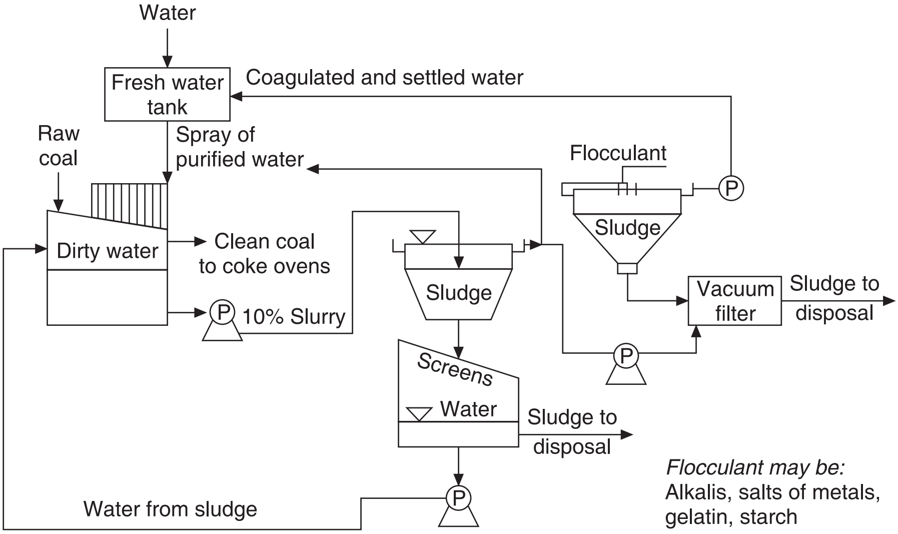

Figure 13.1 Coal washery reuse of water; Ref.: Southgate, B.A., *Treatment and Disposal of Industrial Wastes,* H.M. Stationery office, London, 1948.

Wastes generated during mining operations are characterized by very large quantities, from which a relatively small amount of useful material is recovered. Further, each of the stages forming the coal cycle, viz. coal mining, coal transportation, coal preparation, coal conversion and combustion plus utilization produces wastes, either in solid, liquid or gaseous forms. Each of these wastes has to be handled by dfferent methods for protection of the environment.

Nandusekar [3] lists the adverse effects of mining activity as follows: pollution of air and water, noise pollution, leaching effect from overburden, injuries due to falling rocks and ground vibration during blasting. Loss of (a) productive land, (b) land and property by underground fires and surface subsidence, (c) flora and fauna, (d) top soil due to erosion, (e) forest area also takes place. In addition, adverse socio-economic effects also need consideration. An environmental impact assessment of the mining project is recommended in order to anticipate the ill-effects, provide adequate preventive measures and protect the environment. Pandey [4] gives an overview of available options for managing water pollution problems due to mining activity. Problems associated with mining, transportation, preparation, conversion into usable product and its combustion, and their solutions are listed.

A coal washery works on the principle of differences in specific gravity of coal and impurities present with it. Specific gravity of pure coal ranges between 1.23 and 1.7. Raw coal is crushed into small size and is introduced into a suspension or solution, whose specific gravity is adjusted so that the coal floats at the surface and impurities settle as sludge. Suspended solids in the effluent from a coal washery may range from 5,000 to 30,000 mg/l, with average value of 20,100 mg/l [5]. Water pollution problem due to mining in Jharia coal fields in the vicinity of Damodar river have been described in detail by Ghose and Kumar [6, 7]. They observed that a coal washery in the area under study discharged 300–500 m^3 of effluent per day into the river, along with 6–10 tonnes of good quality coking coal. After studying the characteristics of the effluent, they tried various coagulants and coagulant aids for removal of the suspended coal fines. They found that synthetic polyelectrolyte was very effective. They have also described the location of tailing dam site and its construction. Revegetation on the tailing dumps is discussed in order to provide an aesthetic terrain. Rao and Sastry [8] applied alum alone and alum aided by *Nirmali* (*Strychnus potatorum*) seeds for the removal of suspended solids from coal washery wastes and found that *Nirmali* seed alone could give high efficiency of removal. The optimum pH, flocculation and settling times for *Nirmali* seeds were: 6.5–8.0, 20 minutes and 15–30 minutes, respectively. Starch and caustic starch (3 parts of caustic soda and 30 parts of potato starch in 100 parts of water) were not found to be effective.

The black solid material from coal cleaning operation contains finely divided clay, black shale, and other materials with coal. Waste water carrying these impurities is first thickened and the centrate is returned to the washing circuit. The thickened sludge is filtered, or may be pumped to a settling pond, where the solids are allowed to settle. If their content of fine coal is large, it is recovered and gives good economic returns [1].

13.1.1 Acid Mine Drainage

As already mentioned, formation of acid mine drainage water is due to the reaction of pyrites (FeS_2) with oxygen in the presence of moisture. Two microorganisms, *Ferrobacillus ferrooxidans* and *Ferrobacillus thiooxidans* are believed to accelerate the process of oxidation of pyrites. But these organisms work in a very narrow range of pH (approximately 3.5). Their activity is greatly reduced if the pH is above or below this value.

The acidity of mine drainage is a function of degree of contact between flowing water, oxidized acid-producing materials and the amount of alkaline material, which the water may contact and dissolve. The pH varies between 6.0 and 2.8. An average acid mine drainage contains 500–1000 mg/l acidity as $CaCO_3$, 100–300 mg/l iron, and total dissolved solids about 3000 mg/l. It rarely contains high concentration of chlorides and almost never contains oxidizable organic matter [1].

Among the methods proposed and used to prevent or minimize the formation of acid mine drainage are the following:

- Provision of siphon-trap seal chambers to prevent the flow of air into and out of the mine. But the method is not effective because of the presence of hidden openings in the mine.
- Inhibiting the reaction between pyrites and oxygen by using antioxidants, which are to be applied through gaseous transfer, aqueous transfer and direct spraying. This method is not economically attractive.
- Permanently flooding abandoned mines. This is possible for mines, which are below drainage level. The method cannot be used for above-drainage mines. Moreover, such flooding may interfere with operations in active adjacent mines.
- Placing acid-forming materials and thoroughly covering them with a compact layer of earth during surface mining. If the degree of compaction is great enough, the flow of oxygen is greatly reduced. This method has been successfully used in many surface mines.
- Control of water flow in both, underground and surface mines. This ensures that the products of reaction and water do not come in contact with each other.
- Biological treatment [1, 17].

A coal-mining company in Pennsylvania, USA proposed to mine an area using the truck-shovel mining method instead of the traditional dragline-mining method. This technique offers a more flexible alternative for cut sequencing and selective placement of waste material which should not result in formation of acid mine drainage [9]. Addition to sulphide tailings and waste rock of 2-mercapto-1-methyl imidazole or a 1-3-4-thiadiazole compound prevents acid mine drainage formation by inhibiting the oxidation of sulphides, according to Gould et al. [10]. Georgopolou et al. [11] suggest that pyrrhotyte coated with iron phosphate may provide a long-term relatively inexpensive solution to acid mine drainage formation. Acid mine drainage, treated with lime, was spray irrigated on acidic sandy soil planted with agricultural and cover crops. Improved crops and higher pH were observed by Jovanovic et al. [12]. Treatment of acid mine drainage with kaolin amorphous derivative (KAD) resulted in more than 99% heavy metals removal from the drainage within 1 hour. In addition, metals could be recovered and reuse of KAD material after stripping was possible [13]. Sulphate reducing bacteria (SRB) were used in two-step biological process to remove sulphate and metals from mine waste water. First, SRB convert sulphates to sulphide and sulphide oxidizing bacteria convert H_2S into elemental sulphur. The metals precipitate as metal sulphides after reacting with H_2S [14]. A system for remediation of acid mining drainage (AMD) using a porous medium bioreactor and SRB was evaluated. The results supported the concept of using SRB for treatment, as they were found to survive pH 3.0

for a long time [15]. Run-off water from a coal pile was biologically treated, raising the pH from 2.0 to 7.0 while removing heavy metals with a specific mixed culture of *Bacillus* and *Pseudomonas* under aerobic and anaerobic conditions [16].

13.1.2 Conversion of Coal into Coke

The production of coke by carbonization of coal consists of heating bituminous coal in the absence of air at 1000°C for 12–18 hours in an oven or retort, driving off volatile products which are recovered as tar, light oil and gas. Many plants have facilities to process light oil further into pure benzene, toluene, xylene, and solvent fractions, for distilling tar into useful distillates, and to recover hydrogen, ethylene, sulphur, hydrogen sulphide, ammonium thiocyanate, naphthalene, phenol, pyridine and other products.

Coal, properly sized and mixed, is heated in the ovens in the absence of air. Gases formed due to heating are cooled to about 80°C, thus condensing most of the tar. The gases then pass through primary coolers where they are washed and cooled further to 30°C, when additional tar and crude ammonia liquor condense. The red hot coke is pushed into quenching cars, where it is cooled by spraying water over it. Surplus water sprayed on the coke drips down into tanks located below the quenching cars. Water for cooling is also pumped into these tanks. About 30% of the cooling water evaporates and the rest collects impurities in it. In some coke ovens, condensates containing phenols and ammonia are also used for quenching. But this is an objectionable practice because it leads to severe corrosion of the quenching cars. The cooled coke is further crushed and graded for use in blast furnaces, foundry cupolas, gas production or for household use [2, 18]. The flow chart of coke production is shown in Fig. 13.2(a).

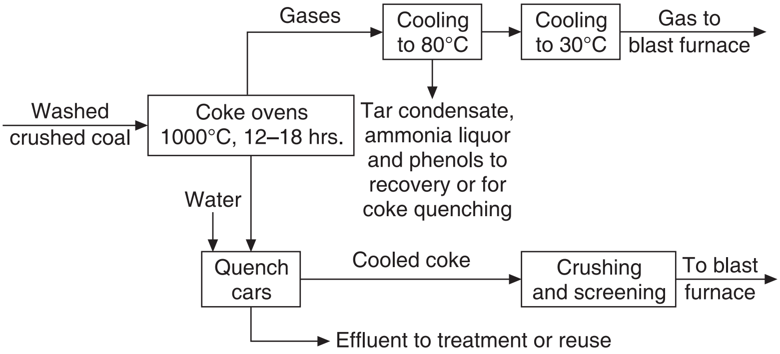

Figure 13.2(a) Manufacture of coke.

Waste water streams in a coke oven are: (1) from coke oven gas cleaning plant which contains mainly phenol and ammonia, and

(2) by-product recovery plant, which contains oil and grease, aromatic compounds and other organics. These streams are combined and treated in the waste water treatment plant. Sureshkumar et al. [19] have given the analysis shown in Table 13.1.

Table 13.1 Analysis of Waste Water from Coke Oven

Parameter	Range
pH	7.5–8.0
Temperature	50°–55°C
Suspended solids	130–140
Chemical oxygen demand	4600–5000
Biochemical oxygen demand (5-day 20°C)	1200–1500
Phenol	750–800
Cyanide	4.1–4.7
Oil and grease	300–350
Total ammonia	1000–1100
Thiocyanate	600–650
Sulphide	40–60
Thiosulphate	60–80

Note: All values except pH and temperature are expressed in mg/l.

Prasad and Singh [20] have given the analysis of waste waters from coke oven plants in Jharia coal fields. The effluents were analysed for pH, total dissolved solids, total suspended solids, DO, COD, BOD, phenol, ammonia, cyanide, and oil and grease. Similarly, Gupta and Mozumdar [21] have given the analysis of spent liquor from ammonia stills from different plants in various countries. The average quantity of waste water released per tonne of coking coal varies between 0.25 and 0.3 m^3 [22].

13.1.3 Treatment of Coke Oven Waste Water

In view of the toxic nature of coke oven waste water, treatment by physical, chemical, biological means and by suitable combinations of the above three have been tried out. Rao et al. [23] used the oxidation ditch for treating phenolic waste. They saw that acclimatized activated sludge could easily tolerate phenol concentration up to 1000 mg/l and destroy it by 86%. Aeration period of 8 hours was enough to destroy phenols almost completely, besides getting moderate BOD (82.9%) and COD (58%) removals. The raw waste was diluted to 6%, while MLSS in the ditch were maintained at 10,000 mg/l. It was also seen that the usual indicators of good activated sludge were replaced by the fungus *Geotrichum*.This fungus may alone be useful in phenol degradation.

Pilot plant studies on treatment of phenolic wastes using deep trickling filter (3.66 m) were carried out by Rao et al. [24]. After acclimatizing the biological film developed on the filter medium with diluted phenolic waste, 90% phenol destruction was obtained. The maximum phenol loading was 0.173 kg/m^3/day and the corresponding BOD load was 0.27 kg/m^3/day.

Gupta and Mozumdar [21] have listed various methods of phenol removal, viz. activated carbon adsorption, chemical oxidation with potassium permanganate, sodium dichromate, sodium peroxide, manganese ores, chlorine, chlorine dioxide and ozone, biological oxidation by activated sludge process and trickling filtration and continuous cultivation method in which a small volume of waste water is diluted to get a constant concentration of phenols, it is supplied with nutrients and is fed into the aeration tank containing aerobic bacteria, giving phenol destruction from 1.25 to 1.875 kg/m^3/day. Patwardhan and Desai [25] reviewed the various methods of phenol removal including (a) physical—catalytic incineration, deep well disposal, use of electrostatic forces, oil-water separation, evaporation and burning, and steam stripping, (b) chemical—oxidation with chlorine, chlorine dioxide, ozone, adsorption on activated carbon, ion exchange and solvent extraction, and (c) biological methods—single-stage and two-stage filtration, deep trickling filters, activated sludge process, spray irrigation and use of water hyacinth. Raw wastes as such have intolerably high phenol and ammonia concentrations. So, they have to be pretreated by physical or chemical means to reduce these two pollutants to levels where microbes can handle them successfully.

Porous, weakly basic anion exchangers on acrylic matrix were studied by Reddy, Anand and Dasare [26] for the absorption of phenolic compounds. The ion exchange and surface characteristics of the resins and the nature of the adsorbates were found to govern their absorption performance. They found that the rate of absorption was pH dependent and depended on the presence of electrolyte (TDS) in the waste water being treated. An alkaline solution was a suitable elutent for the absorbed phenol, which could be completely removed from the resin.

Bhatt, Bhargava and Panesar [27] used a moving media reactor for studying its phenol removal efficiency. They used charcoal particles of specific gravity 1.215 and geometrical mean diameter of 280 microns as the moving medium and kept influent phenol concentration, inflow rate and size of charcoal constant, but changed the pH of the influent from 3–10. When the mass of charcoal input was varied from 2 gm/min to 17 gm/min, it increased charcoal input, reduced the adsorption of phenol and the reactor worked efficiently at pH 3. In a bid to find a cheap adsorbent for phenol removal from waste water, Singh and Mishra [28] used $Fe(OH)_3$ impregnated sawdust in Fe(III) form. They found that the sawdust could be reused three times after regeneration.

Kumaran [29] studied for a year the performance of an oxidation ditch specifically designed for phenol removal. The initial phenol concentration was 4027–7389 mg/l, COD from 14,918–44,640 mg/l. In addition, it had high ammonia concentration associated with carbonates, bicarbonates and hydroxyl ions, resulting in a pH of 8.5–9.5. The ditch was found to perform poorly due to the presence of high concentration of phenols, as was observed from the values of effluent ammonia. Banerjee [30] used a four-stage bench-scale rotating biological contactor (RBC) to determine the phenol removal kinetics. He concluded from his studies that the mass-transport (MT) and first-order plug flow (PF) reactor models were not applicable to the RBC. For a phenol loading of 2.1 g/m^2/day, removal was almost complete in 2 hours, while at a loading rate of 16 g/m^2/day, removal was about 80% in 2.5 hours. Temperature, rotational speed and organic load had a significant effect on the performance. A paper by Shivaraman and Pandey [31] gives the characteristics of phenol-bearing waste water from coal carbonization. Various bioreactor systems and microorganisms responsible for phenol degradation have been tabulated. They suggest further work on the following:

1. Settleability of activated sludge biomass.
2. Economical method for colour removal from the treated waste water.
3. Biomass characteristics of existing coal carbonization waste water treatment units.

Singh et al. [32] have made a critical review of the effects of radiation on coal-mine environment. In coal mining, the major occupational exposure comes from decay products of Radon gas, while coal ash radioactivity is due mainly to the presence of uranium, thorium and their derivatives. The authors have suggested conducting a detailed survey in mining belts and coal-based power plants, fly ash tanks, etc. to monitor radiation levels and a thorough health survey with due emphasis on radiation of radio-nucleids. Kumar et al. [33] evaluated the performance of a full-scale coke-oven waste water treatment plant working on a two-stage activated sludge process. They observed poor settling of MLSS in the two settling tanks of the two stages, low MLSS in both the aeration tanks (541 and 981 mg/l in the two stages), overall COD reduction of 87% and of BOD 95%. The recycled sludge from the two settling tanks was found to have solids concentration of 522 mg/l and 1518 mg/l respectively, against the design values of 10,000 and 20,000 mg/l. Destruction of thiocyanate and cyanide was also poor, while the total ammonia in the treated effluent was higher than the stipulated value. Therefore, treatability study was carried out at site, using downflow trickling filter with optimum hydraulic loading rate of 2 m^3/m^2/day and organic loading rate of 1.5 kg COD/m^3/day. The performance of the trickling filter was found to be satisfactory. Therefore, the authors proposed adding the trickling filter downstream of the existing activated sludge system.

Pandey, Rao and Kane [34] conducted studies on two separate pilot plants, one treating phenol-bearing waste formed from low temperature coal carbonization and the other, cyanide-bearing waste, from an alkali cyanide manufacturing unit. The purpose of the pilot plants was to get an idea about the cost-effectiveness of the proposed method of treatment, viz. completely mixed activated sludge (CMAS) process. It was found that phenol removal and COD removal were 99.32% and 53.04%, respectively, showing that the chosen treatment was appropriate. Based on the performance of the pilot plant, the authors were able to devise design parameters for a full-scale plant.

Kumaran [35] has listed phenols and other related aromatic compounds, viz. phenol, catechol, o-, m-, p- cresol, resorcinol, hydroquinone, pyrogallol, polyaromatic hydrocarbons (PAH), pyridines, picolines, lutidines, xylenes, toluenes, benzoic acid, which are likely to be present in coal refining wastes. He worked on synthetic phenol-bearing waste in the laboratory and developed suitable cultures for degradation of phenols. He recommends the use of such specialized cultures for startup of a pilot or full-scale plant and claims that they enhance recovery process in a plant upset by hydraulic or organic overloads. Srinivasan [35A] isolated bacteria from garden soil, which could degrade phenols upto 1200 mg/l in a temperature range of 22°C–35°C in a laboratory-scale activated sludge unit.

13.2 MINING OF FERROUS AND NON-FERROUS METALS

The operation of removing ores from the earth is done both in open pits and in underground mines. Ore processing steps include one or more of: crushing and grinding, froth flotation, filtration, screening, gravity concentration, magnetic separation, leaching, roasting and smelting, drying, ion exchange, pelletizing, amalgamation, cyanidation. Most of these operations require water. Waste waters generated from the above operations contain settleable solids. Most domestic ores contain from 1% to 10% of the desired component; hence, the bulk of excavated material must be discarded. Chemicals used in froth flotation and those used in leaching operation are also present in the waste water. Some ores may give rise to acid mine drainage. However, the pollution potential from such waste water is low [36].

The principal way to control the waste water is to provide ‘tailings’ ponds, which act as settling tanks. These are used for pH correction, chemical precipitation, storing reuseable water, and in a few instances, for recovering value-added metals.

1. **The iron industry** uses water primarily for washing the ore and reuses the water stored in its ponds. Overflow from the ponds can be safely discharged into public waters [36].
2. **Copper ore,** when washed, gives rise to acid mine drainage water in which small amount of copper is dissolved. This is easily recovered and the drainage water is stored in the tailings pond for recycling [36].
3. **Uranium ore** is extracted by the resin-in-pulp method. The ore is crushed, grounded and leached with sulphuric acid, coarse

sand is separated and uranium is stripped from the ore. It is a common practice to sink monitoring wells around the tailings ponds so that possible groundwater movement of radioactivity can be detected [36].

4. In **zinc production**, the usual steps are: crushing, grinding, flotation, thickening and filtration. It produces considerable mine drainage, its average composition being 1450 mg/l zinc, 800 mg/l iron and pH 2.3. The above observation applies also to industries processing lead-zinc, copper-zinc, and complex lead-zinc-silver-gold-copper ores [36].
5. **Gold mining** involves amalgamation of the gold ion with cyanide ion; in addition, the waste water contains zinc, copper, nickel and arsenic. A number of technologies such as alkaline chlorination, ozonation, ion exchange, electrochemical treatment have been used for destruction of cyanides from gold mining wastes. Natural degradation of free and metal-complexed cyanide in tailings ponds has been very effective. Reduction of cyanides from 68.7 mg/l to 0.08 mg/l was observed in one pond in about 70 hours holding time [37].

A cheap method of recovering gold from effluents was developed by a Japanese team at Hiroshima University. It consists of adding a cyclic polyamine dissolved in chloroform to the waste water of which pH is reduced to less than 1.0. After settling, the gold is found to have formed a complex with chloroform at the bottom of the reaction tank. The chloroform fraction is separated and mixed with water at 60°C at pH 8.0 and allowed to settle for 30 minutes, during which time the gold dissociates from the amine. Better than 90% recovery was reported from 1 litre solution containing 1 millimole gold [37A]. Physico-chemical characteristics of waters entering a tailings pond are important from the point of view of determining their suitability for recycling or for recovery of value-added metals. Thukral, Joshi and Chand [38] analysed the sediments from the tailings pond of Khetri Copper Complex, Rajasthan. They found high silt and fine sand contents, no organic matter and high concentration of heavy metals. Ghose and Sen [39] emphasize the need for studying soil properties, foundation conditions, construction material and conduct of sedimentation test in order to design a reasonably sized tailings pond. They site the instance of a pond designed on an empirical basis of 5 days' hydraulic retention time, and surface area of 400–1000 m^2 for every 1000 tonnes tailings discharged, which gave a size of 10,000 m^2, whereas sedimentation test indicated an area of only 3155 m^2. The same authors [40] find that the constituents of iron tailings slime are mostly silica, alumina and iron ore in the form of oxides, in addition to oxides of manganese, chromium, cobalt, nickel, copper, zinc, etc. Results of sedimentation test indicated subsidence rate of 0.008 m/hour. For a flow of 130 m^3/hour, the pond area required was 6270 m^2, against 10,000 m^2 worked out by empirical formula.

Mining in high mountainous areas requires tackling different problems such as steep terrain with high potential for rockslides, landslides and avalanches, freezing temperatures, and high seismic conditions. Mining industry uses currently one of the four options for tailings disposal, viz. cycloned tailings, thickening, filter pressing and conventional wet disposal. In addition, lining of the ponds may be necessary in order to protect groundwater quality [41]. Baur [42] discusses the aspects of monitoring and data management for mines which have stopped producing. The discussion includes pit lake studies for mine closure, surface water control and treatment, and environmental monitoring and data management.

An efficient and environment friendly way of extracting minerals from ores is bioleaching. Microorganisms leach low-grade ores and mine tailings and extract expensive minerals like copper, uranium, etc. which are otherwise very costly to recover by conventional means. Organisms involved are generally chemolithotrophic, autrotrophic, thermophilic and acidophilic. *Thiobacillus ferooxidans, T.thiooxidans, T.organoparus*, etc. are the chief varieties used for this purpose [43].

13.3 MANUFACTURE OF IRON AND STEEL

The process involves melting of iron ore with coke and limestone in the presence of air. Production of a unit weight of pig iron requires 1.5 units of ore, 0.6 units of coke, 0.2 units of limestone, 0.2 units of cinder, scale and scrap and 2.5 units of air. During production, 0.5 tonnes of slag is formed, which floats on top of the molten iron at the bottom of the blast furnace. Air pollution occurs due to the fumes formed; particles of iron ore, sinter and coke are thrown off with the furnace gases, which contain carbon monoxide. The dust contains about 30% iron, 15% carbon, 10% silicon dioxide and small quantities of aluminium oxide, manganese oxide, calcium oxide and other materials. The gases and fumes so formed are treated by initial settling, dust catching and are then passed through venturi scrubbers and/or wet type electrostatic precipitators. To some extent, the cleaned gases are also used to fire coke ovens, blast furnaces, etc. [22]. The dust, separated from the gases, is recycled to the blast furnace. A general manufacturing flow sheet is given in Fig. 13(b).

Steel is produced in open hearth or basic oxygen or electric furnaces, which are fed iron ore, scrap, limestone and alloying material (as required). They also produce gases and fumes, which have to be collected, cleaned and disposed of.

Water is required during the production for cooling the furnaces, for use in the wet scrubbers, for condensing steam, for cooling hot flue gases, for pig casting, sintering, indirect cooling of the important parts of steel-making equipment, for human consumption in canteens, toilets and residential colonies of the steel works, etc. The rate of consumption is quite large, e.g. make-up water for the operation of the plant may be anywhere between 4000 m^3/h and 6000 m^3/h, wet gas coolers take 13.5 m^3/min and scrubbers require about 4.5 m^3/min. Water demand of the basic oxygen furnace is about 180 m^3/min while the open hearth and electric furnaces consume from 3.5m^3/min to 5.5 m^3/min. In general, the total water demand ranges from 13.5 m^3/min to as high as 55 m^3/min, out of which 75–90% is used for cooling. A 2.5 million tonne steel plant shows a rough breakup of water consumption as follows: 5% for coke ovens and by-product units, 10% for blast furnaces, 9% for blast furnace gas cooling system, 2% for open hearth furnaces, 14% for rolling mills, 50% for steam boilers and turbo blowers and 10% for miscellaneous uses [22]. Some part of the water gets contaminated and needs treatment before discharge to the environment, but that fraction which is only used for indirect cooling can be easily recirculated after cooling. Even the treated effluent can be reused within the premises of the mill, thereby achieving substantial saving of fresh water.

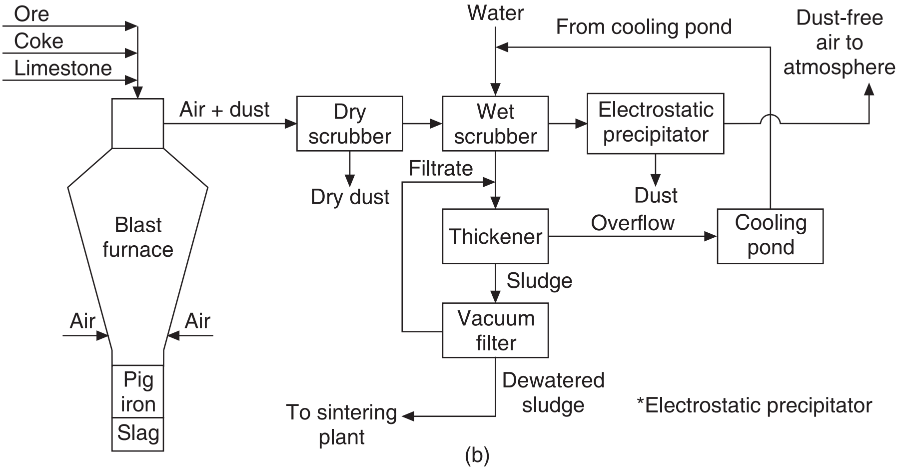

Figure 13.2(b) Manufacture of pig iron.

