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WASTE WATER TREATMENT TECHNOLOGIES AND RECENT ANALYTICAL DEVELOPMENTS

Edited by **Fernando Sebastian García
Einschlag** and **Luciano Carlos**

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Waste Water - Treatment Technologies and Recent Analytical Developments

<http://dx.doi.org/10.5772/3443>

Edited by Fernando Sebastian García Einschlag and Luciano Carlos

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Published by InTech

Janeza Trdine 9, 51000 Rijeka, Croatia

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Publishing Process Manager Iva Lipovic

Technical Editor InTech DTP team

Cover InTech Design team

First published January, 2013

Printed in Croatia

A free online edition of this book is available at www.intechopen.com

Additional hard copies can be obtained from orders@intechopen.com

Waste Water - Treatment Technologies and Recent Analytical Developments, Edited by Fernando Sebastian García Einschlag and Luciano Carlos

p. cm.

ISBN 978-953-51-0882-5

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Preface

The generation of wastes as a result of human activities has been continuously speeding up since the beginning of the industrial revolution. Waste water is very often discharged to fresh waters and results in changing ecological performance and biological diversity of these systems. Consequently, the environmental impact of foreign chemicals on water ecosystems and the associated long-term effects are of major international concern. This makes both waste water treatment and water quality monitoring very important issues.

The main sources of waste water can be classified as municipal, industrial and agricultural. Depending on the nature of the waste water, effluents may have high contents of harmful organic compounds, heavy metals and hazardous biological materials. Heavy metals are released during mining and mineral processing as well as from several industrial waste water streams. On the other hand, large quantities of organic pollutants such as polychlorinated biphenyls, organochlorine pesticides, polycyclic aromatic hydrocarbons, polychlorinated dibenzo-p-dioxins and dibenzofurans have been released to the environment especially during the last 50 years. Furthermore, relatively new organic substances, namely pharmaceuticals, cosmetics and endocrine disrupting chemicals, have been found in natural waters close to urban sites in the last 15 years and are now viewed as emerging contaminants. Finally, raw sewage can carry a number of pathogens including bacteria, viruses, parasites, and fungi.

The book offers an interdisciplinary collection of topics concerning waste water treatment technologies and the evaluation of waste water impact on natural environments. The chapters were invited by the publisher and the authors are responsible for their statements. The book is divided into two sections: the chapters grouped in the first section are mainly concerned with management and remediation technologies, while the chapters grouped in the second section are mainly focused on analytical techniques and the evaluation of environmental impact. The first section covers basic knowledge concerning the most frequently used waste water treatment technologies. The suitability of different techniques according to the nature of the effluent to be treated is discussed taking into account advantages and drawbacks. The chapters grouped in the second section of the book cover several aspects of modern techniques for the analysis of trace pollutants. Monitoring of water quality is required to assess the effects of pollution sources on aquatic ecosystems. Sensitive and selective techniques, often necessary for the evaluation of the effects of waste water streams on natural waters, are comprehensively overviewed.

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We hope that this publication will be helpful for graduate students, environmental professionals and researchers of various disciplines related to waste water. We would like to acknowledge the authors, who are from different countries, for their contributions to the book. We wish to offer special thanks to the Publishing Process Managers for their important help throughout the publishing process.

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Management and Remediation Technologies

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Waste Water Management Systems

Jelenka Savković-Stevanović

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51741>

1. Introduction

As mankind eventually adopted a more settled, non-nomadic way of life, people become increasingly involved in the technical aspects of water. To a large extent, the primary concerns in the beginning were utilization and improvement of existing water resources, together with protection against the hazards and potential harm associated with uncontrolled natural water. It was only toward the end of the nineteenth century that wastewater become an issue in science, technology, and legislation, specifically, its production and treatment, in terms of both municipal and industrial sources [1]-[5].

As early as 4500 years ago the first prerequisites were met for urban and agricultural water management. This encompassed irrigation and drainage systems, canals, and sewage facilities. Even so, the treatment of waste water in formal waste treatment plants by means of the microbial degradation of wastewater components was reported for the first time 1892. It was municipal wastewater, including that from artisans, craftsman, and small factories, typical for larger cities of that time. Much earlier, in Greco- Roman times extensive facilities were erected and maintained for supplying drinking water to cities. Waste water in those days presented no major problems, and sewage systems were regarded less as a means of collecting water for reuse than as way of draining off potential sources of hazard and preventing pollution of the streets, with the attendant risk of a spread of vermin and epidemics.

Development of the organized utilization of water as an essential resource for human beings, animals, and plants led to further technical strides, such as dams against flooding or for storage purposes, waterways designed for transport, and harbors on the sea coast and along inland waterways. Problems of wastewater arose gradually during the same period in conjunction with the increase in urban population as the natural self purification capacity of surfaces waters proved no longer able to keep pace with development. Risks related to groundwater contamination are associated not only with emissions in the form of wastewa-

ter, the ground -air cycle plays a role as well via atmospheric deposition. The state of a particular body of water can be described by a set of code numbers, but the core of the problem is in fact a sum of all the processes leading to the observed state. In this case, the essential element is the kinetics of two opposing processes the rate of pollution, and the rate of cleansing. Each of these is in turn a combination of natural and anthropogenic phenomena applicable to the site in question. Most of the problems are derived not from absolute numbers, but rather from population densities, production densities, or productivities, in the various urban centers of the industrialized world, all of which actually have access to an adequate supply of natural water.

In the terminology of water economics, consumption of water refers to a loss of quantity, not a decrease in quality. In this sense, consumption represents that part of the water supply that is lost in the course of use, primarily through evaporation. This fraction of the water is permanently withdrawn, at least from the local water cycles, and is thus no longer available for further utilization, so it must be replenished with water from precipitation, springs, or wells.

As industrialization proceeded, two unique characteristics of water acquired rapidly increasing importance, its high specific heat capacity, and its rather high solvent power with respect to many inorganic and some organic substances. The consequences of these factors in the context of the production and disposal of wastewater are quite different, however. Water that is intended to serve as a heat reservoir, cooling agent, steam source, must be cleaned before use in order to prevent corrosion and erosion in turbines and heat exchangers, and it is subsequently returned to the environment in a purified state, albeit at a higher temperature. On the other hand, water in its function as a reaction medium, or even a reaction partner, has now developed into the most significant source of wastewater in industry. Entire branches of manufacturing are based on production processes carried out in the aqueous phase, where water is used as a solvent, dispersing agent, transport medium, and reagent. This is perhaps most evident in the case of breweries, in sugar, paper, and pulp factories, in dye works, tanneries, and the like where the real problem is one not only of the actual content of the wastewater, but also its quantity [6].

Water is drawn by industry from many different sources. It may be taken directly from a river, a lake, a well, or from a privately impounded supply, or it may be obtained from a neighboring municipality. Both the amount drawn by the industry and the degree of treatment accorded the water so withdrawn varies widely from industry to industry and from plant to plant. The quality of treatment may vary considerably within a given plant depending upon the particular uses to which the water is put. The amounts of water withdrawn by various industries for different uses, and the quality of water that have been used by different industries before being subjected to various degree of treatment are varied.

Water has been used in abundant quantities by chemical, petrochemical, petroleum refining and other process industries. However, in recent years, the increased cost of wastewater treatment to meet environmental requirements and the scarcity of less expensive industrial water have provided process industries with strong incentive to minimize the amount of water consumption and wastewater discharge. The major concern is to emphasize the im-

portance of water reuse and a number of effort have been made towards achieving the goal of extensive water reuse in various process industries [3].

There have been presented many ideas for wastewater recovery and reuse in the in industries[5]-[9]. These paper have exclusively described wastewater treating systems for the realization of zero discharge. As for the optimal design methods for wastewater treating systems, several attempts have also been made by using system approaches. Much information on the optimization studies on process units for waste water treatment can be acquired from this survey [10]-[50]. In addition, a method of utilizing the system structure variables is considered to be useful to eliminate difficulties due to combinatorial problems. The studies presented so far, however, only cover wastewater treating systems. The amount of wastewater was given beforehand and its reduction was not taken into consideration. As far as the authors know, the optimal design problem including water reuse for the total system consisting of water-using system and wastewater -treating system has not yet been solved.

2. Basic principle

In the last decade, a number of studies, on wastewater reuse or optimal designs of waste water treating systems have been presented. Though those studies have received much attention, they have been carried out exclusively on wastewater treating systems without paying attention to water using systems. However, the authors extensive survey on the present status of water use in a industry has shown that there is enough room to reduce a large amount of both fresh water and wastewater. The reduction can be accomplished by optimizing water allocation in a total system consisting of water using units and wastewater treating units. The problem of maximizing water reuse can be considered as a problem of optimizing water allocation in a total system. Furthermore, the problem of determining a system structure is defined as a parameter optimization problem by employing structure variables. Due to the approach, the difficulties associated with combinatorial problems are resolved.

For the year 2000, a global balance of quantities and fluxes shows an overall water supply of 2500 km³ and water demand 6000 km³, representing 24% of the directly usable supply [6]. When this allocated among the major consumers and account is taken of the corresponding levels of specific water consumption (evaporation), several trends with regard to quantities and types of wastewater are discernible. (Table 1)

Consumption category	Percentage of total demand (6000 km ³)	Consumption (evaporation) as a percentage of demand
Domestic	8	20-30
Industry	29	15-20
Agriculture	59	75
Storage losses	4	100

Table 1. Types of wastewater.

Water circulation through the atmosphere contains 13000 km^3 , ca. 0.02% of the overall liquid, global water reserve of $1.3 \times 10^9 \text{ km}^3$. The annual quantity subject to evaporation, which is equal to the annual amount of precipitation, is estimated at 475000 km^3 . This corresponds to a 35-fold annual turnover of the atmospheric content, which means water exchange between the atmosphere and the surface of the earth is complete every 9.5 days. In some cases local circumstances lead to considerable deviations from these global values.

Waste water treatment becomes especially important in times of water scarcity. This is particularly true when agriculture, domestic water needs, and industry find themselves in vigorous competition. the greatest increase by far is anticipated for agriculture assuming for the year 2000 a world population $6\text{--}6.5 \times 10^9$ (Fig.1).

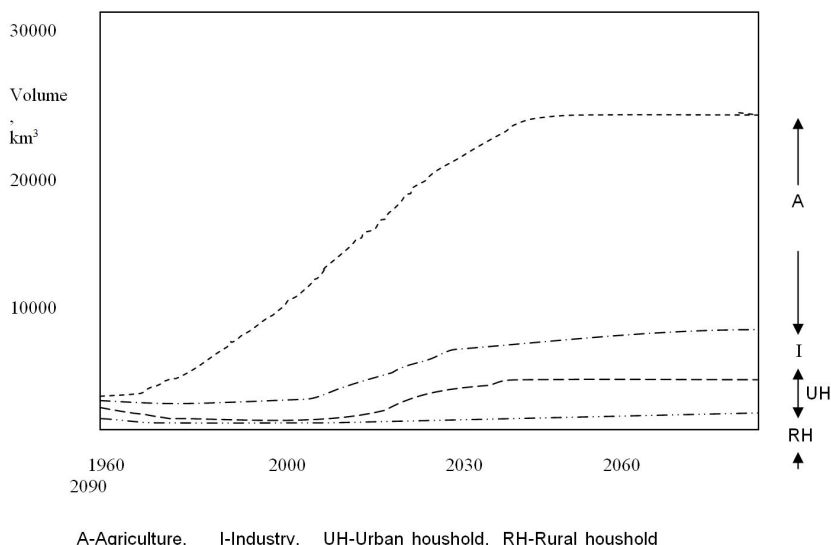


Figure 1. The increasing worldwide demand for water.

Water as regarded as chief raw material problem of the future, elevating wastewater treatment to the status of a recycling technology. This involves substance protection in the sense of sustainable development, together with the maintenance of an adequate supply of drinking water, an emphasis that goes beyond the earlier concern directed almost exclusively toward environmental protection, especially the protection of natural waters.

Each of the processes described below has its place in the broad spectrum of technical possibilities. The question of what is the best process should thus be replaced by a search for the most suitable process in a particular circumstance, taking fully into account the nature of certain definable problem cases. Modern technological development of wastewater treatment has occurred largely in and with the aid of the chemical industry. However, the waste water problem and its treatment is of interest not only to this particular aspect of industrialized society. Numerous other branches, often to an even greater extent (Fig.2).

There is no shortage today of diverse international experience in the construction and operation of waste- treatment plants. In fact, in some places this has developed into its own separate branch of process engineering. It is still worth noting with respect to terminology, however, that some of the reasoning applied to wastewater concepts and standards of evaluation has been borrowed from neighboring disciplines, especially biology.

3. Industrial water treating systems

The authors have carried out an expensive study on the present status of water use in a typical industry. As the result it has been shown that there enough room to reduce a large amount of wastewater by maximizing water reuse and waste water recovery. Further increases in the efficiency of water use can be expected by the change of process conditions. In solving such large complex problems, it has been found more methods.

Water is drawn by industry from many different sources. It may be taken directly from a river, a lake a well, or from a privately impounded apply, or it may be obtained from a neighboring municipality. Both the amount drawn by the industry and the degree of treatment accorded the water so withdrawn varies widely from industry to industry and from plant to plant [10]-[36]. The quality of treatment may vary considerably within a given plant depending upon the particular uses to which the water is put. Table 2 shows the amounts of water withdrawn by various industries for different uses[37]-[40].

In the chemical industry, economic factors usually dictate the inclusion of a wastewater separation system. Thus, wastewater that is not in need of treatment, clean water, especially cooling water, is separated from that which does require treatment. Clean water can be discharged directly into the receiving stream. If the wastewater requiring treatment fails to meet the quality specifications for biological waste treatment it must first be subjected to decentralized chemical-physical pretreatment, after which it can be fed into the central wastewater treatment plant for purification as shown in Fig.2.

Specific wastewater loads can be reduced or even avoided through measures of the type recommended in conjunction with process integrated environmental protection.

The entire wastewater regime is also reflected in the approach taken to wastewater decision making. For each type of wastewater, all the following questions must be rigorously addressed to ensure consistent and disposal (Fig.3).

Can be amount and contamination level of the waste water be reduced or even eliminated by process integrated means?

Does all the wastewater in question in fact require treatment?

Is the waste water suitable in its present form for biological treatment, or should it be subjected to decentralized pretreatment?

These considerations apply, for companies that have their own central wastewater treatment plants, and indirect discharge, for companies that dispose of their wastewater via a public wastewater facility.

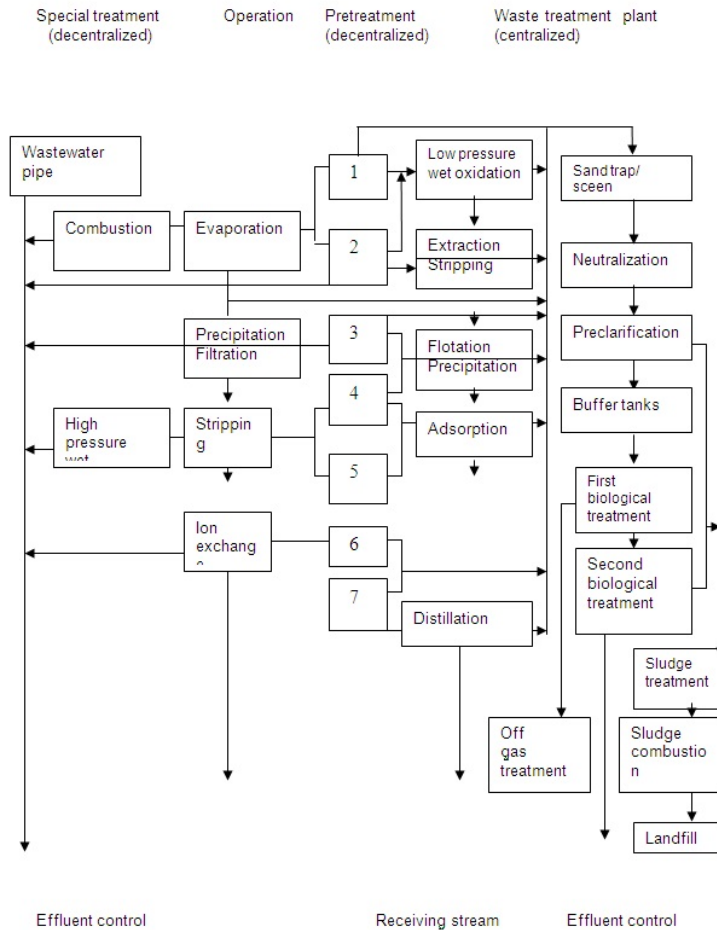


Figure 2. Decentralized and centralized aspects of waste water treatment.

Suspended solids removal, particularly of the coarser materials from 5μ up, such as sand and heavy silt may be removed in sedimentation basins. Such basins usually serve a dual purpose, preliminary removal of suspended solids, and storage to balance variations in supply with the relatively constant demand of the plant processes. In these basins, detention time is measured in days, the amount depending upon the likelihood of interruption or reduction in the supply. A 30th-day detention is not uncommon in some circumstances. Particles smaller than 1μ are generally not affected by the detention. The effect of continued aeration and sunlight in oxidizing organic peptizing substances may cause a certain amount

of flocculation. Algal growth, particularly of the free floating type, occurs in warmer climates and may indeed contribute to the total turbidity emerging from the basin. Control of algal growth is usually accomplished by the addition of copper sulfate sprayed in aqueous solution on the water surface from a boat or spread by solution from solid material in burlap bags towed behind power boats that traverse the surface of the reservoir in a pattern. In the warmer climates, addition of copper sulfate every several months in the amount of one ppm, based on the top one foot of water, may be employed. In some exceptional circumstances in very arid regions with short water supply, evaporation control may be practiced by the addition of fatty alcohols which form a monolayer on the surface.

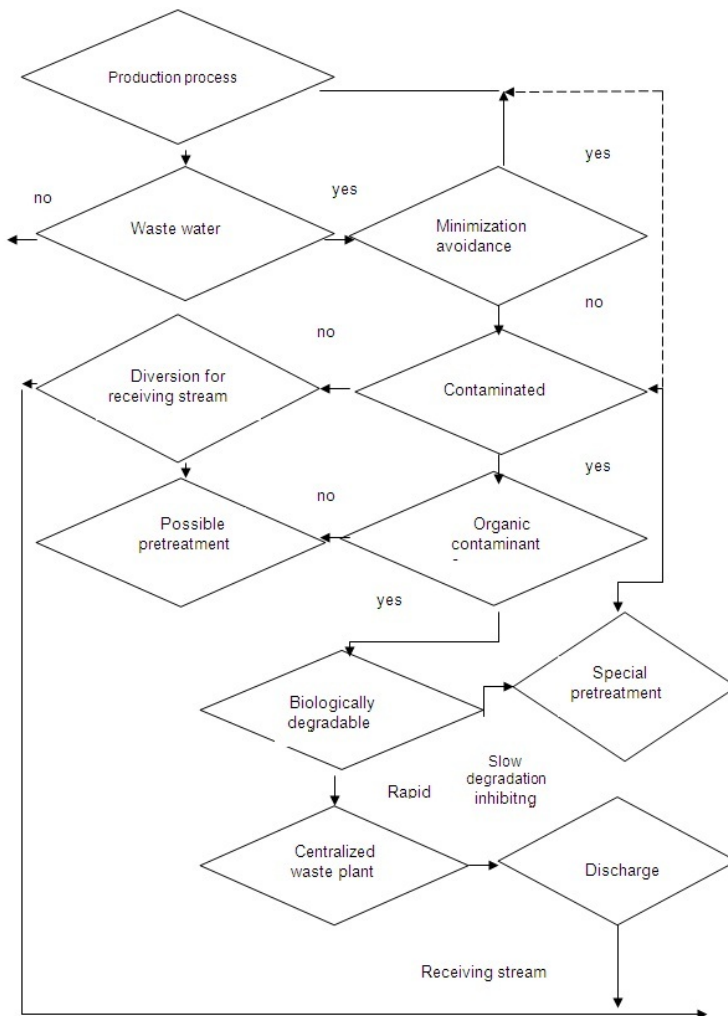


Figure 3. Decision diagram dealing with for waste water formation, avoidance, separation and treatment.

The degree of clarification applied to the water from the source of supply is governed both the intended use of the water and by the level of turbidity that is to be removed. Two processes, singly or in combination, are generally employed for clarification. The first of these is filtration where turbidities are generally less than 50 ppm, and clarification can be accomplished simply by passing the water through a filter. Filters may be of three configurations, the most common being a single granular medium such as sand, typically of effective particle size of 0.4 mm at flow rates ranging from 1 to 8 gal/minft².

A small amount of a coagulant such as alum may be added ahead of the filter amounts varying from 5 to 15ppm. Such rapid sand filters may either be operated by gravity, relying solely on a head of water over the filter medium to force the water through, or they may be completely enclosed in a cylindrical tank with pump pressure used to force the water through the medium. Pressure drops typically range from 1 to a maximum of 8 ft of water. The depth of bed employed is commonly from 2 to 3 ft. Finely divided anthracite coal of effective particles size of 0.6 mm may be used instead a sand. When anthracite is used, the addition of coagulation chemicals is usually required. The coagulation chemicals added serve the purpose of agglomerating the colloidal dispersed solids and aid in their adherence to the filter media and hence their removal. Clarification efficiencies measured as the ratio of suspended solids entering are commonly 0.90-0.99. The sand or anthracite coal in earlier designs was supported on a bed of graded gravel, but in current practice is more commonly supported directly on the filter bottom which is provided with strainers sufficiently fine to prevent sand or anthracite from passing through.

Previously most filters, both pressure and gravity, were of a single medium, sand or anthracite. Currently, many new installations are being designed with a mixed media or graded density filter. In this case, filter media of different types such as sand and anthracite are employed together, with the anthracite, being the more coarse and lower density medium, appearing on the top of the filter, 49 mm (20 in) of 1.0 mm anthracite coal may be placed on top of 14.7 mm 6 in (6 in) of 0.4 mm sand. When the filter backwashed to remove the suspended impurities that accumulate during the run, the less dense medium, the coal, is washed to the top by the upward flow of water and the heavier medium, the sand, even though finer, remains on the bottom. The suspended solids that have been removed, being much lighter than, either medium and in flocculated form, are carried out by the up flowing water and washed to waste. In both types of filters, single medium and mixed media, the amount of backwash water required is approximately three percent of the total throughput of the filter during a run, the end of which is controlled by a given limit on the quality of the effluent. The advantages of the mixed media filter are that the coarser material on top causes removal of a large percentage of the suspended solids in the entering water and allows the solids removed to accumulate in the depth of the bed rather than forming a mat on the top. The remaining amount of suspended solids is removed on the finer media. The net results is an ability to handle an influent water with a much higher suspended solids content, and to process a greater quantity at higher flow rates without deterioration of effluent quality than is possible with a single medium filter. Where mixed media filters are employed, flow rates

vary from 3 to 6 gal/minft². Total head loss is limited to approximately results in a penetration of suspended solids through the filter medium into the effluent.

Industrial Group	Water intake, billion (gal/year) ^b -cooling and condensing	Water intake, billion gal/year -boiler feed sanitary service etc.	Water intake, billion gal/year -proc Ss	Water intake, billion gal/year -total	Water intake, billion gal/year -water recycled	Water intake, billion gal/year -gross water use, including recycling	Water intake, billion gal/year -water consumed	Water intake, billion gal/year -water discharged
Food and kindred products	392	104	264	760	520	1280	72	688
Textile mill products	24	17	106	147	163	810	13	134
Lumber and wood products	71	24	56	151	66	217	28	123
Paper and allied products	607	120	1344	2071	3045	6016	129	1942
Chemicals and allied products	3120	202	564	3880	3688	7574	227	3650
Petroleum and coal products	1212	99	88	1399	4768	6162	81	1318
Leather and leather products	1	1	14	16	2	18	1	15
Primary and metal industry	3387	195	995	4578	2200	6778	266	4312
subtotal	8814	762	3432	13008	15347	28355	817	12191
other industries	571	197	271	1039	1207	2246	71	968
Total industry	9385	959	3703	14047	16554	30601	888	13159
Thermal Electric Plants	34849	c		34849	5815	40665	68	34781
Total	44234	959 ^d	3703	48896	22869	71265	956	44940

^a [37])a Source census of manufactures [37], b gal means British gallon 1gal= 4.54 L, c Boiler feed water use by thermal electric plants is estimated to be equivalent to sanitary service, in industrial plants etc., d Total boiler feed water(excluding sanitary service in industrial plants).

Table 2. Industrial plant and thermal-electric-plant (Water intake, Reuse, and Consumption, 1964.

4. Adsorptive, chemical and incineration systems in wastewater treatment

Adsorption processes have been successfully applied in the chemical industry for the purification of water generally, as well as for various solutions and individual wastewater streams.

In the chemical, physical, and biological purification of wastewater dissolved constituents are eliminated not only by use of special absorbents, but also in many cases by adsorption on the surface of undissolved substances already present. Elimination occurring by the latter mechanism cannot be examined separately, so it is simply described to the treatment process as a whole.

The deliberate application of adsorption is always in competition with other chemical, physical, and biological approaches to the purification of wastewater. Ecological and economic considerations are decisive in the choice of any particular process or process combination [10]. The question as to whether adsorption is technically and economically feasible, either alone or in combination with other processes, must be examined separately in each individual case. To this end it is necessary to consider the adsorption phenomenon itself in conjunction with the preparation and regeneration of the adsorbent, since from a process engineering stand point the two processes constitute a single entity. In addition, reuse or disposal of material arising in the course of the process should be taken into account as appropriate.

Adsorption causes dissolved organic wastewater constituents to accumulate at the surface of one or more adsorbents. Adsorption must therefore be regarded as a physical concentration process taking place at a liquid solid phase boundary, one that competes with other concentration processes occurring at liquid-liquid [11]-[13] (extraction or membrane processes) and liquid-gas boundaries (evaporation, distillation, stripping)[34]. In the unified examination that follows, it was necessary that some attention also be devoted to such oxidative processes as aerobic biological treatment, chemical oxidation, wet oxidation, and combustion, treated elsewhere in this contribution in detail.

In general, it may be assumed that adsorption processes have already established themselves as valuable for dealing with fairly small wastewater streams containing low concentrations of adsorbable substances. Adsorption is especially common in decentralized wastewater treatment, both alone and in combination with other processes.

Dissolved wastewater constituents are potentially subject to attachment at the surfaces of solids. An accumulation of this type is known as adsorption, and it is attributable mainly to van der Waals forces, particularly dipole-dipole interaction, though coulombic forces also often play an important role. The fixing of dissolved substance to a sorbent can sometimes lead to an enrichment factor of 10^5 or greater. In most cases the adsorbent-adsorbate mixture must then be worked up in a second processing step. Regeneration of a contaminated sorbent frequently takes advantage of the reverse counterpart to adsorption-desorption.

The equilibrium state that is established after a sufficient amount of time has elapsed defines the equilibrium concentration of a solute in a liquid and the loading of an adsorbent. This

state can be described in terms of so called adsorption isotherms. An isotherm is applicable only to a specific, defined temperature, although the influence of temperature is very small in liquid-solid systems in contrast to gas-solid systems. The curves themselves are usually determined empirically, but their shape can also be described mathematically.

One of the first attempts at developing an isotherm equation was reported by Langmuir, who was concerned originally with the adsorption of gases, basing his work on methods of statistical thermodynamics. The Langmuir equation assumes the presence of a adsorbent surface, and it is therefore valid only to the point of a monomolecular covering of the relevant surface. In general, Langmuir homogenous isotherms are described by the equation:

$$X = X_m \frac{c}{b + c} \quad (1)$$

where X is equilibrium loading, X_m is loading for monomolecular coverage, c is residual solution concentration remaining after establishment of the adsorption equilibrium, and b is a constant.

