CHAPTER 21

MANUFACTURE OF ORGANIC CHEMICALS

CHARACTERISTICS OF THE WASTE WATER

This branch of the chemical industry produces a wide range of organic chemicals, and consequently analysis and data of the waste water from the industry show a similar variety. It is obviously very difficult to give some general facts about the composition of waste water from the manufacture of organic chemicals.

Water is used for cooling, for transportation of wastes, as a solvent and as a raw material.

Examination of the following parameters should give a general picture of the waste water:

1. The temperature of the waste water is important, as it might cause thermal pollution and change the ecological balance of the species in the ecosystem.
2. The aggressiveness of the waste water is important, if it is to be discharged into the sewer system. The waste water must be neutralized before discharge under all circumstances.
3. On the basis of the BOD_5 of the waste water it is possible to determine whether the waste water can be discharged into the municipal waste water treatment plant or into the receiving water, or whether the water must first be treated biologically before it is discharged.
4. The BOD_5/COD ratio gives the ratio between biodegradable and non-biodegradable material. A small value indicates that the waste water contains refractory material and a biological treatment method is in this case not attractive. The waste water might even contain toxic compounds.
5. The TOC (total organic carbon) expresses the total concentration of organic compounds. Complete oxidation by dichromate sometimes do not take place, in which case the TOC gives a better picture.
6. The concentration of suspended matter gives an indication of what can be achieved by direct settling.
7. The alkalinity and acidity determine how much acid or base must be used for neutralization.

8. If toxic compounds are present it is necessary to control their concentration carefully. Toxic compounds can harm the fauna and flora of the receiving water or inhibit the biological treatment.
9. From an aesthetical point of view it is important to record the odour and colour of the waste water.
10. The presence of phenols and other organic compounds are detrimental to the taste of fish, even in concentrations substantially lower than the toxicity limits.
11. If the waste water contains nutrients it might be necessary to remove at least phosphorus or nitrogen to be able to control the eutrofication in the receiving water. Furthermore, the biological treatment processes can be affected if the BOD_5:N:P ratio is significantly different from 100:15:1.
12. The quantity of waste water is of great importance since it is the concentration of the different compounds in the receiving water or in the total municipal waste water which is critical.

The number of organic chemicals produced is increasing rapidly and the toxicity limits for fish, biological treatment plants, etc. are far from being known for all the chemicals manufactured. If the industrial waste water is discharged into the municipal sewage it is necessary to test whether it will affect the biological treatment plant. The industrial waste water is diluted with different quantities of domestic sewage and it should be determined, which ratio will affect the biological oxidation.

<u>Survey of the organic chemical industry</u>

It is difficult to make a survey of all the types of waste water being discharged from this industry (Trobisch, 1969)

However, it is possible to make a classification on the basis of the raw materials and the chemical composition of the products:

1. Production of organic softeners: phthalic acid, maleic acid.
2. Production of raw materials for the plastics industry, which involves the production of monomeric compounds such as butadiene, styrene, ethene, propene, acrylonitrile, isocyanate, acrylates, methyl acrylates, ethylene oxide, phthalic acid derivatives, and others.
3. Production of raw materials for the dye industry: aniline, nitrobenzene, azo dyes, etc.
4. Production of insecticides: organic phosphates, parathion compounds, chlorine compounds.

5. Production of alcohols: methanol, ethanol, propanol, isopropanol, etc.
6. Production of glycols: polyvalent alcohols.
7. Production of raw materials for the pharmaceutical industry: a wide range of organic compounds.
8. Production of organic acids.
9. Production of additives to oils.
10. Production of ketones and aldehydes.
11. Production of organic solvents: esters (propyl acetates, butyl acetates) and chlorine compounds such as dichloroethene, dichloromethane, etc.

Table 21.1 gives a characteristic analysis of waste water coming from the manufacture of organic chemicals. Due to the great possibility for variation, the data can only be taken as a characteristic example and not as general figures valid for all the industry.