13.3.1 Treatment of Waste Water

Waste water from a steel mill is treated for removal of suspended solids, destruction of phenols, removal of ammonia, recovery of by-products and cooling of hot water for recirculation. Effluent from wet scrubber is subjected to settling, the sludge is dewatered and the clarified effluent is returned to the scrubber. Dewatered sludge is sent to the sintering plant for recharging to the blast furnace. Coke oven effluents are passed through catch pits to separate the tar, oil and benzol contents; excess ammonia is converted into ammonium sulphate and dephenolizing column is used to recover phenol and cyanide from the ammoniacal liquor. The effluent thus treated may be used for coke quenching, or may be subjected to biological treatment. Uncontaminated cooling waters may be cooled in cooling towers or cooling ponds and recycled. Coke oven gas coolers discharge waste water containing high suspended solids, which is clarified after coagulation with lime and chlorinated copperas. The sludge is dewatered and disposed of, and the clarified water is recycled or used for coke quenching. Ammoniacal liquor and gas resulting from coke manufacture contains ammonia which is recovered by solvent extraction, or by the semidirect process, viz. by bubbling the gas through dilute sulphuric acid, when ammonium sulphate is formed [2]. The waste is treated by biological means when ammonia concentration is low. Activated sludge or trickling filtration is used for this purpose. It is possible to recover hydrogen sulphide formed during coal carbonization. The gas containing H_2S is passed over layers of iron oxide mixed with sawdust. The spent iron oxide is regenerated by calcining, and the sulphur dioxide evolved is used in the manufacture of sulphuric acid [2].

Among the non-ferrous metals, aluminium occupies an important position. It is the most abundant metal in the earth's crust. Bauxite, the main source of aluminium, is a mixture of similar minerals containing hydrated aluminium oxides. One tonne of aluminium metal is obtained from 2 tonnes of bauxite. Bauxite is washed, ground and dissolved in caustic soda at high temperature and pressure. The undissolved bauxite residue, containing iron, silicon and titanium, precipitates to the bottom of the reaction tank and is known as 'red mud' and accounts for about 35%–40% of the raw material. It may be disposed of by landfilling, or by use in the manufacture of cement, or converting into bricks, roofing sheets and polymer doors [44].

Jena and Singh [45] have reviewed the various methods of recovering iron, titanium and alumina from red mud. It can be used as a soil conditioner for the treatment of acidic soils because of its alkalinity. It also helps the soil by holding the nutrients, retaining moisture and raising pH. Red mud is used in flue gas desulphurization, as a coagulant in water treatment, for removal of heavy metals from industrial wastes, for removal of phosphorus from wastewater and as a neutralizing agent for acidic waste water.

13.4 PICKLING, GALVANIZING AND PLATING

Metals, as they are extracted from the ores, are subject to reaction with atmospheric oxygen and form oxides of the metals at their surfaces. This layer of oxide must be thoroughly removed before the metal surface is given any treatment for protection against corrosion.

13.4.1 Pickling

Pickling is a process in which the metal is dipped in an acid (sulphuric, hydrochloric, nitric, hydrofluoric, phosphoric, individually and in combination) for a fixed length of time, rinsed with water and stored for further use. Sulphuric acid is by far the most commonly used acid for this purpose. Steel pickling results in the formation of ferrous sulphate. During this process, the initial concentration of the acid, which dissolves the scales on the metal surface, decreases gradually till it is down to 5–9% in continuous operation and 0.5% to 2% in batch operation. A corresponding increase in the concentration of ferrous sulphate also takes place in the acid. When the acid is spent, it may be disposed of in deep wells, cavernous limestone, abandoned mines, exhausted oil and gas sands or artificial lagoons [46]. But it is worth treating the waste water and recovering ferrous sulphate from the spent pickle liquor rather than disposing of it as above. Methods of treatment are: neutralization, electrolysis, evaporation, ion exchange, refrigeration, chemical conversion, extraction, dialysis. Lime is the most common neutralizing agent used because it is cheap, but produces large volume of 'difficult to dewater' sludge. Evaporation results in recovery of ferrous sulphate and free acid. Differential solubility is also used to reduce the solubility of ferrous sulphate. Spent liquor can be used to extract manganese from low-grade ore, to extract magnesia from dolomite and to produce ferric phosphate from phosphate rock. Ion exchange offers acid in its free form from the spent liquor [47].

Dialysis is a simple, cheap method of recovering acid from the spent pickle liquor, because it does not involve the use of power or chemicals. However, it alone does not solve the problem of disposal. A change of acid from sulphuric to hydrochloric is economical in the continuous pickling method. But it requires provision of hoods over the pickling line to extract the fumes of hydrochloric acid [48]. A process called 'turbulator' is used to regenerate hydrochloric acid and iron oxide, which simply reverses the action taking place during pickling. A small amount of acid is lost, but can be easily made up [49]. Besides ferrous sulphate and pickling acid, it is also possible to recover copperas, ferric sulphate, iron oxide, electrolytic iron, iron powder, iron oxide pigments and ammonium sulphate, the last named being recovered when the spent pickle liquor is treated with coke oven effluent [46].

Ferrous sulphate and sulphuric acid are recovered by adding scrap iron to the pickle liquor till all acidity is neutralized. The liquor is evaporated or refrigerated to crystallize ferrous sulphate. The crystals are separated by centrifugation and the centrate containing sulphuric acid is concentrated to 28%, at which value, 80% of the ferrous sulphate precipitates out. The acid is concentrated further to 80% when the remaining ferrous sulphate precipitates out. The acid is returned to the pickling bath.

Pickling of other metals is also done with a mixture of nitric acid and chromic acid for aluminium, 15% sulphuric acid for copper, brass and bronze, 10% sulphuric acid for nickel and monel metal.

13.4.2 Galvanizing

Galvanizing is a process, in which the metal surface is covered with a thin coat of zinc for protection against corrosion. The articles to be galvanized are first dipped in a flux containing zinc chloride and ammonium chloride; they are then dried in a furnace with the help of hot flue gases. Next, they are immersed in a tank containing molten zinc maintained at 460°C. Oxidation of the zinc is prevented by a floating layer of ammonium chloride and brine in glycerine. The articles are lifted out of the bath with a crane and are held over the bath for some time to allow excess molten zinc to drain back into the galvanizing tank. They are rinsed with water, dried and stored. The volume of waste water produced ranges between 2400 and 9000 litres per tonne of material. Treatment consists of neutralizing with lime, soda ash, caustic soda or limestone. Lime produces large amount of sludge, which is difficult to dewater. Soda ash and caustic soda are expensive but produce little sludge. Limestone is cheap, but its surface gets coated with the product of neutralization; this slows down or even stops the process of neutralization.

If the entire bath is spoiled and has to be dumped, it is first stored in a separate tank and is gradually mixed with dilute rinse water and then treated as mentioned.

13.4.3 Plating

Plating is a process of forming a thin coat of one metal over the surface of other metal (or non-metal) in order to: (1) alter the surface properties of the other metal, (2) improve its appearance, (3) improve resistance to corrosion and tarnishing, chemical attack, etc., and (4) increase hardness. Electrochemical forces are used for this purpose. Coating of chromium, cadmium, copper, zinc, silver, gold, etc. can be given by electroplating, in which these metals are made to form complexes with cyanide ion in order to increase their 'throwing' power. Typically, double cyanide baths are used, one containing cyanide of the metal to be plated and the other containing excess of alkaline cyanide. The latter bath serves to dissolve the metal cyanide and to maintain an excess of cyanide [50].

Effective plating is ensured by thoroughly *cleaning* the surface to be plated. This is achieved by using organic solvents like trichloroethylene or perchloroethylene, or an emulsion made from kerosene, a wetting agent and an alkali, or electrolytic cleaning using an alkali plus a wetting agent plus a chelating agent. The surface to be cleaned is made the anode. Chemicals used in the cleaning operation are removed by *rinsing* with water. Acid or alkali dipping is done next to get *chemical cleaning* of the surface, depending on whether the earlier step has used an alkali or an acid as a component of the cleaning solution. The surfaces are cleaned with water to remove reacting chemicals and products of the earlier reactions. The next step is that of *plating*. Here the objects to be plated are made the cathode, while the metal, which is to plate the objects, is made the anode. Direct current is used for the plating operation. If the objects to be plated are small, they are placed in a barrel, which is dipped in the plating bath. This is known as barrel plating. After the desired time period, the plated objects are lifted out of the plating bath, are held over the bath to allow draining of the bath contents. The plated objects are then *rinsed* with good quality water (preferably demineralized water) and are *dried with hot air*. Every care is taken to ensure that there is no spillage of the plating bath contents and economical use of rinse water is done, so that the same water can be recycled for further rinsing. When the cleansing power of the rinse water is exhausted, it is topped up with the necessary plating chemicals and returned to the plating bath. Countercurrent rinsing or fog rinsing is also practised as a measure of water conservation.

Process flow diagrams of pickling, galvanizing and plating are given in Fig. 13.2(c). The contents of the plating bath are highly toxic and must be destroyed (especially cyanides and other heavy metals such as chromium, cadmium, copper, zinc, etc.) or their concentrations must be reduced to safe limits. Various methods of treating cyanide-bearing wastes are used, viz. alkaline chlorination, ozonation, acidification and natural aeration by lagooning, acidification followed by forced aeration into a tall stack, treatment with ferrous sulphate, electrolytic oxidation in the presence of chloride ion, treatment with addition products, etc. The most commonly used method is alkaline chlorination.

A very important step to be taken in the plating area is to separate all acidic waste streams from cyanide-bearing streams to avoid even accidental formation of hydrocyanic acid (HCN), a highly toxic chemical. Cyanide destruction can be done on a batch basis or on a continuous basis. Batch destruction is preferred because it is possible to ascertain the extent of destruction without using elaborate analytical instrumentation, which would be essential if continuous destruction is to be practised. Oxidation of cyanides by chlorine under alkaline conditions is carried out upto cyanate (CNO^-) stage, or upto carbon dioxide and nitrogen stage, depending upon discharge requirements. The chemical reactions are as follows:

$$NaCN + Cl_2 = CNCl + NaCl \tag{1}$$

$$CNCl + 2NaOH = NaCNO + NaCl + H_2O \tag{2}$$

$$2NaCNO + 4NaOH + 3Cl_2 = 6NaCl + 2CO_2 + N_2 + 2H_2O \tag{3}$$

The first reaction is instantaneous at all pH values, while the second reaction takes about half an hour to go to completion at pH value above 8.5. It is also temperature dependent. The cyanate formed is about 1/1000th as toxic as cyanide and hydrolyses under acidic conditions to ammonia and carbon dioxide in receiving waters. The third reaction requires 4.09 parts chlorine and 3.09 parts NaOH per part of cyanide. Although the reaction is most rapid at pH 6.5 to 8.5, a pH of 8.5 is preferred to simplify operation, eliminate formation of nitrogen trichloride

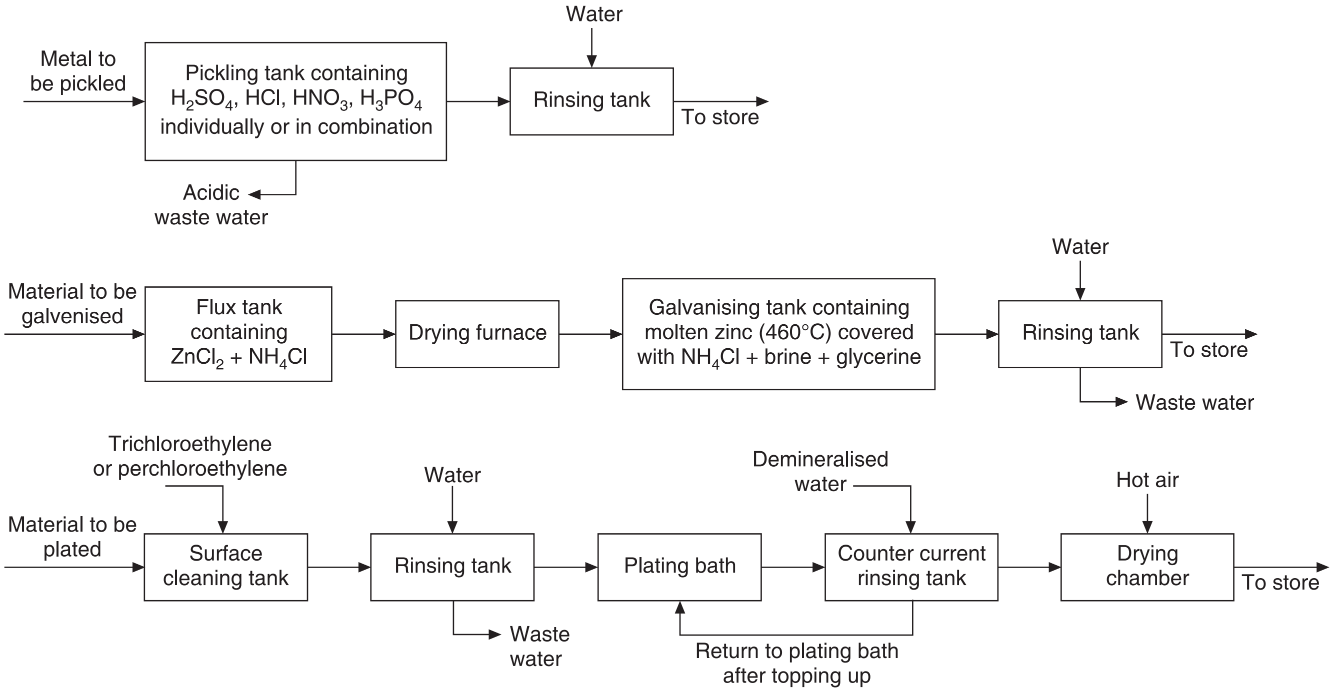

Fig. 13.2(c) Pickling, galvanising and plating operations.

and permit reactions 2 and 3 to occur sequentially in a single treatment unit. At pH 8.4, the reaction is complete in 10 minutes, while at pH 9.6, it takes 40 minutes [51].

Solid cyanide compounds are formed during the process of hardening metal surfaces. Commercially available solutions containing 50% sodium cyanide and potassium cyanide are used for this purpose. When repeated use reduces the concentration of cyanides to 20%, they are added to get the desired concentration. On prolonged use, the bath is emptied. It contains solid cyanide compounds. Gandhi and Varde [52] conducted laboratory-scale experiments to treat solid cyanide waste by chlorination with bleaching powder. Five grams of solid cyanide waste was dissolved in water, filtered and was mixed with different concentrations of bleaching powder. After a contact time of 1 hour, the samples were analysed first for residual chlorine and, after dechlorination, for residual cyanide. They found the optimum ratio of cyanide to chlorine as 1:3.4.

Ozone is a suitable oxidant for cyanides. The reaction is usually written in the form:

$$CN^- + O_{3--} \rightarrow CNO^- + O_2$$

The theoretical requirement is 1.84 kg ozone per kg of cyanide, but the actual figure is 1.5 kg, implying some degree of auto-oxidation. This method has the advantage of not increasing chlorides in the treated waste water, but is costly compared with alkaline chlorination [53].

Acidification and natural aeration or forced aeration is suitable for cyanide destruction in remote areas like gold mines, where the HCN formed due to acidification can be adequately dissipated in the surrounding air, or is absorbed in caustic soda [53].

Reaction with ferrous sulphate, electrolytic oxidation or use of addition products, are methods which are not commonly used in practice for destruction of cyanides. But biological treatment of cyanide-bearing wastes is possible with acclimated microorganisms. Kaul et al. [54] conducted laboratory-scale experiments with a two-stage system consisting of completely mixed activated sludge (CMAS) process, followed by oxidation pond. At an inlet concentration of about 200 mg/l of cyanides, the CMAS system was operated at a hydraulic retention time (HRT) of 24 hours, followed by oxidation pond with HRT of 7.5 days. The effluent cyanide concentration ranged between 0.12 and 0.23 mg/l. Laboratory-scale studies were conducted by Agate [54] for destruction of thiocyanate-bearing waste water by using acclimated microbial mass in an activated sludge process. The waste water had a pH of 13.0 and a thiocyanate content of 9000 mg/l. This waste was successfully treated. Alagarsamy, Vijayaraghavan and Gandhirajan [55A] studied the performance of a full-scale treatment plant for cyanide (solid and liquid) waste treatment, based on alkaline chlorination process. They found that it was not possible to reduce cyanides to less than 0.8 mg/l from liquid cyanide waste, while it ranged between 0.2 and 2.5 mg/l for solid cyanide waste. The study also showed that the treated effluent would have chlorine residual concentration of 100–250 mg/l, indicating a need for dechlorination (if adequate dilution water was not available), before discharge to the environment.

The plating industry produces waste water containing unacceptably high concentrations of heavy metals, chromium in its hexavalent form being a common pollutant. It may be present either as a single pollutant or in company with other elements such as copper, cadmium and zinc. In view of their high toxicity, it is necessary to remove them before discharge to the environment. The most common method of chromium removal involves reduction of hexavalent chromium to its trivalent form with ferrous sulphate under acidic conditions and precipitating it as chromium hydroxide by neutralizing the acidity with lime. Other methods are also used, a few of which are described here.

Deshpande et al. [56] suggest a combination of a membrane bioreactor with ion exchange and electrochemical forces to separate and reduce hexavalent chromium. It involves application of a potential difference to an ion exchange membrane to achieve this purpose. Low-cost adsorbents, made from waste material, have also been used for chromium removal. Thus, Manju and Anirudhan [57] used coconut fibre pith-based pseudo-activated carbon in their batch experiments. They found that the efficiency of the carbon depended on adsorbent dose, initial concentration of the adsorbate and time of contact. The reaction was exothermic. The best pH was 2.0. The spent carbon could be regenerated with 1M sodium hydroxide.

Brick kiln ash and flyash were tried by Rai and Surendra Kumar [58] as adsorbents. They found good potential for both the materials. At a pH of 1.3, inlet Cr^{6+} concentration between 10 and 50 mg/l, particle size between 124 and 853 millimicrons, temperature between 25°C and 50°C and a mixing speed of 100–200 rpm, flyash was found to be better than brick kiln ash. Patnaik and Das [59] used blast furnace flue dust (BFD) in their batch experiments and observed better than 95% Cr^{6+} removal under ambient temperature and pH conditions. The removal process was seen to follow first-order kinetics with respect to Cr^{6+} ion concentration. Rice husk, treated with sulphuric acid, followed by CO_2 activation, produced an activated carbon which removed 88% total chromium and gave better than 99% Cr^{6+} removal. A waste, containing 300 mg/l of Cr^{6+} was treated with this carbon, which gave a removal capacity of 45.6 mg Cr^{6+}/gm against 35.4 mg/gm with commercial carbon [60]. Singh and Lal [61] produced an adsorbent by treating spent tea leaves with sulphuric acid. At an optimum pH of 2, the breakthrough was found to occur at 39.3 mg/gm. The spent adsorbent was regenerated with 3M NH_4OH. Recovery of Cr^{6+} was 85%. Sarkar and Gupta [62] treated chromium plating waste water with activated alumina. They found that pH had no effect on adsorption process. Based on their observations, they recommended continuous treatment in a column 1 m tall, 50 cm diameter, containing activated alumina, which could treat waste water containing 130–140 mg/l of Cr^{6+} in 8 hours. Gupta and Tiwari [63] used aluminium oxide as an adsorbent and found it to follow Freundlich isotherm in removing Cr^{6+}. The highest removal took place at pH 4.0–6.0. At 120 mg/l Cr^{6+} concentration, removal was 90–97%. The ultimate adsorption capacity was found to be 11.7 mg/gm at pH 4.0. The adsorption capacity was seen to decrease in the presence of other anions such as cyanides.

Besides cyanides and chromium, there are other heavy metals, which are toxic and need to be removed effectively. Some of the attempts towards this end are briefly described here. Reeve [64] discusses various means of reducing, recycling and recovering wastes in metallurgical industry. M/s EPA Vic. conducted a survey of electroplating filter cake wastes for recovery of nickel, zinc, copper and chromium. Local metal extraction companies were approached for handling the cakes collected, remediated, dried and pelletized by member companies of the local waste management association. Economic evaluation indicated that nickel and copper could be profitably recovered, while zinc and chromium should be recovered at source itself. Other methods followed include colloid flotation, electrolytic recovery, membrane technology, dissolving metals as amine complexes, etc. Lewis [65] has presented case studies on successful recycling of industrial wastes, particularly zinc and copper. Waste from galvanizing can contain from 60% to 90% zinc. It is possible to recover 40%–60% zinc from this waste by treatment with sulphuric acid, filtration, evaporation, crystallization and centrifugation. Brass is usually made by alloying electrolytic zinc and copper. The waste produced from remelting brass is called brass ash. It can be subjected to wet processing, because brass metallics do not react with water. During remelting, the zinc in brass oxidizes and is skimmed off. The brass ash is pulverized, zinc ash, containing 94% Zn and 4% Fe is added to the molten metal to adjust the copper content to 60%. The metal is then ingoted. Kalyani et al. [66] experimented with flyash in natural and acid-treated forms to assess its adsorption capacity for nickel. The adsorption of nickel was found to depend on the amount of flyash, concentration of metal ion, contact time and pH of the metal solution. The optimum pH was 6.2. Equilibrium adsorption data were correlated by Freundlich, Langmuir and Redlich-Peterson isotherms. The maximum monolayer capacities of flyash in natural and acid-treated forms were 41.7 mg/gm and 62.9 mg/gm. respectively.

Gaikwad and Bharadwaj [67] also used flyash to remove zinc from viscose rayon waste water. The experiment was conducted using (i) a packed column, and (ii) a clarifier, the purpose being to find out the requirement of flyash for the same removal in each unit, along with reduction in COD and Zn. The packed column gave 94% removal of zinc, in the first run, which was drastically reduced in subsequent runs, indicating the need for regeneration. The ratio of flyash to waste water was 1:1, which was very high. The clarifier experiment required only

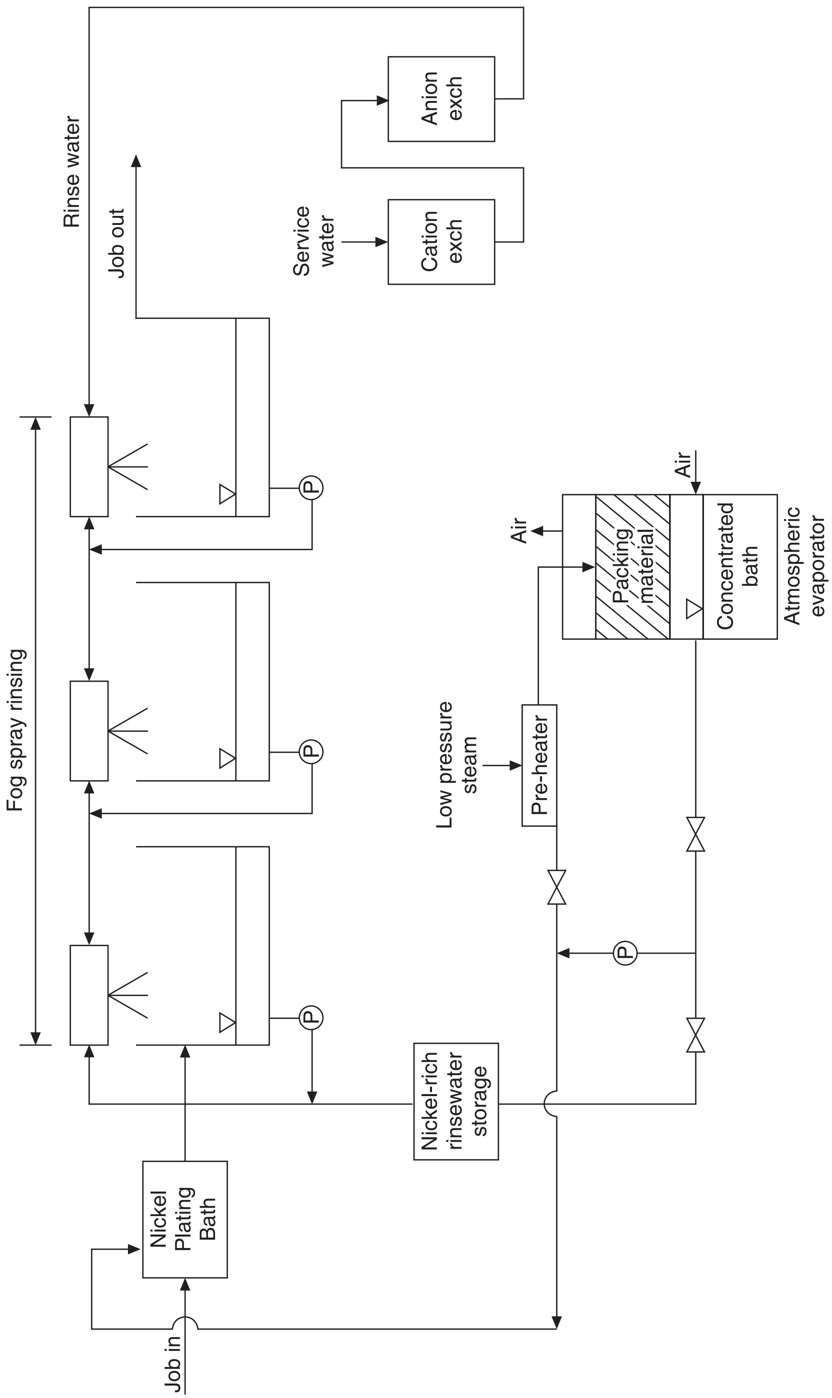

Figure 13.3 Nickel recovery system.

3%–5% flyash for treating 30 litres of waste water per hour. Although zinc removal was only 50% in the clarifier, the amount of flyash required was much less than that in the packed bed. COD reduction in both the cases was appreciable. Removal of copper from acidic effluent produced during the manufacture of printed circuit boards was attempted by Seshadri et al. [68]. They used an activated carbon column as electrode. Removal of copper was found to be a function of applied current, initial concentration of copper and surface area of the cathode. Optimum values obtained were: current—0.5 amp, surface area—180 cm^2 for initial copper content—1–10 gm/l. The advantage of the method is that recovery of copper is done without addition of chemicals.

Bottom ash from thermal power station was used by Rao et al. [69] to study its use as adsorbent of nickel ion from waste water. Maximum removal was obtained at pH between 11.5 and 12.0. Rai et al. [70] employed water hyacinth for removal of copper (II) from simulated water. The plant was exposed to concentration of copper from 0.1 mg/l to 20 mg/l. Rapid absorption was observed during the first 96 hours, the rate remaining nearly constant thereafter. Sequential exposure of the plant to the waste water showed it to be capable of absorbing copper, but at progressively reduced rates. The property of granulated slag from steel plant, containing iron and manganese in a state suitable for electrochemical reduction of a number of extraneously added metal ions, was studied by Loomba and Pandey [71]. They found that by controlling parameters such as weight of slag used, pH, concentration of the metal, rate of flow and applied EMF, it was possible to selectively remove metals such as mercury, lead, copper and zinc from waste water.

Lead plating and cadmium plating is done in fluoborate bath, which produce effluents containing 100–250 mg/l of lead and 7–50 mg/l of cadmium. Removal of these heavy metals by chemically activated carbon was done by Muthukumaran, Balasubramanyam and Ramakrishna [72]. Coconut shell, treated with sulphuric acid in the presence of potassium persulphate or hydrogen peroxide, was used as activated carbon in the pH range of 3.0–6.5 for lead and 4.0–9.5 for cadmium. This carbon was found to be superior to steam activated carbon. The column capacities were found to be 133.3 mg/gm for lead and 66.7 mg/gm for cadmium. Regeneration was possible with dilute mineral acid. The carbon retained its adsorptive capacity even after five cycles of regeneration.

Hanra and Prabhakar [73] used reverse osmosis membrane for separation of cadmium from waste water. They found that polyamide membrane was better than cellulosic membrane for this purpose. The permeate could be reused in the plating process and the reject could be treated further for recovery of cadmium.

Narayana and Krishnaiah [74] determined the optimum pH value for adsorption of Cr^{6+}on bituminous coal and optimum pH for reduction of Cr^{6+} to Cr^{3+} for its removal from waste water. The pH values they found were 2.0 for adsorption and 1.0 for reduction.