The isotherm equation proposed by Freundlich as early as Langmuir was established empirically. Because of its relatively simple form it is an excellent device for describing adsorption from an aqueous solution:

$$\frac{X}{M} = kc^n \quad (2)$$

where X is amount of adsorbed substance, M is weight of adsorbent used, c is residual concentration remaining after establishment of the adsorption equilibrium, and k and n are constants specific to a given adsorbent-adsorbate mixture.

Plotting this equation in log-log function, $\log(X/M) = \log k + n \log c$, produces a straight line, which greatly facilitates practical application of the method (Fig.4 and Fig. 5).

The Langmuir equation is clearly limited to low degree of loading, whereas in the case of the Freundlich equation there is no formal concentration-dependent limitation to the expression's validity. In practice, however a flattening of the Freundlich isotherm does become evident with increasing concentration, which means that the Freundlich exponent (n) increases with decreasing concentration. Thus rigorous application of the Freundlich equation is limited to a rather narrow concentration range.

Multicomponent mixtures are the rule in practical waste water treatment, and these can be characterized only by such cumulative parameters. Individual substances included in a collective analysis compete for occupation of the available adsorption sites.

Since different substances usually have very different adsorption behaviors, the Freundlich isotherms actually obtained in such cases are curved, or even bent at sharp angles as shown in Fig.5.

Despite the complications created by isotherms whose course is not straight, the Freundlich isotherm method is frequently used as a way of rapidly acquiring information regarding absorbability on adsorbents. Moreover, such isotherms make it possible to estimate adsorbent consumption rates as well as the achievability of particular concentration targets.

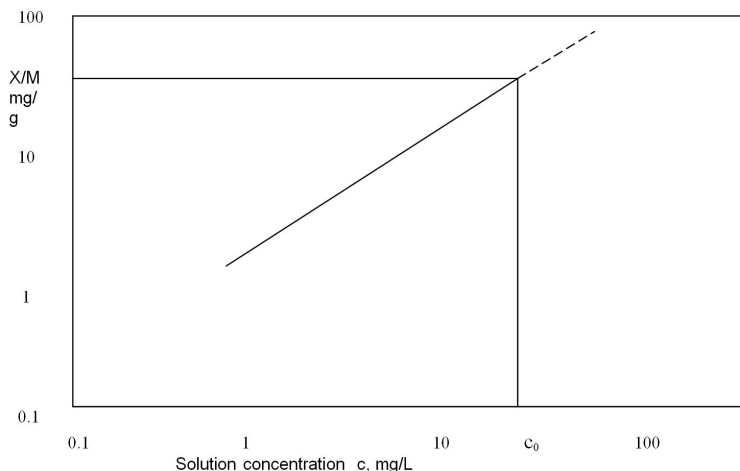


Figure 4. A well behaved Freundlich isotherm.

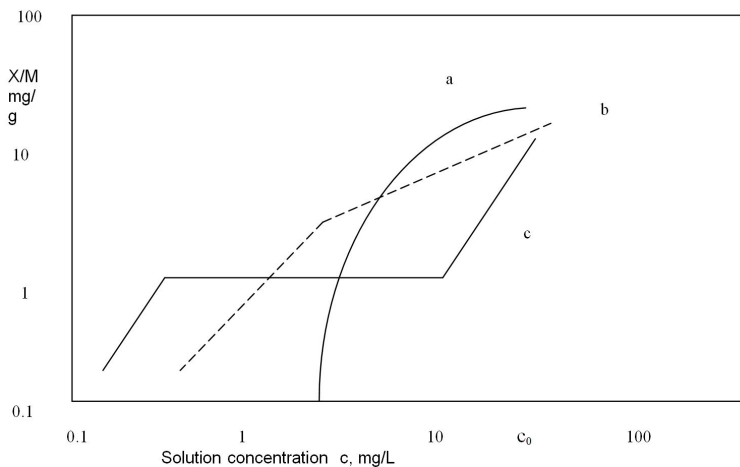


Figure 5. Typical non-linear Freundlich isotherms (a,b,c) obtained with different mixtures of solute.

In the last twenty years special processes have been developed to utilize chemical reactions directly for the degradation of water contaminants. Some have been developed to the point of technical maturity, and without exception these are oxidative processes. The methods for the oxidative and reductive elimination of wastewater components are old.

The active oxidizing agents are oxygen containing radicals in the vast majority of cases the radical H-O. The oxidizing agents actually introduced are usually air, oxygen, hydrogen peroxide, or ozone. Process engineering characteristics distinguishing the individual methods vary quite considerably. What differentiates one process from another, and distinguishes all of these approaches from the microbial route, is a consequence largely of the nature of the wastewater itself and the extent to which its components should or must be degraded. It should also be noted that advantage is sometimes taken of several either direct chemical or biochemical methods, as well as combinations of the two together.

The generally more drastic reaction conditions or more aggressive reactants associated with a purely chemical method, and the often higher degradation rates achieved, lead easily to the impression that direct chemical methods are inevitably superior to biochemical methods. This is not necessarily the case, however. Material degradation is the first and

foremost a kinetic problem, and reaction mechanisms and catalysis play decisive roles. To describe a substance as "not degradable" is basically an unwarranted oversimplification, because it implies that "degradability" is a fixed property of a substance, whereas it is in fact matter of behavior, i.e., some degradation will indeed occur, but at a rate that is unacceptably low. In drawing any methodological comparison, various direct chemical methods must be taken into account, and especially from the following points of view [41]-[45].

1. Energy costs and not only with regard to requisite temperature levels, but also the required duration of action and any energy expenditures associated with separation and enrichment steps, especially in the case of dilute wastewater.
2. Irregular waste from and how to cope with peak volumes or concentration. Microbial processes function best when volumes and concentrations are relatively constant. Large fluctuations, especially toward higher values, can often be managed with the aid of subsequent or parallel chemical process steps.
3. Mixed wastewater and the separation of partial (split) streams containing slowly degradable or interfering wastewater components [41],[42]. Major grounds for the separation and individualized treatment of specific production wastewater streams include the following:
 - a. A certain partial stream is characterized by high volume and the presence of contaminant amenable to degradation by means of the simple and inexpensive low pressure wet oxidation process, resulting in a secondary wastewater suitable for introduction into a control biochemical wastewater-treatment plant.
 - b. A partial stream contains wastewater components that degrade only slowly, suggesting that high-pressure wet oxidation. This process is quite elaborate and involves relatively high operating costs, so a more economical alternative might be to pursue chemical degradation only up to the point of suitable fragmentation, assigning the responsibility for further degradation, as above, to a central biochemical wastewater-treatment plant.

- c. A partial stream contains such a high level of salts that a cell culture would no longer be capable of functioning. Wet oxidation on the other hand might not be feasible either if in the case of certain salt-like companion substances the threat of corrosion rules out both low- and high-pressure oxidation. Such a case could be dealt with only by strictly thermal oxidation based on combustion, after appropriate concentration.

Generally, speaking, chemical treatment is restricted to special wastewaters characterized by components that are degraded too slowly in conventional waste-treatment plants or that interfere with the biochemical degradation of other substances. Chemical waste degradation processes listed in order of increasing operating temperature and pressure.

1. Atmosphere pressure wet oxidation by means of hydrogen peroxide, ozone, or air, with iron oxide or titanium dioxide as catalyst.
2. Low-pressure wet oxidation with air, based on an iron/quinone catalyst.
3. High-pressure wet oxidation with air, using copper as the catalyst.
4. Thermal oxidation, i.e., evaporation of water and combustion of the residue.

There is no such thing as a single best process, one clearly characterized by an ecological maximum and economic minimum. What is instead required is extensive experimental investigation to establish the limits and possibilities associated with each individual case, thereby providing a sound basis for meaningful comparisons. The question of how one should proceed with a particular wastewater source can then be answered reliably.

Thermal processes must generally be ruled out in cases involving low concentrations of degradable substances because of excessively high specific energy costs per unit volume. The use of hydrogen peroxide is often advantageous here, especially if the substances in question accumulate on an irregular basis. With higher contaminant concentrations, either high-pressure or low-pressure wet oxidation can be implemented. Evaporation followed by combustion becomes the method of choice if there is the added complication of high concentrations of inorganic salts. Wastewater of this type is derived largely from the chemical and materials industries.

The direct oxidation of organic compounds by hydrogen peroxide under acidic conditions is a well-known but relatively seldom-employed process. The oxidation potential of H_2O_2 can be increased above that of ozone through catalysis, usually with Fe^{2+} . Oxidation with hydrogen peroxide was investigated in the second half of the 20th century in conjunction with the treatment of municipal sewage [42] and waste water from industrial production, especially effluents containing sulfur and phenols [10], [43]. Successful hydrogen peroxide treatment of wastewater from hardening plants and tanneries has also been described.

In special advantage of this process is that the technological effort required is small, an especially positive factor in the case of dilute wastewater (<10 g COD /L). Non biochemical treatment is of special importance for wastewater fractions with low concentrations of contaminants, because the corresponding large volumes determine the size of the required

treatment facility, and thermal processes are excluded because of the enormity of the associated energy requirement.

Oxidation with H_2O_2 proceeds at atmospheric pressure and room temperature within 60-90 min. Hydrogen peroxide is not toxic, is easy to handle, and decomposes into the environmental products oxygen and water. Large scale use of this otherwise virtually universal oxidizing agent is restricted by the high price of H_2O_2 itself, together with the fact that although self-decomposition proceeds with the formation of oxygen, the resulting oxygen contribution almost nothing to the oxidation process.

Hydrogen peroxide is not merely an oxygen-transfer agent that facilitates work in a homogeneous aqueous phase, indeed, one should make every effort to avoid conditions favoring the self-decomposition of hydrogen peroxide:



More the point is the fact that catalysis by iron (molar ratio $H_2O_2 : Fe^{3+} = 15 : 1$, pH= 3.0), leads-as in the reaction of the Fenton reagent-to the formation of the H-O' radicals, and it is these that constitute the actual oxidizing agent.

The redox potential E_0 for the reaction sequence:



has been determined to be 2.28 V. For the analogous reaction with ozone the redox potential is 0.21 V lower:



In the case of substance that oxidize only slowly even under these conditions, or via oxidation chains starting from them, it has been observed that self-decomposition of H_2O_2 - which is of no value for COD degradation-becomes appreciable. It is therefore necessary to establish the extent of utilization of introduced H_2O_2 , and to complete this with the applied dosage in that particular case. The dosage should then be decreased until a utilization of nearly 100% is achieved [44]. If a dosage is calculated based on the stoichiometry corresponding to complete oxidation all the way to CO_2 , an almost equivalent COD degradation can usually be achieved with 60% of the calculated dose, resulting in almost 100% utilization of the added H_2O_2 .

The heat of reaction has also been determined under these conditions, leading to the following values established with a flow calorimeter, isothermal [45]:

$$\begin{aligned} Q_1 &= 4.59 \text{ cal} / \text{mgCOD} \cong 19.22 \text{ J} / \text{mgCOD} (\pm 3\%) \\ Q_2 &= 2.48 \text{ cal} / \text{mgH}_2\text{O}_2 \cong 10.39 \text{ J} / \text{mgH}_2\text{O}_2 (\pm 4\%) \end{aligned} \quad (8)$$

The extent to which different classes of substances differ in their behavior is illustrated by the data in Table 3. From an economic stand point, the selected conditions in this study were appropriate only for the last two substances listed. The process can be regarded as non-specific with respect to the various classes of organic substances typically encountered in wastewater. It also shows little dependence on the salt load.

The degradation of more than 100 individual compounds as well as authentic industrial wastewater has been described [46]. As a results of adsorption on flocculated material during the neutralization step the process leads to an effective reduction of COD roughly 10-15% greater than the level of true degradation.

The process can be operated continuously in the form of a cascade. On a pilot-plant scale ($\leq 500\text{L}$) the residence time is 60-90 min with a dosage of 20-80% $\text{H}_2\text{O}_2/\text{COD}$. Partial oxidation with maximum utilization of H_2O_2 is pursued only to the point at which the wastewater can be subjected to subsequent degradation in a biological wastewater-treatment plant without impairing biochemical processes there. The type and level of salts present is of some importance, even though the actual oxidation with H_2O_2 is largely insensitive to salts. Considering only the COD value of the wastewater, partial oxidation with H_2O_2 is still technically feasible with dilute effluent in the concentration range 0.5-10g COD/L, where thermal processes must be excluded because of the associated energy demand.

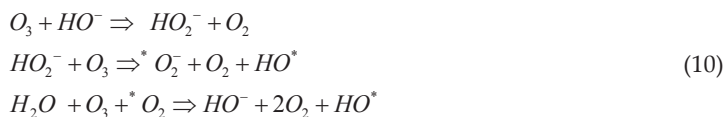
Radical formation based on hydrogen peroxide has also been achieved by UV irradiation for wastewater-treatment purposes [47].

Use ozone for the oxidative elimination of wastewater components has also been known for a long time. Ozone was used even earlier for the sterilization of air and the treatment of drinking water. Its effectiveness is highly dependent on the pH and is based essentially on two mechanisms.

1) So-called direct oxidation occurs under acidic conditions. This is fairly slow process, but the conversion can be accelerated greatly if the energy necessary for radical formation is provided in the form of UV high from a Hg low pressure radiation source.



2) Alkaline oxidation also takes place via the intermediate formation of hydroxyl radicals:



Ozonization of organic halogen compounds leads to both inorganic halides, from dehalogenation at C-Cl, and the ensuing formation of new organic halides.

The formation of organic halides has also been detected in wastewater containing a combination of chlorine free organic materials and inorganic halides originating from the accompanying salt load. Compounds formed in this way generally reflect the presence of oxidizing agents, especially ozone or hydrogen peroxide.

In this system, oxidative degradation of C-H and C-C bonds and the formation of the new C-Halogen bonds in the presence of the appropriate salts is strongly pH dependent. Radical reactions produce the intermediate hypochlorite, which in alkaline medium also acts as an oxidizing agents. Chlorination at carbon is clearly apparent under acidic conditions, as implied by an equilibrium shift in the system



This effect is even more pronounced in the case of the higher halides as shown by the following Data on C-Halogen formation in conjunction with oxidation (Table3).

Halide	Threshold pH
Chloride	<5
Bromide	<10
Iodide	<15

Table 3. Halogen formation vs. threshold pH.

Oxidative cleavage predominates in all three cases at a pH>4.

The oxidative treatment of wastewater containing salts requires the prevention of simultaneous and persistent halogenation. A high chloride content must be anticipated in seepage water from landfills and in certain effluent streams derived from product ion lines in chemical processing plants.

Bromide in drinking water leads to the formation of organobromine compounds upon ozonization. Special measures must be instituted in dealing with bromide- and iodide-containing wastewater derived from the processing of color negative films and the production of printing plates. In the case of iodide containing wastewater it is useful to remove the iodide prior to oxidation of other constituents. With bromide-containing wastewater it is possible

to degrade the adsorbable organic halide (AOX) formed in situ during the course of oxidation by introducing an excess of oxidizing agent.

Radicals derived from natural ozone, and from natural, extracellular sources of hydrogen peroxide in the soil, especially the hydroxyl radical $\text{H-O}^\bullet$ [48], also produce halogenated intermediates in the presence of ubiquitous salts, including halogenated metabolites. Some of the latter are intermediate products with a limited lifetime in the mineralization process, whereas others are persistent excretion products in the form of humic acids with halogenated aromatic groups. Similar processes are observed in the ocean and in inland waters.

Corresponding process in industry, i.e., oxidative degradation reactions with the simultaneous formation of intermediate organic halogen derivatives, has so far not been reported, although oxidative degradations in the formed natural decomposition and decay induced by natural oxygen sources together with biochemical catalysts: oxidizes, peroxidases have been simulated in the laboratory [49]. Specific proposals were developed in conjunction with this study for the industrially very important degradation of lignin in the wastewater released from paper and pulp mills.

Semiconductors catalysts such as the oxides of titanium, iron, or zinc, together with atmospheric oxygen as the oxidizing agent and sunlight as a source of the requisite activation energy, constitute systems for the treatment of dilute wastewater. These systems have already been investigated in the context photochemical degradation of organic substances in the atmosphere [48],[49].

Apart from studies involving individual substances, the behavior of actual wastewaters has also been investigated in a thin film fixed-bed reactor (Fig.6), including groundwater, seepage water, influents to biochemical wastewater-treatment plants, and the corresponding effluents.

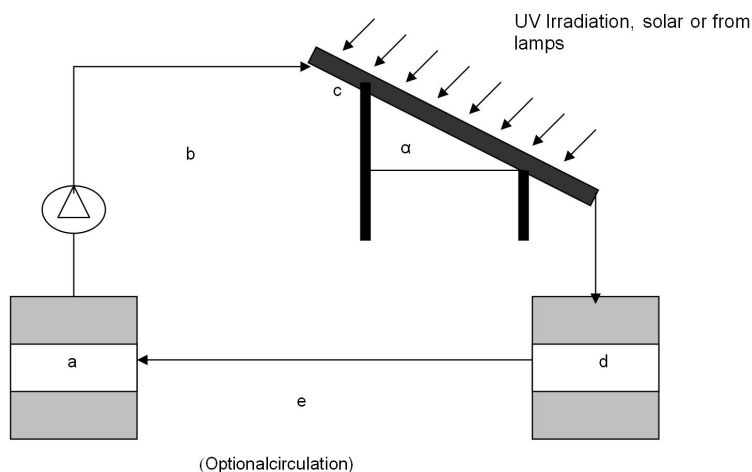


Figure 6. A thin-film fixed-bed reactor for solar detoxification.

A consideration of the associated energy factors shows that titanium dioxide absorbs light only at wavelengths below 390 nm because of its relatively large band gap of 3.2 eV. Accessible sunlight with a radiant power of 20-30 W/m² in the wavelength range 300-400 nm makes available 0.2-0.3 photons per m² per h. Quantum yields of 0.1-10% have been reported at TiO₂ surfaces. Assuming an average quantum yield of 1%, this energy source would suffice for the degradation of 2-3 mmol of wastewater compositions per square meter of surface area per hour. For substances with molecular masses of ca.100 present in concentrations of ca. 1mg/kg, the potential wastewater throughput would be 200-300 L/h for an absorption surface area of one square meter. Lamp panels equipped with standard fluorescent lamps of the type developed for tanning benches have also been used as sources of near-UV radiation. The corresponding degradation reactions proceed more rapidly with hydrogen peroxide as a sole or supplementary source of oxygen.

Variants such as parabolic channel reactors have been found to be much less effective than thin-film fixed-bed reactors. Such chemical variants as hydrogen peroxide in conjunction with mixed oxides based on Fe (III)/Ti(IV) have led to better utilization of the available visible light, because α -Fe₂O₃ absorbs at wavelengths under 540 nm.

Photo-reactivity has been found to increase in the presence of mixed oxides of this type as a result not only of photo-oxidation but also photo-addition, which may prove to be of some importance in the context of degradation intermediates.

Wastewater for which biological, chemical and physical purification processes either fail or prove too expensive can, if necessary, be purified by combustion of their organic constituents. In principle, all organic substances can be oxidized in a flame, and volatile inorganic substances formed can be separated in a flue-gas scrubber. Oxidation in a flame and the associated breakdown of organic materials depends on temperature, residence time, oxygen content, and turbulence in the combustion chamber.

The incineration of organic constituents is a specialized process for treating those industrial wastewater in which the organic constituents, and under some circumstances the inorganic constituents as well, are chemically utilizable at high temperature with the aid of atmospheric oxygen, the accompanying water matrix "gas phase oxidation" is also used in conjunction with this type of combustion to distinguish it from processes such as wet oxidation.

5. Waste water management system

Waste water management involves analysis of elements, their attributes, behavior and parameters estimation, real time optimization and safety. Optimization provides optimal working conditions, services, troubleshooting, advanced control and hazard minimization. However, these will support people decision to prevent abnormal situation, not replace the people.

Waste water treatment operation makes history data base of manipulates entity variables. Supervision can make different service databases model. A model manager, which shows how does seek out a new way to create optimal waste water policy and how does model pretreat-

ment and post treatment waste water network life cycle, and how does make management history was developed. Management systems will be available to analyze environment requirements and performed information processing in the aim objective achieving [51]-[58].

There is no safety reason to discontinue operation, when monitoring devices respond at the boundary between normal operating and admissible error ranges of waste water variables. Damage minimizing systems come into action when the waste water system is in no specified operation and when an undesired event occurs.

To use models to support decision making is proliferating in both the public and private sectors was the aim of this chapter. As powerful decision aids models can be both beneficial and harmful. At present, few safeguards exist to prevent model builders or users from deliberately carelessly data, or recklessly manipulating data to further their own ends. Perhaps more importantly few people understand or appreciate, the harm can be caused when builders or users, fail to recognize the values and assumptions on which a model is based or fail to take into account all the groups who would be affected by a model's results.

5.1. Waste water safety

Waste water from cities, industrial and the others manufactures are transported with various sewerage systems. Under infrastructured system understand process systems which using for recieving, collecting, evacuation and waste water treatment. Dependent of that how is collected and evacuation of waste water system can be general, separation and partical separated type.

At the general system all waste water is transported with one channel. The separation system are performed transport of all waste water from industry hausholders, and atmospha separated channels. The partial separation systems mixing industrial water with hausholderswater or industrial and atmospheric water. Behinde these systems can made various combination in different parts of city. The waste water transport systems are consist from more connected elements. There are collectors, pipelines, valves, pumps which distributed in more streams as shown in Fig.7.

Maintenance waste water treatment and evacuation are very important. Safety of the waste water transport system is ecological significant. Because a diagnostic system for risk analysis and supervision of the waste water system is developed. In the safety analysis and operation the simulation getting started with data of the process components. For accident detection the derived model is forecasted the future behavior of the system and risk parameters are determined. The system is consisted of streams and process units data as well as the basic faults and symptoms.

This chapter illustrate the waste water transport safety protection system as shown in Fig. 8. In simulation, both qualitative and quantitative analysis are often applied together. Usually, qualitative decision efficiently made with symbolic and graphic information, and quantitative analysis is more conveniently performed by numerical information.

The diagnostic expert systems have important role how in risk analysis and accidents prevention of the production systems such as in transport systems (Fig.8). A diagnostic systems for supervision and maintaining process systems were developed [20]-[25].

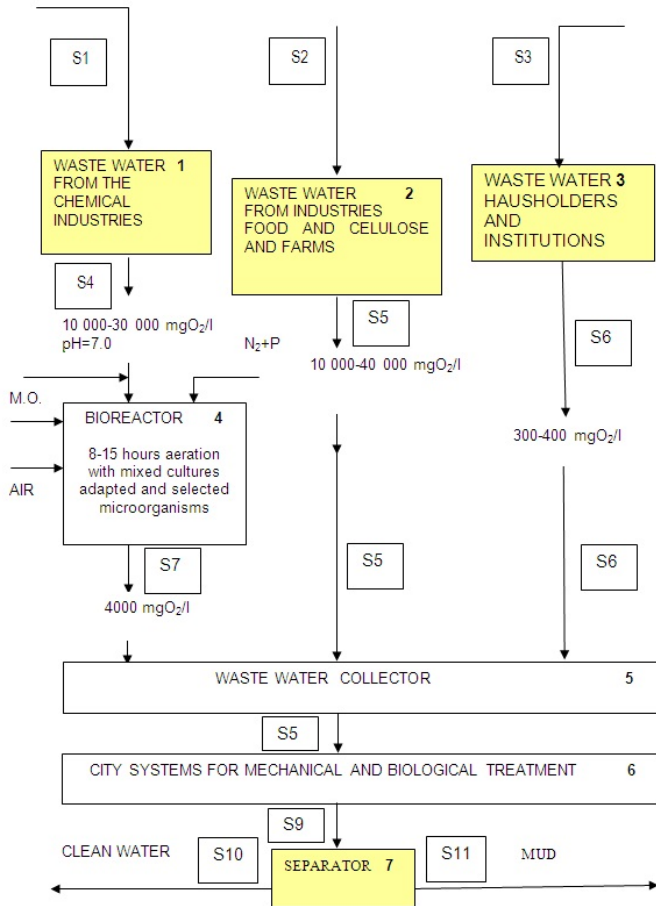


Figure 7. Waste water system evacuation.

Maintenance waste water treatment and evacuation are very important. Safety of the waste water transport system is ecological significant. Because a diagnostic system for risk analysis and supervision of the waste water system is developed. In the safety analysis and operation the simulation getting started with data of the process components. For accident detection the derived model is forecasted the future behavior of the system and risk parameters are determined.

The system is consisted of streams and process units data as well as the basic faults and symptoms. The diagnostic expert systems have important role how in risk analysis and accidents

prevention of the production systems such as in transport systems. A diagnostic systems for supervision and maintaining waste water sewerage systems was developed in literature [1].

Operation makes history database of manipulates and object variables, symptoms and scenarios. Likely scenarios are typically generated by instantiating parameter values in a parametric model according to the given situation. Modelling of the risk parameters were involved uncertain processing.

The level of aggregation is defined by the modular component interconnections which define propagation paths of attributes within the system. Initial research starting by the phase of the development of a conceptual framework which will facilitate the modular specification of models, and second phase the development of a logic framework which will permit object using attributes and simulation techniques to be linked into executable models. The fault event of a system are in the first instance generally formulated in an IF-THEN form. This can be immediately reformulated using the operators AND, OR and NOT in Boolean form, if one can assume that the primary events have only two states existence and non-existence.

System identification involves identification of variables, element and equipment as well as material supplies. System variables are defined in three discret states low, medium and high. The equipment states are defined as blockage and leakage, system state as normal and does not work. Supply exists or not exists. As system variables consider pressure, flow and level.

The considered system consists of 11 waste water streams, four supply streams and 7 process units. A diagnostic system as a support decision system was built. The data base has involved data streams and process units data as well as the basic faults and symptoms which connecting by semantic network (Fig.8).

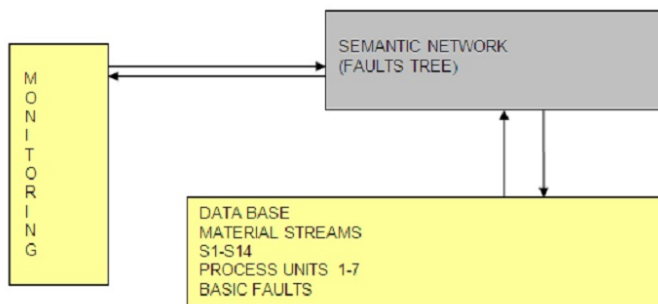


Figure 8. Sucture of the waste water diagnostic system.

The diagnostic system can assist to maintain waste water system safety transport. Waste water evacuation and treatment system safety is ecological very important problem. Fig.8 presents safety information support system, for waste water transport system diagnosis. The problem at hand is a problem of diagnosis, in which a major part of the solution consists of informing supervisor and action.

Such as systems can be used as a plant maintenance aids.

6. Proactive decision of the waste water management

A decision system on the process system which consists of operation and goal parameters was built. In the world mostly systems are used for solving structural problems, and they use retrospective view. These systems are used data from data base and directed to goal, but they have not view in front of and ability for unstructured problems solving. The process system for wastewater transport is unstructured. Goals and assumptions and decision support tools are examined such as events tree.

In recent years the study of systems management has successfully elucidated some basic techniques for generalizing concrete examples to more abstract descriptions [51]-[58]. These include heuristics for generalizing particular data types, candidate elimination algorithms, methods for generating decision trees and rule sets, back propagation of constraints through an explanation tree, function induction, and synthesis of procedures from execution traces [56],[57]. No coherent methodology has emerged for describing and categorizing management techniques to make them readily accessible to potential users. In fact there almost as many paradigms for management as there are systems and the variety of different, evocative, connotation laden words used to describe simple mechanism is one of the biggest problems in mastering the field. The apparent richness and variety of these approaches may give a misleading impression of a field teeming with fruitful techniques, with a selection of well defined methods for tackling and given problem [2]-[4].