TABLE 21.1

Characteristic analysis of waste water from the production of organic chemicals

Product	BOD_5 (mg/l)	COD (mg/l)	Suspended matter (mg/l)
Phthalic acid anhydride and maleic acid anhydride	-	150-300	20-50
Methyl acrylate acid	-	7000-12000	6000-12000
Butadiene and styrene	4000-8000	800-1500	200-500
Acrylates	1000-2000	2000-3200	50-100
Ethylene and propylene	400-600	800-1200	20-40
Isocyanates	300-600	900-1600	40-75
Methyl and ethyl-parathion	2000-3500	4000-6000	50-100
Acrylic nitrile	200-500	600-1200	80-150
Raw materials for the pigment industry	200-400	1000-2000	80-200
Esters	5000-12000	10000-20000	20-100
Acetaldehyde	15000-25000	40000-60000	150-300
Organic acids	300-600	5000-15000	100-200
Ketones	10000-20000	20000-40000	50-100
Organic phosphate compounds	500-1000	1500-3000	200-400

Biological treatment

Decision of whether a biological treatment is possible or not is based on the composition of the waste water (Gloyna et al., 1967).

It might in some cases be possible to treat the waste water by a separate biological method. The waste water will harm the municipal treatment plant (Bauer et al., 1968) as the biological culture must be adapted to the composition of the waste water (Bock et al., 1968). It is possible, for instance, to treat waste water containing 10-30 mg/l phenol biologically; however, the municipal biological treatment plant will still be affected by this concentration of phenols. It is therefore important in all circumstances to distribute the waste water discharge over as long a time period as possible.

Table 21.2 gives a survey of biodegradable and non-biodegradable organic compounds (Ludsack et al., 1960). On the basis of this it is possible to obtain a first impression of whether the biological treatment process is possible or not.

TABLE 21.2

Survey of biodegradable and non-biodegradable organic compounds

Biodegradable organic compounds	Non-biodegradable organic compounds
Aliphatic acids	Ethers
Aliphatic alcohols	Ethylene chlorine hydrine
Aliphatic primary and secondary alcohols	Isoprene
Aliphatic aldehydes	Butadiene
Aliphatic esters	Methylvinyl ketone
Alkylbenzene sulphonates	Naphthalene
Amines	Various polymeric compounds
Mono- and dichlorophenols	Polypropylene benzene sulphonates
Glycols	Certain carbon hydrides, especially of aromatic structures, including alkyl-aryl compounds
Ketones	
Nitriles	Tertiary benzene sulphonate
Phenols	Tri-, tetra- and pentachlorophenols
Styrene	
Phenyl acetate	-

Some general rules can be stated (Popescu et al., 1970):

1. High molecular weight compounds are generally more difficult to oxidize biologically than smaller molecules.
2. The concentration of a wide number of organic compounds is important. Biological oxidation is more difficult, the higher the concentration.
3. Aliphatic compounds are usually more easy to treat biologically than aromatic compounds.
4. Unsaturated compounds are generally more easily oxidized biologically than saturated compounds.
5. Tertiary carbon atoms are generally not possible to oxidize biologically.
6. Substitution or addition of functional groups will reduce the possibility for biological treatment.

Table 21.3 gives information about biological treatment of a wide range of organic chemicals.

A study of the partition characteristics of trichloroethylene--bearing waste has demonstrated that considerable sorption of trichloroethylene onto sludge solids takes place.

The maximum quantity of TCE that can be adsorbed onto the sludge solid is 3000 mg TCE/kg of solid, but this concentration will cause difficulties in the anaerobic digestion system. However, air stripping has been shown to be a feasible method for the removal of TCE, eliminating the probability of TCE causing problems in activated sludge systems.

Cresols in aqueous solutions may be destroyed by photo-oxidation, a process that uses visible light as a direct energy source. Dye-sensitized aerobic photo-oxidation as a waste water treatment process may successfully employ the conventional engineering method of biological treatment methods.

Methylene blue is an effective sensitizer for the photo-oxidation of cresols and will probably sensitize the photo-oxidation of other refractory molecules as well. There is an optimum concentration of dye in an aerobic dye-sensitized photo-oxidation system. For cresol solutions of 10-300 mg/l this concentration is 5-10 mg/l. A first-order reaction describes with reasonable accuracy the rate at which cresols are photo-oxidized, but the reaction mechanisms is probably not a simple first-order one. The photolysis of cresol occurs as much as 2.8 times faster in an aerobic system than in anaerobic conditions.