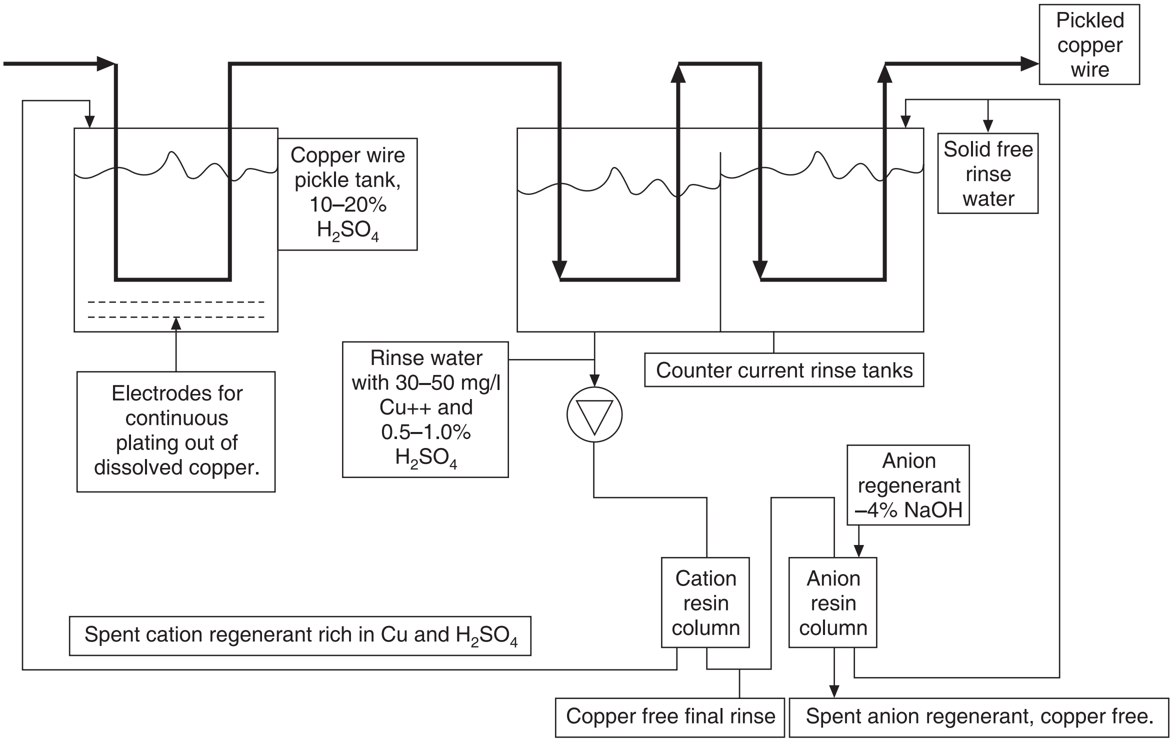

Figure 13.4 Copper rinse waste recirculation system.

FOR REFERENCE PURPOSES ONLY

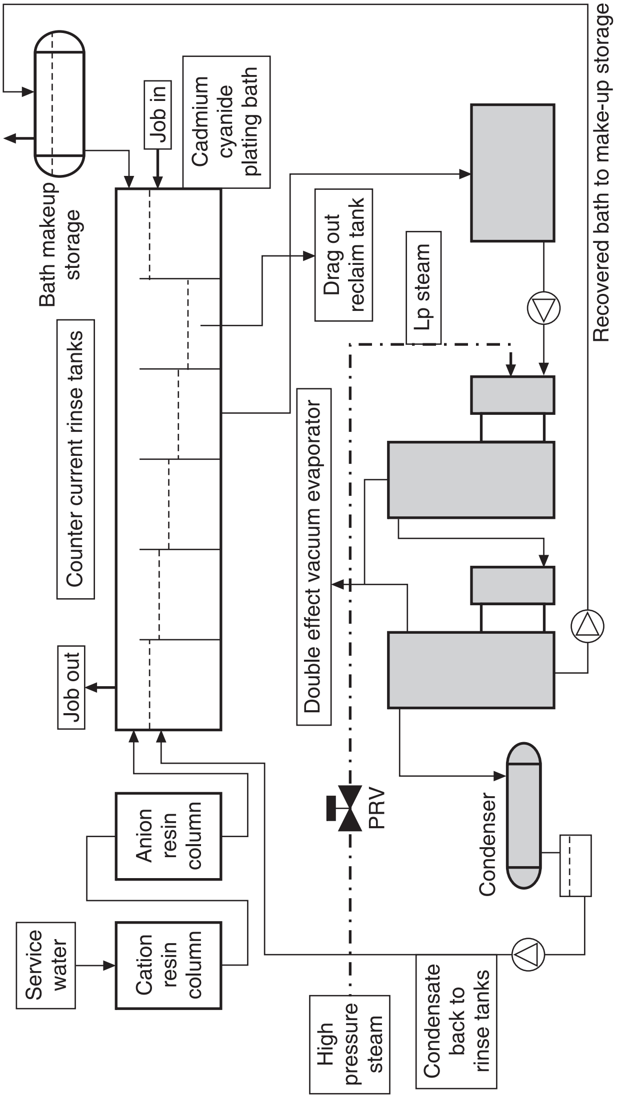

Figure 13.5 Cadmium cyanide plating bath recovery.

Information about the steel manufacturing plants in India at Bhilai, Durgapur, Rourkela and Bokaro has been given in [22]. Sharma and Naik [75] analysed the effluents from Bhilai steel plant for their physico-chemical characteristics and to find out their suitability for irrigation. The samples were collected 15 km downstream of the steel plant. They found that pH, phenol and ammonia contents were lower than those reported for integrated steel plants, but the values for phenols and ammonia were greater than the limits for discharge to inland surface waters. Singh [76] described the various measures taken by M/s Lloyds Steel Plant at Wardha for control of air pollution and water pollution. The volume of water recirculated per tonne of steel produced is 135 m^3 while the estimated actual consumption is only 6 m^3.

Thiruppathi [77] has given a detailed description of water and waste water management measures taken at M/s Sterlite Industries (I) Ltd., a non-ferrous metal manufacturing company in India. The industry is a ‘zero discharge’ plant. It smelts copper. It has its own sulphuric acid and phosphoric acid plants. Sulphur dioxide produced during smelting is used for manufacturing sulphuric acid, which in turn is used for producing phosphoric acid from rock phosphate. The volume of water received in the plant is 15.9×10^6 l/day; but recycling, conservation of water and replacing cooling water by air wherever feasible, has resulted in a saving of about 9×10^6 l/day of water. In addition, a collection pond is constructed to make rainwater available for use in the plant.

A new source of toxic wastes containing heavy metals and other organic components, which can contribute substantially to pollution, is electronic waste. It comes from unwanted computers, monitors, TV sets, stereo systems, copiers, fax machines and household electronic gadgets. Pollutants present are: lead and cadmium in circuit boards, lead oxide and cadmium in monitor cathode ray tubes, mercury in switches and flat screen monitors, cadmium in computer batteries, polychlorinated biphenyls (PCBs) in older capacitors and transformers, brominated flame retardants on printed circuit boards, plastic casings, cables and PVC cable insulation that releases highly toxic dioxins and furans when burned to recover copper from the wires. Devi, Shobha and Kamble [78] suggest a number of measures to mitigate this problem such as adoption of cleaner technologies, ecofriendly design of products, zero waste discharge, reduction of waste at source, recycle and reuse of waste material, incineration and landfilling. In addition, formulation of an ‘e-policy’ by government and corporate sector is expected to reduce the problem of e-waste.

Among measures which can save water and facilitate recovery of valuable metals in the plating industry are: (i) providing static rinses instead of running rinses to the plated surfaces, (ii) increasing draining time of plated material, (iii) using countercurrent washing system, in which the plated object is passed through static rinsing tanks from left to right, while rinse water is supplied only to the last rinsing tank. Its overflow is collected in the tank upstream of the last tank and, thus, rinse water flows in a direction counter to the direction of movement of the plated object, i.e. from right to left. The contents of the first rinse tank can be topped up with necessary chemicals and returned to the plating bath. Alternatively, they can be subjected to demineralization treatment for recovery of precious metals on one hand and reusable water on the other. Hesler [79] has described various applications of the ion-exchange process for achieving the above goals. A few ways in which water and plating chemicals can be recovered and reused [79] can be seen from Figs. 13.3, 13.4 and 13.5.

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Chapter 14

PETROLEUM REFINING INDUSTRY

The manufacture of petroleum products involves: (1) extraction of crude oil from the earth, (2) transportation of the crude oil to the refinery, (3) refining it with the help of a number of unit operations and unit processes, and (4) distributing the end products to their respective points of consumption. Each of the principal operations mentioned above is capable of producing pollution, e.g. *extraction* includes mud lost during drilling operations, oil losses and oil field brines, which invariably accompany the crude oil; accidental spillage and equipment failure during *transportation*; operations such as pressure and vacuum distillation, thermal and catalytic cracking, reforming, polymerization, and alkylation during *refining*, which require water for indirect cooling, for washing lube stocks, steam condensate from processing operations, etc. Distribution and storage of petroleum products can result in pollution due to spillage which reaches inland water bodies if it is not controlled [1].

Drilling muds are used to seal subsurface pressures, to lubricate and cool the drill and to remove drill cuttings without interfering with the drilling operation. They are specially prepared fluids of controlled density, viscosity, surface tension and water retaining capacity. Chemicals used in preparing them include amorphous silica, iron oxide, strontium sulphate, complex phosphates, sodium silicate and barium sulphate. Caustic soda, tannin, gallic acid, humic acid, etc. may also be used. In general, drilling muds are carefully conserved on account of their high cost. Oil field brines constitute from 4% to 96% of the total volume of oil and water produced by an oil well. These brines are usually disposed of by injection into ground, or by solar evaporation, or by controlled diversion into surface waters. If the oil well is located in the sea, or near the seashore, the brine can be conveniently discharged into the sea. It is possible to recover magnesium, iodine and bromine from oil field brines [2].

Crude oil is subjected to distillation, cracking, hydrocracking operations to give naptha, kerosene, diesel oil, gasoline, fuel oil, lubricants and LPG, along with asphalt, grease, coke and waxes. The gaseous products are sent to the fractionating columns, where light products such as kerosene, light fuel oil and gasoline are recovered after processing. All streams of the atmospheric distillation unit are suitably processed to give products in required proportions [3].

Refining operations consume as much as 30–80 litres of water per litre of crude oil processed. About 80% of this water is used for cooling. Liquid wastes produced during refining operations are given in Table 14.1.

Table 14.1 Liquid Wastes Produced During Refining [3]

Refinery process	Liquid waste produced
Distillation	Effluent with ammonia, hydrogen sulphide and phenols
Desalting	NaCl, phenols, sulphides or free H_2S
Vacuum distillation	Phenol and oil
Naptha hydrotreating	Sour condensate
Catalytic hydrotreating	H_2S, oil or phenols
Catalytic or thermal cracking	Phenols, H_2S, ammonia, cyanides
Hydrocracking	Ammonia
Catalytic alkilation	Alkalis from washings and acids from drains
Solvent processes	Solvents like phenol, sulphide, copper acetate, etc.
Treating processes	Organic and inorganic pollutants and emulsified oil.

The quality of the raw waste water from a refinery varies from process to process and refinery to refinery. An average Indian refinery shows the following analysis as in Table 14.2 [3].

Table 14.2 Raw Waste Water Analysis

Item of analysis	Concentration
Free oil	2000 to 3000 mg/l
H_2S and sulphides	10 to 220 mg/l
Phenols	12 to 30 mg/l
Suspended solids	200 to 400 mg/l
5-day BOD at 20°C	100 to 300 mg/l
Alkalinity	10 to 350 mg/l

In general, from 0.03 kg to 0.06 kg and 0.4 kg and 0.9 kg of phenols and COD, respectively, are present per tonne of crude oil refined [3].

Individual streams of waste water are far more polluting than the average waste water as seen from Table 14.3 [4].

Table 14.3 Characteristics of Individual Waste Water Streams

Characteristics	Spent caustic waste stream		Process waste stream			Acid waste stream			
	Benzene sulphonation scrubbing	Orthophenyl phenol washing	Polymerisation	Crude desalting	Catalytic cracking	Sour condensates	Acid wash still bottom	Acid wash orthophenyl phenol	Sulphite wash CP still bottom
Ammonia	—	—	—	20	—	136–6550	—	—	—
Acidity	—	—	—	—	—	—	—	24,200	675
Alkalinity	33,800	30,400	2,99,330	—	—	—	—	—	—
B.O.D. 20°C	53,000	1040	9440	80–160	230–240	500–1000	20,800	13,600	1,65,000
C.O.D.	1,12,000	67,000	50,350	124–470	550–2840	500–2000	2,45,000	23,400	8250
Sulphides	—	—	3060	0–13	—	330–8250	—	—	6
pH	13.2	0–12.0	12.7	7.2–9.1	—	4.5–9.5	1.0	1.1	3.6
Phenol	8.3	5600	22.2	10–25	20–26	100–1000	3800	1500	16,400
Oil and grease	—	—	—	20–516	200–2600	—	—	—	—
Dissolved solids	—	—	—	—	—	—	3,40,500	81,300	1,75,400
Total solids	50,000	40,000	—	—	—	—	4,03,200	82,500	1,79,900
Chlorides as NaCl	—	—	—	0.4–25	—	—	—	—	—
NaOH	1.0	0.2–0.6	—	—	—	—	—	—	—

Note: All values except pH are in mg/l.

Drilling muds, used in drilling operations, have high solid and chemical concentrations used in preparing them. They have to be treated before disposal. Their characteristics are as given in Table 14.4:

Table 14.4 Physico-chemical analysis of raw combined Waste waters from Drilling sites [5]

Item of analysis	Concentration
Colour	Dark muddy
Nature	Highly turbid and viscous
Temperature, °C	35
pH	8.7–8.9
Total solids, %	5.0–6.0
Total suspended solids, %	4.5–6.0
Total dissolved solids, %	0.6–0.7
Chlorides	175–225
Sulphates	800–900
Oil and grease	150
Soluble COD	600–650
Soluble BOD	220–240
Zinc	26
Chromium	10.25
Copper	1.56
Lead	0.16
Iron	170
Barium	56
Cadmium	0.09
Manganese	1.84

Note: Values except pH are in mg/l, unless otherwise stated.

14.1 TREATMENT OF WASTE WATER

Treatment of refinery waste water should begin with removal of oil and grease, as these pollutants are not easily biodegradable; moreover they interfere with gas transfer, so essential for aerobic biological treatment. Gharekhan [6] has discussed the principles of design of oil-water separators, their construction aspects and has suggested measures to improve their performance. He recommends the minimum size of oil globules to be 100 millimicrons and retention time of not less than 90 minutes. Miranda [7] has proposed an improvement over the traditional American Petroleum Institute's (API) oil-water separator, in which parallel plates are introduced in the flow of the waste water. This improves the performance of the separator despite its size being smaller than that of the API separator. Deepak et al. [8] conducted laboratory-scale studies on the separation of miscible oil from refinery waste water using ferric chloride ($FeCl_3$). Experiments were conducted in a vertical pipe 1.28 m high and 0.32 m diameter. It was provided with arrangement for bubbling air into the waste water from the bottom of the pipe. Doses of $FeCl_3$ tried were 663, 1061 and 1326.2 mg/l. It was observed that in 2 hours, at pH 5.0, and a dose of 1000 mg/l, the miscible oil concentration was reduced from 1188 mg/l to 98 mg/l. The separated oil was moved up the pipe with compressed air and was skimmed off. The authors felt that using 2 or 3 such units in series could reduce oil and grease to less than 10 mg/l.

Sludges produced during refining operations have to be disposed of properly, for which it is necessary to know their composition. Janiyani et al. [9] collected sludge samples and oil samples from Gujarat Refinery in Vadodara and analysed them for hydrocarbons which were fractionated into saturates and aromatics. According to them, such analysis enables one to decide an appropriate method of sludge disposal and to study the response of individual hydrocarbons towards natural weathering processes and microbial oxidation.

Two commonly found pollutants in refinery wastes are hydrogen sulphide and sulphides. They are responsible for producing high oxygen demand, besides being toxic to microbial life. A number of methods are available for stripping hydrogen sulphide and precipitating sulphides with heavy metals or as elemental sulphur. Sandhya and Pandey [10] worked on a combination of a chemical step, followed by a biochemical step for the removal of sulphide. Hydrogen sulphide was oxidized to elemental sulphur in the presence of ferric sulphate. The reduced ferrous ion Fe^{2+} was regenerated biologically by the chemoautotrophic bacteria *Thiobacillus ferrooxidans,* immobilized in a downflow packed bed column. The regenerated ferric sulphate was recycled for further oxidation of hydrogen sulphide. Removal of hydrogen sulphide was found to range between 89.28% and 98.21%. Biological regeneratrion showed an efficiency of 93%–99% at different loadings of Fe^{2+}.

Treatment of the waste water can be divided into physical, chemical and biological processes. Physical process includes oil-water separation by gravity settling, or by dissolved air flotation (DAF). The API oil-water separator is designed on the basis of removing oil globules 0.015 cm and more in diameter. The surface area to be provided should have a factor of safety of 1.2 to allow for short circuiting [11]. Chemical process aims at de-emulsifying, coagulating and settling for the removal of oil, phenols and suspended solids. The activated sludge process gets upset if the oil content in the waste water exceeds 25–30 mg/l, while a trickling filter shows no ill effect even when the oil content is 100 mg/l. Among the coagulating agents used for de-emulsification are ferrous sulphate, ferric sulphate, chlorinated copperas, calcium chloride, calcium carbonate and hydrated lime and their combinations. Weighting agents such as Fuller's earth can help reduce the oil content. The floc formed adsorbs the oil, and depending on the initial concentration, an effluent with oil less than 10 mg/l can be produced [11]. Iron salts are effective against effluents containing mercaptans and sulphides. But it is economical to remove high sulphides by steam stripping or air stripping. Chakrabarty and Bhaskaran [11] have shown that waste water containing 315 mg/l of ammonium sulphide and 100 mg/l of emulsified oil was successfully treated with 40 mg/l of chlorinated copperas, aerated for 15 minutes at pH 6.8 to 7, during which time sulphides were completely removed. The aerated sample was further treated with 300 mg/l of hydrated lime and 40 mg/l of Fuller's earth. After flocculation for 20 minutes and settling for 1 hour, the oil content was reduced to 8–12 mg/l. Further improvement in the removal of oil and suspended solids (especially coke fines) was observed with the use of coagulant aid. Baruah and Phukan [12] removed oil, grease and colour (due to sulphonated organics) from biologically treated effluents with (i) activated carbon, and (ii) 25 mg/l of alum and 15 mg/l of bleaching powder, in a settling time of 35 to 40 minutes. A packed bed with 240 gm of activated carbon could remove completely oil, grease and colour from 125 litres of effluent. The exhausted carbon could be regenerated thermally at 800°C for reuse.

Biological treatment processes used are trickling filters, activated sludge, aerated lagoons, oxidation ponds, oxidation towers, and trickling filters followed by activated sludge process. In the last case, it was observed that trickling filters worked so efficiently that activated sludge process which followed, could not operate well because of low concentration of soluble organic matter in its influent. In view of the toxic nature of refinery wastes, a completely mixed activated sludge process is better than the conventional activated sludge process. Kumar, Ray and Haldar [13] studied the characteristics of spent caustic generated when cracked hydrocarbons are scrubbed with caustic soda. The waste water has high COD, ranging from 50,000 mg/l to 400,000 mg/l, and contains sulphides, mercaptides, sulphates, sulphonates, cresylates, naphthanates, carbon dioxide, hydrogen sulphide, etc. The last two gases are acidic in nature. Treatment normally followed consists of precipitating the sulphides with chlorinated copperas, but it generates sludge which is difficult to dispose of. Further, the process does not remove phenols from the waste water. Care has to be taken to maintain the pH of the precipitated sulphides above 8.0 to avoid the possibility of evolution of hydrogen sulphide. The authors recommend the use of hydrogen peroxide (H_2O_2) in order to avoid the above problems. Stoichiometrically 1 kg of hydrogen peroxide oxidizes 1 kg of hydrogen sulphide. But in actual practice, 3 to 4 times more hydrogen peroxide has to be added to meet the demand from other reactive materials. If sulphides are present in dissolved form as Na_2S, stoichiometrically 4.25 kg of H_2O_2 react with 1 kg of Na_2S. The authors propose a flow sheet consisting of flash mixing, in which acid/alkali (as per requirement) and H_2O_2 are added, then flocculation, followed by dissolved air flotation.

Disposal of treated refinery waste water for irrigation was tried by Ozair, Iman and Siddiqi [14]. They conducted split-plot field experiments for growing triticale (a fertile hybrid cereal obtained by crossing wheat and rye) with the available ground water and compared the growth and other parameters of the crop with that grown on treated refinery effluent. They noted that in general, better growth, yield and more nutrients were obtained from the crop grown on treated effluent than that grown on ground water. However, the effluent-treated crop showed lower carbohydrate and protein contents. Three irrigations with treated effluent were found to be equivalent to four irrigations with ground water. Chakravarty [15] has described the effluent management practices followed at the Indian Oil Corporaton Limited (IOCL) refineries. Treatment consists of primary (oil-water separation), intermediate (oil-water separation + emulsified oil treatment and spent caustic treatment), secondary (BOD removal) and tertiary (holding basins, pressure filtration, chlorination and activated carbon) treatment.

Kaul and Roy [16] have presented the practice of reusing treated effluents from the Gujarat Refinery Complex consisting of (a) Gujarat Refinery (GR), (b) Gujarat refinery Expansion Project (GREP), (c) Gujarat Refinery Secondary Processing Facilities (GRSPF), and (d) Gujarat Hydrocracker Complex (GHC). The four units treat about 700–800 m^3 of waste water/hour, of which 300–400 m^3/hour is reused after adequate treatment for firewater make-up and in cooling towers.

Sastry [17] mentions that biological treatment of refinery waste water is possible by activated sludge process, trickling filtration, aerated lagoons and waste stabilization ponds. Oil and grease greater than 30 mg/l in the waste water affects activated sludge process. But the use of iron salts with the waste water helps the microbial mass and $Fe(OH)_3$, formed in the aeration tank, to flocculate and remove BOD, phenol and oil simultaneously. Deep bed high-rate trickling filters are also effective. Aerated lagoons with a hydraulic retention time (HRT) of six days work well, but the biomass formed is very light. Therefore, a number of ponds in series are required to improve the quality of the effluent. Waste stabilization ponds with an HRT of 60 days have shown BOD and phenol reduction of 43–96% and 61–99%, respectively.

Wood et al. [18] describe the performance of a sequencing batch reactor (SBR) treating refinery waste in Spain. They found the SBR to work well under stringent environmental requirements. Effective removal of selenium from refinery wastes was observed by Adams and Murchison [19] with the use of selected microbes and microbial consortia, which have a range of selenium reducing capabilities. Hansen et al. [20] used 36 hectares of constructed wetlands for treating refinery wastes and found that although most of the selenium was removed by immobilization into sediments and plant tissues, biological volatilization may have accounted for 10–30%. Nurdogan [21] found that a dose of 50 mg/l of $FeCl_3$ as Fe was required to reduce the selenium concentration to less than 50 ppb at all times in laboratory and plant scale experiments. Arabindoo et al. [22] used alum and $FeSO_4$ as coagulants, while Demirci et al. [23] used alum, $FeSO_4$, $FeCl_3$ and lime as coagulants along with

Turkish clays as coagulant aid and found that the clay was as efficient as bentonite. Viraraghavan and de Maria Alfaro [24] used peat, flyash and bentonite as cheap adsorbents for removing phenol from refinery waste water and found that equilibrium was reached in the three cases at 16, 5 and 16 hours respectively, at optimum pH of 4.0–5.0 and a temperature of 21°C.

Ballinger et al. [25] observed that there was considerable diversity of ammonia-oxidizing bacteria of class Proteobacteria, while treating synthetic refinery waste by the activated sludge process. Kapoor et al. [26] examined four immobilized mixed bacterial organisms including *Pseudomonas aeruginosa, Pseudomonas fluorescens, Serratia sp. and Yersinia sp.* for their ability to degrade phenols, and found that the immobilized biomass degraded phenols 100% in 96 hours while the free cells could destroy only 80%. Doctor [27] has given a detailed coverage of petroleum refinery wastes in terms of their characteristics, environmental effects, treatment methods, organisms capable of degrading aliphatic, alicyclic, aromatic and polycyclic aromatic compounds and problems faced during treatment. Copeland and Cole [28] noted that the performance of an activated sludge process could be improved by providing equalization capacity, addition of hydrogen peroxide and separate aeration of return sludge to provide unstressed biomass recycle. Givens *et al.*[29] found during pilot testing that the two-stage treatment, consisting of anoxic step followed by aerobic treatment, gave BOD, COD and total nitrogen removal efficiencies of 99%, 98% and 80%, respectively. Francis and Choudury [30] used a bench-scale four-stage rotating biological contactor (RBC) with polyurethane foam support media and got removal efficiencies of greater than 80% for oil, 90% for ammonia nitrogen and 80% for PhOH at different hydraulic loadings. Hirata and Hosaka [31] used RBC to treat waste water from the washing of oil and chemical drums. Triet et al. [32] used a three-stage biological pond with water hyacinth, chlorella and reeds for post-treatment of petroleum waste water in Vietnam. Poddar and Kumar [33] employed water hyacinth for the removal of phenols, chromium, cadmium, nickel, zinc and lead from refinery effluent.

Physical and physico-chemical processes were also tried out. Alkhatib and Thiem [34] reported removal of emulsified oil by dissolved air flotation (DAF) at optimal air:oil ratio of 0.058:0.077 for API oil water separators as well as parallel plate separators. Fang et al. [35] used electrophoresis for removal of emulsified crude oil from produced water. Bolto [36] found that magnetic particle technology was effective in removing metals from slurries, sludges, muds and effluents with suspended solids. Tur et al. [37] offered nanofiltration as a suitable substitute for low-pressure reverse osmosis treatment of secondary effluents after activated carbon, where waste water reclamation is required. Zubarev et al. [38] observed that cellulose acetate membrane MGA-100 was effective in effluent desalination with 98–99% retentivity. This could facilitate recycling and eliminate surface discharges. Elizardo [39] found that ferrous ion and ultraviolet rays were important catalysts in the use of hydrogen peroxide for oxidizing sulphides and cyanide compounds. Abdrakhimov [40] suggested the use of sulphurous caustic solutions containing caustic, Na_2S, mercaptides, and carbonates generated during pyrolysis of naphtha, for removal of heavy metals, especially mercury. Kale et al. [41] presented the planning and investigations carried out for utilizing Mathura refinery effluent for irrigation. The evaluation was done with respect to soil properties, areas suitable for irrigation, cropping pattern, water requirement, irrigation management and crop scheduling, environmental impact and benefits of the system were also included.

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Chapter 15

PETROCHEMICALS INDUSTRY

Chemicals derived from petroleum or natural gas are called petrochemicals. Petrochemicals are usually intermediates and are used for the production of solvents, detergents, synthetic resins and rubbers, synthetic fibres and pesticides, fertilizers and other chemicals. In a petrochemical plant, the petrochemical fraction is processed to get intermediates and the final product is synthesized by a more complex process. Primary processes consist of combustion, cracking, catalysis, oxidation, pyrolysis, etc. Secondary processes include chemical reactions, recovery, purification, condensation, scrubbing, recycling, distillation. End products from these operations are ethylene, methanol, acetaldehyde, ethylene oxide, acetic acid, ethylene glycol, polyethylene, propylene, butadiene, styrene, acrylonitrile, butanol and caprolactum [1, 2].

Waste water from petrochemical industry includes traces or large concentrates of raw materials, all intermediate products, all final products, coproducts and byproducts and auxillary or process chemicals used during manufacturing process. It is neither necessary nor desirable to determine the concentration of each pollutant present in the waste water. But analysis by compound or class of compound is useful in tracking down the source of pollution and devising in-plant control measures. For overall pollution control, it is preferable to use the familiar parameters such as BOD, COD, solids, colour, odour, etc. plus toxicity, foaming tendency and oil and grease [3].