From standpoint of knowledge engineering, concept management systems differ in their representation of concepts and examples, ways of biasing the search involved in determining a concept and model. This potential is rarely realized in practice because the field management is in turmoil and few useful general principles have been articulated. A model for decision making generates effective procedural, or rule based from a goal based architecture which further supports the development of secondary goals, as mental models.

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In this paper a model for decision making generates effective procedural, or rule based from a goal based architecture which further supports the development of secondary goals, as mental models.

The most important distinction in a knowledge acquisition framework is how systems represent what they manage. Knowledge representation has always been a central topic in process management [20],[21]. For both inductive and deductive concept the formalism above suggests representing concepts in an appropriately powerful form of logic (Fig 9). However, although formal logic provides a sufficient basis for deduction, as a foundation for induction it is at once too narrow and too powerful. On the other hand, logic is too powerful because the need to acquire knowledge automatically from environment and integrate it with what is already knows means that only the simplest representations are used by pro-

grams for system management. Any one representation will not encompass the broad application of concept management techniques, procedures or expressions composed of functions. These reflect fundamental formulations of computing that have been realized in logic, functional and imperative programming styles. Although equivalent in expressive power, the different representations are more or less appropriate for particular concept management problems, depending on the nature of the examples, background knowledge, the way the complexity of concepts are measured, and the style of interaction with the environment. For example, decision trees are naturally represented as logic expressions, polynomials as functions and tasks as procedures. Functional representations incorporate the powerful mathematics available for numbers. Procedures embody the notions of sequencing, side effects and determinism normally required in sequential, real word tasks. There is an obvious overlap between logical and non-numerical function representations. For example, the concept of appending lists can equally well be written in logical and functional styles. The difference is that the logical form expression a pure relation without distinguishing input and output, while the functional representation acts on the input list to construct the output. Many management methods apply to examples that can be expressed as vectors of attributes in a form equivalent to propositional calculus. The values an attribute can assume may be nominal, linear, or tree structured. A nominal attribute is one whose values form a set with no further structure for examples the set of primary colors. A linear attribute is one whose values are totally ordered for example natural numbers. Ranges of values may be employed in descriptions. A tree structured attribute is one whose values are ordered hierarchically. Only values associated with leaf nodes are observable in actual examples: concept descriptions, however, can employ internal node names where necessary. Attribute vectors, propositional calculus are not powerful enough to describe situations where each example comprises a scene containing several objects.

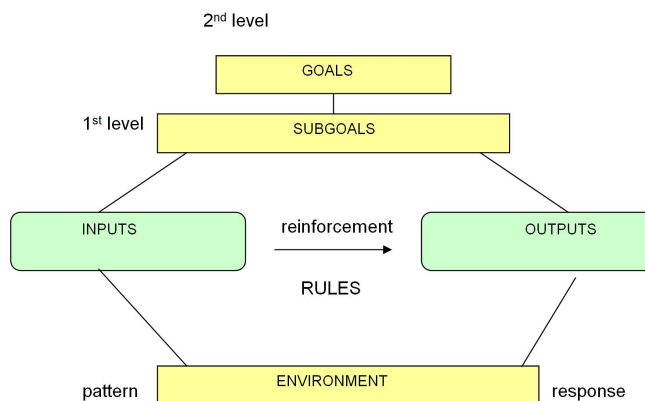


Figure 9. The goal based information system development.

Objects are characterized by their attributes. Moreover, pair wise relations may exist between them. This means that variables must be introduced to stand for objects in various relations.

Such relations can be described by predicates which, like attributes, may be normal linear or tree structured. Objects and concepts are characterized by combinations of predicates.

Functional expressions include many natural laws, as well as relationships between quantities and parameters. Functional representations are appropriate for nested and recursive numeric or non-numeric expressions. Any functional relationship $f(x)$ can be represented in logic and this is no surprise since the two forms are expressively equivalent. But in a framework for induction, it is preferable to treat functional expressions separately and omit explicit quantifiers. An important difference is that functional representations of concepts must be single valued, while logical expressions do not need to be this greatly affects the search space involved.

A more suitable form of representation might be the functional calculus, or some incarnation of it in pure or in functional programming languages. Work on programming language semantics, also partly based on functional calculus and often coupled with function programming languages may suggest appropriate forms of expressly prohibit aspects that distinguish functional from procedural representations in the framework, namely side effects and reliance in sequential execution. Work on programming language semantics, also partly based on functional calculus and often coupled with function programming languages may suggest appropriate forms of representation. Existing function induction systems are specially designed for particular domains with little attention to more general forms.

Typical concepts in procedures category include procedures for assembly welding, and standard office procedures. The procedural formalism suitable for representing sequential execution where side effects, such as variable assignment and real world outputs like movements, make it vital to execute the procedure in the correct order. To describe a procedural language formally, a binding environment model of execution is needed, instead of the simpler substitution model that suffices for pure functional representations must be deterministic to be useful procedural concepts.

Note the generalization of execution traces into a procedure is not reducible to an equivalent problem involving the generalization of non-sequential input/output pairs as such a reduction will lose information about sequential changes in state.

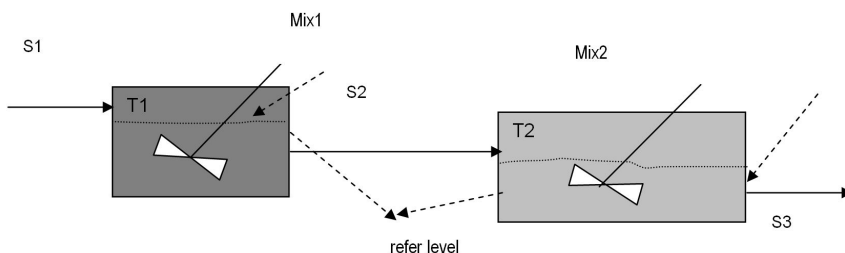


Figure 10. A simple wastewater flow system.

Let consider a simple process system wastewater transport as shown in Fig.10. The system consists of a two tanks, two mixers and pipes.

This system can be represented by qualitative events model expressed by logic algebra, M, B, and L are independent logic variables representing the basic events malfunction, blockage and leakage, respectively.

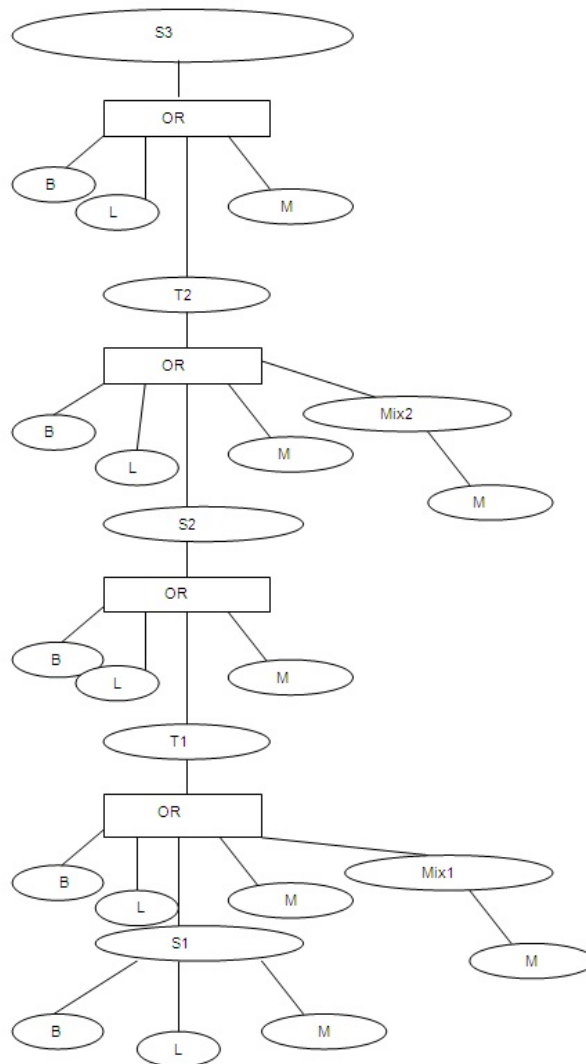


Figure 11. Fault tree diagnostic model.

The study of fault detection and supervision control of the flow system is concerned with designing a system that can assist a human operator in detecting and diagnosing faults as shown in Fig.11.

The two areas of model development and analysis are addressed through the discussion of generic simulation environment. The knowledge based simulation environment is an expression of some control law or cognitive theory. To the extent that the rule base is derived from set of assumptions about the environment and performance expectations, it is a belief system. However, in the existing form, the goals are not expressed and the underlying assumptions are not evident.

When expressed in hierarchical form the relationship that exist between goals and subgoals provide a basis for relating overall goal based system performance to specific assumptions about the variability and contribution of the supporting subgoals. In this form, the belief system is a full expression of some control theory in that the system's relationship with the environment, as expressed in a set of feasible state conditions, can be related either in overall system performance measures to be relationships and the subgoals that manage them.

Knowledge based system must represents information abstractly so that it can be stored and manipulated effectively, although experts have difficulty formulating their knowledge explicitly as rules and other abstractions. They find it easy to demonstrate their expertise in specific performance situations.

Concepts and examples are the output and input of the management acquisition system, what is manage and what is provided by a external agent. To be useful, a framework for representing concepts must provide knowledge engineers with methods for selecting appropriate representations for examples, concepts and background knowledge. Separate representations are required for examples and concepts.

Expert systems can be used to develop rules, based models and augment other types of models. Since can capture the experience, of experts, they can be used to forecast problems, advice, operators, validate data and ensure that the results from other are reasonable.

A functional approach to designing expert simulation systems was proposed many authors. They choose the differential games models is described using semantic networks. The model generation methodology is a blend of several problem solving paradigms, and the hierarchical dynamic goal system construction serve as the basis for model generation. Discrete event approach, based on the geometry of the games, can obtain the solution generally in much shorter time. Cooperation between systems is achieved through a goal hierarchy.

6.1. Decision support system

The distinction between deductive and inductive concept management can be viewed as a modern reincarnation of the long philosophical tradition of distinguishing necessary from contingent truths.

The best way to solve complicated problem by expert systems is to distribute knowledge and to separate domain expertise. In such case, several expert systems may be used togeth-

er. Each of them should be developed for solving a subdomain problem. Here, it is faced the problem of knowledge integration and data management (Fig.12).

Many expert systems can only be used alone for a particular purpose inflexibility. There are lack of coordination of symbolic reasoning and numeric computation, lack of integration of different expert system, lack of efficient management of intelligent systems and capability of dealing with conflict facts and events among the various tasks, being difficulty in modifying knowledge bases by end users other than the original developers.

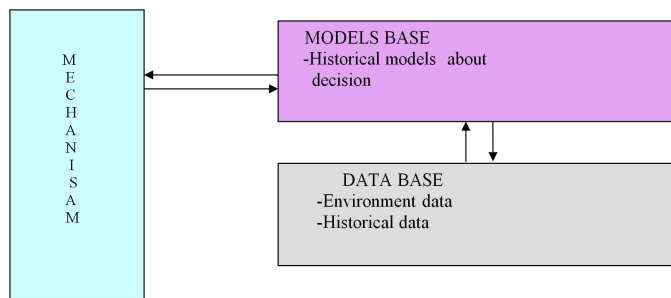


Figure 12. Decision support system building.

A knowledge based decision support system building is consisting from the following steps:

1. Wastewater system and treatment method identification
2. Goals and subgoals definition
3. Rules networking
4. Decision mechanism definition.
5. Monitoring system support

It can be indicated two possible approaches to complex contains modelling. The first, identified with structural knowledge, follows a deductive reasoning approach in which one tries to deduce from an existing theory model relationships for a given problem. The second, identified with a posterior empirical knowledge, follows an inductive approach in which one tries to develop a model from the sampled data. Ideally, these two approaches act as complementary stages of the modelling process.

One follows all six steps with model calibration and model validation serving as an empirical test bed for a prior model as a learning tool. Yet, in some situations characterized by difficulties in obtaining empirical data due to a budget and time constraints or preliminary scope of the analysis, the model specification may be reduced to the a priori stage.

In the traditional view of modelling the behavior of natural system these six steps, although logically connected, comprise separate tasks. Therefore, the development of an operational structure model is a rather lengthy and expensive undertaking. There is a strong need for a

more integrated framework for modelling of system in general that would better link the steps leading to model development and implementation.

The best way to solve complicated problem by management systems is to distribute knowledge and to separate domain expertise. At this, several expert systems may be used together. Each expert system should be developed for solving a subdomain problem and it is faced the problem of knowledge integration and management.

The coordination of symbolic reasoning and numerical computation is required heavily for simulation with expert systems. A few developers tried to develop expert systems with conventional languages. Other suggested to field expert systems in conventional languages, in order to achieve integration. Another disadvantages is that the procedural language environment cannot provide many good features that the symbolic language provides, such as easy debugging allowance for interruption by human experts.

Many integrated intelligent systems are a large knowledge environment, which consists of several symbolic reasoning systems and numerical computation packages. They are under the control of a supervising intelligent system, namely, meta-system. The meta system manages the selection, operation and communication of these programs.

For example, decision support building for wastewater treatment management can outlines in four stages:

1. The physical control of information by computer, which became more complex as the volume of information increased, due to system growth, diversification and government regulation.
2. The management of automated technologies, where the introduction of data processing etc., led to fragmentation and uncoordinated activities.
3. Process system resources management, where data processing, office automation etc., converged along with central and personal computing resources.
4. Technology management, where the physical and technical management of information is integrated with decision making, planning and operations.

Waste water plant operation management support system aimed at helping engineers and managers optimize all phases of process plant design, operations, optimization and process safety. Decision support system is useful for supervision of process plant operations, real - time optimization, advanced interactive control and process hazard analysis. Some techniques are very important for implementing and evaluating decision support systems which expand such diverse areas as computer supported cooperative work, data base management, decision theory, economics, mathematical modeling, artificial intelligence, user interface management system and others [25].

Decision support system principles, concepts, theories and frameworks develops methods, tools, and techniques for developing the underlying functional aspects of a process plant management support systems, solver/model management in plant operation support sys-

tems, rule management and artificial intelligence in process plant system coordinating a plant management systems functionality within its user interface.

Decision of wastewater treatment process design and operation support system interfaces develops methods, tools, and techniques for developing the overt user interface, user knowledge, help of a facilities, coordinating interface event, with its functionality events.

Wastewater plant operation decision support system impacts shows economics, system measurements, decision support system impacts on individual users, multi participants users, evaluating and justifying.

A process plant management system was considered in papers [47]-[57]. Plant management decision support systems was studied in the paper [58]. Process plant information system and process safety management support system were investigated in the paper [5], [4],[17],[18].

The computer supported cooperative work with data base management and mathematical modeling and simulation of process plant provide intelligent plant management support. The model plant operation manager workflow is shown in Fig. 12. The plant manager workflow can be used for the new product quality improvement, the model operation network optimization and generating new data and specified tools. Real-time software need to build intelligent process management applications.

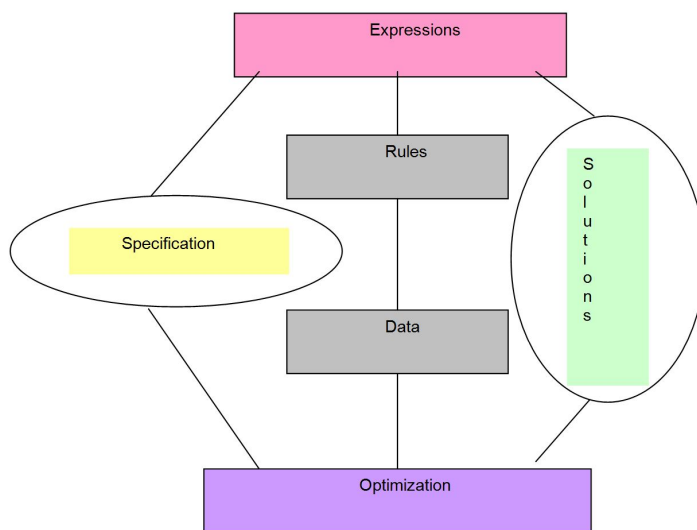


Figure 13. Management activities optimization.

Automatically create process operation models requires a windows based software tool for system identification which claimed to enable users to automatically create high fidelity models of physical systems, processes and plant.

System identification is technique that creates model of a plant operation process from input and output data, eliminating the need for detailed knowledge of the system physics. The new software automated the process, enabling engineers to perform modelling and simulation studies without having to create the underlying mathematical models from first principles.

Advanced commercial simulation systems also come, with in intelligent graphical user interfaces, which speed the development of error-free simulation problems and provide some help with thermodynamics and modelling.

Model operation manager shows how do you seek out a new way to create process operation, how do you model the plant life cycle and how do you make plant operation history in the process waste water treatment. A model plant manager is given by eq.(12).

$$MM = \sum_i^n M_i < T, P, A, F, E, Q(T), Q(P), Q(A)Q(F), Q(E) > \quad (12)$$

where T – set of elements, P -set of syntax rules, A –set of expression, F - set of

semantic rules, E - set stochastic events, $Q(J), J=T, P, A, B, E$ changeable functionality, M_i - operation model and MM -management model.

In the process operation and control safety models “What if ” help to build intelligent process management applications. They shoot stochastic events a day to day. It is improves plant operation reliability.

Process waste water operation involves sensitivity analysis of manipulate and object variables, parameters estimation, noises identification, dynamic simulation, detect process disturbance before they cause significant disruption (Fig.14).

Waste water treatment optimization provides optimal process condition, equipment services life, troubleshooting, advanced process control and minimization.

Superior customer support requests model evaluation. This future model is called “asses and control” as shown in Fig. 15. Where asses means:

- uncertainties not currently amenable to mathematical solution,
- people involvement, and
- advanced technologies support people

and control means:

- must work automatically,
- uncertainties can be handled rigorously,
- people eliminating, and advanced technologies support automatic operation.

Inherent softness exists in product pieces and forecast demands. In this frame it will throw lots of technology at these uncertainties or soft areas expert systems, neural networks, data reconciliation etc.. However, these will support people decision to prevent abnormal situation management, not replace the people.

Also, user can make a new overview this spreadsheet and printout. User can make input data tables, tables of consumption's and tables of flow rates.

6.2. Database management

User can make different waste water plant database models. From the result summary user can extract and flow rates, conditions and consumption. If user wishes to see input and output streams results between stages should to mark on the appropriate block. When block menu appeared, select stream results for retrieval material and energy balances.

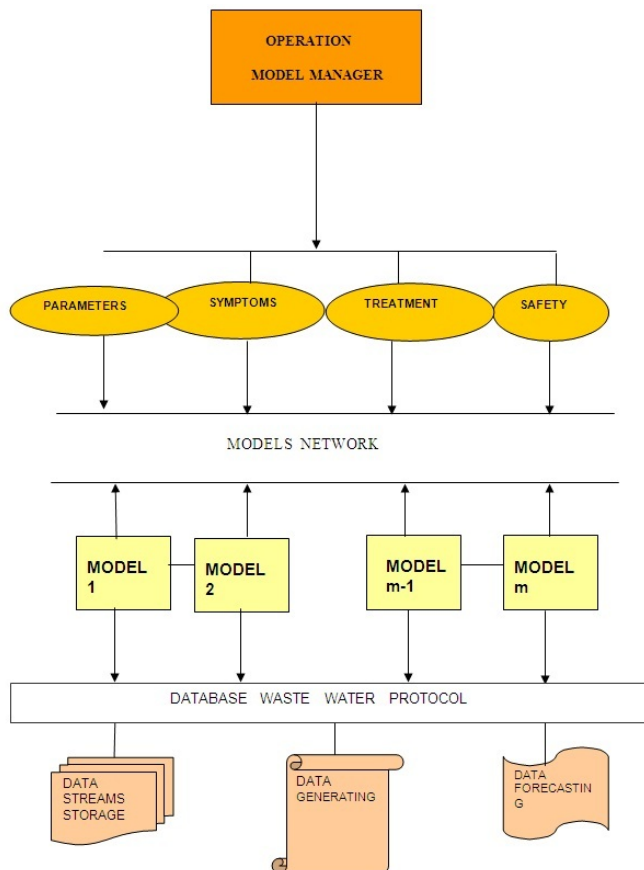


Figure 14. The wastewater operation model manager.

Databases protocol manages all databases, reports and tables. These tables could be distributed and extracted by multimedia databases. User can build hierarchical and relational process plant data bases for the plant management in concurrent operations (Fig.14).

The networks optimization requests maximum product capacity, minimum costs, concern the assignment problem, the matching and the minimum spanning trees, computer implementations and heuristics.

Process hazard analysis creates a resource allocation model by linking risk with cost and database of the values of basic events. In order to predict complete life cycle of the plant the plant life cycle reliability and the life cycle of the cost should be included.

Policy modeling emphasizes formal modeling techniques serving the purposes of decision making. These systems Computer aided process engineering-CAPE, Computer aided control-CAC, Computer integrated manufacturing-CIM, Computer aided safety-CAS make distributed computing.

The use of mathematical models to support decision making is proliferating in both the public and private sectors. Advances in computer technology and greater opportunities to learn the appropriate techniques are extending modeling capabilities to more and more people.

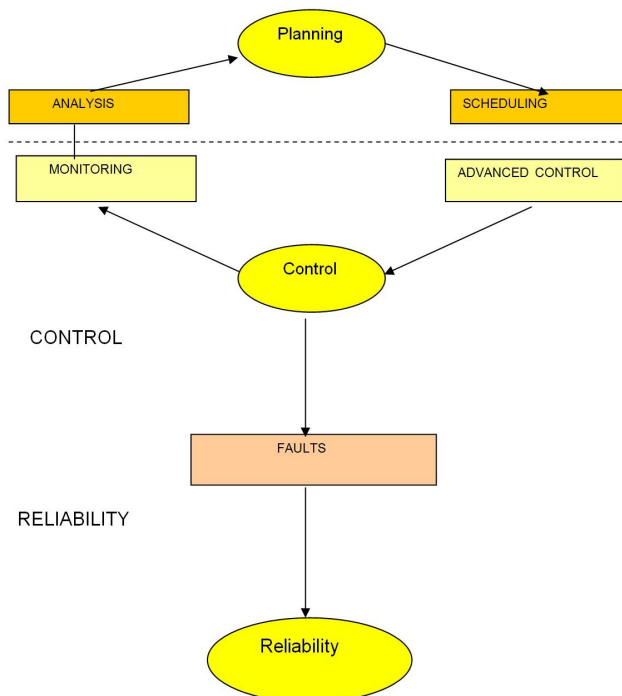


Figure 15. Asses, control and reliability.

As powerful decision aids process operation models can be both beneficial and harmful. At present, few safeguards exist to prevent model builders or users from deliberately carelessly, or recklessly manipulating data to further their own ends. Perhaps more importantly few people understand or appreciate, the harm can be caused when builders or users, fail to recognize the values and assumptions on which a model is based or fail to take into account all the groups who would be affected by a model's results.

Simulation manager models provide a setting for dialog and show the need to continue and define a vocabulary for exploring process operation. It will become increasingly important for model builders and users to have a clear and strong code to guide process plant operation.

The computer supported cooperative work provides explanation based process learning systems. As a cooperate function training is a subsystem within the plant's large organizational system. When training strategies ensure acquisition of knowledge, skills and attitudes which results in improved performance or safety on the plant operation, the training subsystem makes a positive contribution to organizational goal and effectiveness. Process performance, then, is the criterion of success in training.

7. Notation

A-set of expression

c-concentration, mg/L

F- set of semantic rules

k-specific constant

M-model

MM-model manager

P- set of syntax rules

Q- function

T- set of elements

X-equilibrium amount loading

8. Index

i - component

9. Abbervation

COD-contaminants oxidative degradation

AOX- adsorabable organic halide

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Mine Waste Water Management in the Bor Municipality in Order to Protect the Bor River Water

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51902>

1. Introduction

The fact is generally known that all human societies depend on the availability of natural resources (coal, iron, nonferrous metals, precious metals, industrial minerals, etc.) and possibility of their use [1]. One of three main conclusions of The World Summit on Sustainable Development, held in Johannesburg from 08/26/2002 - 4/9/2002, was that the concept of sustainable development underlines that long term efficient development, both for developed and developing countries, has to be based on three favorite topics: environmental protection, economic development and social cohesion, both on national and global levels.

The used minerals to obtain different products are very important for everyday life. Also, they are raw materials for various industries, including ceramics, construction, cosmetics, detergents, drugs, electronics, glass, metal, paint, paper and plastics. Mining and mineral processing has played a vital role in the history and economy of the following Western Balkan countries, comprising Albania, Bosnia and Herzegovina, the Former Yugoslav Republic of Macedonia, Kosovo (Territory under the Interim UN Administration), Montenegro and Serbia. Mining the polymetallic ores, jointly with the metal extraction process, is one of the most powerful industrial sectors. In the period until early 1990, this area was the main European source of copper, lead and zinc but, with disintegration the Yugoslav common market, led to worsening the economic conditions in the region, and after this period came to a sharp fall in industrial production, closing the mines. In a short period, the pollution was reduced as the result of active mining, but at the same time the conditions were created for

continuation of pollution as the result of unclear and incomplete defined legal procedures that did not precisely establish the environmental responsibility in leaving or privatization the mining and mining-metallurgical plants [1].

Very extensive activities, both by the open pit and underground mining, are the essential characteristics of mining activities. These activities in conjunction with metallurgical activities further continue to cause a serious negative impact on the environment generating large amounts of solid waste and hazardous substances, air pollution, negative impacts on the land use and biodiversity, pollution and water availability. Noise and vibrations, the use of energy sources, visual effects are also negative consequences of mining and metallurgical activities. In addition to the active sites, thousands of "old" or "depleted" sites are scattered in the region. Reduction the risk of accident situations and prevention the environmental pollution, with the problems that occur with unresolved issues of ownership of the same locations in such places, is technically and economically very difficult.

Problems of mining sites as a part of industrial hot spots on the Balkan Peninsula are the subject and topic of the Project carried out by the UNDP-led Western Balkans Environment Programme with the support of the Dutch Government and others. Large amounts of solid and liquid waste contain harmful and toxic substances such as cyanides, heavy metals and other harmful and dangerous substances, which have a negative impact on the eco and bio-systems [2, 3]. Cyanide discharge into the Baia Mare River in Romania is the result of incidences the failure of tailing dams at the Baia Mare Gold Mine in Romania and Aznalcollar Zinc, Lead and Copper Mine in Spain that cause many years of pollution the river Rio Tinto in Spain. In general, the environmental impacts of metal mining are likely to be greater than for other minerals, due to the often used toxic chemicals in the separation of minerals [1,2,4].

Copper is one of the essential materials to man since the time of pre-history. The fact that one of the eras of human history called the "Bronze" age and the name comes from copper alloy - bronze. It has found its very wide use thanks to good physical-chemical properties (fatigue resistance, strength, and excellent electrical and thermal conductivity, corrosion resistance). It remains one of the most used and reused of all metals. The demand for copper is due to its good strength and fatigue resistance, excellent electrical and thermal conductivities, outstanding resistance to corrosion, and ease of fabrication. Copper offers the moderate levels of density, elastic modulus and low melting temperature. It is used in the electrical cables and wires, switches, plumbing, heating, roofing and building construction, chemical and pharmaceutical machinery. It is also used in the alloys such as brass and bronze, alloy castings, and electroplated protective coating in the undercoats of nickel, chromium, and zinc.

According to data about the world copper mine production expressed in million metric tons of Cu content for the first years of twenty first century [5], it is clear that there is an almost steady increase of world copper mine production from 12.8 to 14.9 million tones of Cu content in the period from the end of twentieth century till nowadays. The copper ore deposits in Europe are limited and found in Poland, Serbia, Montenegro, Portugal, Bulgaria, Sweden and Finland [6].