TABLE 21.3

Data from the biological treatment of waste water containing organic chemicals

Products	BOD_5 inflow (mg/l)	Efficiency of BOD_5 removal (%)	Flow (m^3/24h)
a) Activated sludge plant			
Phthalic acid anhydride, Phenylsalicylic acid	45	87	30000
Butadiene, Maleic acid	2000	98.8	8000
Ethylene, Propylene, Benzene	600	85	6000
Napthalene, Butadiene	6000	85	1800
Aniline, 2,4-dinitrobenzene, Phenols, etc.	370	76	3800
Acetone, Phenols, p-Cresol	4000	80	800
Ethylene, Propylene oxide	1950	99	600
b) Oxidation ponds			
Butadiene	225	55	75000
Detergents, Alkylates	345	80	10000
Cyclohexane, p-Xylene, Benzene	100	75	2000
Chemicals from lubrication	465	61	800
c) Trickling filters			
Phenols, Salicylic acid, Phthalic acid anhydride	190	70	10000
Softeners, Amines Enzymes	1960	98	4000
Ethylene, Propylene, Butadiene, Benzene, Polyethylene	170	50	2400
Aliphatic acids, Esters, Alcohols, Amines	2000	80	3200
Ethylene, Propylene, Butadiene, Benzene, Phenolacrylonitrile	1300	65	1600

Other treatment methods

Since the composition of waste water from the organic chemicals industry varies considerably, it is often necessary to combine two or more treatment methods to get sufficient purification.

Apart from biological treatment the following methods might come into consideration:

1. Separators for the removal of oil (see also chapter 12).
2. Flocculation. With flocculation it is possible to remove a wide range of organic colloids.
3. Extraction. This method is generally rather costly, but recovery of chemicals will often justify the high cost. The method is mostly used when high concentrations are present in the waste water.
4. Flotation is of special interest when impurities with a specific gravity of less than 1 are present in the waste water.
5. Adsorption. A wide range of organic compounds such as insecticides and dyestuffs can be adsorbed by activated carbon.
6. Sedimentation is only used in conjunction with removal of suspended matters or in combination with a chemical precipitation or flocculation and biological treatment.
7. Oxidation and reduction are mainly used for the treatment of cyanides and chromate.
8. Distillation of waste water is used when the recovery of solvents is possible or when other methods are not available; for the treatment of radioactive waste water, for example.
9. Organic acids and bases can be removed by ion exchange.
10. Filtration can be used for the removal of suspended matter from small quantities of waste water.
11. Neutralization. It is under all circumstances necessary to discharge the waste water with a pH between 6 and 8. Calcium hydroxide, sulphuric acid and carbon dioxide are used for the neutralization process.

Fig. 21.1 shows the solution for treatment of waste water from the organic chemicals industry which produces a wide range of organic compounds.

As seen on the flow-sheet, biological treatment is only used for waste water which does not contain refractory compounds. Waste water containing refractory material must be pretreated by flocculation followed by flotation before the biological treatment. Furthermore, neutralization of this waste water must take place before the biological treatment process.

The cooling water is separated from the waste water and 90% recirculation is achieved.

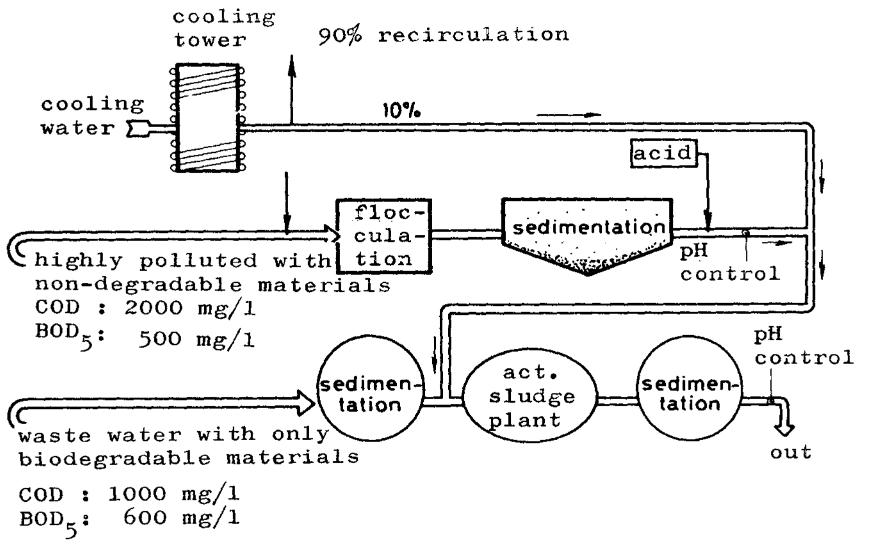

Fig. 21.1. Treatment of waste water from the organic chemicals industry producing a wide range of organic compounds.