Sources of waste water in a petrochemical complex are: (a) direct discharges from production plants, (b) blowdowns from cooling and steam raising systems, (c) sewage from canteens and toilets, (d) contaminated storm discharges from production areas, (e) ballast water from tankers during product handling, and (f) miscellaneous discharges from spills, etc. The quality characteristics of the waste water depend on the specific petrochemical being produced. Table 15.1 shows typical characteristics of petrochemical industry effluents.

Table 15.1 Quality of Effluents [4]

Parameter	A	B	C	D	E	F	G
Alkalinity	4060	365	164	–	–	–	–
BOD	1950	345	225	1950	16,800	16,700	170
Chlorides	430–800	1980	825	800	96,300	1,44,000	800
COD	7970–8540	855	610	1972	21,700	27,500	2000
Oils	547	73	–	547	–	–	45
pH	9.4–9.8	9.2	7.5	–	–	–	–
Phenols	–	160	17	10–50	–	–	400
Sulphates	655	280	–	655	–	–	–
Suspended solids	27–60	121	110	60	700	348	Negligible
TOC	–	–	160	–	–	–	–
Total nitrogen	1160–1253	89	48	1253	40	45	100
Total solids	2191–3029	3770	2810	3029	172467	167221	3000
Miscellaneous	–	Sulphides-150	Phosphates-Trace	–	%Vol. Total solids = 10.5	%Vol. Total solids = 13.2	H_2S=12

Notes: All values except pH are in mg/l

A: Mixed chemicals, including ethylene oxide, propylene oxide, glycols, amines and ethers.
B: Refinery, detergent alkylate.
C: Refinery, butadiene, butyl rubber.
D: Mixed organics.
E: 2,4,5, trichlorophenol.
F: 2,4 dichlorophenol.
G: Nylon.

In view of the great variability of its quality, it is necessary to conduct treatability study on every waste water in order to decide the most suitable form of treatment. Swaminathan and Viraraghavan [5] discuss the various forms of treatment prevalent in the industry, including physical, chemical and biological processes. Some pretreatment in the form of oil-water separation, pH correction, stripping for ammonia and H_2S removal and settling or flotation is necessary before subjecting the waste water to biological treatment. Large balancing tanks are strongly recommended upstream of biological treatment to absorb wide fluctuations in quality and to dilute toxic substances in the waste water. Activated sludge using extended aeration is commonly used. The use of pure oxygen in place of atmospheric oxygen improves the treatment efficiency. Deep shaft aeration provides a high degree of oxygen transfer and low excess sludge production. However, it is a costly process. A patented process [6], using powdered activated carbon with activated sludge, improves efficiency of the process by adsorbing organics not amenable to biodegradation. A drawback of the process is that biological growth can take place on the surface of the activated carbon and reduce its adsorbing power. Further, the process cannot remove compounds which are neither adsorbable nor biodegradable. Deep trickling filters using PVC media can effectively treat petrochemical wastes. Surface hydraulic loading should not exceed 15 m^3/m^2/day and should be just enough to ensure total wetting of the filter media. A high rate filter is designed to remove 70% organic load, followed by conventional activated sludge process to achieve satisfactory quality of the treated effluent. Aerated lagoons are also used as intermediate treatment step, followed by waste stabilization pond. Low MLSS in the aerated lagoons make them susceptible to temperature changes [5]. Anaerobic treatment, usually in a UASB, has been successful for treating low-strength wastes [7]. An anaerobic downflow filter was successfully used to treat low-strength wastes [8]. But anaerobic digestion of effluent from a petrochemical plant manufacturing terphthalic acid in two UASB reactors was unsuccessful [8A]. Mudri, Subrahmanyam and Rao [9] studied treatment of a synthetic waste water resembling petrochemical waste with a combination of aerated lagoon and oxidation ditch. The composition of the synthetic waste water is given in Table 5.2.

Table 15.2 Characteristics of Synthetic Waste

Parameter	1	2	3	4	5	6	Average
pH	3.0	3.1	3.2	2.9	2.9	3.0	–
5-day 20°C BOD, mg/l	1710	1700	1590	1930	2060	1810	1800
COD, mg/l	2735	2720	2625	2900	3010	2810	2800

At a BOD loading of 0.16 kg/kg MLSS/day, BOD removal was 98–99%. The overall BOD removal rate was found to be 0.235/day upto 5 days and 0.098/day from 5 to 12 days. Therefore, an aerated lagoon of 5 days' HRT, followed by extended aeration for 20 hours was recommended. Shah et al. [10] tried aerobic biological treatment of waste water from a DMT plant using biomass support particles and found that the optimum organic loading rate for 90% COD reduction was 14 kg/m^3/day at a hydraulic retention time of 12 hours.

Anaerobic treatment of petrochemical waste water was studied by Nel and Britz [11] from the aspect of influence of substrate pH on the performance of a downflow anaerobic fixed bed reactor. They concluded that: (a) anaerobic treatment at pH 6.0 is not optimal, (b) high Na^+ concentration (used to neutralize acidity with NaOH) inhibited the process, (c) high concentration of volatile fatty acids (acetate> 7000 mg/l, propionate> 2000 mg/l, butyrate>1000 mg/l) even at a feed pH of 3.95 did not inhibit the process, provided NaOH was added at or near its optimum concentration of 0.23 gm/l and (d) reduction of NaOH and final substitution thereof of Na^+, Ca^{++} and K^+ gave substantial savings in the use of alkali. The reduced cation concentrations resulted in a marked stimulation of the process. Although the methane yield at feed pH 3.95 was less than at higher pH, this shortcoming was insignificant compared to the increased rate of the process. Chou et al. [11A] evaluated the effect of molecular structure of 52 petrochemicals on toxicity to methane fermentation. The compounds chosen were on the basis of: double bonds, positions of functional groups, odd or even numbered carbons, length of carbon chain, branching, oxidative state, type of functional group, number of identical functional groups and configuration. Chloro substitution, aldehydes, double bonds and benzene rings showed toxicity to unacclimated cultures. Addition of hydroxyl groups and increased carbon chain length decreased the above toxicity. Acclimation to a toxic compound substantially reduced its toxicity in the case of aldehydes, double bonds and benzene rings.

Katsura, Miura and Hasegawa [12] employed thermophilic aerobic digestion of activated sludge from petrochemical waste treatment plant and achieved minimum excess sludge production, reducing the operating cost by 1/2 to 1/3 compared to dewatering and landfilling. Fan, Wang and Jiang [13] tested a membrane bioreactor (MBR) for treating petrochemical complex waste water. The arrangement consisted of activated sludge process followed by ultrafiltration. Laboratory-scale tests showed average per cent removals for COD, ammonia nitrogen, total phosphorus, oil and total suspended solids as 91%, 85%, 82%, 86% and 92%, respectively. Yang et al. [14] employed low pressure wet catalytic oxidation (LPWCO) method for treating highly concentrated refractory waste water in which a combination of wet air oxidation and Fenton's reagent were used. The process used lower pressure and temperature than used in wet air oxidation and was found to be more efficient than Fenton's reagent alone in COD removal because of synergistic effect.

Disposal of acidic sludge from treatment of petrochemical wastes can pose problems. So Joseph and Rajenthiran [15] treated such sludge with sulphuric acid and prepared activated carbon from it, which was found to be as good an adsorbing agent as commercially available coconut shell activated carbon in the removal of methylene blue colour. Lin. Ma and Huang [16] gave alkaline pretreatment to sludge to enhance its biological hydrolysis in a plant treating waste water from an acrylonitrile butadiene styrene manufacturing unit. The waste water was a high strength nitrogenous stream and was hydrolysed successfully at a temperature of 25°C, HRT of 24 hours with total solids varying from 0.5% to 2%. The dose of NaOH was 50 mg/l. Ries [17] presented laboratory-scale and pilot-scale studies with water hyacinth (*Eichhornia crassipes)* in removing nutrients and metals from inorganic effluents in a petrochemical complex and concluded that zinc and phosphorus could be removed by this plant, provided the system was properly maintained. Gharekhan and Prabhudesai [18] have described their experiences of operating a petrochemical waste treatment plant of Gujarat Aromatics Project at Jawaharnagar, Gujarat with special reference to the control of solids retention time (SRT). They prefer sludge wasting from the aeration system based on the hydraulic flow of waste water through the system plus the return sludge flowrate. Difficulties encountered during operation have also been described in detail.

Caprolactum, an important product of the petrochemical industry, is used as a raw material in the production of Nylon-6. Patel amd Patel [19] studied the characteristics of the waste water generated from its production and got the result as shown in Table 15.3.

Table 15.3 Characteristics of Caprolactum Waste

Characteristics	Minimum	Maximum	Average
pH	5.3	10.0	8.2
Total solids	1956	14478	5713
COD	947	9000	3861
BOD	650	5800	1200
COD/BOD	1.4	2.0	1.6
Total NH_3-N	150	600	300
PO_4	Traces	15	5
Oil and grease	10	85	30

Note: All values except pH are in mg/l.

Laboratory-scale experiments using extended aeration process showed that it was possible to degrade caprolactum and achieve a BOD reduction of 99% at an organic loading rate of 0.50 kg BOD/kg MLSS and a hydraulic retention period of 24 hours. Kadam, Saxena and Shukla [20] conducted treatability studies on caprolactum waste containing 1000 mg/l of ammoniacal nitrogen, 510 mg/l of nitrate nitrogen, 5-day BOD of 3950 mg/l and COD of 9700 mg/l. Biological treatment was given after air stripping of the ammonia. Nitrate nitrogen was removed by providing denitrification before extended aeration. The denitrified waste water was diluted with treated effluent in the ratio of 1:1 and then was aerated, and clarified in secondary settling tank. The BOD and COD were reduced to 325 mg/l and 900 mg/l, respectively. Therefore, the waste was chlorinated and post-aerated. The final BOD and COD values were 190 mg/l and 425 mg/l, respectively. The MLSS/MLVSS ratio was 0.67 in the system at a MLSS concentration of 7300 mg/l.

Resorcinol, like caprolactum, is another pollutant in petrochemical waste water. Swamy et al. [21] studied the possibility of using bagasse flyash for the removal of resorcinol and found it to be as good as activated carbon of laboratory grade and commercial grade. Significant amounts of nitrophenolic compounds are found in petrochemical wastes. Karim and Gupta [22] through an extensive literature review have shown that an anaerobic system capable of holding a large concentration of biomass, can degrade nitrophenols. Further, improvement in degradation can be had if denitrifiers are also present in the biomass. Pretreatment of nitrophenols by way of oxidation with ozone, hydrogen peroxide or potassium permanganate improves biodegradation. Metals present in petrochemical wastes can be precipitated with various chemicals. Eckenfelder [23] lists them in Table 15.4.

Table 15.4 Precipitation of Metals from Petrochemical Waste

Name of metal	Chemicals used	pH value	Remarks
Arsenic	Na_2S or H_2S	6.0–7.0	–
Barium	–	–	Removed as SO_4^{2-}
Cadmium	Co ppt.with $Fe(OH)_3$	6.5	CN^- interferes
Copper	As sulphide	8.5	CN^- interferes
Lead	Na_2S	7.5–8.5	Also ppt. as $PbCO_3$ or $Pb(OH)_2$ at pH 9.0 to 9.5
Manganese	Lime + ClO_2, $KMnO_4$, O_3	–	Cu enhances removal
Mercury	Alum, FeS	–	
Nickel	Lime	10.0–11.0	Can be recovered as CO_3^{2-} or SO_4^{2-}
Selenium	–	6.6	Ppt as sulphide
Silver	Ppt as AgCl	–	–
Zinc	Lime or caustic	11.0	–

Gharekhan [24] has described the pollution control measures taken at the Indian Petrochemicals Complex Ltd., classifying the chemicals as first generation—those obtained from petroleum, second generation—those obtained from crude oil, and third generation—those obtained from gas. He has given the 5-day BOD values of pollutants commonly found in petrochemical wastes. As a part of the pollution control activities, an experimental station is also set up to test the effect of treated waste discharge on soil, crops grown on the treated effluent, air pollution, etc. Recovery of oil, cobalt, etc. and the economics of the recovery are briefly described.

A high degree of selectivity for the recovery of valuable water soluble components from petrochemical waste was shown to be feasible with reverse osmosis. Recovery of glycerine from a waste stream containing inorganics and polyglycerins was achieved with tubular membrane modules of asymmetric cellulose acetate and cellulose acetate type. Sufficient glycerine was recovered to provide an attractive return on the required investment [25].

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Chapter 16

FERTILIZER AND PESTICIDES INDUSTRIES

Fertilizers can be grouped into (a) nitrogenous, e.g. urea, ammonium sulphate, ammonium nitrate, ammonium chloride, (b) phosphatic, e.g. superphosphates, (c) complex, e.g. ammonium phosphate and ammonium sulphate-phosphate, and (d) potassic. Chemicals required in the production of these fertilizers are mainly sulphuric acid, nitric acid, naphtha, carbon dioxide and phosphoric acid. It is convenient for the industry to produce these acids in-house. Raw chemicals required are generally produced during the manufacture of main products. For example, anhydrous ammonia is reacted with sulphuric acid, usually obtained as by-product from other manufacturing plants. Gypsum obtained from phosphatic fertilizer manufacture, is reacted with ammonia and carbon dioxide from ammonia plant. Calcium sulphate, produced during the manufacture of superphosphate, is used in producing ammonium sulphate.

16.1 A FEW MANUFACTURING PROCESSES [1]

16.1.1 Ammonia Synthesis

A mixture of pure nitrogen and pure hydrogen in a proportion of 1:3 by volume is compressed under 200 atmosphere pressure and passed through a chamber heated to 500°–550°C, containing finely divided iron (which acts as a catalyst) and molybdenum (which acts as a promoter). Nitrogen combines with hydrogen to form ammonia. The gases, containing ammonia and unreacted nitrogen and hydrogen, are cooled under pressure, when ammonia is liquefied while the other two gases are recycled to the reaction chamber to get more ammonia. The reaction is exothermic. Ammonia thus generated is used in the manufacture of urea [2].

16.1.2 Urea Synthesis

Naphtha or natural gas is treated with steam and hot air to produce carbon monoxide, carbon dioxide and hydrogen. Carbon dioxide is separated from the mixture and is sent to the urea synthesis plant. Separation is done using potassium carbonate, monoethanolamine, diethanolamine and caustic soda. Ammonia from ammonia synthesis plant is reacted with carbon dioxide to form urea. The liquid is filtered and subjected to vacuum crystallization. The crystals are separated by centrifugation, dried and remelted. The molten urea is pumped to the top of prilling tower and is sprayed in it against a current of hot air. Spherical prills of urea are formed at the bottom of the tower, from where they are collected. Hydrogen produced from naphtha is sent to the ammonia synthesis plant while carbon monoxide is oxidized to carbon dioxide [1]. The manufacturing flow sheet is shown in Fig. 16.1.

16.1.3 Phosphoric Acid

Phosphate rock, or fluorapatite, is reacted with sulphuric acid to form phosphoric acid. An important by-product of this step is hydrofluoric acid, HF. It combines with silica to form fluosilicic acid H_2SiF_6. Another by-product is calcium sulphate sludge, which is used to form ammonium sulphate [1].

16.1.4 Ammonium Sulphate

Reaction between ammonia and sulphuric acid gives ammonium sulphate. Alternatively, calcium sulphate sludge from phosphoric acid plant can be reacted with ammonium carbonate to produce ammonium sulphate and calcium carbonate, which can be used in the manufacture of cement [1].

16.1.5 Diammonium Phosphate (DAP)

Phosphoric acid is neutralized with ammonia and the ammonium phosphate slurry so formed is granulated, or ammonium sulphate is added to the slurry before granulation to get ammonium sulphate phosphate [1].

16.2 SOURCES OF WASTE WATER

Sources of waste water streams are: (i) process water, (ii) process intermediates, (iii) final products, (iv) oil-bearing wastes from compressor house and boiler house, (v) wash water from gas scrubbing towers,

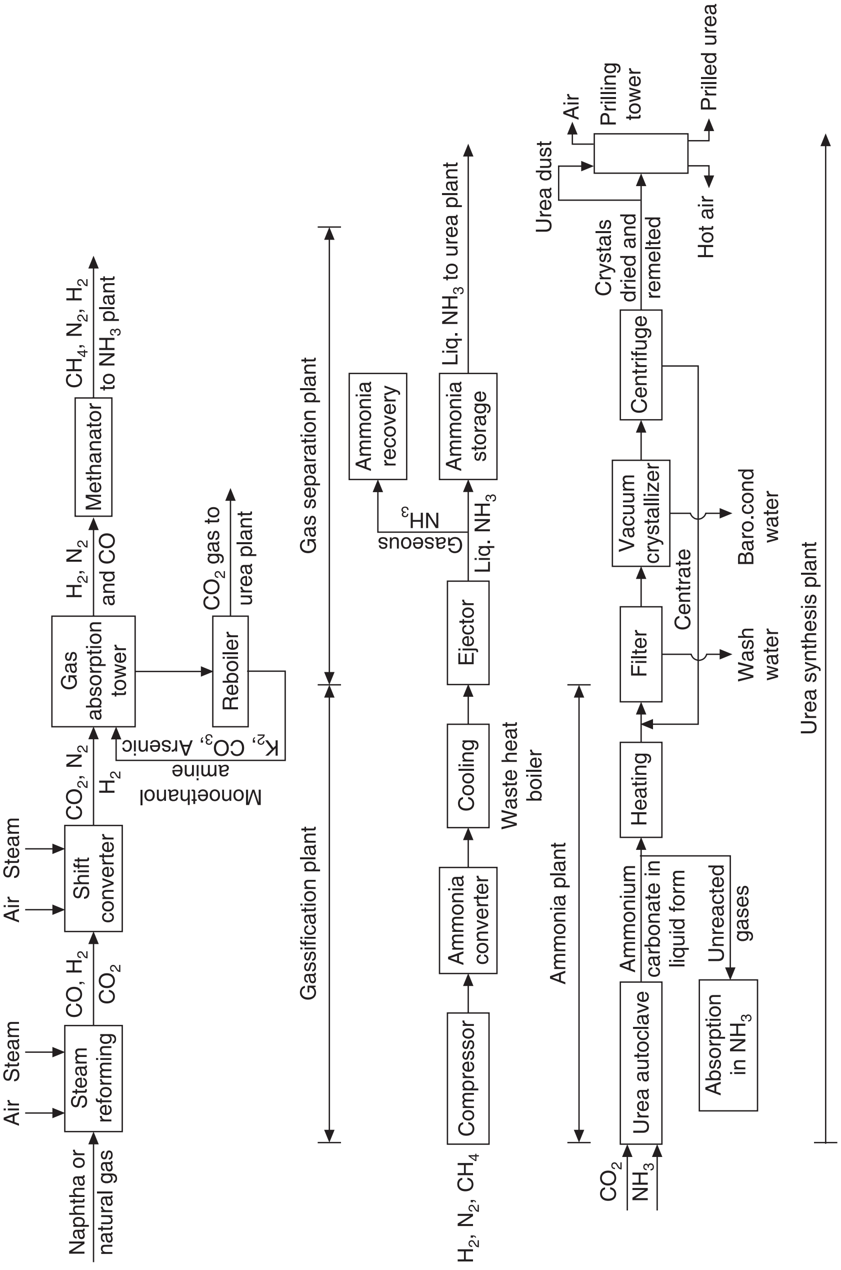

Figure 16.1 Urea synthesis.

(vi) regeneration and rinse waters from demineralization plant, (vii) cooling tower and boiler blowdowns, (viii) phenols and cyanides, if ammonia is extracted from ammoniacal liquor of coke ovens.

Average composition of waste water from a fertilizer manufacturing plant is given in Table 16.1 [3].

Table 16.1 Average Composition

Item of Analysis	Value
pH	7.5–9.5
Total solids	5400
Ammonia nitrogen	700
Urea nitrogen	600
Phosphates	75
Fluorides	15
Arsenic	1.5

Note: All values except pH are in mg/l.

These characteristics vary over a wide range, depending on the raw materials used, method of manufacture, housekeeping practices followed, reuse and recycling practices followed, if any.

16.2.1 Disposal of Waste Water

Methods of disposal include the following:

1. Disposal at sea: Minimum treatment required before disposal is removal of components which could damage, corrode or form incrustations in the pumps, piping and the outfall. In addition, a thorough study of the ocean currents and their mixing characteristics is required to decide the length of the outfall.
2. Disposal into river: Treatment required for removal of toxic substances to avoid fish kills, prevent deterioration of downstream water supplies, avoid eutrophication.
3. Disposal on land: Removal of pollutants harmful to soil organisms and reduction of total dissolved solids to less than 2100 mg/l. This is difficult to achieve, except by dilution. Further, the land required would range between 10 and 20 ha per 1000 m^3 of diluted waste water, the dilution ratio ranging between 3 and 4. So, this alternative would be feasible if adequate land and dilution water were available [1].

16.3 METHODS OF TREATMENT

Efficient treatment can be had if segregation of waste streams and their separate treatment is done before mixing them together for final treatment and disposal, e.g. carbon slurry waste which is generated during gasification of naphtha by the steam reforming process, gas scrubber wastes containing monoethanolamine (MEA), arsenic, potassium carbonate and caustic, urea, ammonia and ammonium sulphate and phosphate-bearing wastes, acid spillages, acidic and alkaline wastes from demineralization plant, oily wastes from equipment, cooling water and domestic sewage [1].

Pollutants, which demand special attention, are (i) ammonia in its free and combined form, (ii) arsenic, (iii) MEA, (iv) urea, and (v) chromium compounds, if they are used as algicides in cooling towers. A number of methods have been devised to take care of these pollutants.

Ammonia removal is done by (a) air stripping, (b) steam stripping, (c) lagooning after pH adjustment, and (d) nitrification and denitrification. Air stripping involves raising pH of the waste to 11.5, when ammonia is liberated as a gas. Vigorous agitation is required at this stage either with compressed air or by stripping towers fitted with fans. Compressed air agitation done for 3 hours at elevated pH effected 90.5% removal [4]. The use of stripping towers filled with redwood slats and supplied with air has shown this method to be efficient (upto 98% removal), provided enough air was supplied and the tower height was about 7 metres [4]. Steam stripping is economical if the ammonia concentration is 3–4%. But the steam requirement is very high, of the order of 240 tonnes/hour. So this method is not economical. Lagooning after raising pH to 11.0 for a day reduced ammonia by 44–61%. The process of nitrification and denitrification can be conveniently combined with carbonaceous BOD removal in the activated sludge process. But fertilizer wastes are deficient in carbon. So, a source of carbon is required for the success of this process. Siddiqi, Ratnaparkhi and Agarwal [5] conducted laboratory-scale study on nitrification of ammonia-bearing waste water, using a submerged fixed film reactor and found it to be four times more efficient than the conventional trickling filter in bringing about nitrification.

Conventional biological method of ammonia removal uses autotrophic nitrifying bacteria for nitrification and heterotrophic bacteria for denitrification. With the discovery of anaerobic ammonium oxidation (ANAMMOX) process, the cost of biotreatment for ammonia removal will reduce greatly, due to low oxygen requirement for nitrification and elimination of a carbon source for denitrification [6]. Shivaraman et al. [7] studied anammox activity in a field pond receiving ammonium nitrate-rich waste water and found that around 9% and 78% of total (ammonium + nitrite) nitrogen fed to the pond was converted to nitrate and nitrogen gas, respectively. It was also found that anoxic conditions are necessary for ANAMMOX organisms to oxidize ammonium in the presence of nitrite.

Urea is a major nitrogenous fertilizer used and is produced from reaction between ammonia and carbon dioxide. It is estimated that a 1000 TPD unit produces urea and ammonia-bearing waste water of 10,000 m^3/day [8]. It is possible to hydrolyze urea to ammonia and carbon dioxide under high temperature and pressure, provided the waste water contains only urea and ammonia. Other waste water streams arising out of spillage, leaks, scrubber washings, etc. cannot be economically subjected to thermal treatment, but contain enough urea and ammonia and must be subjected to some other form of treatment. Aerobic nitrification-denitrification method is available for this purpose, but requires power for oxygen supply and sludge return. Latkar and Chakrabarti [9] conducted laboratory-scale experiments to hydrolyze urea under anaerobic conditions using a fixed film fixed bed (FFFB) reactor. They found that it could handle about two times more urea than a continuous flow stirred tank (CFSTR) reactor. At a urea loading of 2.73 kg/m^3 void space/day, 100% destruction was observed. Influent ammonia loading of 1 kg/m^3 void space/day was easily tolerated by the system. The authors claim that the proposed anaerobic system could replace aerobic nitrification-denitrification system, provided the air/steam stripping technology reduced the $NH_4 \rightarrow N$ in the influent to and effluent from the system to acceptable levels.

Urea manufacturing units use monoethanolamine (MEA) for purification of carbon dioxide and hydrogen in a gas scrubber. Even in small concentrations, MEA exerts a very high BOD, the theoretical value at 30°C being 1,700,000 mg/l. Therefore, Chakrabarty et al. [10] conducted laboratory-scale studies using a Warburg respirometer to determine the maximum concentration at which MEA can be degraded in a biological system. No toxicity was observed upto 30 mg/l MEA, but it was apparent at 50 mg/l and became pronounced at 100 mg/l. It appeared, therefore, that the toxicity threshold lay between 45 mg/l and 55 mg/l.

Phosphatic fertilizers include ammonium sulphate-phosphate, diammonium phosphate (DAP) and superphosphate. Discharge of waste water from phosphatic fertilizer plants gives rise to serious problem of eutrophication in the receiving water and reduces its usefulness for other purposes such as drinking, bathing, etc. Average chemical analysis of waste water from a phosphatic fertilizer plant is given in Table 16.2.

Table 16.2 Analysis of Waste Water from Phosphatic Fertilizer Plant

Characteristics	Phosphoric acid plant	Diammonium phosphate plant
pH value	4.9	7.4
Dissolved solids	16,040	1340
Alkalinity (as $CaCO_3$)	–	275
Acidity (as $CaCO_3$)	760	–
Free ammonia	–	12
Fixed ammonia	–	26
Phosphate (as PO_4)	1800	–
Fluorides (as F)	200	–

Note: All values except pH are in mg/l.

For efficient treatment, it is necessary to segregate the various waste streams and to treat them separately before they are mixed together for final treatment. Streams requiring individual treatment are: (i) oil-bearing wastes, (ii) acidic waste from cation exchange regeneration, and (iii) phosphate and fluoride-bearing waste from phosphatic plant. The oily wastes are passed through an oil-water separator. Acidic wastes are stored separately and mixed with the remaining wastes after ammonia removal. Wastes containing phosphates and fluorides should be separated from each other and should receive treatment for reduction of phosphates and fluorides by lime and coagulant. Chemical precipitation reduces phosphates to 5 mg/l and fluorides to 20 mg/l. Further, biological treatment may take the form of trickling filter, activated sludge and its modifications, aerated lagoons or even stabilization pond.

Arora and Chattopadhya [11] studied the performance of an existing plant in a superphosphate manufacturing unit. Treatment consisted of lime dosing and settling for 7 hours in the holding tank. Settled effluent was mixed with cooling tower water and a part of this mixture was used for irrigation. The authors suggested utilization of the fluoride-bearing effluent for manufacturing fluosilicic acid, an insecticide, or for further conversion to sodium or magnesium silicofluoride, a preservative for cement surfaces. Keshavamurthy and Karanth [12] have listed the methods of ammonia removal with the approximate concentration at which each method may be applied as given in Table 16.3.

Table 16.3 Concentration and Method of Removal of Ammonia

Method of treatment	Applicability to approximate limits
Steam stripping	More than 3000 mg/l
Air stripping	1500–3000 mg/l
Simple lagooning	100–500 mg/l
Ion exchange	Less than 25 mg/l
Chemical method	Less than 5 mg/l
Biological method	About 800 mg/l

They tried steam stripping, air stripping and lagooning for removal of ammonia from process condensates of ammonia plant and urea plant. Steam stripping gave a removal efficiency of 98% for ammonia plant effluent, 99% for urea plant effluent. Air stripping of urea plant effluent gave 30–40% efficiency. Simple lagooning of urea plant effluent was abandoned because it was observed that the ammonia content of the lagoon increased due to hydrolysis of urea with time.