The first mining operations in the Republic Serbia, related to the exploitation of copper ore in Bor, began in the early 20th century, more precisely in 1903. Exploitation of copper sulfide ores is carried out both by underground mining and open pit mining. Further course of ore processing requires a complex treatment in which the low-grade ore is enriched in the flotation concentration process in order to obtain the copper concentrate. This operation is used for material preparation for the pyrometallurgical process to obtain the anode copper. The final stage in the process of cathode copper production, purity minimum 99.95 wt. % Cu, is the process of electrolytic refining the anode copper.

In the period until the 1990s, the copper production from copper sulfide concentrates, which is concentrated in Serbian in the Mining and Smelting Basin (RTB) Bor, presented almost 50%, and since 2003 it accounts 20% of the total European copper production [7,8]. Due to the confirmed ore reserves of about 700 million tons, and the presence of Au and other precious metals, the mining and metallurgical activities on this site are also expected in the future. Exploitation of these ore reserves in RTB Bor and extraction of metals lead to the pollution of region by contamination of soil, air, surface and groundwater. Mining and metallurgical activities also have a negative impact on the health of population of this region.

Due to the imperfection of technological process of ore processing in the immediate vicinity of Bor, it was delayed about 250 000 t of open pit overburden and 88 000 t of flotation tailings which contain hazardous and dangerous materials such as copper, nickel, arsenic, zinc, antimony, mercury, chromium, bismuth. Such large quantities of mining waste require large areas for disposal [9]. In the area of disposal the mining waste, the acid mine water is generated acid mine drainage (AMD) from the mine wastes containing sulfide-rich minerals. Sulfide minerals, mainly pyrite (FeS_2), often present in the mine wastes, can generate AMD when they come in contact with water and O_2 . The oxidation of pyrite produces H_2SO_4 reducing pH in solution. Generally, the pH drops to values below 4, which causes toxic metals to dissolve. Low pH conditions involve the growth of acidophilic bacteria *Thiobacillus ferrooxidans* [10]. These bacteria have the ability to oxidize aqueous Fe(II) to Fe(III) which is then the principal agent for pyrite oxidation in an aerobic or anaerobic environment. At $\text{pH} < 2.5$, a near-steady-state cycling of Fe occurs via the oxidation of primary sulfides by Fe^{3+} and the subsequent bacterial oxidation of regenerated Fe^{2+} [11]. These reactions cannot be carried out without dissolved O_2 [12].

Waste water, generated during metallurgical treatment of copper ore, also leads to transfer of harmful and dangerous materials into local water ways. There are many new processes for treatment of these wastes and some of them using the cheap, locally available adsorbents [13,14].

The following block diagram (Figure 1) shows a simplified diagram of the production process of cathode copper with the indication of place where the waste solutions are generated.

Treatment of waste solutions, produced during the mining and metallurgical activities in the process of ore mining to the finished product – cathode copper, is the basic pre-condition for their release into local water ways.

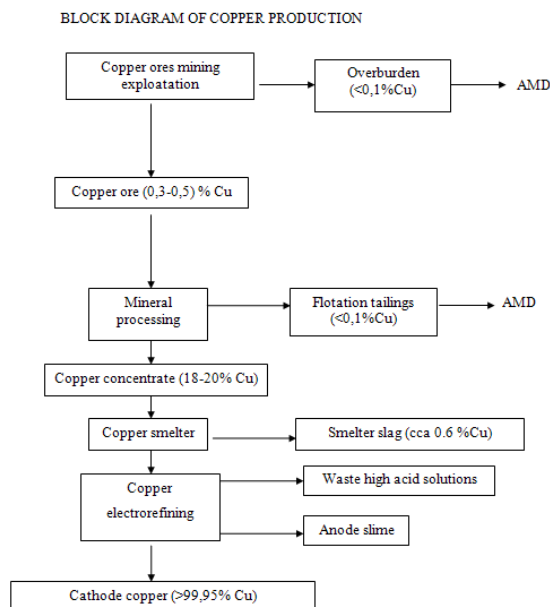


Figure 1. Block diagram of copper production in RTB Bor

Many different biological and chemical technologies exist for treatment of acid mine drainage (AMD) and smelter effluents but neutralization is the most commonly used process for the removal of metals from industrial wastewaters because it offers a most cost effective solution applicable to large operating units [15,16] until different electrochemical and hydro-metallurgical processes are often used in recent years [17-21]. Lime neutralization is most applicable largely due to the high efficiency in removal of dissolved heavy metals combined with the fact that lime costs are low in comparison to alternatives. This treatment essentially consists in bringing the pH of the raw water to a point where the metals of concern are insoluble. These metals therefore precipitate to form minuscule particles. A separation of these precipitates is then required to produce a clear effluent which meets regional discharge criteria. The solid/liquid separation forms a sludge which, depending on the applied process, can contain 1 to 30 wt. % of solids. This sludge must be disposed of in an environmentally acceptable manner. Many studies have demonstrated efficiency of the precipitation in removing various metals (for example, nickel, copper, zinc, cadmium and lead) as sulphide, carbonate and phosphate instead of hydroxide. Besides yield and selectivity, a good knowledge of settling, filterability and dewatering characteristics of the metal precipitates produced is also necessary to evaluate the techno economic performance of different metal precipitation methods.

During the period from 1933 to 1970, the flotation tailing completely degraded the valley of the Bor River, White River and partly Timok. Entire length of the Bor River flow to the emp-

ties into the Krivelj River, about 70 hectares of coastal land was polluted by the flotation tailings. It is estimated that the flotation tailings polluted even more than 2000 ha of the most fertile coastal land of the above rivers. In addition to the physical contamination of the coastal land of the Bor River valley by thousands of tons of flotation tailings, the Bor River is constantly polluted by waste water resulting from draining through the flotation tailings and open pit overburden.

Continuous monitoring the quality and quantity of discharged waste water into the Bor River creates a basis for creating the necessary information base that will be the beginning of an integrated waste water management that, as the result of mining and metallurgical activities in RTB Bor, were discharged untreated into the Bor River. The Bor River belongs to the Timok River basin which flows into the Danube, and thus this river and its coastal region are directly polluted by a number of harmful and dangerous metals. In order to determine the impact of flotation tailings on water pollution in the Bor River, the tailings was subjected to the TCLP test as well as the leaching test.

The reason for this characterization is that the drainage water from the flotation tailing dump cannot be physically sampled because this water is drained through the cracks to the municipal sewer where it is mixed with the utility water. Possibility of metal precipitation from drainage water of the Robule Lake will be tested using 10 wt.% lime milk as well as using FeCl_3 and AlCl_3 as coagulants. Dewatering characteristics of the obtained precipitate will be tested in order to define the conditions for further treatment of the obtained residue. By proper management of mine waste water, the economic effect of copper recovery by chemical or electrochemical methods can be achieved in addition to the environmental effect.

2. Materials and methods

For the purpose of continuous monitoring the quantities and chemical composition of waste water, discharged into the Bor River, at the monthly level, the following samples were taken:

- Drainage water from the Robule Lake,
- Drainage water from the site of flotation tailings deposited on the empty space of the open pit, closed after cessation the exploitation,
- Wastewater generated during metallurgical processes, and
- Water from the Bor River which flows into the above water.

Drainage water of flotation tailing dump cannot be physically sampled because this water is drained into the municipal sewer and thus mixed with the wastewater, utility water. Flotation tailings from Mining and metallurgy copper complex in Bor are deposited on the field, size 380x260 m. Flotation tailing dump, during the earlier period, was sam-

pled in eight drill holes in which the samples in quantities of 5 kg were taken at each 5 m in depth to the value of 20 m [22].

Three samples of 5 kg, originated from the independent drill hole B, were used as representative samples for physic-chemical characterization of determination the material acidity, definition of particle size distribution, apparent density and specific mass, mineralogical analysis as well as the leaching test and TCLP test (B/1-2 m is the sample from depth of 1-2 m from the surface; the sample marked: B/8-9 m is the sample from depth of 8-9 m from the surface and the sample marked: B/15-16 m is the sample from depth of 15-16 m from the surface). The drilling was carried out using the depth prospecting drill set S.K.B-5, by rotary drilling with a simple core tube without the introduction of flush (i.e., dry). Drill holes diameter was 101 mm.

Qualitative-quantitative mineralogical analysis was carried out on a common sample formed from these three samples. Qualitative analysis was carried out using the polarized microscope JENAPOL-U, Carl Zeiss – Jena, and the qualitative analysis was carried out using the software package OZARA v.2.5 in the Pinnacle System for microphotography.

The pH meter WTW INOLAB 720-Series was used to determine the acidity of samples. The sample for determination of acidity was prepared by mixing the flotation tailings with water using the applicable procedure within TCLP test by EPA Test Method 1311 - TCLP.

The water acidity was measured in the field during sampling on the portable waterproof pH meter ROWA as well as in the laboratory conditions after the certain lapse of time using pH meter WTW INOLAB 720-Series.

Flotation tailings is the waste material of extremely uniform structure due to the standard procedure during the flotation process in which the sulfide copper minerals are realized [22]. For these reasons, the sieve analysis of a composite sample, formed from the three samples, was carried out. The method for defining the sieve analysis content depends on the size and type of the raw material. Accordingly, the sieve analysis method was used, in range from 300 to 37 μm . TYLER, MPIF Standard 05 sieving system was used for the sieve analysis, which was confirmed for the last time in 1998 [23].

Atomic emission spectrometry with inductively coupled plasma (ICP-AAS), carried out on a device SPECTRO CIROS VISION, was used to determine Cr, Ni, As, Pb, Cd, Fe and Mn contents in water samples from the Robule Lake, the samples of drainage water from the flotation tailing dump, delayed in the area of empty open pit Bor and water from the Bor River.

In samples of waste water, generated during the metallurgical process, the elements: Cu and Fe were analyzed using the AAS - Atomic Absorption Spectrophotometer (Perkin-Elmer - 100), the elements: As, Pb, Cd, Zn, Ni and Se using the Atomic Emission Spectrometer with inductively Coupled Plasma-ICP-AES (Spectro Ciros Vision).

For determination the contents of suspended solids, the gravimetric method was used, and the turbidimetry was used to determine the content of SO_4^{2-} ions in the analysis of all samples.

Standard EPA Test Method 1311-TCLP was used to determine the toxicity of a composite sample formed from materials of various depths of B drill hole, and the EN 12457-2 method was used for testing the waste in accordance with the relevant legislation in Serbia.

3. Results and discussion

3.1. Characterization of flotation tailings

- a. Mineralogical analysis: The results of quantitative mineralogical analysis showed that pyrite is a dominant mineral and the following: covellite, enargite, chalcopyrite, chalcocite, bornite, tetrahedrite, rutile, limonite, magnetite, leucocosen, sphalerite, sylvanite, arsenopyrite, molybdenite and malachite, and gangue minerals, which were mostly present as quartz, silicates and carbonates. The results of individual samples from drill holes 1-8 [22] show that the composition is very similar for all samples. The average content of a sulphide composite sample, obtained by merging of samples B/1-2 m, B/8-9 m and B/15-16 m is 21.82 wt.%, the average oxide content – 0.454 wt.% and the average ore content does not contain the minerals – 77.8 wt.%.
- b. Sieve analysis, Apparent density and Specific mass: Table 1 shows the results of sieve analysis. Since the material reactivity increases with decreasing the particle sizes, and this is about the material in which the content of fractions finer than 0.038 mm is about 40 wt.%, it can be concluded that there are real pre-conditions for generation the acid main drainage AMD [24].

Size class, mm	W (wt. %)	R – sieve oversize (wt. %)	D – sieve undersize (wt. %)
-0.300 + 0.212	1.20	1.20	100.00
-0.212 + 0.106	7.80	9.00	98.80
-0.106 + 0.075	16.80	25.80	91.00
-0.075 + 0.053	19.60	45.40	74.20
-0.053 + 0.038	15.40	60.80	54.60
-0.038	39.20	100.00	39.20

Table 1. Sieve analysis of the flotation tailing sample

The apparent density was calculated by the following formula:

$$\Delta = \frac{m_2 - m_1}{V} \left(\text{kg/m}^3 \right) \quad (1)$$

where:

V- container capacity, m³

m_1 - mass of container, kg

m_2 - mass of container with sample, kg

Calculated value for apparent density of the wet sample, average value is 2219 kg/m³

Calculated value for apparent density of the dry sample, average value is 2028 kg/m³.

The density (ρ) or a specific mass was defined by the quotient of mass (m) and capacity (V) of homogenous body. In other side, the density equals the mass per 1 m³. Density of the actual sample i.e. a specific mass was done by the glass pycnometer. The following formula was used:

$$\rho = \frac{m_2 - m_1}{(m_4 - m_1) - (m_3 - m_2)} \rho^t \left(\text{kg} / \text{m}^3 \right) \quad (2)$$

where:

m_1 - empty pycnometer mass, (kg)

m_2 – pycnometer mass with sample, (kg)

m_3 – pycnometer mass with sample and water, (kg)

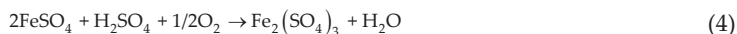
m_4 – pycnometer mass with water, (kg)

ρ^t - fluid (water) density at the measuring temperature, (kg/m³)

The density of the composite sample was 4500 kg/m³.

- c. Acidity of a sample: measurement of acidity showed that the material has higher acidity in the lower depths and the values range from 3.25 in the sample B/1-2 m to 4.35 in the sample B/15-16 m.

After disposal of tailings, the present sulfide minerals are exposed to air and atmospheric effects. As the oxidation process results of present sulfide minerals and above all pyrite, as the predominant mineral, the acid water are created. Generally, the oxidation of pyrite from mining wastes under weathering conditions, and further formation of iron (III) could be represented by the following reactions [25]:



Products of pyrite oxidation are sulphuric acid and iron (III) which further induce oxidation of other sulphide minerals and generation of contaminated Acid Mine Drainages (AMD) with low pH value (2.5-4.5) and increased content of SO₄ and metals ions (Cu, Zn, Pb, As, Cd, Ni i Mn), metalloids. This is confirmed that pyrite (FeS₂) serves as a precursor for the

formation of acid mine drainage, which contains high amount of sulfate ions, metal ions and metalloids and the pH value of solution is between 2.5 and 4.5 [22].

- d. Chemical characterization: chemical characterization of all three samples (Table 2) showed that the values of content the following elements were below the limits of sensitivity of the used analytical methods: Sn, Sb, Cd, Pb, Ni and Mn, while the values of Cu, Fe, As, Zn and Hg contents ranged as follows: Cu-0.67 wt.% max. and 0.097 wt.% min., Fe – 21.22 wt.% max. and 6.42 wt.% min., As – 0.025 wt.% max. and 0.0038 wt.% min., Zn – 0.034 wt.% max. and min 0.026 wt.% min. Hg-0.0001 wt.%. By comparing these values with maximum allowable values, it can be seen that the values for Cu, Zn and As are higher than maximum allowable values of Cu-100 mg/kg, Zn-30 mg/kg, and As-25 mg/kg and that it is realistic to expect that content of these elements in AMD is higher than maximum allowed [26].

Elements, content	Sample of flotation tailings, B/1-2 m	Sample of flotation tailings, B/8-9 m	Sample of flotation tailings, B/15-16 m
Sb, wt %	< 0.005	< 0.005	< 0.005
As, wt %	0.0038	0.015	0.025
Cu, wt %	0.097	0.40	0.67
Hg, g/t	0.2	0.30	0.40
Cd, wt %	< 0.0025	< 0.0025	< 0.0025
Mo, wt %	< 0.001	< 0.001	< 0.001
Ni, wt %	< 0.01	< 0.01	< 0.01
Pb, wt %	< 0.025	< 0.025	< 0.025
Se, wt %	< 0.0040	< 0.0040	< 0.0040
Cr _{total} , wt %	< 0.001	0.012	0.014
Zn, wt %	0.026	0.033	0.034
Fe*, wt %	6.42	5.53	21.22
Al*, wt %	5.62	2.98	2.32
Mn*, wt %	< 0.002	< 0.002	0.0033

Note: values marked with - * - are not regulated by legislation

Table 2. Chemical characterization of copper flotation tailings

- e. Leaching and toxicity: Based on the results of leaching test, which was carried out according to standard procedure SRPS EN 12457-2, this waste is classified in a group of hazardous waste. Copper content is much higher than the legally permitted values. Table 3 shows the comparative values of element contents in different samples of tailings and maximum allowed values according to the current legislation

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Element	Valid legislation	Sample of flotation tailings (B/1-2 m)	Sample of flotation tailings (B/8-9 m)	Sample of flotation tailings (B/15-16 m)
Limit value of concentration, mg/kg dm*	Concentration, mg/dm ³	Concentration, mg/dm ³	Concentration, mg/dm ³	
Sb	5	< 0.1	< 0.1	< 0.1
As	25	< 0.1	< 0.1	< 0.1
Cu	100	1310	1773	2202
Hg	2	< 0.001	< 0.001	< 0.001
Cd	5	< 0.1	< 0.1	< 0.1
Mo	30	< 0.1	< 0.1	< 0.1
Ni	40	/	1,6	1,3
Pb	50	/	9	38
Se	7	< 0.2	< 0.2	< 0.2
Cr _{total}	70	< 0.1	< 0.1	< 0.1
Zn	200	180	237	284
Fe**	/	1290	819	2405
Al**	/	536	495	382
Mn**	/	3,6	4,8	36

Where: dm* - dry mass

** - values are not regulated by the legislation

Table 3. Leaching test, carried out according to the standard procedure SRPS EN 12457-2

Values for the content of following elements: Sb, As, Hg, Cd, Mo, Se, Cr, Bi, Sn, were below the sensitivity limits of the applied chemical methods.

By comparison the obtained values and statutory value for testing the waste and leachate water from the landfills of inert, non-hazardous or hazardous waste, it can be seen that the content of Cu in all samples is far higher than the statutory values by which this waste is classified in a group of hazardous waste; that content of Ni and Pb is within maximum allowable values and that the values for Zn content are above the allowed values for samples (B/8-9 m) and sample (B/15-16 m). The obtained results are in a direct conformity with the results of chemical characterization of tailings (Table 2).

The results of EPA Test Method 1311 - TCLP (Table 4) showed that the value of Cu content of 104.4 mg/dm³ was registered in the sample B/15-16 m almost four times higher than the allowed value according to the current legislation of the Republic of Serbia which is in

agreement with the legislation of the European Union, which classifies this waste in a group of toxic waste.

The increased concentration of Cu in the value of 88.1 mg/dm³ was also registered in B/8-9 m sample while the sample B/1-2 m had lower value than prescribed one. The trend of higher concentrations in samples from lower depths was also observed in other elements that move into eluent during TCLP test.

Element	Valid legislation	Sample of flotation tailings (B/1-2 m)	Sample of flotation tailings (B/8-9 m)	Sample of flotation tailings (B/15-16 m)
Limit value of concentration, mg/kg dm*	Concentration, mg/dm ³	Concentration, mg/dm ³	Concentration, mg/dm ³	
Sb	15	< 0.1	< 0.1	< 0.1
As	5	< 0.1	0.14	0.17
Cu	25	5.7	88.1	104.4
Hg	0.2	< 0.001	< 0.001	< 0.001
Cd	1	< 0.1	< 0.1	< 0.1
Mo	350	< 0.1	< 0.1	< 0.1
Ni	20	< 0.1	< 0.1	< 0.1
Pb	5	< 0.1	0.6	2.6
Se	1	< 0.2	< 0.2	< 0.2
Cr _{total}	5	< 0.1	< 0.1	< 0.1
Zn	250	8.5	11.9	13.2
Fe*	/	12.2	28.5	98.4
Al*	/	12.3	14.6	16.6
Mn*	/	0.13	0.31	1.8

Note: The marked elements* are not on the list of parameters for testing the toxic characteristics of waste such as the obtained values in TCLP test were not discussed.

Table 4. TCLP test, carried out according to the standard procedure EPA Test Method 1311

Content values of Sb, As, Cd, Hg, Mo, Ni, Pb, Sr, Cr_i in effluent were below the values of detection the applied chemical methods.

3.2. Characterization of waste water flowing into the Bor River

1. Drainage water from the Robule Lake

Water from the Robule Lake was analyzed over a period of 12 months, from June 2011 ending to May 2012 (Table 5). Considering the concentration values corresponding to the surface water requirements of Class IV the applicable Rules on dangerous substances in water, it can be seen that the content of all analyzed elements is above the permissible values of the amounts (mg/dm³): Cu - 0.1, Zn - 1.0, Cd - 0.01; Ni - 0.1, Fe - 1.0. By comparison the measured pH values and Rules of prescribed values, which range between 6.0-9.0, it is seen that it is acidic water which presents the polluter of local ecosystem (soil, water).

Robule Lake	pH value	SO ₄ -2 mg/dm ³	Cu mg/dm ³	Mn mg/dm ³	Zn mg/dm ³	Cd mg/dm ³	Ni mg/dm ³	Fe mg/dm ³	Total suspended solids, mg/dm ³
06. 2011	4.08	4907.5	71.6	133.8	29.1	0.09	1.0	575.0	33.0
07. 2011	4.20	4604.2	70.2	122.6	26.4	0.08	0.6	526.4	28.0
08. 2011	2.86	8243.1	69.1	96.0	26.3	0.117	0.738	739.0	12.0
09. 2011	3.49	10570.6	66.9	112.4	25.6	0.11	0.75	812.0	55.0
10. 2011	3.26	7905.7	65.3	108.2	24.3	0.093	0.66	626.8	34.0
11. 2011	2.56	7620.2	53.0	104.3	24.6	0.091	0.72	720.0	32.0
12. 2011	2.70	8243.1	69.1	102.1	26.3	0.117	0.738	739.0	12.0
01. 2012	3.52	10570.6	66.9	98.3	25.6	0.11	0.75	812.0	55.0
02. 2012	3.43	10321.4	64.3	98.8	25.8	0.10	0.68	762.3	52.0
03. 2012	3.54	10518.3	63.2	101.4	26.2	0.097	0.67	581.8	57.0
04. 2012	2.70	7731.7	77.2	96.4	30.4	0.089	0.74	835.6	24.0
05. 2012	3.38	7523.9	64.7	102.3	24.4	0.087	0.67	615.6	29.0

Table 5. Drainage water from the Robule Lake

2. Drainage water of flotation tailings, stored in the area of empty open pit, closed after completion the ore mining operation – RTH

The Old Flotation Tailing Dump (fields 1, 2 and 3) was in the operation since 1933 and it was operational until 1987, after which the storage of flotation tailings from the Old Flotation Plant Bor is done in the empty area of the open pit RTH (after ending the ore mining). Large amount of stored open pit overburden presents a generator of acid drainage water (AMD) generated by the action of rainwater and groundwater (often acid rain precipitation formed at the contact of falls and SO₂ gas) in the oxide, sulphate and carbonate copper minerals, contained in the stored open pit overburden and flotation tailings. This water is characterized by slightly higher pH value than the pH value of drainage water from the Robule Lake, what can be seen comparing the shown values in Tables 5 and 6. Also, the content of elements, registered in drainage water of flotation tailings, stored in the area of empty open pit

and closed after completion the ore mining operation – RTH, is lower than the content on these elements in the Robule Lake.

RTH water	pH value	SO ₄ -2 mg/dm ³	Cu mg/dm ³	Zn mg/dm ³	Cd mg/dm ³	Ni mg/dm ³	Fe mg/dm ³	Total suspended solids, mg/dm ³
06. 2011	4.60	4366.7	18.9	11.4	0.03	0.5	155.1	111.0
07. 2011	4.86	4022.4	16.8	10.2	0.021	0.32	155.1	106.0
08. 2011	5.30	3882.9	11.0	8.65	0.044	0.227	190.1	81.0
09. 2011	5.17	3878.4	12.4	8.42	0.035	0.25	190	97.0
10. 2011	4.08	4298.2	17.9	10.8	0.032	0.48	160	88.0
11. 2011	5.97	4102.2	12.6	10.2	0.036	0.38	100.1	86.2
12. 2011	3.94	3882.9	11.0	8.65	0.044	0.227	190.1	81.0
01. 2012	3.28	3990.6	14.3	7.8	0.28	0.220	184.2	68.0
02. 2012	3.60	4008.4	16.8	7.4	0.32	0.28	162.1	56.0
03. 2012	3.37	4143.4	27.8	7.1	0.36	0.36	86.6	46.0
04. 2012	2.88	3792.1	29.2	7.7	0.024	0.31	148.2	12.0
05. 2012	3.60	3343.4	27.4	6.73	0.03	0.34	103.1	15.0

Table 6. Drainage water from flotation tailings, stored in the area of empty open pit, closed after completed the ore mining operation (RTH)

Regarding to the concentrations of Cu, Zn, Cd, Ni and Fe with the concentration values that correspond to the requirements of surface water Class IV the applicable Rules on dangerous substances in water, it can be seen that the content of all analyzed elements is above the permissible values. Measured values are not also in the range of values defined by the same Rules and the values indicate the fact that it is acid water.

3. Waste water generated in the metallurgical process

Those are composite samples that present total waste water generated in a part of metallurgical production the cathode copper that includes the following production units: electrolytic copper refining, electrolyte regeneration, production of precious metals and sulphuric acid production (Table 7).

Comparing the concentration values that correspond to the requirements of surface water Class IV the applicable Rules, it can be seen that the content of all analyzed elements is above the permissible values as follows (mg/dm³) : Cu – 0.1; Pb – 0.1; Zn – 1.0; Cd – 0.01; Ni – 0.1; Se – 0.01; As – 0.05; Fe – 1.0. Considering the measured pH values with the Rules of prescribed values, it is seen that the values are far lower than the prescribed ones, and by

comparison with the pH values for drainage water from the Robule Lake and drainage water from the site of RTH tailing dump, it is seen that the acidity of this water is the highest.

Metal. complex water	pH value	SO ₄ ⁻²	Cu	Pb	Zn	Cd	Ni	Se	As	Fe	Tot. susp. sol.
mg/dm ³											g/dm ³
06. 2011	3.12	2813.1	514	4.7	457	11	36	8.7	167	3169	2.60
07. 2011	3.24	3228.1	216	5.8	43.9	<0.1	13	31	51.4	3340	2.42
08. 2011	3.62	3567.9	123	4.1	118	2.4	6.4	19.2	45	3760	4.38
09. 2011	3.42	3470.4	335.8	3.7	132	3.7	21	8.2	95	3730	2.80
10. 2011	2.40	5569.1	541	2.8	102	2.4	45	12	134	4766	4.28
11. 2011	2.02	1624.2	86.2	3.0	110.6	2.2	12.1	6.8	120.6	382.2	26.1
12. 2011	2.45	1554.2	58.5	3.1	6.02	0.055	1.53	<0.2	2.55	214.7	71.0
01. 2012	3.06	2880.2	69.2	2.8	8.4	0.080	1.26	<0.2	2.64	368.2	62.2
02. 2012	3.21	3124.6	72.4	1.86	8.8	0.090	1.20	<0.02	2.48	364.2	54.3
03. 2012	2.99	3334.0	75.8	1.50	9.2	0.091	1.15	<0.2	2.85	395.1	48.0
04. 2012	1.89	4976.7	158.2	0.18	8.1	0.033	15.2	<0.2	<0.10	247.5	24.0
05. 2012	2.95	2930.2	158.7	1.6	16.9	0.22	2.2	0.25	3.24	289.0	2.0



Figure 2. Downstream view of the Bor River Valley, 30/04/2012



Figure 3. Point of connection the Bor River and Krivelj River, 30/04/2012

Characterization of water from the Bor River is given in the Table 8:

Bor River	pH	SO ₄ -2 mg/dm ³	Cu mg/dm ³	Pb mg/dm ³	Zn mg/dm ³	Cd mg/dm ³	Ni mg/dm ³	Fe mg/dm ³	Total suspended solids, g/dm ³
06. 2011	3.26	1234.0	10.9	<0.1	3.3	0.03	0.4	85.3	166.0
07. 2011	4.10	1138.0	12.8	<0.1	3.4	0.04	0.6	88.6	184.0
08. 2011	4.26	1157.5	19.2	0.830	3.35	0.031	0.420	86.8	376.0
09. 2011	5.16	998.3	9.9	0.33	2.3	<0.02	0.30	35.6	272.0
10. 2011	4.84	1111.9	14.9	<0.1	2.7	<0.02	0.50	2.3	218.0
11. 2011	5.05	110.3	27.0	0.75	3.1	<0.02	0.48	130.0	342.6
12. 2011	4.53	1157.5	19.2	0.83	3.35	0.031	0.42	86.8	376.0
01. 2012	4.60	998.3	9.9	0.33	2.3	<0.020	0.30	35.6	272.2
02. 2012	5.20	1086.2	8.7	0.24	3.0	<0.02	0.26	12.3	234.2
03. 2012	5.83	1130.0	10.2	<0.1	2.0	<0.020	0.13	2.6	256.0
04. 2012	5.99	782.7	1.5	<0.1	0.98	<0.020	0.16	1.1	219.0
05. 2012	5.67	674.2	2.25	<0.1	1.0	<0.02	0.12	3.32	196.0

Table 8. Water in Bor River

Content of some elements in the Bor River water is also higher than maximum permitted content of for water of Class IV, and the Bor River water must fall into the water with hazardous substances that may endanger the life or health of humans, fish and animals.