Chemical oxidation

Many organic compounds are refractory and cannot be treated biologically, although in many cases chemical oxidation is possible.

Generally, compounds containing OH, NH_2 and azo groups (N:N) can be oxidized chemically, while it is more difficult for compounds with NO_2, COOH and SO_3H groups.

Table 21.4 surveys the possibility of oxidizing various compounds chemically and biologically. The results are based on laboratory experiments. Chemical oxidation took place with chlorine at 70°C and pH 4.0. The reaction time was 30 minutes. 133-250% of the theoretical chlorine amount was used. The starting concentration of the components was 1000 mg/l.

Biological oxidation took place at 20°C. 1 ml of 1% sodium nitrite to 300 ml solution and a phosphate buffer of pH 7.2 were added. 15-30 mg of the chemicals under investigation and 50 mg of activated sludge were used. The biological oxidation was allowed to continue until the carbon dioxide production ceased.

TABLE 21.4

Efficiency of chemical and biological oxidation

Components	Functional groups	Efficiency of chemical oxidation (% COD)	Efficiency of biological oxidation (% BOD_5)
Phenol	OH	92.3	90.5
2-chlorophenol	OH, Cl	78	91.5
Pyrocathecole	OH	91.5	39.8
Aniline	NH_2	83.8	90
Benzene acid	COOH	92	
2-aminophenol	OH, NH_2	86	54,7
4-aminophenol	OH, NH_2	78.8	46.1
2-nitrophenol	OH, NO_2	78.8	46.1
3-nitrophenol	OH, NO_2	90.1	60
4-nitrophenol	OH, NO_2	77.8	25.7
Sodiumbenzene sulphate	SO_3Na		74.6
Sulfanil acid	NH_2, SO_3H	80	86.8
Phenol-4-sulphonic acid	$OHSO_3H$	89.6	27.1
1-naphtol	OH	46.2	
1-naphtylamine	NH_2	70.5	
1-naphthalene sulphonic acid	SO_3H	41.8	60.7
2-naphthalene sulphonic acid	SO_3H	23.8	86.8

All monosubstituted benzenes and naphthalenes with OH, NH_2, SO_3H and COOH groups are easily bio-oxidized. The disubstituted benzenes and naphthalenes are more difficult to decompose, and will depend on which two groups these aromatic compounds contain. Benzene and naphthalene substituted by three or more groups are not possible to bio-oxidize. Often the waste water from this industry contains a wide variety of organic compounds that it is necessary to combine the chemical and biological oxidations. It is then possible in most cases to achieve a reasonable efficiency of COD and BOD_5 removal (80-90% reduction is often obtained).

Fig. 21.2 gives an idea of the BOD_5 and COD values met with in this industry. The cumulated frequency is shown.

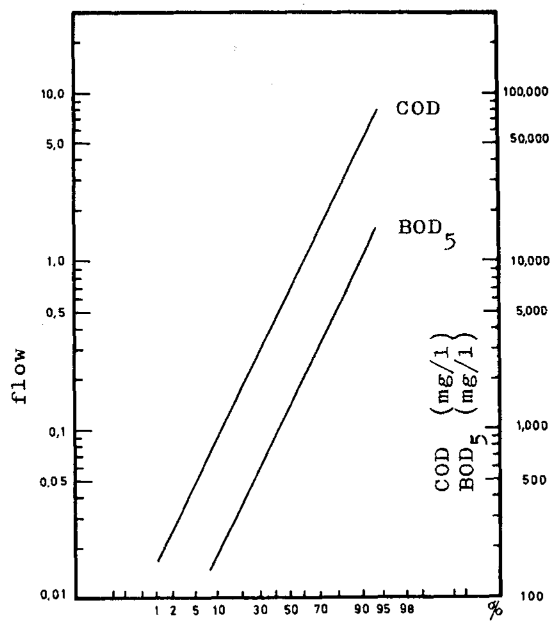

Fig. 21.2. BOD_5, COD and flow is plotted versus cumulative frequency.

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