Conservation and reuse of water and waste water as practised at the Gujarat Narmada Valley Fertilizer Company Ltd., Bharuch, India was described by Karia [13]. Water requirement of the factory was about 45×10^6 l/day, while production activities produced an effluent of about

18×10^6 l/day. Measures taken to reuse treated water and waste water were as follows:

1. 60% of filter backwash water was recycled to the raw water reservoir.
2. Spent alkali from anion regeneration unit was used to raise pH of ammonia plant effluent, saving about 400 m^3 of fresh water per day.
3. About 70% of DM plant regeneration water was used as DM plant make-up water.
4. Continuous effluent (40 m^3/hour) from hydrolyzer in urea plant, 1200 m^3/day of ash settler overflow, 300 m^3/day of effluent from hazardous chemical removal plant, 900 m^3/day of treated sewage, were used for irrigation, instead of fresh water.
5. Ash slurry preparation was done with about 9000 m^3 of treated effluent per day. These steps resulted in substantial saving of fresh water.

Pakkala [14] has described various measures taken at Rashtriya Chemicals and Fertilizers Ltd., Bombay, to control air and water pollution. Liquid effluents from ammonia and urea plants are treated by steam stripping. Ammonia-free effluent from the stripper is used as cooling tower make-up water. Phosphatic fertilizer plant effluent is treated with chemicals, settled and the clarified effluent is used in dust scrubbers, cooling towers, and for washing purpose. The Indo-Gulf Fertilizers and Chemicals Corporation Ltd. (IGFCC), (UP) practises reuse and recycling of treated effluents from its factory in the following ways [15]: (i) sludge from clarifier and backwash water from filters are treated and reused as cooling tower make-up water, (ii) acidic discharges from water treatment and cooling towers are used to neutralize the effluent from DM plant, (iii) ammonia condensate water is demineralized and used as boiler feed water, (iv) urea process condensate is treated under high temperature and pressure, ammonia and carbon dioxide produced in this step are recycled and the treated water is passed through a DM plant for boiler feed, and (v) condensates from turbines in ammonia, urea and utilities plants are collected, demineralized and used as boiler feed water. The average raw water consumption in December 1990 was found to be 655 m^3/hour against the designed figure of 1700 m^3/hour, because of the above measures.

The National Fertilizers Ltd., Vijaipur (MP) practised water conservation, waste water treatment and recycling of treated effluents to reach a ‘zero discharge’ status. Ammonia and methanol from the process condensate were removed and the water was used as boiler feed water. Backwash water from filters was recycled to the water treatment plant inlet. Chromate-based cooling water treatment was replaced by nonchromate-based chemicals. Reverse osmosis plant was used to produce make-up water for cooling towers. The entire treated effluent was used for agriculture, i.e. in kitchen gardens, lawns, nurseries, green belt development, etc. [16].

Chemical oxidation of urea was studied by Mehta and Dasare [17] using hypochlorite, hypobromite and polybromide resin. The effect of temperature, presence or absence of promoters was also studied. They concluded that if the theoretical amount of hypochlorite is used, only half of the urea is oxidized. Increase of contact time and raising temperature had no effect on oxidation. Addition of copper salt and bromide increased oxidation of urea. Passing of urea solution through a cation exchange resin in hydrogen form, in the presence of sodium nitrite, gave industrially useful water and the resin capacity used was 80% of its total capacity. A chemical process for purification of phosphogypsum, produced during the manufacture of phosphoric acid, was proposed by Singh [18]. The impurities of P_2O_5, fluoride and organic matter were removed by hot ammonium sulphate and subsequent washing with water.

Microbial hydrolysis of urea in an upflow anaerobic filter was tried by Pathe, Patkie and Lohani [19] using synthetic waste, containing 840–1040 mg/l of urea, 358 mg/l alkalinity, 61 mg/l of suspended solids and 1011 mg/l COD. The anaerobic system gave 67–79% hydrolysis of urea at a urea loading from 0.76 kg/m^3/day to 3.03 kg/m^3/day. Gas production ranged between 0.03 m^3/kg and 0.1 m^3/kg COD destroyed per day.

Muthukumar and Subrahmanyam [20] were successful in simultaneously removing phosphates and fluorides from phosphatic fertilizer waste water with the help of lime and phosphogypsum. The waste water characteristics are tabulated here.

Parameter	Range
pH	1.6–2.7
Acidity to pH 4.3 ($CaCO_3$)	850–4360
Total solids	8800–16880
Suspended solids	550–2480
Fluoride, F	3150–4350
Phosphate	735–1545
Ammonia nitrogen, N	730–3200
Chloride, Cl^-	35–130
Sulphate, SO_4^{2-}	1500–6250
Cadmium, Cd	0.045–0.35
Chromium, Cr	0.1–0.45
Copper, Cu	0.15–0.2
Iron, Fe	3.5–5.0
Lead, Pb	0.05–0.2
Manganese, Mn	0.1–0.14
Nickel, Ni	0.37–0.42

Note: All values except pH are expressed in mg/l.

Mooney et al. [21] had provided two-stage treatment for a similar waste. In the first stage, the pH was raised to 3.5–4, when more than 85% fluoride was precipitated as $CaF_{2,}$ with marginal phosphate removal. In the second stage, the pH was raised to 8.5, when highly insoluble hydroxyapatite $Ca_5(OH)(PO_4)_3$ and fluorapatite, $Ca_{10}\ F_2(PO4)_6$ complexes were formed and the fluoride and phosphate concentrations were reduced to 10 mg/l and 5 mg/l, respectively. In the present case, it was seen that lime alone was unable to supply enough calcium ions for high removal of fluorides, unless the calcium ions were supplemented by some other calcium salt. The by-product phospho gypsum, formed during the manufacture of phosphoric acid, was used for this purpose, and simultaneous removal of fluorides and phosphate was achieved to limits below those stipulated by MINAS for phosphatic fertilizer industry. Mehta and Dasare [22] proved the feasibility of decomposing urea by electrolytic oxidation. Small amounts of potassium bromide and sodium chloride were required to be present in the waste water.

16.4 PESTICIDES INDUSTRY

Pesticides commonly used in agriculture can be grouped as: (a) insecticides: organochlorines, organophosphates, carbamates and synthetic pyrethroids; (b) organic fungicides and bactericides: dithiocarbamates, dicarboximides, systemic fungicides and benzimidazoles, and (c) organic herbicides: phenoxyaliphatic acids, nitroanilines, arylaliphatic acids and bipridylium. These pesticides persist in water and soil for a long time, the factors affecting their persistence depending on the nature of pesticide, nature of water, properties of the soil, etc. Table 16.4 shows the stability periods of some pesticides.

Table 16.4 Persistence in Soils of Different Chemicals [25]

Insecticides, herbicides and their groups	Persistence
Toxaphene	6 years
Heptachlor	9 years
Aldrin, dieldrin	9 years
Dichlorodiphenyl trichloroethane (DDT)	10 years
BHC	11 years
Chlorodane	12 years
2,4,5-T	6 months
Diuron	16 months
Simazine	17 months
Atrazine	18 months
Mohuron	3 years
Carbamate	2–8 weeks
Aliphatic acids	3–10 weeks
Organophosphates	7–84 days

Most pesticides undergo partial or complete decomposition when exposed to light; the photodecomposition is limited to only the upper layer of the soil. Therefore, the residue under the surface is not affected. It is possible that the radiation-induced reactions result in products which are vulnerable to microbial attack [24].

Pesticides may gain access to ground and surface water supplies through direct application or through percolation or runoff from treated areas. Some of them are toxic to fish and other aquatic life at very low concentrations. They also tend to concentrate in aquatic plants and animals to very high values. In general, the chlorinated pesticides are most resistant to biological degradation. The organic phosphorus pesticides tend to hydrolyze quickly at pH values greater than 7.0. The carbamates are known for their low toxicity and high susceptibility to biodegradation [25].

16.4.1 Manufacturing Processes of a Few Pesticides

DDT: Monochlorobenzene is condensed with chloral in the presence of concentrated sulphuric acid. The reaction temperature is maintained at less than 30°C. The DDT formed is recovered by crystallization and caustic washing.

Carbaryl (Sevin): Alphanaphthol is reacted with sodium-1-naphthoxide, which is reacted with phosgene and the resulting chloro-formate is reacted with methylamine to get the final product.

Parathion and Methyl Parathion: Methyl or ethyl alcohol is reacted with phosphorus pentasulphide, followed by chlorination. The phosphorothio chloridate reacts with sodium nitrophenoxide to give the final product.

Malathion: Reaction between o-o-dimethyl-phosphorodithioic acid with diethyl maleate, using triethyl amine as catalyst and hydroquinone as polymerization inhibitor is carried out for several hours at 50°C to 60°C. After completion of the reaction, the mixture is diluted with benzene, washed with water and sodium carbonate, the solvent is removed under pressure and the final product separated.

Benzene Hexachloride (BHC): Benzene is chlorinated in the presence of actinitic light (usually a mercury vapour lamp) at atmospheric pressure. This is followed by treatment with methyl alcohol or acetic acid. Final product is obtained by fractional crystallization.

A very wide variation exists in the chemicals used and the methods of manufacture of pesticides. Hence, the chemical characteristics of the waste water are also different from each other. However, general values of the various constituents are given in Table 16.5 [26].

Table 16.5 Chemical Characteristics of Some Pesticide Waste

Parameter	DDT	Sevin	Parathion	2,4, 5-T	2, 4-D	Herbicides	Diolefin-based insecticide
pH	0.5–2.0	7.0–10.0	2.0	7.9	9.5	–	2.0
Total solids	6215	10,000	27,000	1,72,467	1,67,221	62,000	1000
Suspended solids	50	–	–	700	348	10	100
Chlorides	11	100	7000	69,000	72,000	30,000	High
Sulphates	3840	20,000	3000	–	–	5540	–
Organic nitrogen	256	500	–	40	45	–	–
Nitrates	–	–	20	–	–	–	–
Phosphates	–	Nil	250	–	–	–	–
Sodium	–	8000	6000	–	–	–	–
COD	3680	10,000	3000	25,700	23,600	3600	500
BOD_5	260	Nil	700	16,680[a]	16,680[a]	2000	50
COD/BOD	14	–	4.3	1.5	1.5	1.82	10

[a] BOD estimated using 50-50 dilution of 2,4 D and 2,4-5 T and acclimated seed (below toxic levels).

It is seen from Table 16.5 that the wastes have high total solids, mostly inorganic, low suspended solids, high COD:BOD ratio, show high variation in pH values and are nutrient deficient. Some constituents of these wastes are highly toxic to man, animals, plants, wild life and aquatic life. Therefore, adequate treatment of the wastes is always required before they are discharged into the environment.

16.5 METHODS OF TREATMENT

Methods of treatment include, chemical, physico-chemical, biological and physical steps, the general sequence being: (a) in-plant control, (b) pH correction, (c) coagulation, (d) adsorption, and (e) biological treatment. pH correction is done using lime, or sodium hydroxide or anhydrous ammonia.

Chemical treatment involves lowering pH to less than 2.0 to remove mercaptans with organophosphorus pesticides and rapid dehydrochlorination of aldrin, dieldrin and endrin.

Oxidation with chlorine, chlorine dioxide, ozone, potassium permanganate and hydrogen peroxide has been successful in removing the active components of the pesticides. Ozone dose of more than 4000 mg/l removes greater than 80% COD from BHC waste. Potassium permanganate can treat heptachlor and 2,4 D. Toxins in organophosphate wastes are almost completely removed by it. Chlorine can treat parathion and aldrin, but they are oxidized by chlorine and ozone to form paraxone, which is more toxic than the original compounds. Moreover, chlorination of pesticides can lead to the formation of chloro-organics, which are suspected carcinogens. Further, chemical treatment is very costly in view of the large doses of chemicals required.

Coagulation with alum, followed by filtration, removes DDT easily, but lindane, parathion, aldrin, dieldrin, BHC and malathion are not affected because their solubility plays an important part in successful coagulation.

Adsorption removes most of the chlorinated hydrocarbon pesticides which are hydrophobic. It is observed that adsorption on clays is relatively irreversible. This is important in view of application of certain pesticides to soil. Adsorption on activated carbon is commonly done. It removes herbicides, fish poisons, solvents and emulsifiers also. Parathion is the most amenable to activated carbon treatment, while lindane is the least amenable. Banerjee and Kumar [27] used a dose of 85 gm/l of activated carbon for 100% removal of pesticide Acephate. Langmuir adsorption isotherm was followed. The adsorptive capacity of the carbon was found to be 0.04614 gm/gm. Although the method was costly, the authors recommend it because activated carbon also removed colour, odour, suspended solids, BOD, COD, detergents and virus. Bharadwaj [28] studied adsorption on activated carbon alone and activated carbon plus flyash for the removal of DDT, aldrin, dieldrin and malathion. Adsorption was greatly reduced after one run in both the cases, indicating the need for regeneration. Raising pH of the waste to 11.9 had no effect on the amount adsorbed. Pretreatment of both the beds with 0.5 N HNO_3 helped to increase sorption capacity. Anil Kumar et al. [29] studied the interaction between potassium phosphonate fungicide and laterite soil. They found that phosphonate followed Freundlich isotherm at high concentration and Langmuir isotherm at low concentration. Calcium content of the soil had a marked effect on adsorption, but high pH lowered the adsorption. Hanumantharaju and Awasthi [30] observed that the degradation pattern of Metalaxyl, Mancozeb, and its metabolite ethylene thiourea (ETU) followed first-order kinetics in soil. The degradation was predominantly biological and chemical in nature.

Other physico-chemical methods include photochemical degradation, liquid-liquid extraction, benzene extraction for DDT and foam fractionation for aldrin and dieldrin [26].

Biological treatment processes include activated sludge process, trickling filtration, aerated lagoons and waste stabilization ponds.

Anaerobic digestion has also been successfully used. Pilot-scale and full-scale treatment with activated sludge can treat parathion waste, either with or without dilution with sewage. BOD and COD removal efficiencies of 90% and 97% respectively, are reported, along with reduction of phenols to 0.1 mg/l. Malathion upto 100 mg/l can be easily treated by the process. Actinomyces, filamentous fungi and streptomyces can degrade PCNP and dechlorinate DDT to DDE, but have no effect on dieldrin. In general, activated sludge process requires high concentration of MLSS and extended time of aeration to be successful. Trickling filters are used as high-rate filters and serve as roughing filters. Aerated lagoons are low in cost but produce a poor effluent because of the presence of organic suspended solids in it. Waste stabilization ponds are used as polishing units. Long detention times of the order of 20 days allow the microorganisms to degrade relatively bioresistant compounds. Organic loadings are usually restricted to 20.4 to 33.5 kg BOD/ha/day. As algal growth is of importance, waste water with colour, turbidity or emulsions cannot be treated adequately. High sulphur-containing wastes allow sulphur-utilizing bacteria to grow and reduce light penetration and, hence, efficiency of the ponds.

Anaerobic treatment of pesticide wastes was studied by a number of people. Mitra and Jones [31] observed the limitations for toxaphene transformation in such contaminated soil. Anaerobic conditions supplemented with nutrients like alfa alfa would help transformation at high temperatures during summer. Karim and Gupta [32] reviewed various anaerobic methods of treating waste water containing nitrophenols (NP). The process of UASB reactor was very useful in degrading more than 94% of 2-NP, even when its concentration in the feed was increased to 300 mg/l at a residence time of 0.66 days. At influent concentrations of 260 and 30 mg/l for 4-nitrophenol and 2-4 dinitrophenol respectively, destruction was 99% and 68%. The corresponding nitroaromatic loadings were: 910 mg/l for 2-NP, 790 mg/l for 4-NP and 91 mg/l for 2-4 DNP. In addition, nearly 75% of volatile fatty acids were reduced in the reactor. An anaerobic fluidized bed reactor, using activated carbon as the medium was found to give more than 90% COD removal at a retention time of 0.6 days and NP loading of 0.9 kg/m^3/day at 35°C. Pretreatment of the waste by chemical oxidation was found to improve the degradation of nitrophenols. In all the cases of anaerobic degradation of pesticide wastes, it is essential to provide adequate acclimatization period for the microorganisms in order to reduce the lag period.

Lindane is easily degraded anaerobically. The increasing order of persistence of pesticides under anaerobic conditions is: Lindane, Heptachlor, Endrin, DDT, DDE, Aldrin, Heptachlor epoxide and Dieldrin [26].

Methods of disposal of solid, semisolid and concentrated liquid wastes from the manufacture of pesticides are as follows:

1. **Incineration:** Most of the organic matter in these wastes can be easily burned, but high salt content may create problems of

corrosion, feed system and burner maintenance problems. Nitrogen compounds in the wastes give rise to oxides of nitrogen. Sulphur and phosphorus compounds, when burned, cause air pollution problems. Compounds containing heavy metals, such as lead, mercury and arsenic produce dangerous aerosols when burnt. Therefore, if incineration is to be practised, a well-designed air pollution control system must accompany the incinerator [26].

2. **Burial:** It is believed that pesticide compounds move very little in soil, hence they can be safely buried. In non-homogeneous soils, where ground water table is high, contamination with the pesticide compounds must be guarded against [26].
3. **Ocean disposal:** Industries located on or near the seashore can economically dispose of their concentrated liquid and semisolid wastes deep into the sea, if the volume of waste material is large and the pollution control authorities permit this form of disposal [26].

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Chapter 17

VEGETABLE OIL, FOOD AND ALLIED INDUSTRIES

This chapter deals with waste waters generated from processing raw materials of vegetable origin for the manufacture of products fit for human consumption. It includes vegetable oil industry, fruit canning industry, starch and liquid glucose manufacturing industry, confectionery industry and rice and coffee processing industry.

17.1 VEGETABLE OIL INDUSTRY

Raw material used may be cotton seed, sunflower, soya, mustard, rice bran, *mahua, til*, etc. Chemicals commonly used during the manufacturing process include mineral acids, caustic lye, bleaching earth, salt, nickel catalyst, phosphoric acid, etc. The end products include vanaspati oil, soap, acid and oils. Generally, 30–40% of the supplied water ends up as waste water and includes, besides process waste, boiler blowdown, water treatment plant waste water, floor and equipment wash water, etc. [1, 2].

The main sources of waste water are: hydrogenation plant, filter wash water, soap plant, acidified oily effluent, spent vacuum pump oil, etc.

Table 17.1 Characteristics of Waste Water [2]

Item of analysis	Soap section	Hydro-genation	Combined effluent (i)	Combined effluent (ii)
Temperature	Ambient	Ambient	Ambient	Ambient
pH value	8.5	2.5	5.8	9.0

(Contd.)...

Table 17.1 Characteristics of Waste Water [2] *(Contd.)*

Item of analysis	Soap section	Hydro-genation	Combined effluent (i)	Combined effluent (ii)
Colour	Whitish	Whitish	Whitish	Whitish
Total solids	12,500	5,900	9,040	4,460
Dissolved solids	8,200	4,800	5,400	3,600
Suspended solids	4,300	1,100	3,640	860
Chlorides	1,360	1,050	1,235	400
COD	8,800	6,370	4,160	2,368
BOD	2,500	2,360	800	980
Oil and grease	2,600	400	3,400	1,200
Sulphates	1,250	3,100	3,000	295
Ammoniacal nitrogen	4.5	2	3.6	8
Total volatile solids	2,620	815	2,100	–
Per cent sodium	0.8	0.2	0.3	–

Note: All values except temperature, colour, pH and sodium are in mg/l.

It is seen from Table 17.1 that waste water requires adequate treatment for oil and grease removal, pH correction, suspended solids removal and biological treatment before discharge to the environment. Kadam and Vashi [2] subjected the waste water to oil skimming, pH correction with lime to pH 9.0 and coagulation with ferrous sulphate and ferric chloride and achieved 82.9% oil removal, 41.9% BOD reduction and 69.8% COD removal. Ferrous sulphate was a better coagulant than ferric chloride, but the dose of lime was high, of the order of 2000 mg/l. Plain settling followed by extended aeration was not effective. Oil skimming, coagulation and settling, followed by extended aeration was found to be the most effective treatment; it produced an effluent with BOD of 45 mg/l, COD of 90 mg/l and no oil and grease.

17.1.1 Palm Oil Refineries

Palm oil refineries are classified as (a) physical refining and dry fractionation (A), (b) physical refining and detergent fractionation (B) and (c) physical and chemical refining and dry/detergent fractionation (C). For every tonne of oil, the effluent produced is 0.2 tonnes for physical refining and 1.22 tonnes for chemical refining and soap stock splitting. The waste water generated includes neutralization wash water, spent liquor, cooling water, boiler blowdown, floor wash, carrier liquid of unwanted oil fractions and spillages [3]. Composition of the waste water produced is given in Table 17.2.

Table 17.2 Composition of Waste Water [4]

Item of analysis	(A)	(B)	(C)
Temperature	35	42	57
pH	5.3	4.9	3.0
BOD	530	2640	4180
COD	890	5730	7700
Suspended solids	50	12	6
Phosphorus	4	1	12
Total fatty matter	220	1580	3550

Note: All values except pH and temperature are in mg/l.

The treatment of waste water is done by sedimentation and dissolved air flotation after coagulation and flocculation with lime, alum and polyelectrolyte. COD reduction upto 90% is achieved, but the treatment produces large amount of sludge. Biological treatment by activated sludge process with MLSS of 1500–2000 mg/l, F/M ratio of 0.2–0.5, HRT of 24 hours and SRT of 3–10 days gave an effluent with BOD and suspended solids less than 50 mg/l each [5].

Agamuthu [6] has given a detailed description of the production of palm oil from the fresh fruit bunch (FFB). Approximately, 60% of the FFB comes out of the mill as palm oil mill effluent (POME), which is about three times the palm oil production. In addition to the liquid effluent, other wastes included are felled palm trunks, palm fronds, empty bunches and fibre and shell. Raw POME has a BOD of 25,000–31,000 mg/l and COD of 62,000–68,000 mg/l. Other constituents of the waste are as given in Table 17.3.

Table 17.3 Proximate Analysis of POME (After Partial Treatment) [6]

Parameter	Quantity*
pH	7.64 + or – 0.14
Moisture (%)	95.7 + or –1.5
Ash % on DM	37.3 + or –2.0
Total nitrogen	3140 + or –1116
Ammoniacal nitrogen	906 + or –312
Phosphorus	517 + or –340
Potassium	3900 + or –379
Magnesium	1225 + or –290
Calcium	637 + or –198
Manganese	26 + or –14
Copper	7 + or –2
Zinc	14 + or –6

(Contd.)...

Table 17.3 Proximate Analysis of POME (After Partial Treatment) [6] *(Contd.)*

Parameter	Quantity*
Iron	516 + or –196
BOD	2330 + or –346
COD	44662 + or –15479
Total solids	47213 + or –13894
Suspended solids	30045 + or –18623
Oil and grease	459 + or –134
Crude fibre	3256 + or –744

*–mg/l on FW unless otherwise stated.

17.1.2 Treatment of Waste Water

The palm oil industry uses (a) waste stabilization pond system, (b) open digester followed by extended aeration, (c) closed digester with biogas recovery and land application, or (d) thermophilic anaerobic contact process.

1. **Waste stabilization ponds:** They are used for suspended solids removal and biological treatment of the waste water. The effluent is passed through oil removal tank, followed by anaerobic pond, 5–7 m deep. The effluent of anaerobic pond is passed through a facultative pond 1–1.5 m deep. For a total retention time of 66 days, the treated effluent has a BOD of less than 150 mg/l. The suspended solids in the raw waste are high. Therefore, it is necessary to remove sludge from the ponds frequently and dewater it on drying beds.
2. **Open digestion followed by extended aeration:** In this system, two-phase open top digesters are used with organic loading of 0.8–1 kg BOD/m^3/day and are followed by extended aeration. Settled solids have to be removed regularly and are used as fertilizers in the fields.
3. **Closed digester with biogas recovery and land application:** This system produces an effluent with BOD of 1000–2000 mg/l, which is used as fertilizer. The organic loading rate is 4.8 kg volatile solids/m^3/day and hydraulic retention time is 8–10 days, the operating temperature being 42–50°C. Mixing is done by gas circulation.
4. **Thermophilic digestion:** At 55°C, it reduces retention time considerably, but the process is not used commonly [6].

   Other uses of POME include employing the trunk of the palm tree for paper production, mulching of fibre for growing mushrooms, raw waste for growing *Aspergilus niger* and

Neurospora sitophila, filtrate produced during treatment for growing *Saccharomyces cerevisiae* and digested effluent for producing *Euglena sp.* and *Chlorella sp.* [6]. Setialdi et al. [7] determined the effect of recirculation of anaerobically treated effluent on the performance of a baffled anaerobic reactor and found that a recycle flow of 15 times the inflow was enough to maintain pH above 6.8 without adding alkalinity.

Non-edible oil seeds such as castor, *karanja, kusum, mahua, neem, sal*, etc. can be profitably used for generating biogas from the seed cake after the extraction of oil. Rao and Konnur [7A] found that about 3.5 kg of castor cake and 30 litres of water are enough to produce 1.2 m^3 of gas, which can meet the cooking requirements of a family of 5.

5. **Olive oil mill waste waters** and their treatment were studied in detail by a number of workers. The commonly accepted form of treatment consists of anaerobic digestion, followed by aerobic treatment and tertiary treatment, where the treated effluent was recycled or reused.

17.2 THE FRUIT PROCESSING INDUSTRY

This is a seasonal industry. The essential steps involved in processing are as follows [8]:

1. Preparation of raw material by thorough cleaning for removal of soil, dirt, dried juices, insects and chemical residues
2. Sorting according to colour and degree of ripeness of the fruit
3. Trimming to remove blemishes
4. Peeling and coring
5. Dilute alkali wash
6. High pressure water wash to remove fruit skin and excess alkali
7. Canning and sealing [8].

A lot of solid waste, sometimes up to 50% of the raw fruits processed, may be produced. The methods of their disposal consist of: (i) ensilage, (ii) production of alcohol, (iii) drying and use as cattle feed, (iv) using the press juice as syrup after giving it adequate treatment, (v) composting, (vi) incineration, (vii) discharge to the effluent treatment plant; this step can increase the organic load on the plant by as much as 60% and is not desirable because of the seasonal nature of the industry, (viii) ocean disposal, and (ix) inclusion of comminuted waste solids into spray-irrigated liquid wastes [8].

The volume of liquid wastes produced is equal to the amount of water supplied minus water lost by evaporation, leakage and water present in the final product. It is advantageous to separate cooling water from the rest of the waste water in order to reduce the size of the treatment plant. Treatment of the waste water consists of pH correction, coagulation and settling, followed by anaerobic and aerobic treatment. Activated sludge process can be upset by a high concentration of canning waste, while trickling filters can take the loads easily. The wastes require nutrient supplementation before biological treatment. Chemical treatment alone with lime and ferrous sulphate has shown BOD reduction of only 20% [8]. The advantage of segregation of the different waste streams at design stage was brought out by Cabrera [9] in a food processing plant, where the volume of waste water was reduced by 50%. In the fruit canning industry, cooling waters from evaporators and retorts can be used for initial can washing. Dry skin peeling machines are installed in place of those using water under pressure for this purpose. Low-pressure, high discharge washdown hoses are replaced by high-pressure hoses with nozzles, which shut off on release. These steps can reduce cooling water outflow by 63%, fruit peeling water requirement by 59% and floor washing water by 60%.

Rao et al. [10] carried out an in-plant study of a fruit processing industry during mango and tomato processing seasons. The characteristics of the composited waste waters were as given in Table 17.4.

Table 17.4 Fruit Processing Waste Water

Parameter	Mango processing	Tomato processing
Flow, m^3 per day	130	130
pH	5.1	4.3
Alkalinity as $CaCO_3$	910	200
Total solids	2910	1760
Dissolved solids	1790	1320
Suspended solids	1120	440
BOD	2205	1260
COD	4410	2970
Chlorides	182	160
Sulphates	12	32
Calcium	64.4	58.4
Magnesium	66	20.6
Total nitrogen	16.2	16.1
Phosphorus	2.2	2.0
BOD load, kg/day	286.7	162.8
Suspended solids load, kg/day	146.6	57.2

Note: All values except pH are in mg/l.