Waste water flow from the specified locations is measured quarterly and values are shown in Table 9, where it is seen that the lowest value was measured during the winter while the values for the fall and spring are close.

3.3. Neutralization process and dewatering characteristics of metal precipitate

The principle of lime neutralization of acid mine drainage (AMD or ARD for acid rock drainage) lies in the insolubility of heavy metals in alkaline conditions. By controlling pH to a typical set point of 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated. Other metals such as nickel (Ni) and cadmium (Cd) require a higher pH, in the range of 10.5 to 11 to effectively precipitate the hydroxides. The precipitates can be formed individually as minuscule particles smaller than a single micron.

Neutralization and metal precipitation process was carried out by adding 10 % lime milk in the sample from Robule Lake. The mass of lime is calculated relative to chemical composition of waste water. Compounds FeCl₃ and AlCl₃ were used as coagulants. The effect of different operating parameters on the precipitate characteristic was investigated. The precipitation process is stopped on pH = 9.88. Obtained precipitate settling, compaction and dewatering characteristics were studied too, as a part of this research.

Flow rate measured in autumn 2011		
Waste water	Month of measurement	Flow rate, m ³ /h
Robule Lake	September 2011	7.20
RTH drainage	September 2011	32.4
Metallurgical ww	September 2011	312.8
Bor river	September 2011	2106.4
Flow rate measured in winter 2011		
Waste water	Month of measurement	Flow rate, m ³ /h
Robule Lake	Nov/Dec 2011	5.40
RTH drainage	Nov/Dec 2011	28.6
Metallurgical ww	Nov/Dec 2011	302.2
Bor river	Nov/Dec 2011	1620
Flow rate measured in spring 2012		
Waste water	Month of measurement	Flow rate, m ³ /h
Robule Lake	April/May 2012	6.78
RTH drainage	April/May 2012	30.3
Metallurgical ww	April/May 2012	305.5
Bor river	April/May 2012	1818

Table 9. Flow rates measured in period September 2011 – May 2012

3.3.1. Precipitation process experimental procedure

Neutralization process was carried out on 50 dm³ of real waste water from Robule Lake with the next characteristics (mg/dm³): Cu - 71.3; Ni - 0.7; As <0.1; Fe - 788; Mn - 133.8; Zn - 31; Cr < 0.02; Pb <0.1; Cd - 0.17; SO₄²⁻ = 10047.2; Cl⁻ - 14.71; NO₂⁻ - 0.1; NO₃⁻ - 38.6; consumption KMnO₄ - 41.08; solid residue at 105 °C - 16664.0; Total suspended matters - 23.0, pH value - 2.48.

First step of the neutralization process is lime dissolution. This lime must first be hydrated and fed to the process as slurry. The hydrated lime then dissolves to increase pH. The increased pH then provides hydroxide ions which combine with the dissolved metals to produce precipitates. The following equation shows the general reaction for produce the metal precipitate [27]:



The reaction (5) is characteristic for the next metal cations involved in waste water from Robule Lake: Al³⁺; Co²⁺; Cu²⁺; Fe²⁺; Fe³⁺; Ni²⁺; Pb²⁺; Zn²⁺.

Neutralization process was carried out by adding 10 % lime milk (sample 1). Mass of lime is calculated relative to chemical composition of wastewater. Compounds $FeCl_3$ (sample 2) and $AlCl_3$ (sample 3) were used as coagulants. The effect of different operating parameters on the sludge characteristic was investigated. The neutralization process is stopped on $pH = 9.88$.

Chemical analysis of water during the neutralisation process were performed on a laboratory portable device DR/890 Colorimeter HACH and the results for the Cu and Fe are presented in Table 10.

	pH	Cu, mg/dm ³	Fe, mg/dm ³
start	2.49	71.3	788
I st step	5.34	3.47	4.57
II nd step	7.40	0.04	< 0.1
III rd step	9.88	< 0.1	< 0.1

Table 10. Waste water characterization during the neutralization process

The complete chemical characterization of water samples after the neutralization process showed that the values of Cu, Fe, Mn, Cd, Ni, Zn were below the sensitivity of applied chemical methods

3.3.2. Dewatering characterization

The mass of sample of 5 g was transferred to a measuring cylinder of a 50 ml. The sample level was measured. After adding the volume of 30 ml distilled water, the level of suspension was measured. Then water was added to ratio solid: liquid = 1: 8. After the manual stirring, solution was left to settle and measured the time of settling. Filtration was carried out by gravitational and vacuum methods. Water volume, which can be separated by gravity, was measured in measuring cylinder using filtration of suspension with filter funnel through filter paper marked Quantitative Ashless, 100 circles 5A, 125 mm, and ash contents of filter paper 0.11 mg /circle. Protocols of experiments were the same for both methods gravitational and vacuum and in both cases of neutralization. Only difference was that, in the case of vacuum method of dewatering, the suspension was vacuum filtered through glass filter crucible, G3.

Dewatering by gravitational method

Obtained results are presented in Table 11 and it could be seen that for all samples are similar. The addition of different coagulant reagents did not give a difference in results of dewatering in different samples. Filtration times are similar too.

Obtained results show that settling of sludge comes in a short time and the content of liquid phase in samples after filtration is about 90 %.

Description	unit	sample1	sample2	sample3
Dry sample mass	g	5	5	5
DM water vol.	ml	40	40	40
Sample volume	ml	4.5	4.5	5
Vol.of suspen.	ml	44.5	44.5	45
Settling time	s	25	25.2	26
Filtration time	s	38	40	42
Wet sam. mass	g	9.75	9.25	9.6

Table 11. Parameters and results of dewatering analysis of sludge obtained after gravimetric filtration.*Dewatering by vacuum method*

The obtained results for vacuum filtration are similar. By comparing the values for dry and wet samples it is obvious that the usage of vacuum filtration achieves better dewatering of liquid phase from sample, percentage of water in the samples is about 50 %.

Description	unit	sample1	sample2	sample3
Dry sample mass	g	5	5	5
DM water vol.	ml	40	40	40
Sample volume	ml	4.5	4.5	5
Vol.of suspen.	ml	44.5	44.5	45
Settling time	s	25	25.2	26
Time vac. filt.	s	15	15.6	15.8
Wet sam. mass	g	7.24	7.35	7.4

Table 12. Parameters and results of dewatering analysis of sludge obtained after vacuum filtration.**4. Conclusion**

The results of leaching and toxicity tests of flotation tailings, i.e. the solid waste, originated as the result of mining-metallurgical activities in the area of East Serbia, showed that it is a dangerous and toxic waste. This waste is a constant source of water, soil and air pollution.

The results of chemical analyses of waste water, generated from the investigated sites, showed that water individually presents a pollution source of the Bor River.

The precipitation process of water from the Robule Lake has confirmed the effective purification of this water prior to discharge into the Bor River.

Content of some elements in the Bor River is higher than the statutory maximum allowable lead content for water of the Class IV, and that neither this water should be discharged into the local water ways. It can be said that the Bor River water must be placed into the water with dangerous substances that may endanger the life or health of humans, fish and animals.

The proposed Waste Water Management, in order to reduce the water pollution in the Bor River, cannot immediately or within a short time bring in a properly and clean condition one “dead” river and the black ecological point (or rather the river in which even the bacteria cannot survive). However, what gives a practical contribution of this work to cleaner water in the Bor River, in the coming period, is to establish a mechanism for waste water management. The implementation of waste water management creates the conditions for gradual reduction the newly-formed acid mine water, with the ultimate aim of completely control its creation in the future.

Acknowledgment

This work is financially supported by the Ministry of Science, Republic of Serbia: “The Impact of Mining Waste from RTB Bor on the Pollution of Surrounding Waterways with the Proposal of Measures and Procedures for Reduction the Harmful Effects on The Environment”, No. TR 37001.

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Applications of Magnetite Nanoparticles for Heavy Metal Removal from Wastewater

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/54608>

1. Introduction

Because access to safe drinking water is the key to protect public health, clean water has become a basic need of all properly functioning societies [1]. Despite their presence at low concentration ranges, environmental pollutants possess serious threats to freshwater supply, living organisms, and public health [2].

Contamination of water with toxic metal ions (Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III)) is becoming a severe environmental and public health problem. In order to achieve environmental detoxification, various techniques like adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation and biosorption processes are extensively used [3-5]. Among these, adsorption is a conventional but efficient technique to remove toxic metal ions and bacterial pathogens from water.

Development of novel and cost-effective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention. Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology [6-7].

The synthesis of magnetite nanoparticles has been intensively developed not only for its fundamental scientific interest but also for many technological applications: such as magnetic resonance imaging, ferrofluids for audio speakers, magnetic targeted drug delivery, and magnetic recording media [8]. In particular, the use of magnetite nanoparticles as adsorb-

ents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields.

Bare magnetite nanoparticles are susceptible to air oxidation and are easily aggregated in aqueous systems [9]. Thus, for the application of these nanoparticles in various potential fields the stabilization of the iron oxide particles by surface modification is desirable. The magnetic structure of the surface layer, which is usually greatly different from that in the core of the nanoparticles, can have a notable effect on the magnetic properties of nanoparticles [10]. The control of the size and the polydispersity are also very important because the properties of the nanocrystals strongly depend upon the dimension of the nanoparticles. It is interesting to mention that only magnetite particles with size of less than 30 nm have a large surface area and exhibit super paramagnetic properties that make them prone to magnetic fields and they do not become permanently magnetized without an external magnetic field to support them [11]. These properties are highly useful in the development of novel separation processes [12].

To understand the behavior of the colloidal ferrofluids of the particles and to improve their applications or develop new ones, careful studies related to fluid stability, control of surfactants, particle sizes and physical behavior are essential [8].

We here present recent developments on the use of magnetite nanoparticles (NPs) and magnetite-containing composite nanomaterials for the removal of heavy metals from waters.

2. Synthesis of Fe_3O_4 nanoparticles

For different applications, several chemical methods can be used to synthesize magnetic nanoparticles: co-precipitation, reverse micelles and micro-emulsion technology, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, and electrospray syntheses [8]. The synthesis of superparamagnetic nanoparticles is a complex process because of their colloidal nature. For metal removal applications, an adequate surface modification of the nanoparticles is a critical aspect regarding both selectivity and aqueous stability of these materials. To this end, in the last decade, organic and inorganic functionalized Fe_3O_4 nanoparticles have been developed and modifications of the synthesis methods mentioned above have been proposed. A brief description of the methods most widely used for preparing materials with applications in metal removals is given below:

Co-precipitation: This method is probably the simplest and most efficient chemical pathway to obtain magnetic particles. Magnetite is usually prepared by an aging stoichiometric mixture of ferrous and ferric salts in aqueous medium. The precipitation of Fe_3O_4 is expected at a pH between 8 and 14. The size and shape of the nanoparticles can be controlled by adjusting pH, ionic strength, temperature and nature of the salts [13-14]. Particles with sizes ranging from 5 to 100 nm have been obtained using this method. The addition of chelating organic anions, such as carboxylate ions (e.g. citric, gluconic, or oleic acid) or polymer sur-

face complexing agents (e.g. dextran, carboxydextran, starch, or polyvinyl alcohol) during the formation of magnetite can help to control the size of the nanoparticles [8].

Reverse micelles and micro-emulsion technology: This method includes amphoteric surfactants to create water-swollen reversed micellar structures in nonpolar solvents. Surfactant molecules may spontaneously form nanodroplets of different sizes, micelles (1-10 nm) or water-in-oil emulsions (10-100 nm) [15-16]. In these nanodroplets, aqueous iron salt solutions are encapsulated by a surfactant coating that separates them from a surrounding organic solution. Thus, this system act as nanoreactor for synthesizing nanoparticles as provides a confinement that limits particle nucleation and growth. The main advantage of the reverse micelle or emulsion technology is the diversity of nanoparticles that can be obtained by varying the nature and amount of surfactant and cosurfactant, the oil phase, or the reacting conditions. In addition, the size of the magnetite particle can be controlled by the temperature and the surfactant concentration [15].

Thermolysis of precursors: Organic solution-phase decomposition of the iron precursor at high temperatures (higher than 200 °C) has been widely used in iron oxide nanoparticle synthesis [8]. This method has improved significantly the control of the mean size, the size distribution and the crystallinity of magnetic iron nanoparticles. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products. Many iron precursors have been tested. For example, Sun and Zeng [17], have prepared monodisperse magnetite nanoparticles with size of 3 to 20 nm by reaction at high-temperature (265 °C) of iron acetylacetonate, $\text{Fe}(\text{acac})_3$, in phenyl ether in the presence of alcohol, oleic acid, and oleylamine.

Hydrothermal reactions: Hydrothermal syntheses of Fe_3O_4 nanoparticles have been reported in the literature during the last decade [18-20]. These reactions are performed in aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200 °C. There are two main routes for the formation of magnetite via hydrothermal conditions: hydrolysis and oxidation or neutralization of mixed metal hydroxides. These two reactions are very similar, except that only ferrous salts are used in the first method. In this process, the reaction conditions, such as solvent, temperature, and time, usually have important effects on the products. In the hydrothermal process, the particle size is controlled mainly through the rate processes of nucleation and grain growth.

Magnetic nanocomposites: Fe_3O_4 nanoparticles can be coated with inorganic material such as silica, gold or silver [21-23]. These coatings not only improve the stability of the nanoparticles in solution but also provide sites for covalent binding with specific ligands to the nanoparticle surface. These nanoparticles have an inner iron oxide core with an outer shell of inorganic materials. For example, the use of silica confers great stability to the nanoparticles dispersion against changing of pH and concentration of electrolytes [24]. Chang et al. [25] prepared three types of nano-scale composites comprised of magnetite, silica and aluminosilicate as SPASMs (i.e., aluminosilicate materials incorporated with superparamagnetic particles) via three sequential steps: formation of magnetite by chemical precipitation, coating of silica on magnetite through the acidification method or the sol-gel route, and development of aluminosilicates via the sol-gel route.

3. Characterization of Fe₃O₄ nanoparticles

Among the methods widely used in the literature for Fe₃O₄ nanoparticle characterization and surface determination are: Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Powder X-ray Diffraction (XRD) Technique, Atomic Absorption Spectroscopy (AAS), Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Electrical Conductivity Measurement.

Among the methods used for the determination of the size and size distribution of nanoparticles, a few are applicable in various chemical environments, i.e. small-angle X-ray scattering (SAXS) and dynamic light scattering (DLS). One particular advantage of SAXS is that it can be used to analyze dispersions as well as powders or solids, whereas DLS is limited to dilute solutions. Comparing SAXS with an image-guided method like transmission electron microscopy (TEM), SAXS benefits from a higher statistical quality in the size distribution determination providing information about primary particles and aggregates from a single scattering experiment. Additionally, no high vacuum is required, which limits the samples to solid state samples. TEM has its specific benefits as it delivers direct images and local information on size and shape of nanoparticles. Therefore, these two techniques are complementary and combining both methods can lead to superior information with regard to shape and size of nanoparticles in dispersions or powders [26]. A less common technique to obtain a particle size distribution is the analysis with nitrogen sorption. The evaluation according to BET theory (Brunauer–Emmet–Teller) allows obtaining information on the size of non-agglomerated and dense particles [27].

Comparison between the results obtained by the different techniques in the literature seem to support the view that comprehensive information on particle size, size distribution and shape require the use of more than one characterization technique. Each of the techniques has its specific advantages: TEM delivers direct images, from which information on size and shape of nanoparticles is obtained, SAXS is able to measure powders, solids and also particles in solution, DLS is a fast and cheap method to measure a high number of samples, and BET give the size of nanoparticles as a by-product from the main aim of the method, e.g. the determination of phases within a sample or the specific surface. For many nanomaterials it is observed that DLS exceeds SAXS and TEM by a factor of two or higher. Significantly larger values from DLS might be attributed to larger hydrodynamic shells, as a complex shape of particles as well as their aggregation can influence the numerical evaluation from DLS.

Powder XRD and electronic diffraction patterns (ED) are used to determine the crystal structure and characterization of the bulk Fe₃O₄ nanoparticles. Elemental analysis and surface coverage of magnetite particles may be measured by energy dispersive X-ray spectroscopy (SEM/EDS, EDAX). XPS is used for the analysis of the surface chemistry. Raman and Fourier transform infrared (FTIR) spectroscopy have been used to characterize the phase of the magnetic core of magnetite nanoparticles [28-29]. FTIR spectra yield information on the chemical bonds between the Fe₃O₄ core and the organic surface coverage [30].

Because of the peculiar magnetic properties of magnetite, the particles magnetization as a function of temperature and the hysteresis cycle of both magnetite and composite particles is also used for the characterization of the particle. Normally, magnetite nanoparticles exhibit overall magnetic behavior characteristic of soft magnetic particles, with a narrow hysteresis cycle, and a small coercive field and remnant magnetization. The presence of nonmagnetic shells covering the nanoparticles is evidenced by the fact that magnetization is reduced compared to that of pure magnetite and the initial magnetization field dependence is steeped in the latter case [31]. In general, particle intrinsic coercivity (H_c) and the saturation magnetization are determined by vibrating sample magnetometer (VSM) [32]. However, the effective magnetic core size of the particles may be measured by magnetic relaxometry (MRX) investigating the relaxation behavior in liquid suspensions [33].

Mössbauer spectroscopy analysis may also be performed to distinguish crystallographic phases [34]. Magnetite particles exhibit ferromagnetic properties for observation times shorter than the relaxation time, while superparamagnetic properties are exhibited in the opposite case. Since the time of relaxation increases with the particle size, the Mössbauer spectrum of a dispersed system of magnetic nanocrystals is usually a superposition of a Zeeman sextet, corresponding to the large-size ferromagnetic particles, with a superparamagnetic doublet, corresponding to the particles of smaller size. However, since the time of relaxation in the system of interacting superparamagnetic particles can change due to correlation bonds arising between magnetization vectors of neighboring particles, the shape of the Mössbauer spectra depends both, on the inter-particle interaction and on the superparamagnetic properties of an individual particle. Therefore, interpretation of Mössbauer spectra yields information on particle size and on strong inter-particle interactions [34].

FTIR spectra yield information on the chemical bonds between the Fe_3O_4 core and the organic surface coverage [30].

Thermogravimetric and differential thermal analyses are essential for the determination of the weight of surfactant covering the particle surface per mass of magnetite, and for the determination of desorption binding heat of the covering layers [35-36].

Given that the surface properties of oxides are extremely sensitive to pH variations in the dispersion medium, determinations of the electrophoretic mobility and zeta-potential of the particles are also of importance for their technological applications [28].

4. Metal removal

In the present section we will describe recent literature results related to the application of magnetite nanomaterials for the removal of heavy metals and metalloids from water, mainly copper, chromium, mercury and arsenic.

Yantasee et al. [12] prepared superparamagnetic iron oxide (Fe_3O_4) nanoparticles with a surface functionalization of dimercaptosuccinic acid (DMSA) and employed them as an effective sorbent material for toxic soft metals such as Hg(II) , Ag(I) , Pb(II) , Cd(II) , and Tl(I) ions which effectively bind to the DMSA ligands and for As(III) which binds to the iron oxide lattices. The nanoparticles could be separated from solution within a minute with a 1.2 T magnet. The authors compared the chemical affinity, capacity, kinetics, and stability of the magnetic nanoparticles to those of conventional resin based sorbents (GT-73), activated carbon, and nanoporous silica (SAMMS) of similar surface chemistries in river water, ground-water, seawater, and human blood and plasma. $\text{DMSAFe}_3\text{O}_4$ showed a capacity of 227 mg of Hg/g , a 30-fold larger value than that of GT-73.

Singh et al [37] prepared magnetite nanoparticles functionalized with carboxyl (succinic acid), amine (ethylenediamine) and thiol (2,3-dimercaptosuccinic acid) groups. These nanoparticles were used for removal of toxic metal ions (Cr(III) , Co(II) , Ni(II) , Cu(II) , Cd(II) , Pb(II) and As(III)) and bacterial pathogens (*Escherichia coli*) from water.

Liu et al. [38] developed humic acid (HA) coated Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4/\text{HA}$) for the removal of toxic cations such as Hg(II) , Pb(II) , Cd(II) , and Cu(II) from water. $\text{Fe}_3\text{O}_4/\text{HA}$ were prepared by the coprecipitation method. TOC and XPS analyses showed that the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ contains ~11% (w/w) of HA fractions abundant in O and N-based functional groups. TEM images and laser particle size analysis revealed that the $\text{Fe}_3\text{O}_4/\text{HA}$ (with ~10 nm Fe_3O_4 cores) aggregated in aqueous suspensions to form aggregates with an average hydrodynamic size of ~140 nm. Sorption of the heavy metals to $\text{Fe}_3\text{O}_4/\text{HA}$ reached equilibrium in less than 15 min, and agreed well to the Langmuir adsorption model with maximum adsorption capacities ranging from 45 to 100 mg/g. The $\text{Fe}_3\text{O}_4/\text{HA}$ was able to remove over 99% of Hg(II) and Pb(II) , and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH.

Badruddoza et al. [39] fabricated carboxymethyl- β -cyclodextrin modified Fe_3O_4 nanoparticles (CM β CD-MNPs) for removal of copper ions from aqueous solution by grafting CM β CD onto the magnetite surface via carbodiimide method. The characteristics results of FTIR, TEM, TGA and XPS show that CM- β -CD is grafted onto Fe_3O_4 nanoparticles. The grafted CM- β -CD on the Fe_3O_4 nanoparticles contributes to an enhancement of the adsorption capacity because of the strong abilities of the multiple hydroxyl and carboxyl groups in CM- β -CD to adsorb metal ions. The adsorption of Cu(II) onto CMCD-MNPs was found to be dependent on pH and temperature. The thermodynamic parameters reveal the feasibility, spontaneity and exothermic nature of the adsorption process. FTIR and XPS reveal that Cu(II) adsorption onto CMCD-MNPs mainly involves the oxygen atoms in CM- β -CD to form surface-complexes. In addition, the copper ions can be desorbed from CMCD-MNPs by citric acid solution with 96.2% desorption efficiency and the CMCD-MNPs exhibit good recyclability.

Goon et al. [40] studied the controlled adsorption of polyethylenimine (PEI) onto 50 nm crystalline magnetite nanoparticles (Fe_3O_4 NPs) and how these PEI-coated Fe_3O_4 NPs can be used for the magnetic capture and quantification of ultratrace levels of free cupric ions. The authors were able to systematically control the amount of PEI adsorbed onto the Fe_3O_4 mag-

netic nanoparticle surfaces by varying the concentration of polymer during the adsorption process. This work demonstrated that the NPs ability to bind with copper is highly dependent on the amount of PEI adsorbed on the NP surface. It was found that PEI-coated Fe_3O_4 NPs were able to capture trace levels (~2 ppb) of free cupric ions and concentrate the ions to allow for detection via ICP-OES. They also showed that due to the amine-rich structure of PEI, the PEI-coated Fe_3O_4 NPs selectively adsorb toxic free cupric ions but not the less toxic EDTA complexed copper.

Chou and Lien [41] prepared dendrimer-conjugated magnetic nanoparticles (Gn-MNPs) combining the superior adsorbent of dendrimers with magnetic nanoparticles (MNPs) for effective removal and recovery of Zn(II). The adsorption efficiency increases with increasing pH. At pH less than 3, Zn(II) is readily desorbed. Hence, the Gn-MNPs can be regenerated using a diluted HCl aqueous solution (0.1 M) and Zn(II) can be recovered in a concentrated form. It was found that the Gn-MNPs still retained the original removal capacity of Zn(II) after 10 consecutive adsorption–desorption stages.

Wang et al. [42] developed amino-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanomaterial with a core–shell structure to remove heavy metal ions from aqueous media. The structural, surface, and magnetic characteristics of the nanosized adsorbent were investigated by elemental analysis, FTIR, N_2 adsorption–desorption, transmission electron microscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, vibrating sample magnetometry, thermogravimetric analysis, and zeta-potential measurement. The amino-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoadsorbent exhibited high adsorption affinity for aqueous Cu(II), Pb(II), and Cd(II) ions, resulting from complexation of the metal ions by surface amino groups. Moreover, the adsorption affinity for heavy metal ions was not much affected by the presence of a cosolute of humic acid or alkali/earth metal ions (Na^+ , K^+ , etc.). The metal-loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ nanoparticles could be recovered readily from aqueous solution by magnetic separation and regenerated easily by acid treatment.

Shishehbore et al. [43] reported a method for the pre-concentration of trace heavy metal ions in environmental samples. The method is based on the sorption of Cu(II), Cd(II), Ni(II) and Cr(III) ions with salicylic acid as chelate on silica-coated magnetite nanoparticles. The adsorbent was characterized by XRD, SEM, BET and FT-IR measurements. The method was successfully applied to the evaluation of these trace and toxic metals in various waters, foods and other samples.

Wu et al. [44] showed that Fe_3O_4 can be used to disperse nano- Fe^0 and thus sustain Cr(VI) mitigation by nano- Fe^0 . Fe^0 nanoparticles can attach to the surface of Fe_3O_4 by addition of large Fe_3O_4 -NPs into the reaction solution during the preparation of Fe^0 nanoparticles. The introduction of Fe_3O_4 prevents the aggregation of Fe^0 nanoparticles and keeps the high efficiency of the nanocomposite for Cr(VI) reduction. Their results suggest that higher proportions of Fe_3O_4 in the nanocomposites could increase the rate of Cr(VI) reduction, and the optimal ratio of $\text{Fe}_3\text{O}_4\text{:Fe}^0$ for Cr(VI) reduction was determined to be 40:1. The authors also showed that solution pHs significantly affect the rate of Cr(VI) reduction, with reactions occurring faster under acidic or neutral than basic conditions.

Cutting et al. [45] showed that nanomagnetites produced by the bacterial reduction of schwertmannite powder were more efficient at reducing Cr(VI) than either ferrihydrite “gel”-derived biomagnetite or commercial nanoscale Fe₃O₄. Schwertmannite-derived biomagnetite proved capable of retaining more (~20%) ⁹⁹mTc(VII) than ferrihydrite-derived biomagnetite, confirming that the production of biomagnetite can be fine-tuned for efficient environmental remediation through careful selection of the Fe(III) mineral substrate supplied to Fe(III)-reducing bacteria.

Wang et al. [46] investigated As(V) speciation resulting from different sorption processes on magnetite nanoparticles, including both adsorption and precipitation. Using X-ray absorption fine structure (XAFS) spectroscopy and transmission electron microscopy (TEM), they conclude that As(V) could form complexes at the surfaces of the small nanoparticles and could be progressively incorporated in their structure with increasing As loading. These results provide some of the fundamental knowledge about As(V)-magnetite interactions that is essential for developing effective water treatment technologies for arsenic.

Chen et al. [47] synthesized multiwalled boron nitride nanotubes (BNNTs) functionalized with Fe₃O₄ nanoparticles (NPs) for arsenic removal from water solutions. Adsorption experiments conducted at neutral pH (6.9) and room temperature using the developed nanocomposites revealed effective arsenic (V) removal. The Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms were tested for a range of As(V) initial concentrations from 1 to 40 mg/L under the same conditions. The equilibrium data well fitted all isotherms, indicating that the mechanism for As(V) adsorption was a combination of chemical complexation and physical electrostatic attraction with a slight preference for chemisorption.

Chowdhury and Yanful [48] investigated the adsorption of arsenic and chromium by mixed magnetite and maghemite nanoparticles from aqueous solution. These authors employed a commercially grade nanosize ‘magnetite’, later identified in laboratory characterization to be mixed magnetite-maghemite nanoparticles in the uptake of arsenic and chromium from different water samples. Their results showed 96-99% arsenic and chromium uptake under controlled pH conditions. The maximum arsenic adsorption occurred at pH 2 with values of 3.69 mg/g for As(III) and 3.71 mg/g for As(V) when the initial concentration was kept at 1.5 mg/L for both arsenic species, while at the same pH Cr(VI) sorption capacity was 2.4 mg/g with an initial Cr(VI) concentration of 1 mg/L. Their results also showed the limitation of arsenic and chromium uptake by the nano-size magnetite-maghemite mixture in the presence of a competing anion such as phosphate.

Yang et al. [49] studied the effect of Zn(II) on both the kinetic and equilibrium behavior of arsenic adsorption to magnetite nanoparticles in the pH range 4.5-8.0. At pH 8.0, adsorption of both arsenate and arsenite to magnetite nanoparticles was significantly enhanced by the presence of small amount of Zn(II) in the solution. The adsorption rate also increased signifi-

cantly in the presence of Zn(II). The adsorption enhancement effect of Zn(II) was not observed at pH 4.5-6.0, nor with ZnO nanoparticles, nor with surface-coated Zn-magnetite nanoparticles. The enhanced arsenic adsorption in the presence of Zn(II) cannot be due to reduced negative charge of the magnetite nanoparticles surface by adsorption of Zn(II) because other cations, such as Ca(II) and Ag(I), failed to enhance arsenic adsorption. Formation of a ternary surface complex by zinc, arsenic and magnetite nanoparticles was proposed as a possible mechanism controlling the observed zinc effect. Zinc-facilitated adsorption provides further advantage for magnetite nanoparticle-enhanced arsenic removal over conventional treatment approaches.

Zhang et al. [50] showed that the application of starch as a stabilizer in preparation of the Fe_3O_4 particles is able to efficiently reduce particle aggregation, and thus, effective particle size, resulting in much greater specific surface area and adsorption sites. Moreover, the presence of starch leads to the formation of more effective adsorbing sites on magnetite particle surfaces. By employing the XAFS technique, the authors showed that arsenate is adsorbed on starch-stabilized magnetite nanoparticles mainly as inner-sphere bidentate and monodentate complexes. The coordination numbers of As-Fe binding increases with increasing starch concentration, which indicates that the arsenate is more firmly adsorbed at higher starch concentrations.

An et al. [51] prepared and tested a new class of starch-bridged magnetite nanoparticles for removal of arsenate from spent ion exchange brine. Maximum uptake was observed within a pH range of 4-6. The Langmuir capacity coefficient was determined to be 248 mg/g at pH 5.0. The final treatment sludge was able to pass the TCLP (Toxicity Characteristic Leaching Procedure) based leachability of 5 mg/L as As.

All the results described in this section are summarized in Table 1.

5. Perspectives

As illustrated in this book chapter, the use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removing the contaminants by applying external magnetic fields. In particular, technologies based on the utilization of magnetite nanoparticles for the removal of heavy metals from wastewaters are under active development as highly effective, efficient and economically viable nano-adsorbents. Among the main advantages of these nanomaterials is the possibility of surface modifications with different organic or inorganic coating agents to allow the removal of a wide range of heavy metals with specificity. However, the application of these methods is still limited in the early stage and more research in the field is certainly necessary.

In conclusion, there is much recent interest in the use of engineered magnetite nanoparticles in wastewater treatment. However, uncertainties over the health impacts and environmental fate of these nanomaterials need to be addressed before their widespread application. Research on their fate and impact in the environment is required due to the discharges already occurring to the environment.

Synthesis Method	Coating agents	Surface functionalized group	Metal removed	Ref.
Thermolysis of precursors	dimercaptosuccinic acid	Thiol group	Hg(II), Ag(I), Pb(II), Cd(II), Ti ⁺	[12]
Co-precipitation	succinic acid	Carboxylic group	Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), As(III)	[37]
Thermolysis of precursors	ethylenediamine	Amine group		
Thermolysis of precursors followed by ligand exchange process	dimercaptosuccinic acid	Thiol group		
Co-precipitation	Humic acid	Carboxylic and phenolic group		
Co-precipitation	carboxymethyl- β -cyclodextrin	Carboxylic group	Cu(II)	[39]
Crystallization from ferrous hydroxide gels	polyethylenimine	Amine group	Cu(II)	[40]
Co-precipitation	dendrimers	Amine group	Zn(II)	[41]
Co-precipitation followed by a sol-gel process using sodium silicate ($\text{Fe}_3\text{O}_4@\text{SiO}_2$)	(3-aminopropyl) trimethoxysilane	Amine group	Pb(II), Cd(II), Cu(II)	[42]
Co-precipitation followed by hydrolysis of TEOS, ($\text{Fe}_3\text{O}_4@\text{SiO}_2$)	salicylic acid functionalized silica	Carboxylic group	Cu(II), Cd(II), Ni(II), Cr(III)	[43]
Stabilization of Fe^0 nanoparticles with Fe_3O_4	-	-	Cr(VI)	[44]
Bacterial reduction of schwertmannite	-	-	Cr(VI), Tc(VII)	[45]
Co-precipitation	-	-	As(V)	[46]
BNNTs functionalized with Fe_3O_4 nanoparticles	-	-	As(V)	[47]
Commercially available magnetite-maghemite mixture nanoparticles	-	-	As(V), As(III), Cr(VI)	[48]
Commercially available magnetite.	-	-	As(V), As(III)	[49]
Modification of co-precipitation method	Starch	hydroxyl group	As(V)	[50]
Modification of co-precipitation method	Starch	hydroxyl group	As(V)	[51]

Table 1. Application of magnetite nanomaterials for the removal of heavy metals from water.

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The Effect of Solar Radiation in the Treatment of Swine Biofertilizer from Anaerobic Reactor

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51946>

1. Introduction

The intensive process of creating confined pigs generates large amounts of waste, characterized as polluters of great impact to the environment. According to the Brazilian environmental legislation, Law No. 9.605/98, the amount of effluent produced by swine requires appropriate destination, and the producer may be held criminally responsible for damage caused to the environment, human health and animals.

The diet used to feed swine has a high nutritional value, and what is effectively utilized by the animals is approximately 50% and the remainder is excreted in their feces. In relation to the organic load, the pig manure has a greater power of pollution than the domestic sewage. However, the effluent of these animals contains important chemicals that are necessary in agriculture which, when added to soil, can act as fertilizer, replacing part of chemical fertilizers. However, irrigation with wastewater from pig farms, especially in growing vegetables, generates constant concern about the risks of contamination by pathogenic organisms.

In this sense, the efficiency of a disinfection process to reduce these pathogens in water or wastewater is essential. The disinfection may be performed by chemical and physical processes. In chemical processes what is mainly used are: chlorine gas, sodium hypochlorite, chlorine dioxide and ozone. In the physical processes what is mainly used is the heat and

light produced by the Sun, specifically ultraviolet radiation. Therefore, in this chapter the aim is to demonstrate the effect of ultraviolet radiation on bacteria and endoparasites present in pig biofertilizer.

2. Pig industry in Brazil and worldwide

According to the Brazilian Association of Producers and Exporters of Pork [1], the world production of pork in 2011 was 101.13 million tons. Brazil ranks fourth in the world ranking of production, behind China, European Union and the United States. Another relevant fact is that pork production in Brazil is growing year after year. On the issue of Pork exports, Brazil occupies a prominent position in at fourth place.

The main Brazilian producers are the states: Santa Catarina, Rio Grande do Sul, Parana and Minas Gerais, but the State of Mato Grosso do Sul is who has achieved the highest growth rates [1]. With the increasing swine production, environmental pollution by waste and dejects is a problem that has escalated alarmingly.

Recent assessments have shown a high level of contamination of rivers and surface waters that supply both the rural and urban areas [2]. According to this author, using the concept of equivalent population, a pig, on average is equivalent to 3.5 people in terms of contamination by effluent. The pollutant capacity of a pig is higher than any other species. In other words a farm with a population of 1,000 animals pollutes the environment more than a city of 3,500 inhabitants.

The pig deject is composed of feces, urine, drinking and cleaning waste water, wasted feed, and dust caused by the breeding process [3]. The main causes of sewage pollution by swine effluents is due to its untreated release into waterways, which causes an imbalance due to the reduction of dissolved oxygen in water, the spreading of pathogens and soil and water contamination by nitrates, ammonia and other toxic elements [2].

However, the search for ways to reduce the impact on the environmental, such as the methanogenic fermentation of biodigesters, whose product is rich in nitrogen, phosphorus, potassium and biogas, still continues.[3, 4].

The production of effluents by pig farms has brought great concern due to its high rate of contamination and its large volume as shown in Table 1. Table 2 shows the minimum, average and maximum for the physical-chemical characterization of pig manure obtained in the unity of the waste treatment system of Embrapa (Brazilian Agricultural Research Corporation) in the City of Concord in the State of Santa Catarina - Brazil.

2.1. Risks of pollution from pig manure

The improper disposal of pig waste can contaminate surface water with organic matter, nutrients, fecal bacteria and sediment. Nitrates and bacteria are components that affect the quality of underground water systems [2].

Category	Manure (kg/day)	Manure + Urine (kg/day)	Liquid Waste (Liters/day)
Pigs (25 – 100 kg)	2,30	4,90	7,00
Sow gestation	3,60	11,00	16,00
Lactating sow + piglets	6,40	18,00	27,00
Neck	3,00	6,00	9,00
Weaning piglets	0,35	0,95	1,40

Table 1. Daily production of pig manure in different production phases Source: Adapted from [4].

Parameter (mg.L ⁻¹)	Low	Medium	High
COD	11.530	25.543	38.448
Solids	12.697	22.399	49.432
Total Volatile Solids	8.429	16.389	39.024
Fixed Solids Total	4.268	6.010	10.409
Settling Solids	220	429	850
Nitrogen Total	1.660	2.374	3.710
Phosphorus Total	320	578	1.180

Table 2. Physical-chemical characterization of pig manure in Concordia, Santa Catarina Source:[5]

Ceretta et al (2005), studying the importance of runoff as a phenomenon of loss of nitrogen and phosphorus applied through pig slurry in an area cultivated with the rotation oat / corn / turnip, concluded that losses by disposal of nitrogen and phosphorus for the nutrition of plants are considered small, but their concentrations in the major peaks are at risk of eutrophication sources of bodies of water.

Fertilization with excessive or continued swine waste can cause undesirable environmental impacts such as biological and chemical imbalances in the soil, water pollution, loss of productivity and quality of agricultural products and reduce the diversity of plants and soil organisms [8].

The production of pigs can generate other types of pollution such as the odor that occurs due to evaporation of volatile compounds that cause harmful effects to human welfare and animal. The types of airborne contaminants are more common in waste are ammonia, methane, volatile fatty acids, H₂S, N₂O, ethanol, propanol, dimethyl sulfide and carbon. The emission of gases can cause severe damage to the breathing airways of both man and animals, as well as the formation of acid rain through discharges of ammonia in the atmosphere and contribute to global warming [9,10].

2.2. Disinfection of waste

During effluent treatments, the pathogen reduction is essential and this process can be chemic, with the use of disinfectant, or by physical process, destroying or inactivating these agents [11]. The efficient disinfection of the water supply and waste effluent can considerably reduce the transmission of diseases by water [12].

Chlorine is widely used to treat waste water. However, reacting with natural organic matter, this chemical agent generates sub products as chloroform, monochloroacetic acid, trichloroacetic and dichloroacetic. These compounds are considered potentially harmful to human health [13].

It is therefore necessary to develop ways of disinfection without risk to the environment and to humans, while at the same time, maintaining the efficiency provided by chlorine disinfection [14].

Alternative methods of disinfection are being developed in order to replace chemical products, reducing the formation of precursors of trihalomethanes or other byproducts with carcinogenic potential [15].

The use of ultraviolet radiation is an alternative to chemicals in the process of disinfection of drinking water and also wastewater [16], with the advantage of not generating unwanted byproducts and it does not keep waste that could affect the balance of the ecosystem where the effluent is being released [14].

2.3. Ultraviolet

Ultraviolet radiation corresponds to the portion of the electromagnetic spectrum which lies between the X-rays and visible light [14]. Ultraviolet radiation can be an alternative to using traditional chemicals in the process of disinfection of drinking water and wastewater [15].

The effect of ultraviolet light on living beings can be divided into UV-A, UV-B, UV-C and UV-vacuum. The UV-A radiation has wavelength between 315 nm (90.8 kcal / einstein) and 400 nm (71.5 kcal / einstein). UV-B has a wavelength between 280 nm (102 kcal / einstein) and 315 nm (90.8 kcal / einstein). The UV-A radiation is less harmful to humans because has low energy and the "black light" be present. This radiation is used to produce florescence in materials, in phototherapy and artificial tanning [17].

According to Ryer (1997) quoted by [17], UV-B radiation is the most destructive form of light, by having enough energy to cause damage in biological tissues, and the minimum amount that is not completely absorbed in the atmosphere. This radiation is responsible for causing skin cancer.

UV-C has a wavelength ranging from 200 nm (143 kcal / einstein) at 280 nm (102 kcal / einstein), is the ultraviolet radiation used as a germicide. The photons of light in this range concentrate significant amounts of energy in collisions with oxygen, resulting in the formation of ozone and are absorbed in a few hundred meters [17]. The range of the wavelength used as a germicide high-power deactivation of microorganism is between 245 nm (116.7 kcal / einstein) and 285 nm (100.4 kcal / einstein).

The vacuum-UV radiation has a wavelength 40 to 200 nm. The first scientists to report the germicidal effect of sunlight were the British Downes and Blunt in 1877 [18]. Initially, this radiation was used for disinfection of air, pharmaceuticals products and compact stations of drinking water treatment, especially on shipping vessels [14]. The bactericidal effects of UV radiation were proven more accurate form by Barnard and Morgan in 1903, who utilized electrical currents to produce radiation with a wavelength between 226 nm and 328 nm [17].

2.4. Mechanism with ultraviolet disinfection

The main mechanism of action of ultraviolet radiation in the disinfection process, using the wavelength in sunlight, is by interfering in the biosynthesis and cell reproduction. The microorganisms are inactivated by ultraviolet radiation as a result of photochemical damage caused to nucleic acids, hampering the normal functioning [16, 15].

The UV radiation does not inactivate the microorganisms by chemical reaction, as with most of the disinfecting agents used in water. The inactivation of microorganisms occurs by the absorption of high-energy, which promotes photochemical reactions with the fundamental components of cells, disrupting the mechanism of duplication or killing the same [18].

The ultraviolet disinfection occurs due to absorption of radiation by proteins and nucleic acids DNA and RNA. With the UV absorption of proteins present in the cell membranes there is a rupture of these membranes and consequently cell death. The absorption of low doses of ultraviolet radiation by DNA can just interrupt the reproduction of microorganisms, preventing them from contaminating the environment [15].

Frequently the absorption of ultraviolet light present in the DNA molecules, such as purines and pyrimidines, becomes more reactive. The maximum absorption of ultraviolet radiation by DNA occurs at 260 nm, suggesting that inactivation by radiation is measured by direct absorption of the purine and pyrimidine molecules, leading to the formation of dimers and hydrates [15]. The ultraviolet radiation passes through the cell wall and is absorbed by nucleic acids and to a lesser extent, by the proteins and other molecules that are biologically important [12].

Ultraviolet radiation absorbed by DNA nitrogen bases may result in the formation of pyrimidine dimers. These molecules deform the helical structure of DNA and impair the replication of the nucleic acid. If replication occurs, the new cells will be mutant descendants unable to replicate (WEF, 1995 quoted by [17]. According to Daniel et al. (2001) this is the fundamental mechanism of disinfection by ultraviolet radiation as shown in Figure 1.

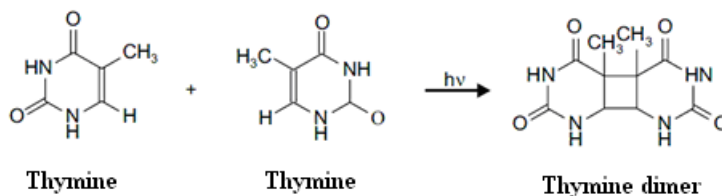


Figure 1. Dimerization photochemical thymine of two bases. Source: [14].

2.5. Advantages and disadvantages of ultraviolet

The advantages of using ultraviolet radiation as a disinfectant agent in water treatment are [14]:

- Ultraviolet radiation is effective for wide range of bacteria and viruses, using relatively small doses;
- Minimum health risks - the formation of byproducts is minimal;
- Gives no residual action, which could react with organic substances in commercial or industrial applications - for example, discoloration is not produced, or a change of flavor, when using ultraviolet radiation in the food industry;
- Safety and acceptance by the operators and the public - no toxic chemical is transported, stored or handled;
- Simplicity and low costs of operation and maintenance - ultraviolet radiation equipment is simpler than the equipment for generating ozone and chlorine dioxide;
- Short contact time, therefore, does not require huge tanks of contact, effective disinfection doses are achieved in a few seconds, compared to the period of 10 to 60 minutes for other disinfecting technologies, being that it is system with an external power source.

Among the disadvantages of disinfection with ultraviolet radiation, are:

- The repair mechanisms of damage DNA caused of microorganisms, if a sub lethal dose is employed;
- The material dissolved or suspended reduces the intensity of radiation as it passes through the water depth;
- It doesn't confer effect to the distributed water because its action is immediate.

However, the fact that ultraviolet radiation does not leave a disinfectant residual in the water has arguably been appointed as an argument for the use of chlorine, because in reality, there is potential for biofilm formation in water distribution networks. If the water contains nutrients (mainly, assimilable organic carbon), these can accumulate around the pipes, supporting microbiological growth and, furthermore, the presence of 1 mg / L free chlorine residual does not guarantee that the biofilm is not formed on the surfaces of pipes and coliforms at 45°C are not found in drinking water [19].

According to Daniel et al. (2001), the disinfection with ultraviolet radiation is most effective for water with a small value of color and turbidity due to the need of light penetration in the center, therefore the quality of water to be treated is an important factor in using this process.

3. Materials and methodology

This study was conducted at the Experimental Farm Professor Hamilton Abreu Navarro (FEHAN), Institute of Agricultural Sciences (ICA) of the Federal University of Minas Gerais, Regional Campus Montes Claros / MG.

The FEHAN is located 7 km from the city center and has an area of 232 ha. Montes Claros is situated at latitude $16^{\circ} 43' 41''$ South and longitude $43^{\circ} 52' 54''$ west (Figure 2). For this municipality, the average altitude is 646 meters in an area of 3568.93 km² and a population estimated at 361.9 thousand inhabitants [20].



Figure 2. Geographical location of the municipality of Montes Claros – MG; Source: Available at: www.skyscraperpcity.com.

At FEHAN, the number of pigs is of 180 animals raised in an intensive production system with complete cycle, i.e., raise, reraise and fatten. The animals are confined to bays, gestation cages and birthing cages. The slaughter age is around six months, weighing on average 100 kg. The animals' diet is based on ground corn, soybean and vitamins / minerals. Water is provided in abundance through troughs in the form of a pacifier.

The cleaning of the swine area happens in the morning with the scraping of excrements and high pressure hose. The effluent is directed by gravity to the digester Indian model with functional load capacity of 17.42 m³ for treatment (Figure 3).

After treatment in the biodigester, for a period of 45 days, samples were collected from 40 liters of effluent and placed in the disinfection device, that we developed, made from recyclable transparent "Pet" bottles, as Figure 4, with the principle of thermosyphon, given the denomination of Ultraviolet Radiation Treatment System (SITRU), the samples were then exposed to ultraviolet radiation for eight consecutive days. The SITRU consists of five columns of

transparent 2 liter containers of "Pet" each, connected by drainpipes (200 mm) and silicone. Connections are of 32 mm PVC whose function is to link the five columns of "Pet". A 20 liter container is at the top as a reservoir of effluent, which is connected to SITRU through a pipe of 32 mm at the top and a pipe of 32 mm at the bottom, as can be seen in Figure 4. The SITRU was placed towards the west at an inclination of 30° . The temperatures of the effluent in the ultra-violet treatment system were collected at two periods (Figure 5, Table 3).



Figure 3. Biodigester Indian Model.



Figure 4. Ultraviolet Radiation Treatment System (SITRU) - Effluent



Figure 5. Temperature measurement of the effluent.

The laboratory tests were conducted with the aim of verifying the disinfecting power of solar radiation. Analyzed, the presence of helminth eggs protozoa and oocysts per gram of feces in the biofertilizer in triplicate, at the start of the treatment in the SITRU and at the end of treatment in the SITRU, i.e. parasitological tests were carried out in two stages.

Day	Time	Effluent temperature °C	Temperature range (Δt) °C
12/09/2010	15:00	21	-
13/09/2010	9:00	18	9
13/09/2010	15:00	27	
14/09/2010	9:00	19	15
14/09/2010	15:00	34	
15/09/2010	9:00	20	13
15/09/2010	15:00	33	
16/09/2010	9:00	20	14
16/09/2010	15:00	34	
17/09/2010	9:00	19	14
17/09/2010	15:00	33	
18/09/2010	9:00	20	14
18/09/2010	15:00	34	
19/09/2010	9:00	19	14
19/09/2010	15:00	33	

Table 3. Monitoring the temperature of the effluent in the SITRU reservoir during the days in the field experiment.



Figure 6. Sample collection for laboratory analysis.

The disinfection efficiency of the biofertilizer by solar radiation was assessed in parasitological and microbiological analyzes in the laboratories of the Institute of Agricultural Sciences - UFMG.

Parasitological analyzes were performed at the Parasitological laboratory and the method used was the sedimentation technique for counting eggs per gram of feces / biofertilizer in a Sedgewick Camera for the detection of helminth eggs and protozoan oocysts [21]. In the first stage, the tests evaluated the *biofertilizer* at the beginning of the treatment in the SITRU; in the second step, analyzes were performed at the end of eight days of treatment in the SITRU. The results of the parasitological analyzes were transformed into $\log(x + 1)$ and the means compared the test "t" Student with significance level of 5%.

Microbiological analyzes were performed in the Microbiology laboratory in accordance with [22] using the method of most probable number (MPN / mL) achieved from the application of the multiple tube technique, which consists in the inoculation of decreasing volumes of sample in a suitable environment for growth of the target organisms, each volume being inoculated in a series of 3 tubes for total coliforms count at 35 °C, fecal coliforms count at 45 °C and for the identification of *E. coli* in the sample of biofertilizer.

Following APHA (2001), another method used the Agar Mac Conckey. The samples were transferred to plates containing this medium to obtain isolated colonies. Each plate colonies were used for confirmatory biochemical analyzes. The colonies that had characteristics of presumptive *E. coli*, were analyzed, taking into consideration its aspects. For confirmatory

biochemical tests, tubes were used, containing Middle Rugai modified with lysine. The collected samples were taken daily in a volume of 200 mL, refrigerated and sent to laboratories. Analyses were performed immediately after collection.

4. Results and discussion

Tests of the microbiological samples of disinfection with solar radiation in the SITRU were performed in two steps. In the first step the determination results of the MPN / ml of total coliforms and fecal coliforms are shown in Table 4. It was not possible to perform the test for *E. coli* using the NMP / mL, considering that no gas was formed in the pipes of Durham present in the E.C. As shown in Table 4. In the second stage, the research results obtained from *E. coli* are shown in Table 5.

The samples collected on days 12, 13, 14, 15, 16 and 17 of September 2010, tested positive for *E. coli*. However, the samples of days 18 and 19 of September 2010 were negative for this microorganism, thereby showing that after seven days of exposure to solar radiation, the treatment system SITRU is effective in the control of *E. coli*, even though the suspended solids and turbidity values were high.

The ability to resist ultraviolet radiation, for any microorganism, reduces with the increase of applied dose and among microorganisms, even within of the same species; there are large differences in resistance [14]. These results agree with [15] who claims that ultraviolet radiation is more effective in waters with color and turbidity of limited value due to the need of light penetration in the middle. Therefore, the quality of water to be treated is an important factor in using this process.

Date	Fecal Samples	Total Coliforms Biofertilizer (MPN / mL)	Fecal Coliforms or thermotolerant Biofertilizer (MPN / mL)
12/09/2010	A1	">1.100	< 3,0
13/09/2010	A2	">1.100	< 3,0
14/09/2010	A3	">1.100	< 3,0
15/09/2010	A4	">1.100	< 3,0
16/09/2010	A5	">1.100	< 3,0
17/09/2010	A6	">1.100	< 3,0
18/09/2010	A7	">1.100	< 3,0
19/09/2010	A8	">1.100	< 3,0

Table 4. Results of analyzes of total coliforms, fecal coliforms in the treatment system by solar radiation

Date	Sample	<i>E.coli</i> (Rugai culture medium)
12/09/2010	A1	Positive
13/09/2010	A2	Positive
14/09/2010	A3	Positive
15/09/2010	A4	Positive
16/09/2010	A5	Positive
17/09/2010	A6	Positive
18/09/2010	A7	Negative
19/09/2010	A8	Negative

Table 5. Results of inactivation of *E. coli*.

The effect of suspended solids in the efficiency of the disinfection process, which besides increasing absorbance of the effluent, hide bacteria on its inside. Therefore it was recommended a pre-filtration for a better efficiency in disinfection [11].

According to [16], it was possible to observe that a system equipped with a reactor of UV lamps, had a very efficient operation in terms of *E. coli* inactivation for the conditions of the experiments with retention times of 3 and 5 minutes, both in clearer water, as for turbid waters.

The results for the parasitological analysis are presented in Tables 6, 7 and 8.

Sample	Start of treatment	End of treatment
A1	600	600
A2	1.400	400
A3	1.000	400
A4	1.600	400
A5	800	0
A6	2.200	200
A7	600	400
A8	1.400	1.000
A9	1.000	600
A10	1.600	400
A11	800	400
A12	800	400
Average	1150	433
Standard deviation	470	239

Table 6. Count of oocyst protozoa count in the effluents of the biodigesters before and after the treatment system by ultraviolet radiation.

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Sample	Start of treatment	End of treatment
A1	600	600
A2	2.000	400
A3	1.000	400
A4	800	800
A5	800	0
A6	1.800	400
A7	1.800	400
A8	1.800	600
A9	1.000	600
A10	800	600
A11	1.200	200
A12	400	400
Average	1167	450
Standard deviation	545	211

Table 7. Count of eggs of *Ascaris sp.* in effluents of the biodigester before and after the treatment system by ultraviolet radiation.

Sample	Home treatment	End of treatment
A1	800	0
A2	1.000	400
A3	1.000	400
A4	1.000	0
A5	600	200
A6	800	0
A7	800	200
A8	1.000	400
A9	800	600
A10	1.000	200
A11	400	200
A12	800	200
Average	833	233
Standard deviation	187	187

Table 8. Trichostrongylideos egg count of effluents in the biodigester before and after the treatment system by ultraviolet radiation.