The waste water was treated with 500 mg/l of lime and 400 mg/l of alum to get a BOD reduction of 59.5%. This partially treated effluent was mixed with sewage and was aerated for 12–24 hours. The waste was deficient in nitrogen and phosphorus and was suitably supplemented to get a C:N:P ratio of 100:5:1. Aeration in an aerated lagoon for 4 days could give equally satisfactory quality of effluent as with 12–24 hours aeration.

Raju and Ramalingaiah [11] conducted batch studies on anaerobic digestion of orange processing waste. The solid waste containing peel skin, core seeds, pomace, leaves, etc. was stored and compacted to remove air from it. Anaerobic fixed film bioreactors (AFFB) containing snail shells, burnt coconut shells, pumice stone, PVC plugs were used as media. At a retention time of 20 days, with a batch feed containing 4% solids, all of them showed identical methane content with a gas yield of 0.7–0.72 m^3/kg solids added. The highest methane content was 74%.

In order to meet the effluent quality requirements throughout the year, Collins et al. [12] used pure oxygen activated sludge process for cotreatment of municipal and fruit/vegetable canning waste water during the canning season and a trickling filter/activated sludge treatment process during the rest of the year. They claim that this combination gave the maximum energy efficiency. Warren et al. [13] provided high rate UASB reactor, followed by sequencing batch reactor (SBR) for the treatment of apple and fruit juice waste water to reduce BOD from 6000–9000 mg/l to less than 10 mg/l. Mahadevaswamy and Venkataraman [14] proposed the use of anaerobic treatment of fruit processing wastes for gas production, followed by utilizing the anaerobically treated effluent for rearing fish.

Treatment and disposal of *vegetable processing* wastes was also studied in detail. Tedaldi and Goldman [15] studied the problem of odours arising out of treatment of vegetable wastes. Effluent from settling pond of the waste water was treated with cationic polymer and subjected to dissolved air flotation for removal of odours in the waste water before it was disposed of on adjacent lands for irrigation. Guo and Lin [16] treated potato processing wastes by a combination of a UASB followed by an upflow anaerobic filter. They could achieve better than 95% reduction of COD and suspended solids. Biogas production was 0.31 m^3 CH_4/kg COD removed.

Tay [17] gave biological treatment by activated sludge process to a *soyabean waste* and achieved BOD, TSS, nitrogen and phosphorus removals of 95%, 90%, 67% and 57%, respectively. Aerobic treatment of *potato processing waste* water by complete mix activated sludge process was demonstrated [18] at MLSS concentrations between 2000 and 8000 mg/l, BOD/MLVSS ratio from 0.15 to 0.47, hydraulic retention time from 0.9 to 8.7 days and organic loading between 0.16 and 1.92 kg/m^3/day. Low air temperature did not affect the process adversely. BOD removals of over 90%, when operated as activated sludge system, 70–80%, when operated as flow-through system without secondary clarification, and better than 96% coliform removal were obtained. Menon and Grames [18A] developed a pilot scale and a full-scale Carrousel system for treating potato processing waste, and achieved BOD, TKN amd phosphorus removals of 99%, 92% and 58% respectively, at a hydraulic retention time of 5.2 days and MLSS of 4170 mg/l.

Menon et al. [19] used an anaerobic fluidized bed reactor to treat food processing waste water and could remove 77% COD at volumetric loading of 40 kg COD/m^3/day.

17.3 OTHER FOOD PROCESSING INDUSTRIES

Among other food products, generating waste water requiring treatment are rice, coffee, confectionery, starch and glucose.

17.3.1 Rice

Banerjee and Pande [20] conducted treatability studies on waste water generated from *parboiled rice*. The waste water had a foul odour, pH: 4.9, total solids: 3.96 gm/l, total dissolved solids: 3.75 gm/l, chlorides: 0.53 gm/l, sulphates: 0.2 gm/l, fluorides: 20 mg/l, sodium: 0.41 gm/l, potassium: 0.92 gm/l, calcium: 0.22 gm/l, COD: 2736 mg/l, BOD: 1576 mg/l, Kjeldahl nitrogen: 15 mg/l and phosphorus: 8 mg/l. Chemical treatment with bleaching powder, alum and lime, followed by aeration for 15 minutes gave 58% COD removal and 30.7% total dissolved solids (TDS) removal. Contact with 5 gm of rice husk charcoal for 24 hours, followed by treatment with bleaching powder, alum and lime gave 61.1% TDS removal and 87.7% COD removal.

When activated charcoal replaced rice husk charcoal, followed by the same treatment as in the first case, TDS removal was 75.7% and COD removal was 97.8%. In all the cases, the foul odour was completely removed. Kim and Choi [21] compared the adsorptive capacities of rice hull activated carbon with commercially available activated carbon. They found that the rice hull carbon had a higher adsorption capacity for phenols than the commercial carbon. Moreover, the rice hull carbon could remove ammonia nitrogen, which the commercial carbon could not. Nightingale [22] described the use of extended aeration with a 'moving chain' diffused aeration system and long solids retention time. BOD removal was 99.7%. In another study [23], reduction in sodium concentration and addition of micronutrients, in pilot-scale anaerobic reactors treating rice processing waste water increased COD removal to 93%.

17.3.2 Coffee

Deshpande, Gadkari and Kaul [24] described the dry and the wet processes of treating *coffee fruits* and conducted laboratory-scale studies on the treatment of waste water generated in the process. Average water requirement was 46 m^3/tonne of coffee processed. The raw waste was acidic in nature with a pH of 3.5–3.9, COD of 7235 mg/l and BOD of 3000 mg/l. The waste was subjected to 4 hours of plain settling and gave 20–23% COD reduction, 17% BOD reduction and 57.5% suspended solids removal. Chemical treatment consisted of 1000 mg/l of lime and 300 mg/l of ferric chloride. Results of jar test showed only 30% COD removal and 10% BOD removal. Large volume of sludge was formed, which floated after 2–3 hours. Therefore, lime was used in the later experiments only to raise pH to 7.0. Biological treatment tried out consisted of anaerobic lagooning for 4 days, which reduced BOD by 85%. With 20 days' retention time, BOD reduction was 96%. Nutrient supplementation was required to maintain BOD:N:P ratio of 100:2.5:0.5. The effluent of this treatment was passed through an aerated lagoon with a retention time of 3 days and a MLSS of 500 mg/l. Here also, nutrient supplementation was required, but the effluent was fit for discharge to inland surface waters. Direct treatment of the waste with activated sludge process with 12 hours of aeration and MLSS of 4000 mg/l gave 80.3% BOD and 68.8% COD reduction. Aeration time was increased to 60 hours and BOD reduction was 98.2%. The authors have suggested three alternatives of treatment, viz. (i) screening, flow equalization, 8 days of anaerobic lagooning, followed by extended aeraton at 0.1 kg BOD/kg MLSS at MLSS of 4000 mg/l; (ii) same as above, but replace extended aeration by 3 days of aerated lagoon, followed by polishing pond; (iii) screening, 9 days of anaerobic lagooning, two-stage anaerobic filtration with loadings of 0.5 kg and 0.15 kg BOD/m^3 respectively, and a polishing pond of 5 days' retention time.

Dinsdale et al. [25] conducted studies on continuous anaerobic mesophilic digestion of *coffee wastes* containing coffee grounds. At a loading rate of 1.3 kg COD/m^3/day, they achieved COD and total volatile solids reduction of 60% each.

17.3.3 Confectionery Industry

It forms an important part of the food processing industry. It produces waste water with high concentration of biodegradable material, which can be successfully handled by anaerobic and aerobic methods of treatment. Tuenay et al. [26] assessed the characteristics and treatability of waste water from a confectionery industry producing marshmellow sandwiched between two biscuits and coated with chocolate, caramel bars covered with chocolate cream, chocolate coated wafers, chocolate covered bars of fruit paste and chocolate crème. The characteristics of the waste water were as given in Table 17.5.

Table 17.5 Characteristics of Confectionery Waste Water

Parameter	Composite sample (1)	Composite sample (2)
Total COD	9950	9170
Settled COD	6470	6925
Filtered COD	3520	6650
Total COD/Filtered COD	0.67	0.87
Total 5-day BOD	2970	6640
Settled 5-day BOD	2660	6100
Filtered BOD	2360	5500
Oil and grease	320	570
Total Kjeldahl nitrogen	56	73
Total phosphorus	2.3	3.1
Anionic detergent	–	5.7
pH value	6.0	5.9

Note: All values except pH are in mg/l.

Chemical treatment of the waste water with alum and lime (250 mg/l) gave COD reduction of 30%. Ferrous sulphate and lime (750 mg/l) gave 40% BOD reduction. This effluent was biologically treated after nutrient supplementation in a sequencing batch reactor (SBR). The COD loading rate used was 0.66 gm COD/gm MLSS, which reduced COD by 97%. No improvement in COD reduction followed when the loading rate was reduced further. The treatment process suggested by the authors was: screening, flow equalization, chemical treatment, SBR treatment, chemical treatment for further COD reduction, sludge conditioning with lime and dewatering in a filter press.

17.3.4 Starch

A naturally abundant nutrient carbohydrate, consisting of linked units of D-glucose, found chiefly in the seeds, fruits, tubers, roots and stem pith of plants, finds many uses in the pharmaceutical industry, food and feed industry, textile industry, etc. The waste waters generated during the manufacturing process vary in quality and volume, depending on the raw material used as the source of starch. First-grade tapioca starch process uses a high degree of mechanization, while second grade process is more labour oriented [27]. Chemical characteristics of first-grade and second-grade starch wastes are given in Table 17.6.

Table 17.6 Chemical Characteristics of Tapioca Starch Wastes

Parameter	Second grade	First grade
Flow, m^3/tonne	20–40	30–50
pH	4.0–5.2	3.8–5.0
BOD	1500–4500	3000–8000
COD	2500–7500	4500–10,000
Suspended solids	900–1800	1500–6000
Total nitrogen	35–70	80–120
Total phosphorus	3–7	4–8
BOD, kg/T starch produced	60–90	150–240
COD, kg/T starch produced	100–150	225–300

Note: All values except pH are in mg/l.

Production of starch powder requires from 30 to 50 m^3 of water per tonne while production of chips and pellets is a dry process. *Sago starch* production generates a waste stream with the composition as in Table 17.7.

Table 17.7 Composition of Waste in Sago Starch Production

Parameter	Combined waste water
pH	4.5–5.5
BOD	1800–6800
COD	5500–17,000
Total nitrogen	15–135
Suspended solids	3900–42,000
Acidity as $CaCO_3$	160–200
Phosphorus	Nil

Note: All values except pH are in mg/l.

Treatment of starch waste is usually done by biological means, in which an anaerobic step consisting of anaerobic lagoons, followed by facultative ponds and aerobic stabilization ponds, produce a satisfactory effluent. The treated effluent can be used to cultivate *Spirulina,* a useful cattle feed [28]. Anaerobic treatment using upflow and downflow filters, UASB, fixed film and fluidized bed reactors is also practised. Design capacities of the UASB units range from 5 to 15 kg COD/m^3 at 30°–35°C [29]. These wastes are deficient in nitrogen and phosphorus. Therefore, nutrient supplementation is necessary. Starch, being a relatively insoluble substance, can be recovered from the waste water by installing primary clarifiers [27].

Treatment of starch waste for pollution control, biogas production and using the treated effluent for irrigation and sludge for soil conditioning was very effectively demonstrated by a factory in Thailand. In 2001, it produced 550 tonnes of starch daily and discharged the effluent into open lagoons, which occupied 200 ha of valuable land. The waste was anaerobically digested, but the gas produced was vented to the atmosphere. So, the factory built lined lagoons and covered them with a plastic membrane. The gas generated due to anaerobic digestion was thus collected and used for drying the starch and power generation. About 86% of the power required to run the factory was produced from the biogas. In 2003, the gas production was 80,000 m^3/day. It was expected that with increased production of starch to 750 tonnes per day, a corresponding increase in the volume of waste water produced would boost the gas production to 1,20,000 m^3/day, enough to meet the power requirement of the factory. An added benefit of the project was that more than 3,60,000 tonnes of carbon which was escaping to the atmosphere per year, was saved [30]. A similar case of biogas production and utilization from starch and glucose manufacturing wastes was presented by Tiwari [31]. The factory processed 40,000 metric tonnes of maize and 25,000 tonnes of tapioca tubers every year and produced 1600 m^3 waste water per day, with a BOD of about 6000 mg/l, COD of 12,000 mg/l and a pH between 4.8 and 5.5. A UASB reactor reduced BOD by 80% and COD by 70%, and produced 8000 m^3 of gas per day, which was used in the boiler house for raising steam. The net saving on the fuel account was Rs. 32 lakh per year in addition to Rs. 16 lakh for chemicals, which were required before the commencement of the UASB project. The payback period was about 4 years over the cost of Rs. 1.8 crore for the effluent treatment plant. Rao et al. [32] studied the characteristics and treatment of waste water of a 20 tonne liquid glucose manufacturing unit. The factory used 2550 m^3 water per day, of which 1500 m^3/day was barometric condenser water. The raw material used consisted of chips, starch and tubers of tapioca and sorghum. The characteristics of the waste water excluding barometric condenser water and ion exchange regeneration water, were as shown in Table 17.8.

Table 17.8 Characteristics of Waste Water

Parameter	Value
pH	4.6
Alkalinity as $CaCO_3$	635
COD	8560
BOD	5700
Total solids	8675
Suspended solids	2550
Volatile suspended solids	1950
Total nitrogen	226
Phosphorus	39

Note: All values except pH are in mg/l.

Laboratory-scale tests on the waste water showed 95% reduction of suspended solids, 33% BOD reduction and 30% COD reduction in 4 hours of plain settling. Anaerobic lagoon, seeded with 20% sludge gave 83–97% BOD reduction and 87–94% COD reduction at a holding time of 4–15 days, and a BOD loading rate of 1.4–0.38 kg/m^3/day. Aerobic treatment in an oxidation ditch, loaded at 0.195 kg BOD/kg MLSS, provided 96% and 84% BOD and COD reduction respectively, at an aeration time of 12 hours and MLSS of 4000 mg/l.

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Chapter 18

DYESTUFF AND DYE MANUFACTURING INDUSTRIES

A dye is a substance which is used to impart colour to a surface, while dyestuff is a material which can be used either to impart colour or to produce a dye. Although dyes are used predominantly for colouring fabrics, they find use in colouring diverse materials such as leather, paper, plastics, petroleum products and foodstuffs. Dyes are designed to resist natural elements such as the sun, wind, sunlight, and man-made elements like oxides of nitrogen, hydrolysis, etc. They resist biodegradation, with the exception of dyes used in colouring foodstuffs. Raw materials used in the manufacture of dyes are mainly aromatic hydrocarbons, such as benzene, toluene, naphthalene, anthracine, pyrene, phenol, pyridine and carbazole. A large variety of inorganic chemicals are also used and include sulphuric acid, oleum, nitric acid, chlorine, bromine, caustic soda, sodium nitrite, hydrochloric acid, sodium carbonate, sodium bicarbonate, sodium hydrosulphite, manganese dioxide, etc. The raw materials are converted into a large variety of derivatives (or intermediate products), which are then turned into dyes. Reactions such as nitration, reduction, sulphonation, halogenation, oxidation and condensation are used for the formation of substituted hydrocarbons, which are functional in nature [1].

18.1 TYPES OF DYES

Dyes are classified as [1, 2]:

1. Direct—these are mainly azo dyes.
2. Developed—where one chemical with fabric affinity is used, followed by second chemical for development of colour.

3. Sulphur—they give heavy shades and provide fast colour.
4. Dispersed—they are applied as suspensions with detergents to aid dye penetration.
5. Vat—they are made soluble by sodium hydrosulphite or caustic soda and the adsorbed dye is then oxidized to its insoluble form.
6. Naphthol—they are made by applying wet chemicals to the fabric and are allowed to react with each other on the fabric.
7. Fibre-reactive—they form true chemical bonds between the dye and the fabric.
8. Acetate dyes—they are used mostly for colouring rayon, nylon and synthetic fibres.

Different dyes used in the textile industry are tabulated in Table 18.1 [2A].

Table 18.1 Different Types of Dyes Used in Textile Industry

Types of dyes	Fibres used on
Vat and sulphur dyes	Cotton, rayon, cotton-polyester blends
Direct dyes	Cotton, rayon, polyester-cotton and nylon-cotton blends
Disperse dyes	Acrylic, acetate, polyester
Acid dyes	Polyester-cotton blends, nylon and wool-nylon blends
Basic dyes (Cationic)	Acrylic, polyester, polyester-cotton blend and nylon
Azoic and developed dyes	Cotton, rayon
Fluorescent dyes	Cotton, wool, rayon, polyester-cotton blends
Mordant dyes	Wool
Dye blends	Polyester cotton blends
Indigo dyes	Cotton, cotton-nylon blends
Fibre-reactive anilene black, natural and oxidation-based dyes	Cotton

The pollutional characteristics of dye wastes depend on: (i) type of dye, (ii) type of cloth, and (iii) specifications of the finished cloth. Dye wastes, in general, are highly coloured, have a high pH, high alkalinity, high COD, high temperature and high toxicity, which comes not only from the dyes but also from the chemicals used in the manufacturing process. They are also difficult to biodegrade. The COD:BOD ratio is very high. Hence, the waste water must be given some form of pretreatment, followed by biological treatment. Before treatment of the waste water is considered, it helps to assess the possibility of reducing water consumption, changing the manufacturing process, substituting less polluting chemicals for high pollution potential chemials, recovering useful material from the waste water streams, recycling waste streams (with or without treatment) and following good housekeeping practices.

In view of the high variability of the waste waters in dye and dyestuff manufacture, it is not possible to generalize their quality characteristics. The following paragraphs describe some of the methods of treating these waste waters. Physico-chemical methods include: (i) polymer coagulation, (ii) cation ion precipitation, (iii) carbon adsorption, (iv) ion exchange, (v) high energy radiation, (vi) exposure to sun rays, (vii) electrolytic treatment, (viii) ozone treatment, (ix) lime coagulation and flocculation, and (x) hydrogen peroxide treatment. Biological methods include waste stabilization ponds (aerobic, facultative and anaerobic), aerated lagoons, trickling filtration and activated sludge process.

Table 18.2 gives the chemicals generally present in the various types of dyes and a typical range of pH values, BOD and total solids in their waste waters during dyeing of cotton textiles.

Table 18.2 Dyeing of Cotton Textiles [1]

Type of dye	Chemicals present in the dye	pH value	BOD, mg/l	Total solids, mg/l
Aniline black	Aniline hydrochloride sodium ferrocyanide, sodium chlorite, pigment, soap	–	40–55	600–1200
Developed	Dye, penetrant, NaCl, $NaNO_3$,HCl or H_2SO_4, developer (Beta-naphthol), soap sulphated soap or fatty alcohol	5.0–10.0	75–200	2900–8200
Direct	Dye, Na_2CO_3, NaCl, wetting agent or soluble oil or Na_2SO_4	6.5–7.6	220–600	2200–14000
Naphthol	Dye, NaOH, soluble oil, alcohol, soap, Na_2CO_3, NaCl, base, $NaNO_2$, sodium acetate	5.0–10.0	15–675	4500–10700
Sulphur	Dye, Na_2S, Na_2CO_3, NaCl	8.0–10.0	11–1800	4200–14100
Vat	Dye, NaOH, sodium hydrosulphite, soluble oil, gelatine, perborate or hydrogen peroxide	5.0–10.0	125–1500	1700–7400

The cost of treatment can be reduced to a certain extent by taking the following steps:

1. In-plant measures—reuse of weak dye rinses, storage and reuse of dye bath, countercurrent washing of fabric.
2. Dilution with municipal sewage and treatment thereafter.
3. Activated carbon treatment.
4. Process modification such as combining scouring and dyeing operations in the case of synthetic fibres.

18.2 METHODS OF TREATMENT

18.2.1 Treatment with Polymer Coagulation

Sihorvala and Reddy [3] used cationic polymer Catfloc-T, anionic polymer APH-35 with alum and ferric chloride for treating cotton textile waste. They observed that Catfloc-T was more effective in colour removal than alum and ferric chloride. Moreover, it did not require pH correction, as with alum and ferric chloride. Kabdasli et al. [4] studied the waste water from two plants producing acrylic fabric. Characteristics of the waste waters were as given in Table 18.3. Reactive and acid dyes were used.

Table 18.3 Characteristics of Waste Waters from Acrylic Fabric Production

Plant no.	Sample no.	COD mg/l, total	COD mg/l, filtered	Total suspended solids, mg/l	Cationic detergent, mg/l
I	1	1050	345	175	–
I	2	955	535	165	25
II	1	850	465	140	–
II	2	905	600	60	45

Chemical precipitation with alum, ferric chloride, ferrous sulphate, lime, 1–2 mg/l of polyelectrolyte was tried. It was observed that COD removal was 40%. Biological treatment of this partially treated effluent by activatd sludge process with loading rate of 1.024 kg COD/kg MLSS reduced the effluent COD to 145 mg/l. Complete colour removal could take place only after tertiary treatment with chemical oxidation and precipitation. Namasivayam and Chandrasekharan [5] studied the removal of colour due to reactive dyes such as congo red, fuchsin base, tropeoline, brilliant green, methylene blue and methyl violet from a dyeing industry located at Tirupur, 50 km from Coimbatore, Tamil Nadu. They used Fe^{3+}/Cr^{3+} sludge from a fertilizer factory and red mud from aluminium factory as flocculant and adsorbent. The results obtained were compared with those from the use of lime, alum and $FeCl_3$. Optimum conditions for colour removal were as given in Table 18.4.

Table 18.4 Optimum Conditions for Colour Removal. Volume of Waste Water 100 ml

Flocculant	Dose, mg/l	Agitation time, minutes	Settling time, minutes	Sludge volume, ml
Fe^{3+}/Cr^{3+} sludge*	700	1	1	22
Red mud*	500	1	1	15
Alum*	500	1	2	18
Lime	13,500	1	1.5	25
Ferric chloride*	1500	1	1.5	20

*With lime dose 13,000 mg/l and pH 12.0.

Results obtained on colour removal with different flocculants were: lime alone—88%, Lime + Fe^{3+}/Cr^{3+} sludge—97%, Lime + red mud—91%, Lime + alum—97%, Lime + $FeCl_3$—90%. Bhole and Pawels [6] used anionic, cationic and non-ionic polyelectrolytes, along with alum, aluminium chloride, ferric chloride, ferric sulphate and magnesium chloride as coagulants, for colour removal from a textile mill waste and a handloom yarn dyeing waste. Optimum dose of alum for the former waste was 200 mg/l and 300 mg/l for the latter. The overall colour removal was 97.5%, suspended solids 84% and COD 97.1%. Manjunath and Mehrotra [7] used a combination of alum and lignin sludge from a pulp and paper mill for colour removal. The reactive dye Procian Brill Red H-7B was used in the experiment. At the optimum dose of sludge plus alum, 92% colour removal was achieved. Mehrotra, Prasad and Srivastava [8] applied physico-chemical method for colour removal from dyehouse effluent containing vat dyes, basic dyes and sulphur dyes. Wood charcoal was also used as an adsorbent for colour removal. Coagulants used were magnesium carbonate and ferrous sulphate. At a dose of 1000 mg/l of $MgCO_3$, 92% colour removal was observed, at pH 10. Only 38% of basic dye was removed at pH 11.0. $FeSO_4$, at a dose of 14 gm/l and pH of 10.0, removed 75% vat dye. At a dose of 600 mg/l and pH 9.0, 58% removal was achieved. Untreated wood charcoal removed 42% colour, at a dose of 16 gm/l. Pala [9] studied colour removal from wastes containing indigo dyes by coagulation with lime, iron and aluminium salts along with anionic polyelectrolyte and found that ferrous sulphate + lime + polyelectrolyte was more effective than alum. Mudri et al. [10] conducted laboratory-scale studies for colour removal and further biological treatment on wastes discharged by a factory making textile printing dyes. The waste had high content of zinc (910 mg/l) and dissolved solids. The colour was intensely bluish green. Zinc removal was achieved by correcting pH to 9.2 with lime. As a result, the COD was reduced to 1800 mg/l and BOD to 175 mg/l (determined after zinc removal). Alum dose from 1250 to 1850 mg/l gave COD reduction of 20% to 30%. Chlorine treatment with a dose ranging from 250 to 1250 mg/l gave COD reduction of 30%. Biological treatment using activated sludge process was effective when the raw waste was diluted with sewage four times and acclimated active sludge was used. COD was reduced to less than 100 mg/l after 23 hours of aeration. The residual colour was removed by 25 mg/l of chlorine.

18.2.2 Adsorption

Adsorption has been, by far, the most commonly used method for removal of colour from waste water. In view of the high cost of commercially available activated carbon, a number of cheap materials have been tried out in its place. Thornton and Moore [11] gave adsorbent treatment to wastes using Fuller's earth and activated bauxite. A number of dyes were tried out. They suggested regeneration of spent adsorbents by burning, if the adsorbed dyes did not contain heavy metals. As a matter of further economy, they suggested chemical regeneration of spent carbon, with the possibility of recovering the adsorbed dyes. Rao et al. [12] found a high degree of removal of azo dyes, viz. acid orange 7 and direct Red 31, at pH 7.0 with activated carbon. They also observed that temperature had no effect on the degree of removal. The direct red dye followed Langmuir isotherm, while acid orange dye followed both, Freundlich and Langmuir isotherms. Mittal and Venkobachar [13] used sulphonated coal and *Ganoderma lucidum* leaves as adsorbents for removal of Rhodamine B and Sandolan rhodine. They found that the coal was effective against both the dyes, while *G.lucidum* was effective against Rhodamine only. Singh and Srivastava [14] tried to remove basic dyes with the help of chemically treated *Psidium guyava* leaves. The withered leaves were treated with sulphuric acid and formaldehyde, dried, crushed and sieved. The dyes used were methylene blue and malachite green. Complete removal of 100 mg/l of methylene blue was obtained at a dose of 2 gm/l of the adsorbent, at optimum pH range of 8.0–10.0. The breakthrough and adsorptive capacities for Malachite green and Methylene blue were 105, 127, 180 and 204 mg/gm of adsorbent, respectively. Both, Langmuir and Freundlich isotherms were followed.

Namasivayam and Sumithra [15] used waste Fe^{3+}/Cr^{3+} sludge from a petrochemical industry as adsorbent for removal of Acid brilliant blue and Procion red (reactive azo) dyes and found adsorptive capacities for the two dyes as 10.37 and 3.28 mg/g of adsorbent, respectively. Langmuir isotherm was followed by both dyes. Karthikeyan [16] tried to remove colour from synthetic dye effluents with low-cost materials such as groundnut shell powder (GNSP), red soil, bauxite and flyash. He found the adsorption potential for Congo red, a direct dye, to be Bauxite> Red soil> Flyash>GNSP, while that for Safranine, a basic dye, to be Red soil>

Bauxite>GNSP> Flyash. Singh and Rastogi [17] prepared activated carbon from used tea leaves and tested it for the removal of basic dyes from aqueous solutions. The leaves were impregnated with phosphoric acid and were then carbonized to form active carbon. The dyes tested were Malachite green and Methylene blue. A dose of 1.2 gm/l of the carbon at pH 8.0–10.0 rsulted in complete colour removal. Both Langmuir and Freundlich isotherms were followed in the adsorption process. Rajavel et al. [18] made low-cost carbons from palm nut shells, cashewnut shells and broomsticks by the sulphuric acid process. They were used for removing dark green PLS dye from actual waste water samples and synthetic samples. Adsorption in both cases was found to be from 92% to 95%. It was also possible to reuse the spent carbons five times by reactivating them with mineral acids, steam and hydrogen peroxide. Gupta, Prasad and Singh [19] used low-cost material such as coal, flyash, woollastonite and china clay for adsorption of colour from dyehouse waste containing Omega Chrome, Fast Blue B, often used in textile and carpet dyeing work. The removal efficiency observed was: Flyash> Coal> Woollastonite> China clay. The best adsorption was achieved at pH 2.0, while desorption could be done at pH 12.0 for recovery of the dye. Flyash was also used by Mall and Upadhyay [20] as adsorbent for basic dyes, viz. Malachite green and Methylene blue. Complete removal was obtained at dye concentration upto 20 mg/l, when the carbon content in the flyash was high. The removal kinetics was of the first order. Both Freundlich and Langmuir isotherms were followed.