Statistical analysis of data showed that there was no significant reduction, with 5% significance for the results presented in tables 6, 7 and 8. However, it may be noted reduction of 62.32%, 61.43% and 72% of *Ascaris sp.*, protozoa and oocyst trichostrongylideos eggs, respectively, before and after the treatment system by ultraviolet radiation.

According [17], in general, bacteria and viruses are sensitive to ultraviolet radiation, needing only effective doses of 20 mWs/cm² to inactivate most species. However, the same cannot be reported for protozoa and helminths, endowed with natural protection that allows for their survival in harsh environments. The shapes of the encysted protozoa and helminths eggs are resistant to ultraviolet radiation, requiring extremely high doses and, in most cases, too costly economically to result in efficient inactivation.

During the disinfecting process of biofertilizer in the SITRU, in this present study, it can be observed that the temperature for the experiment ranged between 19 °C to 34 °C. The thermotolerant coliforms are still alive even at 44 °C and for the most coliforms best growth occurs to 35 °C, therefore in this study it was observed that the temperature did not influence the reduction of these bacteria.

According to [16], with respect to the analysis in terms of efficiency, it should be noted that the inactivation of *E. coli* does not determine the safety of the system as a sanitary barrier. For this, it should be the object of verification not only the pathogenic microorganisms of greatest resistance to the process of disinfection by ultraviolet radiation, such as viruses and protozoan cysts, but also those whose dimensions provide a greater protective effect exerted by the particles dispersed in water to the action of ultraviolet radiation. Thus, by establishing a system of disinfection by ultraviolet radiation, it is evident the need to undertake in a comprehensive manner the water's physical-chemical and microbiological characteristics, the dispersed particle size characterization and evaluation of the permanence of these parameters in different seasons of the year.

5. Conclusion

Despite the color, turbidity and suspended solids high values, the ultraviolet radiation treatment system - SITRU was efficient in the reducing the presence of *Escherichia coli*, but less efficiently for *Ascaris sp* eggs, *Trichostrongylideos* eggs and oocysts protozoa.

Acknowledgements

Fundação de Amparo à Pesquisa do Estado de Minas Gerais (Fapemig), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Banco do Nordeste do Brasil (Fundeci) and Pro-Reitorias de Extensão e Graduação of the Universidade Federal de Minas Gerais for financial support for this research.

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The Effect of Solar Radiation in the Treatment of Swine Biofertilizer from Anaerobic Reactor 95
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Analysis and Evaluation of Environmental Impact

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Recent Developments on Mass Spectrometry for the Analysis of Pesticides in Wastewater

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Shang-Da Huang*

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51929>

1. Introduction

The utility of pesticides plays an important role in the production of agronomy and horticulture areas. In recent years, pesticides have been widely used in increasing amount in various fields including agriculture, floriculture and horticulture. Pesticides applications are multidisciplinary involving in addition to man, behind agronomist, biologist, economist, chemists, engineers, medical practitioners and physicists. The ideal pesticide would be one which is effective against the target species and has little or no side effects on human beings, livestock, crop plants and other non-target organisms. The uses of various pesticides are increasing rapidly year by year with the growing awareness among the farmers about the utility of pesticides in maximum their benefits. Pesticides are a group of chemicals intended for preventing/destroying any pest detrimental to man or his interest during production, processing, storage, transportation and distribution of food. These are toxic substances deliberately added to environment. They are used because of toxic and biocidal to kill and harm living things. Pest control is an integral part of the development of every country because the damage done by pests is considerably high. Pesticides are not only destroy crops but also transmit diseases. Hence, the use of pesticides became necessary both in agricultural and household sectors.

In this connection, multidisciplinary nature and applications of pesticides in different fields have been described and shown in Figure 1 [1]. Pesticides are classified based on their intended target groups and depending on their chemical composition and molecular structures. In terms of intended target groups, the pesticides are classified into the following categories [2].

- Insecticides: These are helpful to destroy insects (Stomach poisons and contact poison).
- Fungicides: These are toxic to fungi and help to prevent plant diseases.
- Herbicides: These are helpful to kill weeds and other unwanted vegetation.
- Others: These includes rodenticides (against rats, mice, grass hoppers etc.,) molluscicides (against snails) and nematicides (control microscopic worms).

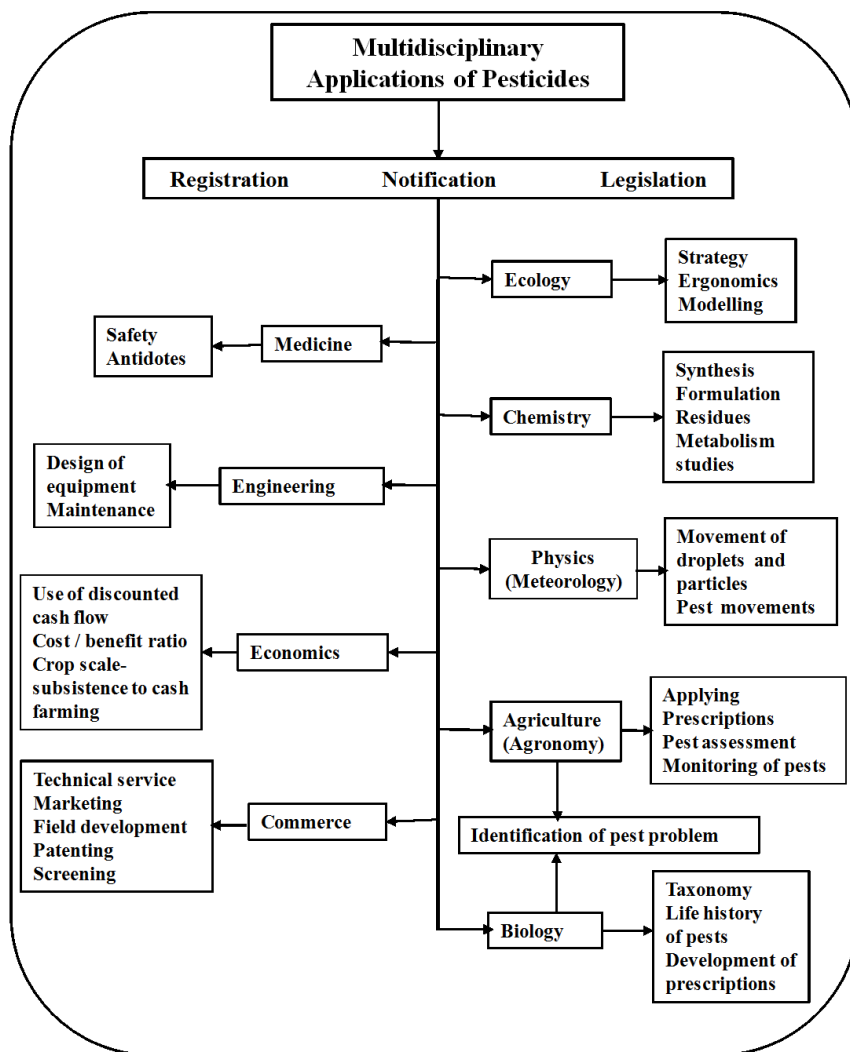


Figure 1. Pesticides applications in multidisciplinary areas.

The persistence of pesticide residues is governed by many factors such as the nature and dosage of pesticide application, its degradation with time, metabolism and conversion into various products along with their movement from one sphere to another through the pesticide cycle [3] and shown in Figure 2. Pesticide residue cycle in the environment starts right from the stage of pesticide application for pest control purposes both in indoor and outdoor. Those are contaminated every component of the environment including food material like food grains, fruits, vegetables and other crops; animal and animal products; water and aquatic animals; non-target organisms; air and soil [4].

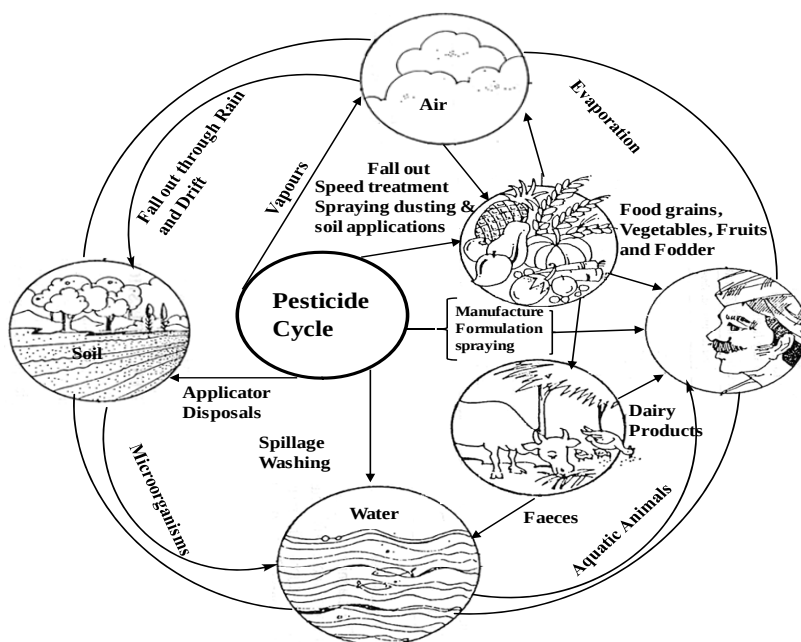


Figure 2. Pesticides cycle in environment

Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our planet. Without the seemingly invaluable compound comprised of hydrogen and oxygen, life on Earth would be non-existent: it is essential for everything on our planet to grow and prosper. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes, and oceans. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at a very alarming rate. In addition to innocent organisms dying off, the drinking water has become greatly affected as is ability to use water for recreational purposes. In order to combat water pollution, we must understand the problems and become part of finding the solution.

Water pollution is referred to an addition in excess of any material or heat that is harmful to humans or animals or desirable aquatic life or otherwise causes significant departures from normal activities of various living communities in a measurement of water. As per the water commission, water is considered as polluted if it is not of sufficient quality to be suitable for variety of uses, people wish to use in the present or in the future. Water pollution according to Environmental Protection Agency (EPA) and World Health Organisation (WHO) are defined as demonstrable and recurrent breach of any physical or chemical or biological criteria of quality of water systems. Water is not a national problem but a global problem. The degree of water pollution depends on both population and living standards of a citizen in a country. As water travels through the hydrological cycle, it changes from pure salt free moisture suspended in the troposphere as clouds to the brine of the sea. Given the ecosystem disruption, the toxicity, and the biological resistance to these pesticides that many insect species have developed organochlorines have largely been replaced with organophosphates and carbamates.

In modern economies, various types of activity, including agriculture, industry and transportation produce a large amount of pesticide pollution. Soil, air and water have traditionally been used as sites for the disposal of all these wastes. Some of them may get into nearby streams, and pollute rivers, lakes and soil. The most common kinds of waste can be classified into four types: agricultural, industrial, municipal and nuclear. Most of the agricultural wastes including a wide range of organic materials (pesticides), animal wastes and timber by-products are laying long time in wastewater. Many of these, such as plant residues and livestock manure, are very beneficial if they are returned to the soil. However, improper handling and disposal may cause pollution.

Persistent Organic Pollutants (POPs) are toxic substances which are produced intentionally for various uses or created as by-products of combustion or industrial processes. They include hexachlorobenzene (HCBs), polychlorinated biphenyls (PCBs), dichlorodiphenyl-trichloroethane (DDT), dioxin, furan, dieldrin, aldrin, endrin, chlordane, heptachlor, toxaphene, and mirex. Some persistent organic pollutants, such as aldrin, chlordane, DDT, HCBs, mirex, and toxaphene are used as pesticides. Others have industrial uses; PCBs, for example, were used for insulating electric transformers. POPs are characterized by their chemical properties. They are substances which are found to be toxic and that are persistent, means they break down very slowly in soil, air, and water and therefore remain in the environment for a long time. Because they persist in the environment, they can be transported long distances through wind or water before they are deposited. According to the United Nations Environment Program, these pollutants have been found on "every continent, at sites representing every major climatic zone and geographic sector throughout the world." This is true even if there is no local source for the pollutants. For example, levels of DDT have been found in the Arctic even though it has never been used there.

The international environmental treaty (the Stockholm Convention on Persistent Organic Pollutants) bans the use of eight POP pesticides immediately: HCBs, dieldrin, aldrin, endrin, chlordane, heptachlor, toxaphene, and mirex, the use of other substances identified as per-

sistent organic pollutants are restricted. Furthermore, the treaty includes measures to provide aid to countries to eliminate the use and production of persistent organic pollutants. At present, near about 1,209 pesticides [4] and their metabolites and degradation products belonging to more than 100 chemical classes in use in food production or present in the environment. Moreover, applications of pesticides are continually expanding, hence their consumption is ever increasing and more of them are infiltrating into the environment. Recent studies have been revealed that European Union countries are consumed more than 300,000 tons of pesticides per annum on crop protection alone [6-8]. In order to determine trace amounts (very low concentrations) of pesticides and their residues in wastewater, it is necessary to follow a series of operations to accurate quantification by using mass spectrometric methods. The series of operations are (i) isolation (extraction and separation) of pesticides from sample matrix (air, water, sediment, living things, etc.), (ii) separation and purification of the pesticide residues from co-extracted, non-target chemicals (sample clean-up), (iii) sample concentration and (iv) pesticide residues identification by mass spectrometry. Therefore, we will focus on the extraction methods coupled with mass spectrometric techniques for the multi-residue pesticides analysis in wastewater.

2. Extraction methods coupled with mass spectrometric techniques

Despite the advances in analytical instrumentation, sample pre-treatment for analyte concentration and matrix removal is frequently the bottleneck in the overall analytical method and inhibits a high sample throughput. Since, sample preparation plays a vital role for the analysis of pesticide residues, and it includes interferent removal and analyte preconcentration. Generally, extraction can define the use of two immiscible phases to separate target species from one phase into the other. The separation or purification of target species involve either by extraction into organic phase, leaving undesirable substances in aqueous phase; or by extraction of unwanted substances into organic phase, leaving desirable solute in aqueous phase. Extraction is a separation process that involves the distribution of a solute between two phases is an equilibrium condition described by partition theory. Extraction efficiency of the method is calculated by the ability of solvent to extract the analyte (inorganic or organic species). This can be defined that the ratio of the concentration of the solute in each solvent at equilibrium is a constant called the distribution coefficient (K).

$$K = \frac{[\text{solute}]_{\text{Org}}}{[\text{solute}]_{\text{Aq}}} = \frac{C_{\text{Org}}}{C_{\text{Aq}}} = \frac{W_{\text{Org}} / V_{\text{Org}}}{W_{\text{Aq}} / V_{\text{Aq}}}$$

where Org and Aq refer to the organic and aqueous layers and C_{Org} and C_{Aq} are the concentrations of solute in each layer at equilibrium in mass/volume (W/V).

(Note that K is independent of the actual amounts of the two solvents mixed)

To date some researchers have also published some reviews as well as book chapters in pesticide analysis in water and food by using extraction methods coupled with mass spectrometric techniques [9-15]. These monographs were mainly highlighted the types of extraction

methods, extraction- and chromatographic -techniques coupled with mass spectrometric techniques for the analysis of multi-residues pesticides in water, soil and food samples. The developed extraction methods-, coupled with used ion sources and -analyzers in mass spectrometry was shown in Figure 3. However, keeping in mind the recent developments in miniaturized extraction techniques coupled with mass spectrometry for the pesticide analysis in today's world, it is hoped that there is still a strong demand for an extensive review with updated literature on recent developments in mass spectrometry for pesticide analysis in wastewater. The aim of this book chapter is to give a comprehensive overview of the recent developments in mass spectrometry for the analysis of pesticides in wastewater.

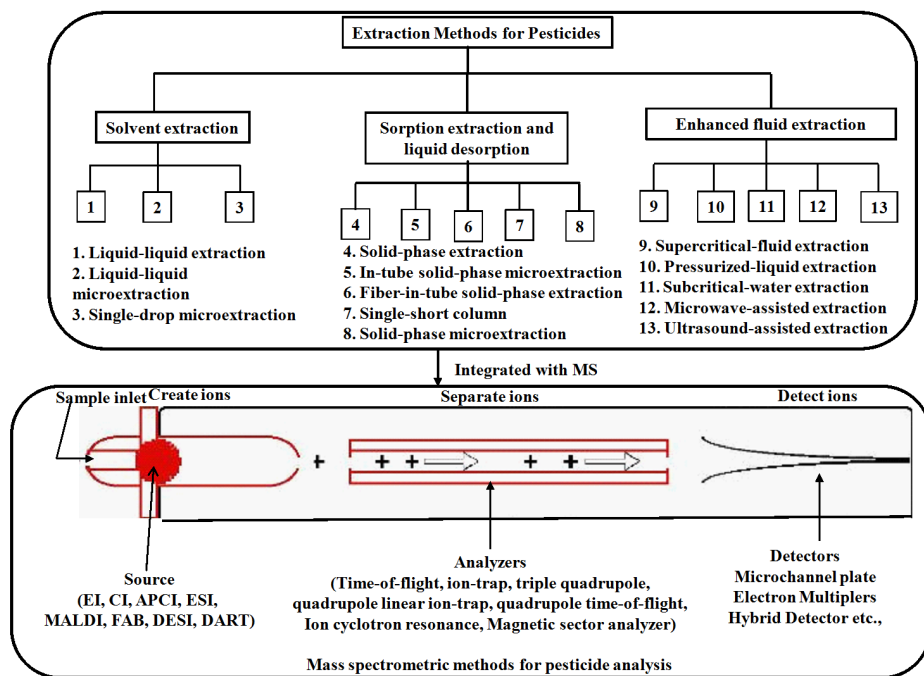


Figure 3. Extraction methods coupled with mass spectrometric techniques

Mass spectrometry coupled to chromatographic techniques (gas chromatography (GC) and liquid chromatography (LC)) is powerful tools for the identification of pesticides in wastewater. Since, these techniques allow selective and routine identification of many pesticide species in parts-per-trillion (ppt) or lower concentrations. In recent years, developments in chromatography coupled with mass spectrometric techniques have been received much attention for the efficient separation and detection of a wide variety of pesticides in wastewater analysis.

Due to the ultra-trace levels of pesticides in environmental samples (ng/L), a preconcentration step is essentially required for the pesticides in wastewater prior to their measurement. Huang's group developed high-performance liquid chromatography coupled with ESI-MS/MS for the identification of 11 chloro- and thiomethyltriazines and metolachlor and its ethanesulfonic and oxanilic acid degradates in water samples [16]. Stir bar sorptive extraction (SBSE) coupled with liquid chromatography/tandem mass spectrometry was used for the determination of pesticides in surface water [17]. Hernandez's group investigated the presence of pesticide transformation products in water by using solid-phase extraction (SPE) coupled with liquid chromatography-mass spectrometry (LC-MS) using different mass analyzers [18]. Moreover, Marin's group described online SPE coupled with LC-MS method for the quantification and confirmation of 27 pesticides including anionic, cationic and neutral species in water samples [19]. Kuster's team developed an automated on-line SPE-LC-MS/MS and LC-MS/MS techniques for the analysis of polar and semi-polar pesticides in nature and treated water samples [20-21]. Moreover, the two dominant ionization methods (EI and chemical ionization (CI)) are used for the analysis of pesticides by GC-MS. Pitarch's group described the use of negative CI mode for the detection of pesticides in water samples [22]. This negative CI mode provided better selectivity and sensitivity than the electron impact (EI) ionization. Meanwhile, several research groups have been developed SBSE methods coupled with thermal desorption low thermal gas chromatography mass spectrometry (TD-LT-GC-MS) and thermal desorption gas chromatography mass spectrometry (TD-GC-MS) techniques for the fast screening of huge number of multi-residue pesticides in water samples with limit of detections (LODs) 10 ng L⁻¹ [23-25]. At the same time, SBSE coupled with automated TD-GC-MS method was used for the sensitive determination of triazines in underground waters [26]. Wang et al. developed GC-MS method for the determination of pesticides in water by solid-phase extraction (SPE) using carbon nanotubes as sorbent [27]. Derouiche's team simultaneously analyzed polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction (HS-SPME) coupled with GC-MS [28].

Designing a fully integrated miniaturized analytical platform for multi-residue pesticides analysis in wastewater studies is a great challenge for any analytical chemist. This can be achieved by imagine of complete platform combining sample preparation, separation methods coupled to a dedicated instrument such as mass spectrometer. Recently, several SPE methods coupled with liquid chromatography – electrospray ionization (ESI) tandem mass spectrometric approaches have been described for the analysis of a wide variety of pesticides in water samples [29-36]. These methods allow efficient ionization of a wide spectrum of compounds with varying polarities and wide linear dynamic ranges. Potter and co-workers developed SPE technique combined with HPLC- atmospheric pressure chemical ionization (APCI) – MS for the analysis of multiresidue pesticides in water samples [37]. A HPLC combined with ESI MS method was described for the direct determination of 300 pesticides in water samples [38]. These approaches have been successfully described that the potentiality of mass spectrometric methods for the analysis of pesticides using various mass analyzers such as ion trap (IT), triple quadrupole (QpQ) and time-of-flight (TOF) which can facilitate to detect pesticides with more accuracy. These

methods are allowed to build homemade libraries (empirical or theoretical) for the identification of pesticides. Moreover, these methods provide a promising direction towards the development of spectral libraries of pesticides by using quadrupole and TOF analyzers. These approaches were successfully provided pesticides full-scan accurate-mass spectra combined with the evidence from isotopic clusters related to the suspected peaks, which allowed the prediction of a reduced number of possible elemental compositions. The confirmation of the pesticide residues was accomplished using characteristic fragment ions with tandem mass spectrometry, which showed the same isotopic profile as the parent molecule. These advances were effectively addressed for the multiresidue determination of wide variety pesticides in water samples. In another application of these methods, exact mass and relative isotopic abundances (RIAs) information of pesticides ions can be obtained using TOF instruments, which allowed to elucidate the elemental composition of organic molecules. By using these methods, all possible elemental compositions of the precursor and product ions and their neutral losses were calculated.

Nowadays, the public has more concerns about the toxic effects of pesticides being widely used for control of insects and weeds, which leads to serious contamination of hydrosphere. Dual-pre-column-based trace enrichment combined on-line with liquid chromatography-diode-array UV and tandem mass spectrometric detection was developed for the determination of a wide polarity range of organic microcontaminants in river water [39]. Tandem MS was used for confirmation and quantification of organic microcontaminants in river water and target species were found at ng/L level. Recently, identification of micro-organic contaminants are very important in wastewater treatment plants. To this, an online HPLC–heated ESI tandem mass spectrometric method was developed and validated for the determination of basic pesticides in effluent wastewaters [40]. Mass resolution was greatly increased to minimize interference from endogenous compounds in the matrix and micro-organic contaminants were effectively detected with improved signal-to-noise ratio and better detection limits. This method was used to detect 11 basic pesticides, such as methoxytriazine, chlorotriazines, chloroacetanilides, phenylurea and carbamate pesticides. Very recently, Santana-Rodríguez's group developed a fully automated on-line SPE system combined with ultra-HPLC-MS/MS method for the detection of 27 endocrine disrupting compounds in sewage samples [41]. This method was effectively separated and detected all the species in a single chromatographic run and analyzed within 4 min. In this method, ESI positive and negative ions modes are used for the analysis of pesticides. Precursor ions included positive ions in positive ion mode ($[M+NH_4]^+$ adducts for short ethoxylated chains AP_nEOs ($n \leq 2$), and $[M+H]^+$ for 19- norethindrone, testosterone and norgestrel) and negative ions in negative ion mode ($[M-H]^-$ for raw alkylphenol (NP and OP), diethylstilbestrol, 17 β -oestradiol, oestriol, 17 α -ethynyloestradiol and bisphenol-A, respectively. Hernandez's developed a multiclass screening method for organic contaminants in natural and wastewater for the qualitative and sensitive identification of trace level organic compounds by SPE coupled with GC-TOF-MS [42]. This method was successfully detected a wide variety of compounds such as polyaromatic hydrocarbons, octyl/nonyl phenols, polychlorinated biphenyls, polybrominated diphenyl ethers, insecticides (organochlorines, organophosphorus, carbamates and pyrethroids), herbicides (triazines and chloroacetanilides), fungicides

and several relevant metabolites. The method was effectively elucidated the possible chemical structures of pesticides by the identification of fragment ions of molecular ions. HPLC combined with ESI-MS/MS technique was used for the simultaneous determination of six selected endocrine disrupter compounds (diltiazem, progesterone, benzyl butyl phthalate, estrone, carbamazepine and acetaminophen) in wastewater samples [43]. Fernandez-Alba's group developed LC-MS/MS method for the analysis of a group of 14 organic pollutants including pharmaceuticals (analgesics/anti-inflammatories, lipid regulators and diuretics), pesticides (diuron) and disinfectants (chlorophene) in wastewater [44]. Mass analysis was performed by using a hybrid triple quadrupole-linear ion trap-mass spectrometer. MS/MS spectra of organic pollutants revealed that losses of 44 amu, assigned to $[M-H-CO_2]^-$ ions, characteristic of the presence of carboxylic acid functionalities in the pollutant molecules. Moreover, the antilipemic agent, bezafibrate, and the biologically-active clofibrate metabolite, clofibric acid were produced $[M-H]^- \rightarrow [M-H-86]^-$ as the main transition-corresponding to the loss of the methylpropanoic acid moiety $[M-H-C(CH_3)_2 CO_2]^-$. Similarly, gemfibrozil gave product ions by the loss of the dimethylpentanoic acid group while diuron and chlorophene lost dimethylamine and chlorine, respectively.

It is well known that the treatments used at the wastewater treatment plants are not exhaustive enough to completely remove organic compounds. Therefore, the effluents of urban waters become a source of many different organic pollutants. Frenich and co-workers developed a rapid multi-residue method for the analysis of 40 herbicides (such as simazine, terbuthylazine and diuron) in waters by ultra-performance liquid chromatography (UPLC) coupled to tandem mass spectrometry [45]. Prior to LC-MS, SPE was used for the extraction of herbicides from water samples. This method describes the advantage of triple quadrupole analysers over ion trap mass spectrometers as there are no restrictions on the maximum m/z value of the product ion. Multi-residue methods are analytical methods for determination of dozens or even hundreds analytes in a single analysis. Nurmi and Pellinen developed a multiresidue method for screening of 84 pesticides in aquatic environments by using SPE-UPLC-TOF-MS [46]. Similarly, SPE-UPLC coupled with ESI MS/MS technique was developed for the validation of 28 basic/neutral pharmaceuticals (antiepileptics, antibacterial drugs, β -blockers, analgesics, lipid-regulating agents, bronchodilators, histamine-2-blockers, anti-inflammatory agents, calcium channel blockers, angiotensin-II antagonists and antidepressants) and illicit drugs in surface water [47].

The trace amounts of organic pollutants (herbicides, fungicides, insecticides, xenobiotics, endocrine disrupting agents and their corresponding transformation products in the water compartment is still of growing and demands a sensitive methods for the preservation and sustainability of the environment. Godejohann's team described the applications of SPE coupled with HPLC-ESI-MS/MS and NMR techniques for the identification of pesticides and their residues in two different wastewater treatment plants in Switzerland [48]. These results confirmed that the presence of pesticides (linuron, metazachlor, ethofumesate, isoproturon, metamitron, propazine and chloridazon desaminometamitron) and their transformation products in wastewater plant. Sauve's group described a simple on-line method for the analysis of 10 compounds including herbicides, pharmaceuti-

cals, caffeine and some metabolites in drinking, surface and wastewater samples [49]. This technique illustrated that the use of on-line SPE coupled with LC-ESI-MS/MS. This method provides detection limits in the range of 2 to 24 ng/L for the pesticide residues, with recoveries from 87 to 110% in surface as well as wastewater samples. The same group described that the development and validation of an on-line -SPE-LC-ESI-MS/MS and -SPE-LC-ESI-TOF-MS/MS methods for the simultaneous quantitation and confirmation of 14 selected trace organic contaminants such as anti-infectives (clarithromycin, sulfamethoxazole and trimethoprim), an anticonvulsant (carbamazepine) and its transformation product 10,11-dihydrocarbamazepine, an antihypertensive (enalapril), antineoplastics (cyclophosphamide and methotrexate), herbicides (atrazine, cyanazine, and simazine) and two of their transformation products (deethylatrazine and deisopropylatrazine) and an antiseptic (triclocarban) in drinking and surface water [50]. This method allowed for the detection and confirmation of trace level organic contaminants by using LC-MS/MS in SRM mode, with a second SRM transition monitored for confirmation of each compound.