Use of soil as adsorbent was studied by Ganjidoust [21] for removal of two dyes, Benzonerol Black VSF 600 (Black dye) and Kayarus Supra Yellow RL (Direct dye), which were passed through 17 mineral soils and 1 agricultural soil. Initial dye concentration was varied between 10 mg/l and 320 mg/l. Acidic pH (4.0) was found to be good for adsorption. Both Langmuir and Freundlich isotherms were followed. Increased temperature did not improve the extent of adsorption, indicating that it was an exothermic reaction. Kousar and Singara Charya [22] used four species of fungi, viz. *Aspergilus niger, Curvularia lunata, Fusarium oxysporum* and *Mucor mucedo*, for their colour removal efficiency from dye-contaminated soil. *A niger* and *M.Mucedo* achieved 92% colour removal and enzyme production, while the other two species were not as effective. Meghana, Venkateswaran and Palanivelu [23] employed an aqueous TBAB (Tetrabutyl ammonium bromide) based biphasic system and inorganic salts, viz. NaCl, Na_2SO_4 and Na_2CO_3 for removing colour due to Cibacron Scarlet LS 2G and Astracyl Red 3B. Both the dyes were separated by 98%, the separation increasing in the order NaCl< Na_2SO_4<Na_2CO_3.

Sarayu and Kanmani [24] used UV/solar photofenton oxidation process, based on generation of hydroxyl free radicals (OH). The Fenton molar ratios (H_2O_2:Fe^{2+}) tried were 25:1, 50:1, 75:1 and 100:1. The maximum removal was observed at 50:1 ratio with pH = 3.0. UV-photofenton exposure for 30 minutes gave 97% colour removal and 70% COD reduction, while Solar-photofenton exposure for 2 hours removed 80% colour and 55% COD. Kanmani and Thanasekharan [25] developed solar photoreactors for colour removal from dye-bearing wastes. In solar photocatalysis, solar UV radiation is used as a source of energy to activate a semiconductor, titanium dioxide. The activated photocatalyst decomposes pollutants such as solvents, alcohols, dyes and fuel oils. TiO_2 is biologically and chemically inert, insoluble, non-toxic and maintains photoactivity during reuse. Synthetic waste water containing dye Cibracron Red (40 mg/l) along with carbonate—0.1 gm/l, chlorides—0.25 gm/l and sulphates—1.5 gm/l was prepared. The catalyst concentration was 1 gm/l. Effective colour removal was obtained with the solar photoreactor, without requiring sun-tracking system or transparent UV walls. No clogging of the system and little power requirement were the other two special features [25].

Biological treatment has been successfully done for dye wastes by a number of workers. Kanekar, Sarnaik and Kelkar [26] used a fixed film bioreactor filled with brickbats as medium, for treating a phenol-bearing dye waste. The reactor was loaded at 1.44 m^3/m^2/day and carried a COD load of 5.67 kg/m^2/day and phenol loading of 0.9 kg/m^2/day. An acclimatized mixed culture of *Pseudomonas alcaligenes* and *P. mendocina* was used. During a study period of 68 days, reductions obtained were: COD—54.4%, TOC—51%, Phenol—97.5% and methyl violet—54.4%. Continuous recirculation was maintained during the study. Dudhbhate and Kulkarni [27] treated complex waste water coming from the production of organic dyestuff intermediates, chemicals, pigments and pesticides. The average composition of the raw waste water was as given in Table 18.5.

Table 18.5 Raw Waste Water Characteristics

Parameter	Average value	Range
pH	–	0.86–10.0
Suspended solids	450	130–2300
Dissolved solids	6440	500–13,800
COD	3100	640–12,800
BOD	1350	300–6950
Total nitrogen	80	10–410
Phosphorus	1	0–21
Sulphates	3210	247–10,500
Acidity	2500	668–4034

Note: All values except pH are in mg/l.

Lime was used as neutralizing agent. After four months of acclimatization and a C:N:P ratio of 100:5:1, the composition of the treated effluent discharged by the laboratory-scale activated sludge unit was as in Table 18.6.

Table 18.6 Treated Effluent Characteristics

Parameter	Average value	Range
pH	–	7.7–8.3
COD	1015	186–2000
BOD	68	30–160
MLSS	6684	3700–11,000
MLVSS	4320	3000–6000

Note: All values except pH are in mg/l.

Palaniappa et al. [28] used a combination of hybrid column upflow anaerobic fixed film reactor and activated sludge aeration for decolourization and biodegradation of synthetic and actual waste water from a textile unit. The raw waste water quality was as in Table 18.7.

Table 18.7 Raw Waste Water Quality

Parameter	Concentration
pH	12.26
Conductivity, mMhos/cm	8800
COD, mg/l	1971
Total alkalinity, mg/l	3120
Total solids, mg/l	6800
Total dissolved solids, mg/l	6000
Sulphates	700
Ammonia, mg/l	3.0
Nitrite, mg/l	0.4
Chlorides, mg/l	1375
Phosphates, mg/l	5.0
Metals, mg/l	
Chromium	0.014
Nickel	0.164
Copper	BDL
Zinc	0.0956
Cadmium	BDL
Manganese	BDL

BDL (Below Detection Limits)

Continuous flow experiments were done on a synthetic waste containing eight different dyes. The anaerobic reactor showed COD reduction of 84.8% and colour reduction of 89%. The removal was 63.9% with actual waste and colour reduction was 50% when the waste was diluted 50%. Weeter and Hodgson [29] assessed treatability of three direct and three acid dyes for biodegradation. The work was done in three phases: *Phase I:* incubation at 20°C for 25 days using seeded sludge. No colour reduction. *Phase II:* acclimated sludge at 2270 to 2400 mg/l MLSS, Colour removal 27 to 63%, but mainly due to adsorption of the colouring matter on the sludge. *Phase III:* non-acclimated sludge and waste-MLSS 1490–2690 mg/l. Colour removal 2–63%. In all phases, good BOD removal was achieved.

The adsorptive capacity of powdered activated carbon was effectively used in treating dye wastes by activated sludge process. Powdered activated carbon was added to the inlet of the aeration tank for adsorption of the colouring matter from the dye waste. Sludge from the secondary clarifier was aerated in a separate tank before its return to the aeration tank. During this aeration, the adsorbed colouring matter was decomposed by the acclimated sludge organisms, thereby decolourising the waste water. In addition, the carbon was regenerated and was returned to the aeration tank for further adsorption of the colour from the dye waste [30].

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Chapter 19

RUBBER WASTES

Rubber is a substance used extensively in everyday life. It may be in the form of natural rubber, made by coagulating and drying tree sap, called 'latex', or synthetic rubber, made from butadiene, styrene and acrylonitrile as the principal raw materials. There are, in general, three sources of rubber wastes: (i) manufacture of rubber commodities, (ii) rubber reclamation, and (iii) synthetic rubber [1]. Manufacture of rubber commodities is essentially a process of washing, compounding, calendaring and curing, followed by actual manufacture. The wastes produced consist of cooling water and impurities removed by washing of the crude rubber. Recovery of the used rubber is accomplished by shredding old rubber, removing iron, cotton, rayon, etc. as impurities by hot caustic treatment under high temperature. The rubber is then washed, dried, milled, strained and refined. The waste water is alkaline, pH being 10.9–12.2. It is treated by settling for recovery of settleable material. The sludge is dewatered, dried and reused. The pH value of the clarified effluent is reduced by bubbling flue gas into it before biological treatment. Synthetic rubber is made by the following process:

1. Production of raw material for polymerization
2. Actual polymerization

The raw waste has an intense odour and is usually treated by equalization, neutralization, settling, oil and grease removal, aeration, chlorination, sodium sulphite dosing, and biological treatment. The waste water needs nutrient supplementation with nitrogen and phosphorus and dilution with sewage in 1:1 proportion. BOD removal upto 95% can be achieved by this treatment [1].

A few studies have been conducted for the treatment of rubber factory wastes. Kothandaraman, Aboo and Sastry [2] made an inplant survey of a factory producing 3200 T of rubber latex concentrate and 200 T of skin crepe rubber per year. Water consumption was 100 m^3/day and waste water produced was 80 m^3/day. Flow-proportionate composite sampling of the waste water was done. Its chemical analysis was as in Table 19.1.

Table 19.1 Raw Waste Water Quality

Parameter	1	2	3	4
Flow(m^3/d)	70	80	80	80
Alkalinity($CaCO_3$)	400	380	390	370
BOD	6100	5800	5240	5800
Suspended solids	5440	4660	3360	3220
Total nitrogen (N)	1500	1880	1500	1560
Phosphate (P)	30	35	40	40
pH	4.2	4.1	4.2	4.0
COD	10600	11200	10800	11000
Total solids	28800	32200	29660	32440
Dissolved solids	23360	27540	26300	23200
Ammonia (N)	630	750	710	650
BOD load (kg/day)	427	464	419.2	464

Note: All values except flow and pH are in mg/l. Nos. 1, 2, 3, 4 indicate sample numbers.

Laboratory-scale studies were carried out on this waste and consisted of ammonia removal by raising pH to 11.0 and aerating for 1 hour, followed by anaerobic lagooning for 30 days at a loading rate of 0.11 kg BOD/m^3/day. The BOD removal was 89.5%. The anaerobically treated effluent was subjected to extended aeration for 24 hours at a loading rate of 0.09 kg BOD/kg MLSS. The BOD of the treated effluent was 32 mg/l. Alternatively, ammonia removal, followed by 6 days of aerated lagoon treatment at 0.16 kg BOD/kg MLSS, produced an effluent with a BOD of 20 mg/l.

Madhu, George and Francis [3] treated waste from a natural rubber processing unit mixed with domestic sewage in proportions 1:1, 1:2, 1:3, 1:4 and 1:5, in an experimental oxidation pond with a detention time of 15 days. The maximum BOD removal of 93% was obtained for a 1:5 mixture of waste and sewage, while nitrogen and suspended solids removal was 20% and 25%, respectively.

Sastry [4] has described the effluent treatment practised in Malaysia. Factories processing rubber get skim latex and concentrated latex by centrifugation of field latex. The skim latex is coagulated with acid to get skim rubber and field latex. The quality of waste water from latex concentrate is given in Table 19.2.

Table 19.2 Analysis of Waste Water

Item of analysis	Value
pH value	3.7
Total solids	7576
Suspended solids	182
BOD	3192
COD	6201
Total nitrogen	616
Ammoniacal nitrogen	401
Sulphates	1610

Note: All values except pH are in mg/l.

The treatment consists of providing a rubber trap for removal of suspended solids and recovery of uncoagulated latex, followed by an anaerobic pond loaded at 0.12 kg BOD/m^3/day. The high sulphate content gives rise to the formation of hydrogen sulphide, which is controlled by maintaining pH above 8.2. The BOD removal coefficient for the pond is 0.061 mg/l/day. Although the system gives 96–97% BOD removal, it is unsuitable for factories located near residential areas. On the other hand, some factories follow high rate digestion at a loading rate of 10 kg COD/m^3/day and use the generated gas in their factories. They give aerobic treatment to the effluent from anaerobic treatment.

Waste waters from rubber goods manufacturing factories are treated by raising pH to 11.0 with lime or NaOH, coagulating with polyaluminium chloride and polyamides and are settled. The sludge formed is wasted, while the clarified effluent is treated with phosphoric acid to correct pH to 7.0 and is anaerobically digested, followed by aerobic treatment to achieve 97–98% BOD removal.

Ramaswamy, Somasekhar and Arekal [5] conducted a one-year study of the effect of rubber tyre factory wastes on algal growth in the receiving stream. The waste water had the following composition as given in Table 19.3.

Table 19.3 Chemical Analysis of Waste Water

Item of analysis	Value
pH	9.0
Dissolved oxygen	3.4
Free CO_2	Nil
Total suspended solids	344
Phosphates	Traces
Ammoniacal nitrogen	2
Iron as Fe_2O_3	31
Potassium as K	4

(Contd.)...

Table 19.3 Chemical Analysis of Waste Water *(Contd.)*

Item of analysis	Value
Temperature	32°C
5 day 20°C BOD	350
Oil and grease	83
Chlorides	240
Sulphates	166
Nitrite nitrogen	Traces
Calcium as Ca	58
Per cent sodium	52
Particle size of suspended matter	Passes 830 micron sieve
Chemical oxygen demand	1688
Total dissolved solids	1041
Fluorides	0.2
Silicates	196
Nitrate nitrogen	0.008
Sodium as Na	108

Note: All values except pH are in mg/l.

They found cyanophyceae as the predominant algal species. A blue-green alga, *Microcoleus,* was also detected. Although the waste water was low in nitrogen and phosphorus, diatoms were found to be abundant throughout the year.

Among the major pollutants in rubber wastes are carboxylic acids, viz. formic, acetic and oxalic, alongwith phenols, alcohols and amines. The acids are not removed by conventional treatment methods. Therefore, Ramu, Kannan and Srivathsan [6] experimented with activated carbon and flyash for the adsorption of these acids. They activated the flyash by treatment with dilute nitric acid, washed, dried and heated it for 5 hours at 110°C. The silica in the flyash helped removal of cations and alumina removed anions. The effect of dose and contact time was studied. Their observations are tabulated in Table 19.4.

Table 19.4 Optimum Conditions for Adsorption of Carboxylic Acids

Condition	Flyash	Flyash	Flyash	Activated carbon	Activated carbon	Activated carbon
	FA	**AA**	**OA**	**FA**	**AA**	**OA**
Dose, gm/l	8.0	7.5	10.0	2.25	2.0	2.5
Contact time, min.	45	50	60	30	35	40
Per cent removal	85	82.5	86	98	95.5	92.5

Note: FA, AA and OA represent formic acid, acetic acid and oxalic acid, respectively.

Initial concentration = 0.2 g eq/l.

The adsorption process was found to obey Freundlich isotherm. The authors recommended flyash as an adsorbent, because it is 25 times cheaper than activated carbon, which is 3 times more effective than flyash.

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Chapter 20

RADIOACTIVE WASTES

The harnessing of nuclear energy and its various uses have given rise to new and complex problems of handling, treating and disposing of solid, liquid and gaseous radioactive wastes, because they are not detectable by human senses. They have certain radionuclides with toxicity greater than that of any other known industrial waste, and there is no known process for destroying radioactivity. The wastes become inactive only by their own decay or disintegration. Radioactive material is used for medicinal, agricultural, industrial and scientific purposes. Wastes generated from these uses have to be managed by complex chemical processes, sometimes under remote control, and require sensitive analytical techniques and control procedures. In view of their peculiar nature, the concentrations of these wastes are expressed in ways different from those used for other wastes, e.g. 1 curie is the quantity of a radionuclide which produces 3.7×10^{10} disintegrations per second. This is nearly equal to the radiation emitted by 1 gm of radium. 1 millicurie = 10^{-3} curie and 1 microcurie = 10^{-6} curie. Concentrations of liquid and gaseous wastes are expressed in microcurie/ml. Concentrations of solid wastes are described by the external radiation delivered to a specific area or volume of receiving material. The most common term used is the Roentgen or Milliroentgen. 1 Roentgen is equal to the quantity of X- or Gamma radiation that produces 1 Electrostatic Unit (ESU) of electricity in 1 cc of dry air, at 0°C and 760 mm pressure. Similarly, 1 Roentgen-equivalent man (REM) is the dose of ionizing radiation that produces the same biological effect as that produced by 1 Roentgen.

Radioactive wastes are classified according to their activity levels as given in Table 20.1.

Table 20.1 Radioactive Waste Activity Levels [1]

Type of waste	Solid wastes (Roentgen/hour)	Liquid wastes (Microcuries/ml)
High level	>2	$>10^3$
Intermediate level	0.05–2.0	10^{-3} to 10^3
Low level	<0.05	$<10^{-3}$

High-level wastes are produced in the chemical reprocessing of spent reactor fuel elements for recovery of plutonium and unburnt uranium. *Intermediate level wastes* are produced from fuel decladding and from the second and third cycles of solvent extraction operation in the chemical reprocessing plant. *Low-level wastes* include wastes generated in laboratory research, medical and industrial use, normal operation of nuclear reactors, and other parts of the nuclear fuel cycle such as uranium mining and milling, feed material purification, and fuel element fabrication [1].

Radiation hazards include effects on structural and non-living materials and physiological injury, even death. Non-living materials are affected by way of discolouring crystalline materials, making pliable materials brittle and catalyzing chemical reactions. The effect on living matter due to exposure is categorized as follows:

1. Acute, which results in shortened lifespan, leukemia or cataract.
2. Chronic, which leads to tumor, induction of cataract, or early death.
3. Genetic, which causes mutation in offsprings.

The health hazards depend on the charge, mass, range and energy of radiation emitted, solubility of emitter in body fluids and affinity of the emitter to various organs [2]. An important property of radioactive material is its natural decay and disintegration and, hence, loss of radioactivity with time. The time required for a radionuclide to reduce its radioactivity to half its original value is known as its 'half-life'. Knowledge of this value helps in deciding the mode of treatment and disposal of the radionuclide. The half-life values of some radioisotopes are given in Table 20.2.

Table 20.2 Half-Life Values of Some Radioisotopes [1A]

Name of isotope	Half-life
Polonium-212	3.04×10^{-7} sec
Carbon-11	20.4 min.
Iodine-131	8.06 days
Calcium-45	165 days
Cobalt-60	5.27 years
Caesium-137	30 years

(Contd.)...

Table 20.2 Half-Life Values of Some Radioisotopes [1A] *(Contd.)*

Name of isotope	Half life
Uranium natural (Insoluble)	4.5×10^9 years
U-233 (Insoluble)	1.62×10^5 years
Plutonium (Soluble or insoluble)	2.41×10^4 years
Carbon-10	19.3 sec
Carbon-14	5,570 years
Phosphorus-32	14.3 days
Potassium-40	1.4×10^9 years
Strontium-90	28 years
Uranium natural (soluble)	4.5×10^9 years
U-233 (soluble)	1.62×10^5 years
Radium-226	1620 years

Measurement of radioactivity is done with the help of a Geiger–Mueller end-window counter.

20.1 HANDLING RADIOACTIVE MATERIAL

Various steps of extraction, refining, using and reprocessing of radioactive material are briefly described as following [1]:

1. **Mining:** Uranium is present in nature as U_3O_8, averaging about 0.25% of the ore.
2. **Milling:** The uranium is extracted from the ore by crushing, blending, roasting, and acid or alkaline leaching. The final product is obtained by ion exchange, solvent extraction, filtration and precipitation. The oxide product averages upto 75% by weight.
3. **Refining:** Uranium is converted to metal or chemical products of acceptable purity for reactor fuels.
4. **Fuel reprocessing:** After a certain operating period, the fission reaction becomes inefficient and the fuel elements are removed from the reactor, with a very small amount of the uranium having been consumed. After 'cooling' for 3–4 months to reduce the extreme radioactivity, the irradiated fuel is sent to a chemical separation plant, where plutonium and unused uranium are recovered. Chemical separation by acid dissolution and solvent extraction produces a large amount of radioactive waste. This is stored in underground tanks [1].

20.2 TREATMENT AND MANAGEMENT

Treatment can be done by one or more of the following:

1. Dilution
2. Evaporation

3. Coagulation and settling
4. Ion exchange with natural clays and synthetic resins
5. Biological processes
6. Metallic displacement
7. Sand filtration
8. Crystallization
9. Solvent extraction
10. Electrolytic separation
11. Differential volatility
12. Electrodialysis

The efficiency of a treatment process is measured by determining 'decontamination factor', which is the ratio between radioactivity in the influent and radioactivity in the effluent.

Management of the wastes includes their safe disposal using the concepts of (a) concentrate and contain, (b) dilute and disperse, or (c) delay and decay. The concept of 'concentrate and contain' is useful for high activity liquid wastes originating from chemical processing of irradiated reactor fuel. The radioactivity is concentrated by volume reduction and is then confined in an area away from human habitation. Containment is achieved by calcinations to oxide, by formation of glass containing high percentage of lead, storing in specially constructed vaults, by chemical treatment and fixation in cement, or by bituminisation of the waste [1, 2]. The concept of 'dilute and disperse' is used for reducing radioactivity by dilution in air or water, but stringent control and monitoring are required to ensure that the safety capacity of the environment is not exceeded. The concept of 'delay and decay' uses the exchange capacity of soil to hold radioactive material within itself. Here again, strict control is required over the level of radioactivity generated due to this form of disposal and the possibility of ground water contamination.

Basic considerations in all the methods of disposal are: (a) specific nature and quality of radioactive material to be handled, (b) characteristics of the receiving environment, and (c) basic radiation protection standards [1]. Coal-based thermal power stations were seen to have changed the concentration of trace elements and radionuclides in the soil surrounding them, as seen by Ramachandran, Lalit and Mishra [3]. They conducted a countrywide survey of the outdoor natural background gamma radiation levels at 214 locations, which showed that flyash from the flue gases definitely changed the radioactivity in the surrounding soil. Similarly, Chowdhary [4] conducted a hydrogeological survey of five wells in Varanasi, India, and found that the well waters showed a much higher radioactivity than is normally expected in drinking water. There was a distinct relationship between radioactivity and bicarbonate alkalinity of the water samples. Disposal of sludges formed during treatment of radioactive wastes can be done by dewatering them to a small volume and storing them in suitable containers. The liquid wastes can be used for making concrete blocks to hold the dewatered sludges, provided the liquid wastes have low or no ammonium nitrate, sodium and calgon, since they inhibit setting of concrete [1A].

Factors requiring careful consideration in burial of the containers include: (a) Precise location records, (b) Geology of the area, (c) Type of container, (d) Depth of root zone in the area, (e) Type of soil, (f) Electrolyte content of the soil, (g) Depth and location of groundwater and its movement [1A].

Methods of treating radioactive wastes were described by Shah [5] and included physical methods of dilution, storage and evaporation, chemical methods of ion exchange, lime-soda softening and chemical precipitation. Biological methods included activated sludge process, trickling filtration, and oxidation ponds. Chemical precipitation as hydroxides can remove Sr-90, Yt-90, Ce-137, I-131, P-32, Ba-137. A decontamination factor of 10 can be achieved by using 75 mg/l of $CaCl_2$, 130 mg/l of Na_3PO_4, 25 mg/l $FeCl_3$, 20 mg/l $CuSO_4$ and 25 mg/l K_3FeCN_6. Ion exchange can be used for small volumes and low concentrations of wastes. A decontamination factor of 10^6 can be obtained with high-capacity resins. Kaolinitic and Montmorillonite clays can remove 80–85% of Caesium and Ruthenium. Vermiculite is also useful for this. Other chemical methods include solvent extraction, recrystallization, fusion into nitrates, etc. Organic phosphorus compounds are useful as solvents, while esters, ethers and ketones are unsuitable. Sinha, Ayengar and Amalraj [6] treated thorium-bearing waste by chemical precipitation, using two systems, viz. calcium phosphate-ferric hydroxide system and caecium oxalate system. They found that suspended thorium was effectively removed by the phosphate-hydroxide system, while dissolved thorium was removed by the oxalate system. Seshadri et al. [7] used electrodialysis and interpolymer membrane to deal with caesium-bearing waste. Electrodialysis is a combination of ion-selective electrode and electrolysis. In order to impart cation selectivity, diammonium salt of phenoldisulphonic acid was introduced into a polyurethane matrix. A decontamination factor of 50 was achieved by this system under laboratory conditions. Seshadri et al. [8] used ceramic membranes to treat radioactive wastes. They treated simulated wastes containing Cs-137 and Sr 90, first with copper ferrocyanide and calcium phosphate coagulating systems. The doses of these chemicals used were 10% and 50% of those used in actual treatment plant. After chemical dosing, the wastes were passed through titania and zirconia membranes with mean pore sizes of 650 nm and 540 nm, respectively. A decontamination factor of 40 was achieved. A pH value of 8.5 was used for the caesium effluent, while pH for strontium effluent was 10.5. The zirconia membrane was found to be more efficient than titania membrane.

Sludges formed during chemical treatment of these wastes must be handled and disposed of safely. Dewatering them is the first step in this direction, the purpose being to reduce their volume to the maximum extent. Seth [9] noted some of the processes used for dewatering as shown in Table 20.3.

Table 20.3 Dewatering of Sludge

Place	Method	Per cent solids (Before)	Per cent solids (After)
Harwell, UK	Freezing, thawing and filtering	3	30–50
Russia	Draining, freezing, thawing and air drying	1–2	90–92
Marcoule, France	Filtering	2	30–40

The dewatered sludges were sealed in drums before sea disposal. The effect of disposal of radioactive wastes in flowing river water and the role of sediments on migration of radionuclides was studied by Nair, Krishnamoorthy and Sarma [10]. They prepared a three-dimensional hydrodynamic model to predict the concentration of radionuclides discharged continuously in a river. The radionuclides were grouped thus: (a) nuclides whose concentration is insignificantly affected due to their long physical half-life, (b) those moderately affected due to their short half-life, and (c) those with short half life, whose radioactivity is confined close to the point of discharge.

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Chapter 21

ORGANIC AND INORGANIC CHEMICALS

Manufacture of some organic and inorganic chemicals gives rise to pollutants, which are toxic, are difficult to biodegrade, can be harmful to aquatic flora and fauna, or can disturb ecological balance, e.g. mercury in the chlor alkali industry, arsenic in the fertilizer manufacture industry, red TNT and yellow TNT in the manufacture of high explosives, etc. This chapter deals with some of these wastes.

21.1 HIGH EXPLOSIVES MANUFACTURE

High explosive products manufactured include trinitrotoluene (TNT), cellulose nitrate, nitroglycerine, cordite, cordtex, tetryl, lead azide, mercury fulminate, lead styphnate, tetracene, cyclonite hexogen (RDX), composite explosives (CE), plastic explosives (PE) and dinitrophenol [1,2,3]. Acids such as sulphuric acid, nitric acid, oleum, required in the manufacturing process, are almost always manufactured in-house. Steps in the manufacture involve use of raw materials such as toluene, cellulose, calcium cyanide, picric acid, glycerine, nitrobenzene, etc. The manufacture of TNT is done by three-stage nitration of toluene with a mixture of sulphuric acid and nitric acid under controlled conditions till alpha-TNT is formed. The crude product is treated with sodium sulphite and washed with water to remove beta and gamma isomers of TNT in the form of soluble sulphonates. The purified TNT is dried, remelted and flaked, or is run into shallow troughs and allowed to solidify [4].

The manufacture of tetryl is carried out by nitration of dimethyl aniline under acidic conditions. The waste acid is run off and the residue is washed, first with dilute acid and next with water till all the acid is washed away. The crude product is purified by dissolving it in acetone containing a small amount of ammonium carbonate. After filtration, the solution is poured into water to precipitate pure tetryl [4]. Similar steps are used in the manufacture of other explosives.

A common factor in the manufacture of explosives is generation of highly acidic effluents, containing toxic and 'difficult to degrade' pollutants, which impart an undesirable colour and taste to the receiving body of water. Disposal of these waste waters on soil leads to pollution of ground water. Adequate treatment of the waste water is, therefore, required. Mudri, Godbole and Parabrahmam [4] characterized the waste water from a high explosives factory discharging its effluents into a nearby river. They reported the presence of dirty yellow colour in the river water even 10 km downstream of the point of discharge. Mudri and Phadke [5] tried various chemical methods for treatment and colour removal from the wastes but could not find an economical solution. They reported that TNT-acclimated activated sludge could treat upto 25 mg/l of TNT-bearing waste water mixed with domestic sewage. Kanekar and Godbole [6] found TNT-degrading organisms in the soil receiving this waste for nearly 50 years. They reported that 15 out of the 66 isolates could degrade TNT in a TNT-peptone medium. Among the various oxidizing agents such as chlorine, ozone, hydrogen peroxide and potassium permanganate, hydrogen peroxide combined with ultraviolet rays was found effective in destroying refractory organics from these wastes [7]. Smith et al. [8] decomposed nitroglycerine and dinitroglycerine with sodium sulphide at pH 10.0 and a contact time of 30 minutes. Chemical hydrolysis of these compounds could also be done with lime at a pH of 11.5. Most of the nitroglycerine was hydrolysed in 60 minutes while dinitroglycerine took 30 minutes. Nitrate esters, viz. propylene glycol dinitrate (PGDN), diethylene glycol dinitrate (DEGDN) and trimethylol ethane trinitrate (TMETN) were successfully destroyed by sodium sulphide alone [8]. Colloidal nitrocellulose (NC) fines could be readily settled with lime (to pH 11.5) plus a suitable cationic polyelectrolyte [8]. Waste water containing nitroguanidine (NGU) was effectively treated with sodium hydroxide and sodium sulphide at pH greater than 11.0. The rate of destruction was found to be a function of the amount of sodium sulphide added. NGU was also found to be non-biodegradable by itself, but required the presence of a readily biodegradable carbon source. The rate of biological metabolism of NGU was found to be a function of, and was limited by, the ratio of NGU and carbon source [8]. Edwards and Ingram [9] found that the colour of TNT wastes could be removed with a chlorine dose of 9000 mg/l, when the waste water and chlorine were intimately mixed in a tower packed with a ceramic medium.

Schott et al. [10] reported that biological trickling filters could handle upto 10% of waste by volume of TNT waste water with domestic sewage, while activated sludge could handle only 5%. Biodegradability of nitroglycerine (NG) using a rotating biological contactor (RBC) was studied, and it was found that there was a direct correlation between the COD of the wastewater and NG concentration. Separate data were collected on destruction of NG at constant COD input and increasing

COD and flowrate with constant NG input. When these data were plotted together, it was seen that the COD removal efficiency was controlled by COD/NG ratio rather than NG concentration alone [8].

It is apparent that waste waters generated during the manufacture of high explosives are more amenable to chemical treatment than to biological treatment. It is possible to provide pretreatment in the form of physico-chemical process, followed by biological treatment. Pretreatment should be provided to individual pollutants and their concentrations should be reduced to a level where they can be mixed together for biological treatment.

21.2 PETROCHEMICAL WASTES

As already mentioned in Chapter 15 (petrochemical wastes), waste waters generated in the manufacture of petrochemicals contain toxic and refractory pollutants, which add significantly to the COD of the waste water. Such pollutants must be treated separately so as to reduce the COD load on the treatment plant and facilitate biological treatment. One such study was conducted [11] at a petrochemical complex discharging toxic, unsaturated aldehydes like crotonaldehydes and aromatic compounds. Upflow anaerobic fixed film reactors were used to assess the treatability of effluent streams from the following:

1. **Chemicals unit**, which discharged
   (a) Croton refining still (CRS) tails
   (b) Ethanol refining Still (ERS) tails
   (c) Acetaldehyde (ACH) stripper tails
   (d) Lean butanol effluent
2. **Olefins unit,** in which the benzene unit residue (BUR) decanter drain was sampled.

Besides having high COD, these effluents also had a high volume. Results of the study are shown in Table 21.1.

Table 21.1 Anaerobic Digestion Studies

Name of effluent	Mode of operation	COD load, (kg/m^3/day)	Hydraulic retention time (days)	Per cent COD reduction
ERS tails	Batch	4	6	90
ERS tails	Continuous	2.5	4	>90
Lean butanol	Continuous	4.5–6	16–6	>90
ACH stripper tails	Continuous	1–1.5	10–16	70–90[a]
CRS tails	Continuous	0.25–1	16	*b*

[a] The reactor failed after 1.5 months of operation and could not be revived.
[b] BUR decanter. Reactor could not take more than 1 kg COD/m^3/day at 30% waste by volume in the feed.

Godbole et al. [12] investigated the microbial degradation of resorcinol under anoxic conditions in a fixed film, fixed bed (FFFB) reactor filled with crushed basaltic rock. At a hydraulic retention time of 20 hours, resorcinol loading rate of 2.93–5.73 kg COD/m^3 void space/day and a COD:Nitrogen ratio of 3.75:1, degradation of resorcinol was found to range between 86.2% and 97.9% after acclimatization. Resorcinol utilization was partially inhibited by paranitrophenol at a concentration of 125 mg/l.

It is known that waste water streams from dimethyl terphthalate wood pulping units and petrochemical industries produce acetic acid-bearing wastes. Acetic acid can be removed from the streams by distillation, solvent extraction, or activated carbon adsorption. Laboratory scale studies using activated jute carbon, bagasse carbon, rice husk carbon and sawdust carbon were conducted by Chand, Majumdar and Kumar [13]. They found that activated bagasse carbon was most efficient and removed 51% at a dose of 6 g/100 ml of solution from an initial acetic acid concentration of 4% by volume, while activated rice husk carbon was the least efficient.

Wet air oxidation can be used to destroy complex structures of certain industrial waste water components at source or to convert them to biodegradable forms. Force [14] describes successful use of the process for treating a waste stream containing para-aminophenol, a byproduct of a pain reliever. Spent caustic liquors from the manufacture of ethylene and from naphtha cracking units in oil refinery were also treated by the process. The temperature and pressure to be maintained in the oxidation process are determined by the degree of oxidation required and constituents of the waste water.

Effluents from a matchstick manufacturing industry were analyzed by Kannan, Rajasekaran and Vallinayayam [15] for calculating water quality index (WQA) of a stream receiving these effluents. The industry uses sulphur, phosphorus, glue and starch in the manufacturing process, all of which contribute to BOD, COD, etc. Correlation coefficients between various pollution parameters were obtained, based on the analysis of effluent samples. The equations developed were:

$$\mathrm{TDS} = -1.15 + 0.70\ \mathrm{EC}\ (r = 1.0)$$

$$\mathrm{HAP} = -161.83 + 0.57\ \mathrm{THA}\ (r = 0.833)$$

$$\mathrm{Mg}^{++} = 0.32\ \mathrm{Ca}\ (r = 0.768)$$

$$\mathrm{HAT} = 162.57 + 0.43\ \mathrm{THA}\ (r = 0.75)$$

$$\mathrm{WQA} = 3144.16 + 4.348\ \mathrm{K}\ (r = 0.699)$$

where TDS = Total dissolved solids, EC = Electrical conductivity, HAP = Permanent (non-carbonate) hardness, THA = Total hardness, HAT = Temporary (carbonate) hardness. A similar study was conducted by Kannan and Rajasekaran [16] on effluents from litho and offset printing presses to predict concentrations of various pollutants in the receiving stream. Samples from set points were collected bimonthly from the receiving stream and were analysed for BOD, COD, magnesium and chloride contents, total hardness (THA), permanent (non-carbonate) hardness (HAP) and electrical conductivity (EC). Equations obtained were:

$$\text{BOD} = -1.295 + 0.5255\ \text{COD}\ (r = 0.995)$$

$$\text{HAP} = -200.031 + 1.042\ \text{THA}\ (r = 0.982)$$

$$\text{TDS} = 312.544 + 0.676\ \text{EC}\ (r = 0.862)$$

$$\text{Mg}^{++} = -419.566 + 0.966\ \text{Cl}^{-}\ (r = 0.826)$$

$$\text{THA} = -169.126 + 0.129\ \text{TDS}\ (r = 0.822)$$

$$\text{HAP} = -390.776 + 0.136\ \text{TDS}\ (r = 0.817)$$

21.3 INORGANIC POLLUTANTS

Inorganic pollutants, commonly present in industrial wastes, include carbon dioxide, chlorine, lead, arsenic and mercury. Their concentrations depend on the manufacturing process, reuse, recovery and recycle systems, if any are used, and housekeeping practices followed. Methods of handling these wastes are briefly described here.

21.3.1 Caustic Chlorine Waste

In a broad-based caustic chlorine industry manufacturing caustic soda, hydrochloric acid, liquid chlorine and hypochlorites, acidic, alkaline and free-chlorine bearing wastes are produced. The average analysis of the waste water is as in Table 21.2.

Table 21.2 Characteristics of Effluent of a Broad-based Caustic Chlorine Industry [17]

Characteristics	Range
pH value	2.4–12.5
Alkalinity as $CaCO_3$	
(i) Phenolphthalein	0–7600 mg/l
(ii) Methyl orange	0–31,800 mg/l
Chlorides as Cl^-	324–10,600 mg/l
Total hardness as $CaCO_3$	2600–13,000 mg/l
Total dissolved solids	2078–62,520 mg/l
Total suspended solids	160–5400 mg/l
Free residual chlorine	45–60 mg/l

Acid wastes could be neutralized by passing them through upflow limestone beds, but aeration of the waste with fresh and partly digested cowdung slurry showed the latter to be more effective in reducing free residual chlorine from 60 mg/l to 7 mg/l in 75 minutes. This method of destroying free residual chlorine is definitely cheaper than using reducing agents such as sulphur dioxide, sodium sulphite or sodium thiosulphate.

21.3.2 Carbon Dioxide

Carbon dioxide, which is the main culprit in global warming, is generated by the burning of fossil fuels such as oil and coal. The worldwide emission of this gas amounted to nearly 6.1 billion tonnes (carbon equivalent, 1996), with India accounting for 4% of the total [18]. Recovery of carbon dioxide from flue gases and converting it into other substances such as methanol or dimethyl ether (DME) is commonly practised today. Salient features of DME are:

1. It is a potential fuel.
2. It is a gas at ordinary temperature and can be liquefied by compressing it.
3. It is chemically stable and is virtually non-toxic.
4. It may prove to be a promising alternative fuel to LPG and light oil in future [18].

Manufacture of ammonia in fertilizer industry produces a large amount of carbon dioxide gas. If a urea plant is also available in the industry, this gas can be conveniently used for manufacturing urea, but where this utilization is not possible, the carbon dioxide gas is vented into air. Carbon dioxide, thus produced can be used as such or can be converted into dry ice and utilized in many industries such as food and beverage industry, for preservation of marine products and transportation of frozen foods, preservation of foodgrains in large silos, for firefighting, for producing certain pharmaceuticals and chemicals, for CO_2-argon welding, shrink fitting, core making in steel foundries, for regeneration of oil wells, in the making of beer, for manufacture of pesticide intermediates, etc. The steps involved in recovering carbon dioxide include moisture and impurities removal, compression to a pressure of 17–20 bar, liquefying the gas to –27°C and releasing it into a closed vessel through a small diameter valve. This action converts it into solid flakes, which are compressed into desirable shapes [19].

21.3.3 Lead

Lead is used in the manufacture of batteries, pigments, explosives, photographic material and paint manufacturing industries, petroleum refining, plating and in producing colour tubes for television sets. Lead mines and lead smelters contribute to pollution.

Most lead wastes are in colloidal and dissolved, inorganic form. However, the tetraethyl lead industry contributes significant amount of organic lead compounds. Removal of lead is achieved by adjusting pH of the waste water between 9.2 and 9.5 with lime, soda ash, caustic soda, phosphate, or dolomitic limestone and precipitating lead as lead hydroxide (with lime and caustic soda), lead carbonate (with soda ash) and lead phosphate (with phosphate compound). Ferrous sulphate is used as a coagulant to separate lead hydroxide. Organic lead compounds are treated by passing the waste through a strongly acid cation exchange bed, eluting the adsorbed lead with caustic soda and treating the eluate with chlorine gas at 95 °C for 45 minutes. The organic matter is destroyed by chlorine and the eluate can then be treated for removal of lead by precipitation [20].

Gajghate and Saxena [21] used activated carbon to remove lead from waste water. They used three grades of carbon to adsorb lead from an aqueous solution at pH values ranging from 2.2 to 10.0. They observed that maximum adsorption took place at pH 2.2, minimum at pH 5.0, which increased to 100% at pH 10.0. Chromium from 5 mg/l to 50 mg/l did not affect adsorption of lead, but 35 mg/l of mercury reduced adsorption efficiency from 99.8% to 90.5% at pH 2.2 and contact time of 4 hours.

21.3.4 Mercury

The major users of mercury are the chlor-alkali and the electrical and electronics industry. It is also used in various forms in the explosives manufacture, the photographic industry, pesticides, biocides, fungicides, slimicides and preservatives, paint, pharmaceutical industry, cosmetic industry, pulp and paper making, sealants used in machines, in thermometers and manometers, etc.

Many methods of treatment of mercury-bearing wastes have been devised. The effectiveness of treatment depends on the chemical nature (organic or inorganic) and initial concentration of mercury, presence of other constituents in the waste water, which can interfere with the process of removal, and the degree of removal required. Among the common forms of treatment are precipitation, ion exchange, adsorption and coagulation, reduction of ionic mercury to elemental form and removal by filtration [22]. Kenney and Hansen [23] classify methods of treatment into three groups, viz. (i) thermal processing, in which the waste is heated to more than 375°C in the absence of air, when mercury volatilizes and the vapours are condensed to get mercury. This method is useful for small volumes of waste waters and high concentration of mercury. In another method, the waste is heated in the presence of controlled volume of air to decompose mercury compounds. Elemental mercury is obtained by condensation and scrubbing; (ii) hydrometallurgical treatment, in which mercury is leached from the waste by a hypochlorite-based system or caustic-sulphide system. The soluble mercury is recovered by cementation, precipitation or electro-winning, and (iii) physical separation for recovering mercury from the soil by washing the soil, screening and gravity separation. Ansari et al. [24] list costly methods such as reduction process, sulphide treatment, ferrous chloride treatment, magnetic ferrites, ion exchange and ion exchange plus use of chelating resin. Sorption on modified peanut skin, walnut expeller meal, redwood bark, western hemlock bark, wool, chicken feathers, soya flour, silk and wheat gluten are considered cheap methods. These authors also tried the use of neem (*Azadirachta indica*) bark to adsorb mercury. They used neem bark powder (size less than 53 micron) at the rate of 0.1% (W/v) and got better than 99% removal from a sample containing 100 mg/l mercury. They observed that the removal was pH independent (pH 1.0–10.0) and was unaffected by the presence of sodium, potassium, calcium, magnesium, copper, zinc, lead, cadmium and nickel upto 500 mg/l. Sulphates, phosphates, acetates had no effect upto 200 mg/l, while high chlorides interfered with removal. The reaction was found to follow Freundlich isotherm.

Chaturvedi and Pandey [25] have suggested control of mercury pollution by its recovery from solid, liquid and gaseous effluents from various operations in the chlor-alkali industry. Sludge produced in the primary and secondary cells, filter sludge from brine house clarifiers and filters contain mostly elemental mercury, which can be recovered by simple distillation. Liquid effluents from cell house, chlorine/hydrochloric acid plant and from brine house contain together 5 to 10 mg/l of mercury, outlet brine from mercury cells contains 1 to 10 mg/l of mercury, which can go upto 1000 mg/l in the case of power failure. Brine house clarifier and filter slurries discharge about 1000 mg/l of mercury, while mercury from the electrolytic cells escapes with hydrogen gas, chlorine gas and as mercury vapour. Cooling of hydrogen gas to 5°C and passing it through activated carbon or chlorinated brine can reduce mercury content to 0.01 mg/m^3. The authors have suggested a precipitation sludge treatment of solid and liquid effluents for effective recovery of mercury and recycling of the treated effluent to the cell house.

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Chapter 22

COMMON EFFLUENT TREATMENT PLANTS

The concept of common effluent treatment plant (CETP) has been accepted as a solution for collecting, conveying, treating and disposing of effluents from industrial estates. The effluents include industrial waste waters and domestic sewage generated in these estates. The CETPs are designed to help small scale and medium scale industries located within the estates to dispose of their effluents, which, in many cases, are small in volume but have a high pollution potential. These industries cannot afford to treat their waste waters individually because of space constraints and financial limitations. But they are expected to give at least preliminary treatment in order to ensure that the common collecting sewer remains free flowing. It may be necessary in certain cases to provide pH correction also before discharging the effluents into the collecting sewer. As is the case with any waste water treatment facility, a CETP is designed on the basis of: (a) the quality and flowrate of the waste water, (b) standard of quality of treated effluent stipulated by the pollution control authority, (c) possibility of recycle, reuse or recovery of treated waste water, (d) availability of land, labour, power for operating and maintaining the CETP, and (e) willingness of the industries located in the industrial estate to contribute towards the capital and operating expenses of the CETP.

A CETP can be changed to a combined effluent treatment plant when it collects domestic sewage from surrounding areas and treats it with industrial wastes. The advantages of such a system are as follows:

1. Dilution is offered to the toxic constituents and inorganic dissolved solids in the industrial wastes.

2. Continuous seeding of microorganisms is possible when the mixture is subjected to biological treatment.
3. Better control over treatment plant is possible than if sewage is treated in a separate plant.
4. Sewage provides nitrogen and phosphorus as nutrients to the microorganisms which treat industrial wastes deficient in these elements. This reduces running cost of adding chemicals to some extent.

CETPs are broadly grouped under two headings, viz. (i) *homogeneous*, in which industries producing similar goods are located in one area, for instance, tanneries or engineering goods, or pulp and paper, etc. and (ii) *heterogeneous*, in which industries producing widely divergent goods are placed together, such as chemical, dairy, food and fruit processing, tanneries, pulp and paper, pharmaceuticals, etc. Designing a treatment plant for the first group is easier than for the second group, as the characteristics of raw wastes produced in the former tend to show lesser variations than the latter.

Advantages of providing a CETP are the following:

1. Small and medium scale industries are relieved of the problem of treating their effluents.
2. Waste water treatment is assured, thereby helping pollution control.
3. The pollution controlling authorities have to monitor only one outlet to check the performance of the CETP.
4. Participating industries have a commitment to generate only waste waters acceptable for treatment in the CETP.
5. Industries can concentrate on finding ways and means of reducing pollution at source, reduce water and power consumption to the extent possible.

Many factors need careful consideration in establishing a CETP.

22.1 OWNERSHIP

Ownership can be either in (i) private sector, (ii) public sector, or (iii) joint private and public sectors [1].

Private sector ownership: In this, individual industries form a co-operative company and become its shareholders. Advantages of this form are:

1. Expression of commitment to pollution control by the industries,
2. Short-term problems of manpower and equipment can be overcome by resources available in member industries. This form of ownership is generally accepted, although there can be conflict among member industries regarding waste water quality and quantity. All participating industries pay a fair share in the cost

of treatment, depending on quality and quantity of waste water. Failure to pay can result in imposing penalty on the defaulting industry by way of non-acceptance of its effluent into the CETP [1].

Public sector ownership: The State Industrial Development Corporations (SIDC) provide all infrastructural facilities including CETPs. But these being government organizations, conflict of interest in regard to compliance and strict enforcement by the State Pollution Control Boards may be difficult [1].

Joint private and public sector ownership: A company is formed by the SIDC and the Industries' Association. This arrangement improves availability of funds, but it can result in delays in defining responsibilities [1].

22.2 TECHNICAL ASPECTS

Technical aspects include:

1. *Basic information*. Information about individual units, their raw materials, products, treatment, if any is being given, quality and quantity of waste water generated, scope for reducing water consumption and waste minimization.
2. *Collection and conveyance*. Waste water is conveyed either by underground drainage system, or by tankers, handcarts, etc., if the volume involved is small.
3. *Pretreatment*. Rational pretreatment to be given by individual units irrespective of the mode of conveyance of the waste water.
4. *Planning*. Master plan and phasewise approach if uncertainty exists about quantity, quality and treatability.
5. *Disposal*. Handling, treatment and disposal of sludge generated either during pretreatment or treatment in the CETP [1].

22.3 FINANCIAL ASPECTS

It is a common observation that the unit cost of treatment becomes very high if the waste water flow is small [1]. Similarly, a group of heterogeneous industries will produce an effluent with varying quality; hence it becomes costlier to treat than if the group consists of homogenous industries. Topographic conditions also play an important part in arriving at the cost of treatment as well as the method of collecting and conveying waste water from member industries.

After a detailed study of 40 CETPs, Kantawala et al. [1] made the following recommendations:

1. A detailed techno-economic study of conveyance of waste waters is necessary, as it accounts for a large part of capital cost.

2. Optimization of pretreatment by individual industries is essential.
3. Phasewise development of a CETP should be seriously considered, but the quality of the treated effluent must meet the standards laid down by the pollution control authorities.
4. Upgradation of the CETP should also be kept in mind in view of the possibility of increased flows, stronger wastes, stricter standards of treated effluent, etc.
5. In-plant pollution control should be encouraged by the Central and State Pollution Control Boards and Ministry of Environment and Forests.
6. Common effluent treatment plants should be converted into combined effluent treatment plants with obvious advantages as mentioned earlier.

The status of CETPs studied is presented in Table 22.1.

Table 22.1 Status of CETPs (upto April 1999) [1]

State	Commissioned	Completed	In progress	Statewise total
Andhra Pradesh	3	–	–	3
Gujarat	5	–	–	5
Haryana	1	–	–	1
Karnataka	2	1	–	3
Madhya Pradesh	1	–	2	3
Maharashtra	3	–	3	6
Rajasthan	2	–	–	2
Tamil Nadu	9	8	13	30
Uttar Pradesh	2	–	–	2
Delhi	–	–	15	15
Total	28	9	33	70

Deshpande and Sen [2] have suggested, besides the usual factors to be considered in the design of a CETP, the classification of wastes as: (a) those amenable to biological treatment; (b) those which can be biologically treated after acclimatization, (c) those which need pretreatment, and (d) those which contain non-biodegradable and toxic pollutants.

They also suggest the three following approaches for the process design of CETP:

1. *Modular approach*, which takes into account changes in the volume of waste water as the industrial estate develops.
2. *Upgradability approach*, wherein the present form of treatment would need upgradation on account of increased flows, stronger wastes, stringent effluent standards and increased possibility of recovery of valuable material from the waste water.
3. *Service centre approach*, which should provide a workshop, garage, library, instrumentation facility and a conference hall.

The CETP at Sarigam, under Gujarat Industrial Development Corporation (GIDC) was studied by these authors. It serves four zones, divided according to activities, viz. zone 1—mechanical and water intensive; zone 2—chemical; zone 3—housing and plastics; and zone 4—mechanical. Total flow 14,200 m^3/day. Treated effluent was proposed to be reused in the estate, used for horticulture, or given to surrounding farmland during dry season. Prabhu [3] presented a case study of a CETP whose development was done in phases. In phase 1, an equalization-cum neutralization (ECN) tank and aerated lagoon was provided. In phase 2, chemical coagulation, settling and sludge handling was introduced between ECN tank and aerated lagoon. In phase 3, an additional intermediate clarifier, second stage aeration tank and secondary clarifier were added. Sewage from nearby residential colony was added at this stage to the industrial waste to dilute high total dissolved solids (TDS) in the waste water and to seed the mixture with microorganisms. In phase 4, dissolved air flotation (DAF) was added downstream of clariflocculator. In addition, sludge thickening and centrifugation were provided. The treated effluent was discharged to the municipal sewer.

A heterogeneous group of industries, numbering 348, including units doing rolling and pickling, textile processing, plating and anodizing, soap making, rubber, plastic goods and candle making was established at Wazirpur industrial area by Delhi Development Authority. The need for a CETP was felt, because the effluents damaged the sewerage system, and air pollution due to the industries had an adverse effect on the health of the workers. Characteristics of the combined waste water were as shown in Table 22.2.

Table 22.2 Combined Waste Water Quality [4]

Parameter	Concentration
pH	3.39–6.85
Turbidity, NTU	65–600
Total suspended solids	404–1573
BOD	72–112
COD	248–900
Nickel	6.02–33.66
Total chromium	6.5–27.33
Iron	117.90–188.63
Cadmium	0.02–0.056
Zinc	1.925–2.5
Copper	1.2–2.45
Cyanide	0.6–0.9

Note: All values except pH are in mg/l.

The waste water was acidic in nature and contained heavy metals. The treatment proposed was, therefore, equalization, neutralization with lime and settling in a clariflocculator. The settled sludge would be stored in a lagoon, while the clarified effluent would be discharged into municipal sewer. Construction, operation and maintenance of the CETP would be the responsibility of Municipal Corporation of Delhi, while the cost of operation and maintenance would be met by the industries.

Another heterogeneous group of industries in a chemical complex was described by Rajagopalan et al. [5]. The industrial complex consisted of a fertilizer unit, a calcium carbide (CaC_2) unit, caustic soda plant, a PVC unit, a cement plant, thermal power station, a water treatment plant and a demineralization plant. Each of these units had its own waste water treatment plant. The authors have described them briefly and have suggested steps to improve their performance.

Rao, Venkayya and Rambabu [6] have described the problems of managing a heterogeneous CETP with bulk drug manufacture as the main contributor of waste water (65%), followed by dye intermediate manufacture (20%) and the rest (15%) miscellaneous products. The CETP received slug flows of waste water, mainly because of batch production by the drug manufacturers. There were wide variations in pH (1.0–10.0), TDS (20–350 gm/l) of which 70% were inorganic, COD (3–95 gm/l). The BOD:COD ratio varied from 0.1 to 0.8. It was, therefore, necessary to segregate high TDS effluents and give them pretreatment. Inorganic TDS in biological treatment could not be tolerated beyond 2.5%. Anaerobic treatment was totally unsuccessful. Even aerobic treatment was possible only after segregating high TDS streams. Since bulk drug making was the main contributor, a screening test to establish toxic/inhibitory nature of a waste stream was devised, based on the oxygen uptake rate. It was interesting to see that Gentamycin, a bulk drug, increased oxygen uptake rate, while Paracetamol decreased it. This was used as a basis for the screening test.

It was also proposed to add about 300 m^3/day of domestic sewage from surrounding areas to the total effluent in order to dilute the TDS and provide continuous seeding of microorganisms. The CETP had a treatment plant consisting of equalization-cum-neutralization, flash mixing, clariflocculation, aerated lagoon, intermediate clarifier and activated sludge process. The treated effluent was discharged into a sewer. The authors suggested improvements to the existing plant, viz. increasing the holding capacity of the ECN tank to five days and converting aerated lagoon to activated sludge process. The treated effluent could then be connected to the sewerage system. The sludge generated would be incinerated using auxiliary fuel.

Rajamani et al. [7] have described a homogeneous CETP for a cluster of 14 tanneries in Bangalore. It consists of a 150 m^3 holding tank, grit chamber, an equalization tank of 100 m^3 capacity, with floating aerators for mixing lime, primary clarifier, acid dosing, activated sludge process with nutrient supplementation, floating aerators for aeration and mixing, and sludge drying beds. Daily flow treated was 1000 m^3. The treated effluent was discharged into Bangalore Water Supply and Sewerage Board's (BWSSB) drainage system, carrying a sewage flow of more than 20,000 m^3/day. In order to minimize the problem of sludge disposal, it was proposed to provide chromium recovery and reuse the plant in the tanneries practising chrome tanning.

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INDEX

Industrial Waste Water Treatment

A.D. Patwardhan

All industrial production processes generate waste waters, which can pollute water bodies into which they are discharged without adequate treatment. It is, therefore, essential to treat such wastes and eliminate their harmful effects on the environment.

This book discusses sources, characteristics and treatment of waste waters produced in industries such as textiles, dairy, tanneries, pulp and paper, fertilizer, pesticide, organic and inorganic chemicals, engineering and fermentation. Many flow diagrams have been included to illustrate industrial processes and to indicate the sources of waste water in such processes. After describing treatment for individual factories, the author discusses the more advanced and economical common effluent plants. The text uses simple and straightforward language and makes the presentation attractive.

This book should prove extremely useful to undergraduate students of civil and chemical engineering and postgraduate students of environmental science and engineering. Industrial design consultants will also find the book very handy. To the Greens, it may offer some of the solutions to their concerns.

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