Recent years, there is an overwhelming evidence of the importance of monitoring programs of pesticide residues on environmental compartments, especially water that constitutes an essential element for animals and human beings. Fernández-Franzón's group developed SBSE coupled with LC-MS/MS with a triple quadrupole analyzer using selected reaction monitoring mode via electrospray ionization for the validation and confirmation of 16 pesticides in surface water [51]. This method was successfully validated in spiked surface water samples at limits of quantifications (LOQs), showed recoveries <62%, and LOQs were found to be 0.03 and 3.0 µg/L for diazinon and simazine, respectively. Fernandez-Alba *et al.* developed and evaluated an analytical method for a rapid automated screening and confirmation of 400 organic micro-contaminants and their quantification in water samples of different types (surface and wastewaters) using LC-electrospray quadrupole-time-of-flight mass spectrometry (LC-QTOFMS) [52]. This method provided detailed fragmentation information of micro-organic species and identified unknown compounds and/or transformation products with similar structures to those of known organic contaminants by in-source CID fragmentation. This method was effectively detected target species and LODs were found to be 2 - 5 ng/L, respectively. Benvenuto's group described that the validation and application of ultra-HPLC-MS/MS method for the quantification and confirmation of 11 compounds (atrazine, simazine, terbuthylazine, terbutometon, terbutryn and their main transformation products) in surface and wastewater samples [53]. This method was optimized full-scan MS and MS/MS spectra of parent pesticides for their identification and confirmation in wastewater. All analytes were measured in positive ionization mode presenting an abundant $[M+H]^+$, which was selected as precursor ion. These approaches were effectively and rapidly identified and confirmed by tandem mass spectrometry and provided cost-efficient separation and screening of multiple compounds in wastewater. Table 1 describes that an overview of extraction methods coupled with mass spectrometric tools for the multi-residue analysis of pesticides and their degradation products in water samples.

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Recent Developments on Mass Spectrometry for the Analysis of Pesticides in Wastewater
<http://dx.doi.org/10.5772/51929>

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Number of pesticides analyzed	Technique	Sensitivity	Reference
11 pesticides	HPLC-ESI-MS/MS	LOD: 0.05 ^a	[16]
16 pesticides	SBSE- HPLC-ESI-MS/MS	LOQs: 0.03-3 ^a	[17]
11 pesticides	HPLC-ESI-MS/MS SPE-LC-ESIMS/MS	LODs: 2-25 ^b LOQs: 50 ^b	[18]
27 pesticides	Online SPE-HPLC-ESI-MS/MS	LODs: < 5 ^b LOQs: 25 ^b	[19]
17 pesticides	Online SPE-HPLC-ESI-MS/MS	LODs: 0.1-2.7 ^b LOQs: 0.2-7.2 ^b	[20]
25 pesticides	SPE- GC-MS/MS	LODs: 25-250 ^b LOQs: 5-150 ^b	[22]
46 pesticides	Dual SBSE-TD-LTM-GC-MS	Not reported	[23]
85 pesticides	SBSE-TD -GC-MS	LODs: <10 ^b	[24]
82 pesticides	Dual SBSE-TD-LTM-GC- MS	LODs <10 ^b	[25]
10 triazines	SBSE-GC-MS	LOQs: 0.7- 11.3 ^b	[26]
12 pesticides	SPE-GC-MS	LODs: 0.01– 0.03 ^a	[27]
15 organochlorines	HS-SPME-GC-MS	LODs: 0.4 – 26 ^b	[28]
7 pesticides	SPE- HPLC-ESI-MS _n	LODs: 5.0-8.1 ^a LOQs: 16.7-26.9 ^a	[29]
14 pesticides	SPE-HPLC-ESI-MS/MS	LOQs: 0.005 - 0.048 ^a	[30]
37 pesticides	SPE-ultra-high pressure-LC-ESI-MS/MS	LOQs: 0.025 ^a	[31]
9 pesticides	SPE-ultra-high pressure-LC-ESI-MS/MS	LODs: 0.1 – 20 ^b	[32]
31 pesticides	SPE-ultra-high pressure-LC-ESI-MS/MS	LODs: ≤ 8 ^b LOQs: 50 ^b	[33]
101 pesticides	SPE- HPLC-ESI -MS	Not reported	[34]
28 pesticides	SPE- HPLC-ESI-MS/MS	LOQs:0.025 - 0.050 ^a	[35]
12 pesticides	SPE-HPLC-ESI-MS/MS	LODs: 0.2-88.9 ^b LOQs: 0.7-296 ^b	[36]
27 pesticides	SPE-HPLC-APCI(+)-MSn	LODs: 0.01-0.1 ^a	[37]
300 pesticides	HPLC-ESI-MS/MS	LODs: 0.1 ^a	[38]
8 polar and acidic pesticides	On-line SPE-LC-ESI-MS/MS	LODs: <1.0 ^b	[39]
11 basic pesticides	On-line SPE-HPLC-ESI-MS/MS	LODs: 0.017 - 0.21 ^a LOQs: 0.045 - 0.63 ^a	[40]
27 pesticides	On-line SPE-ultra HPLC-ESI-MS/MS	LODs: 0.3–2.1 ^b	[41]

Number of pesticides analyzed	Technique	Sensitivity	Reference
150 pesticides	SPE-GC-TOF-MS/MS	LODs: 0.02 – 1.0 ^a	[42]
6 pesticides	HPLC-ESI-MS/MS	LODs: 40 – 130 ^a	[43]
14 organic pollutants	HPLC-ESI-MS/MS	LODs: 0.1 – 10.0 ^a LOQs: 0.1 – 10.0 ^a	[44]
40 herbicides	SPE-UPLC-MS/MS	LODs: 0.002 – 0.02 ^a LOQs: 0.005 – 0.05 ^a	[45]
84 pesticides	UPLC-TOF-MS	LODs: 0.8 – 110 pg/L LOQs: 2.6 – 360 pg/L	[46]
28-basic and neutral pharmaceuticals	SPE-UPLC-ESI-MS/MS	LODs: 0.02 – 2.0 ^a LOQs: 0.2 – 10 ^a	[47]
9 pesticides	SPE-HPLC-ESI-MS/MS	-	[48]
10 compounds including pesticides	SPE-LC-ESI-MS/MS	LODs: 2.0 – 24 ^b	[49]
14 pesticides	SPE-LC-ESI-MS/MS SPE-LC-ESI-TOF-MS/MS	LODs: 0.4 – 3 ^b	[50]
16 pesticides	SBSE-LC-ESI-MS/MS	LODs: 0.01 – 1 ^a LOQs: 0.03 – 9 ^a	[51]
400 micro-organic compounds	LC-QTOFMS	LODs: 2 – 5 ^b	[52]
11 pesticides	ultra-HPLC-MS/MS	LODs: 30 – 780 ^b	[53]
2 pesticides	nanoEESI-MS/MS	LODs: 100 – 600 ^a	[64]
5 pesticides	SPME-DCBI-MS	LODs: 1.0 ^a	[65]

^a µg L⁻¹; ^bng L⁻¹.

Table 1. Over view of multi-residue pesticides analysis using chromatographic techniques coupled with various MS approaches in water samples.

Ambient ionization MS approaches are entirely different from atmospheric pressure ionization techniques, since analytes can be ionized at ambient conditions without applying ionization sources (voltage or heat), which differs from ESI, atmospheric pressure photoionization (APPI), atmospheric pressure chemical ionization (APCI), or AP-MALDI. Briefly, desorption electrospray ionization (DESI) [54] and direct analysis in real time (DART) [55] MS techniques were introduced in 2004 - 2005. These are evidently provided high-throughput applications for the efficient analysis of a wide range of analytes and adapted the underlying methodology to specific analytical needs. After these developments, various research groups have been developed different ionization methods that includes variations of the DESI theme such as desorption sonic spray ionization (DeSSI) [56], later re-

named easy sonic spray ionization (EASI) [57] or extractive electrospray ionization (EESI) [58-59], desorption atmospheric pressure chemical ionization (DAPCI) [60-61] and desorption atmospheric pressure photoionization (DAPPI) [62], respectively. The main function of these techniques is analytes can be ionized without voltage or heat and transported through air into the mass analyzer via a standard API interface, which allows analytes ionization under ambient conditions. Therefore, ambient ionization methods are of great interest for the real-time monitoring of micro-organic compounds since the analytes can be easily ionized and introduced to the mass spectrometer under ambient conditions, which facilitated to eliminate the sample pretreatment process. Recently, Fernandez *et al.* reviewed 290 references those described that the application of ambient ionization mass spectrometric approaches for in-situ and direct analysis of a wide variety of molecules [63]. Even though, these approaches allowed to detect analytes without sample pretreatment, unfortunately limited number of research articles are illustrated that ambient MS tools for the analysis of pesticides in wastewater samples.

Chen's group developed a homemade novel nanoextractive electrospray ionization (nano-EESI) source has been used for in situ mass spectrometric analysis of ambient samples such as pharmaceutical compounds, and pesticides residues without sample pretreatment [64]. The ability of nanoEESI is experimentally investigated by integrating nanoEESI source with a commercial LTQ mass spectrometer for rapid analysis of various ambient samples without sample pretreatment. This method proved as a promising tool for the high-throughput and sensitive in-situ analysis of organic compounds at ambient conditions. Paraquat, β -cypermethrin and pyrethroid pesticides were analyzed by using the nanoEESI MS and peaks were obtained at m/z 186, 93 and 416, which correspond to the paraquat radical ions and protonated β -cypermethrin, respectively. Furthermore, signals at m/z 93 and 185 are correspond to the doubly charged paraquat ions and deprotonated paraquat ions. To confirm the structures of those ions, the CID was carried out and the tandem mass spectra for the ions m/z 186 and 416 are yielded fragmented ions at m/z 171 by the loss of $\text{CH}_3\bullet$ and the other ions at m/z 157, 145, and 131, which due to the loss of $\text{HN}=\text{CH}_2$, $\text{CH}_2=\text{N}-\text{CH}\bullet$, and $[\text{HN}-\text{CH}_2, \text{C}_2\text{H}_2]$, respectively. The ion at m/z 416 yielded the product ion at m/z 388, by the loss of CO , and the other product ions at m/z 191 and 226 are generated by the cleavage of C-O bond in the ester group. Meanwhile, Li's group described that the expanded direct MS analysis to pesticides solution samples by using the desorption corona beam ionization (DCBI) technique in combination with poly(dimethylsiloxane) (PDMS) as substrate solid-phase microextraction of pesticides from sample solution [65]. Pesticides were extracted by using PDMS substrate and then is transferred to MS ion source for desorption and ionization. This approach was effectively improved the detection limit for the direct analysis of five pesticides (acephate, isoprocarb, dimethoate, dichlorvos, and dicofol) in water. This DCBI technique coupled with PDMS sampling is an excellent method for the analysis of organic pesticides in solution and LODs are in the range of 1.0 $\mu\text{g/L}$. Crook's team published a series of papers on ambient ionization mass spectrometric techniques using low-temperature plasma (LTP) [66], paper spray [67] and desorption electrospray ionization [68] methods for the trace analysis of pesticides in foodstuffs. These ambient MS techniques are directly analyzed trace level agro-

chemicals in foodstuffs without sample pretreatment. These approaches were effectively validated and confirmed pesticides by tandem mass spectrometry (MS/MS) at analytes concentration $< \text{pg}$ level. These methods are little or literally not required sample pre-separation, preparation, or derivatization and the analytes mass spectra are most often acquired directly at ambient conditions (open atmosphere, real world and natural environment). Therefore, ambient MS is still a very juvenile field for the analysis of multi-residue pesticides in wastewater samples; however it has already experienced explosive growth in terms of many new variants, hybridization, combinations, and applications for other samples.

3. Final remarks

This chapter has explored the analysis of multi-residue pesticides and their degradation products in wastewater by using different MS approaches over the last few years. Sensitivity of MS methods was enhanced by several ways such as sample pre-concentration, integration of chromatographic techniques and changing MS analyzers. These extraction and chromatographic techniques coupled with MS approaches have brought the promise of simple, validation, high-throughput qualitative and quantitative analysis of trace amounts of multi-residue pesticides in wastewater. These approaches have been demonstrated that effective pesticides analyses were achieved by the integration of chromatographic techniques with different MS platforms, which lead to a higher analysis throughput without compromising separation efficiency and sensitivity. In parallel to the development of multi-residue pesticides analysis MS-based workflows, the newly developed “ambient ionization” techniques (DART and DESI) hold some promise for the direct pesticide residue screening in foodstuffs. Since, these have well ability to inherently operate without chromatographic separation (LC and GC), and sometimes with no sample pre-treatment, are their main attractions but their utility for quantitative analysis in wastewater has not been sufficiently explored. Therefore, new perspectives are to be certainly opened in the near future for trace-multi-residue pesticides monitoring by hyphenation of miniaturized ambient ionization MS systems with various analyzers and detection systems for the qualitative and quantitative determinations of multi-residue pesticides and their degradation products in wastewater.

Acknowledgments

The authors wish to thank the National Science Council of Taiwan (NSC 99-2113-M-007-004-MY3) for financial support. We also thank Mr. Ganga Raju (Doctoral Degree Program in Marine Biotechnology, National Sun Yat - Sen University) and Mr. Hani Nasser Abdelhamid (Department of Chemistry, National Sun Yat-Sen University) for their assistance in searching for literature reprints for this work.

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Selected Pharmaceuticals and Musk Compounds in Wastewater

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/52047>

1. Introduction

In order to achieve sustainable development, environmental protection shall constitute an integral part of the development process and cannot be considered in isolation from it [1]. The environment, especially water ecosystem, is continuously loaded with foreign organic chemicals (xenobiotics) released by urban communities and industries. Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such [2]. In the 20th century, many organic compounds, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) have been produced and, in part, released into the environment [3]. The ultimate sink for many of these contaminants is the aquatic environment, either due to direct discharges or to hydrologic and atmospheric processes [4]. In the 21st century „new“ pollutants namely pharmaceuticals, cosmetics and endocrine disrupting chemicals (EDCs) have become a source of concern. Collectively, they are referred to as PPCPs (Pharmaceuticals and Personal Care Products) and are now viewed as emerging contaminants. A wide range of pharmaceutical and personal care products (PPCPs) is available on the market. From this range various classes, e.g., antibiotics, antiphlogistics, antiepileptics, beta-blockers, lipid regulators, vasodilators, and sympathomimetics, have been detected in drinking water, groundwater, wastewater, sewage, and manure [5]. In last time there is increasing evidence that some of these compounds are persistent in the environment, impacting nontarget organisms in various ways including changes in sex ratios of higher organisms [6,7]. The presence of a xeno-

biotic compound in a segment of an aquatic ecosystem does not, by itself, indicate injurious effects. Traditional chemical measurements alone are an insufficient basis for ecotoxicity assessments. In general, both basic and advanced analytical chemical instruments such as ICP/MS, GC/MS, HPLC/MS etc. are used for water quality analysis. However, it is difficult to distinguish accurately the diverse and complex chemicals, even when using those advance chemical instruments. Furthermore, it is also almost impossible to detect the impact on living organisms in the receiving environment due to their bioavailability and the interaction caused by the synergistic and antagonistic effect of different chemicals. Therefore a new approach of identifying viable and ecologically relevant invertebrate toxicity testing models seems very promising to assess the biological effects and ecological risk of exotic chemicals when released into the environment as a battery of single species bioassays [8].

1.1. Pharmaceuticals

Pharmaceuticals (also drugs, medicaments, medications, medicines etc.) are biologically active substances designated for use in the medical diagnosis, cure, treatment, or prevention of disease [9]. These compounds improve the quality of human life, but due to their increasing production and consumption resulting in their growing input into the environment there is increasing impact of these compounds on the natural ecosystems, caused either by the active compounds contained in medicaments or by their metabolites and transformation products [10]. These compounds are sometimes called as pseudo-persistent pollutants, because in many cases their persistence is not high, but due to continual input their levels in the environment are kept less or more constant. The discharges from waste water treatment plants represent one important source of pharmaceuticals in the water ecosystem, because most of drugs is incompletely removed in waste water treatment plants (WWTP) [11-13]; they could be partially removed by sorption on the sewage sludge or degraded by microorganisms in activated sludge. The removal efficiency depends on many factors like drug properties, type and parameters of the cleaning process, age of the activated sludge. The sludge activity could be also negatively influenced by the presence of antibiotics in treated waste water.

Another important source of pharmaceuticals in the water ecosystem is agriculture, especially livestock production, where growth stimulants are used to increase production and antibiotics are administered as prophylactic medication to animals. Biotransformation of drugs during animal digestion is not very effective; from 30 to 90 % of administered active compounds is excreted unchanged [10,14] and enter the environment directly via urine or faeces, or in manure and suds used as fertilizers.

Non-steroidal anti-inflammatory drugs (NSAIDs) with analgesic, antipyretic and anti-inflammatory effects are one group of the most frequently used medicaments. Ibuprofen and paracetamol followed by diclofenac, ketoprofen and naproxen are the most well-known members of this group. Their extensive use is caused by the fact, that many drugs in this group do not require medical prescription. These compounds also belong to the most frequently detected pharmaceuticals in the European waters. E.g. for ibuprofen the concentra-

tions of units to tens of ng.L^{-1} in surface water, tens of ng.L^{-1} in raw waste water and from tenths to units of ng.L^{-1} in discharged water were found in the Czech Republic [15].

Antibiotics are another important group of pharmaceuticals. This term originally denoted “any substance produced by a microorganism that is antagonistic to the growth of other microorganisms in high dilution” [16]. Nowadays also synthetic compounds are included in this group. Antibiotics have been recently classified as a priority risk compounds due to their high toxicity to algae and bacteria. Hence, these compounds in surface water have the potential to disrupt the key bacterial cycles and/or processes critical to aquatic ecology (nitrification/denitrification), agriculture (soil fertility) and animal production (rudimentary processes) [17,18]. Under long-term exposition the resistance of some pathogenic organisms could develop [11,12].

Macrolide antibiotics are a group of drugs frequently used in human and veterinary medicine. These primarily bacteriostatic antibiotics with a broad antibacterial spectrum are probably the largest group of natural medicines. Macrolides have acquired its name by macrocyclic lactone ring with 14, 15 or 16 carbon atoms, substituted with alkyl, aldehyde, ketone or hydroxyl groups, and with one or more neutral or basic amino sugars bonded to the ring by glycosidic bond. The first macrolide antibiotic, erythromycin, was isolated in 1952 from the metabolic product of fungus *Streptomyces erythreus* [19].

Macrolide antibiotics can be classified into four groups [20]:

1. Natural macrolides of 1st generation have a short half-life; therefore they must be administered in relatively high and frequent doses. There is a potential of interactions with some other drugs.
2. Synthetic macrolides of 2nd generation have more favourable pharmacokinetic properties, applications are therefore less frequent and doses are lower than at first-generation macrolides. There is also a lower incidence of drug interactions.
3. Azalides are formed by incorporating nitrogen into the 14-member lactone ring. From other macrolides they differ with high half-life and very slow release from tissues.
4. Ketolides are the newest and so far little studied group of macrolide antibiotics. These drugs were prepared by replacing sugar cladinose in the 14-member lactone ring by keto-group and by attaching a cyclic carbamate group in the lactone ring. Due to these modifications ketolides have much broader antimicrobial spectrum than other macrolides; besides, they are also effective against macrolide-resistant bacteria, due to their ability to bind at two sites at the bacterial ribosome.

1.2. Musk Compounds

Musk compounds - synthetic fragrances – are substances with pleasant smell which are present in personal hygiene products (perfumes, cosmetics, soaps, and shampoo), in cleaning and disinfection products, industrial cleaning products, air fresheners, etc. to give them characteristic and pleasant scent. These compounds have been marketed since the begin-

ning of 20th century and their industrial production has significantly increased during the last 50 years [21]. Nowadays, four major classes of synthetic fragrances could be met: nitromusks, polycyclic musks, macrocyclic musks and alicyclic (or linear) musks. Nitromusks were the first produced compounds of this type; structure of these compounds is based on two- or threefold nitrated benzene with additional substitution by alkyl-, methoxy- or keto- groups. Musk xylene (MX), musk ketone (MK) and musk ambrette (MA) are the most important members of this group. These compounds show musk-like odour in spite of the fact that their structure is very different from natural musk compounds. They are partially soluble in water (0.15 ng.L^{-1} for MX; 0.46 ng.L^{-1} for MK), but their relatively high octanol-water partition coefficients ($\log K_{ow} = 4.4, 3.8$ and 4.0 for MX, MK and MA, respectively) [22] indicate high bioaccumulation potential in water biota. These compounds are also relatively persistent. According to data published till now, nitro musks show low or none acute toxicity to aquatic organisms, but they are potentially toxic over long time period [23,24]. It has been suggested that their transformation products are potentially highly toxic [25]. The worldwide production of MX and MK (which are the only two nitromusks of industrial importance today) in 2000 was estimated to 200 metric tons and it shows decreasing tendency [26].

Polycyclic musks with several cycles in their structure were discovered in 1950s [27]. Chemically they are indane, tetraline or coumarine derivatives and tricyclic compounds. Currently, these musks are the most widely used. Galaxolide (HHCB) and tonalide (AHTN) in recent years are the most important commercial synthetic musks [21,28] followed by celestolide (ADBI), phantolide (AHMI), and traesolide (ATII). Total worldwide use of polycyclic musks in year 2000 was approximately 4000 tons [26]. These compounds are more resistant against light and bases and bind well to fabric. Nevertheless, HHCB and AHTN are toxic to aquatic invertebrates at concentration levels of ppb to low ppm, but they are almost non-toxic to fish; similar situation occurs during longer exposition [29]. The first report about the presence of these compounds in water and fish appeared in 1984, one year later these compounds were found in human samples [27].

Macrocyclic musk compounds were discovered in 1926 by Austrian chemist Leopold Ruzicka [30,31] who characterized natural musks muscone and civetone as cyclic macromolecules and proposed the method of their synthesis. Since then, many other compounds of this type has been characterized and synthesized. It was found that natural macrocyclic musks are 15- or 17-membered rings, musks of animal origin are mainly ketones, whilst those of plant origin are lactones. These compounds show excellent stability to light and alkaline condition and very good fixation to fabric, nevertheless their synthesis is difficult and usually multi-step procedure, and therefore their production costs are high. Due to this fact the use of these compounds is limited, but they are expected to be of increasing importance in future [27].

Alicyclic musks, known also as linear musks or cycloakyl esters, represent the youngest group of synthetic musks. Their structure is formed by modified cykloalkyl esters. The first compound of this group – cyclomusk - was introduced in 1975 [32]. In 1990, the first commercially successful linear musk – helvetolide – was launched, another linear musk – Ro-

mandolide – was described ten years later [33]. Due to relative novelty there is lack of information describing their occurrence in the environment and their ecotoxicity. A wide range of musk compounds of this group are produced and marketed by the Czech company Aroma Prague Ltd.

2. Environmental Analysis

2.1. Target Compounds

For this study six frequently used acidic non-steroid anti-inflammatory drugs (NSAIDs) were selected. Figure 1 shows their structures and Table 1 summarizes their physical-chemical properties.

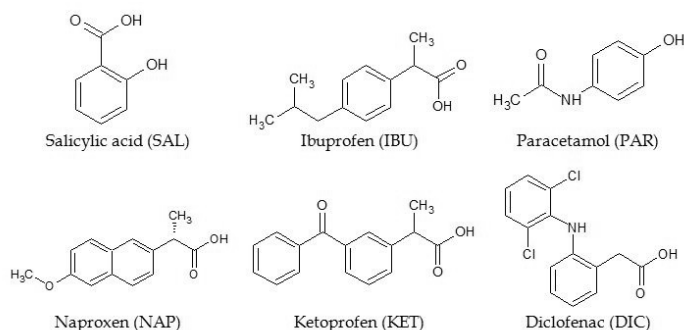


Figure 1. Structures of selected NSAIDs.

Compound	CAS No.	Molecular mass (g.mol ⁻¹)	pK _a	log K _{ow}
Salicylic acid	69-72-2	138.1207	2.97	2.4
Ibuprofen	15687-27-1	206.2808	4.91	3.6
Paracetamol	103-90-2	151.1626	9.38	0.4
Naproxen	22204-53-1	230.2592	4.15	2.8
Ketoprofen	22071-15-4	254.2806	4.45	3.2
Diclofenac	15307-86-5	296.149	4.15	3.9

Table 1. Physical-chemical properties of selected NSAIDs [34-37].

From the group of macrolide antibiotics following drugs were selected:

Erythromycin is a mixture of macrolide antibiotics that are produced by the microorganism *Streptomyces erythreus*. The main ingredient is erythromycin A. Erythromycin is a white to pale yellow powder or form a colourless to pale yellow crystals. It is slightly hygroscopic, poorly soluble in water, soluble in ethanol and methanol. It is metabolized in the acidic environment of the stomach to inactive by-products (ketones, alcohols, ethers), which are responsible for its low bioavailability and gastrointestinal side effects. This bacteriostatic macrolide antibiotic is used for treatment of respiratory infections caused mainly mycoplasma, chlamydia, staphylococci or streptococci, as well as of infections of the skin or urinary tract.

Clarithromycin is used for treating of respiratory infections caused mainly by mycoplasma, chlamydia, staphylococci or streptococci, as well as of infections of the skin or urinary tract. Clarithromycin has strong antibacterial properties and is more resistant against acidic environment than erythromycin; it has also improved pharmacokinetic properties and is better tolerated in the GIT. Clarithromycin is a white crystalline powder, practically insoluble in water but soluble in acetone.

Roxithromycin is a newer macrolide antibiotic with better tolerance than that of erythromycin. It is used to treat the same diseases as erythromycin and also to treat isosporiasis.

Chemical structures of selected macrolide antibiotics are in Figure 2.

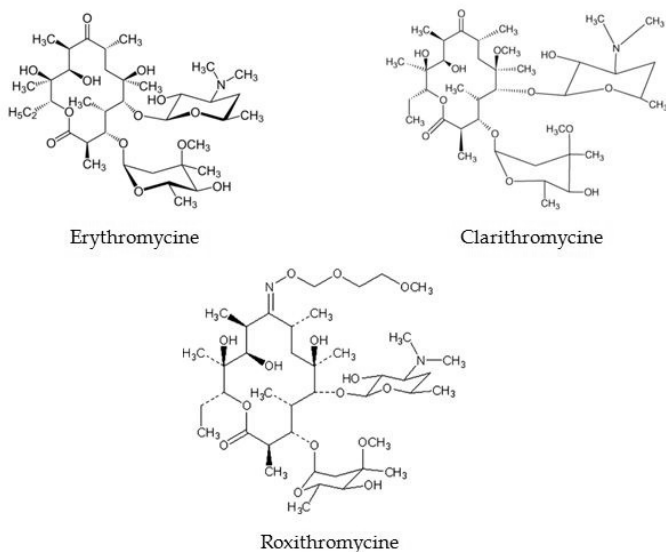


Figure 2. Structures of selected macrolide antibiotics.

Compound	CAS No.	Molecular mass (g.mol ⁻¹)	log K _{ow}
Erythromycine	114-07-8	733.93	3.06
Clarithromycine	81103-11-9	747.95	3.16
Roxithromycine	80214-83-1	837.05	2.75

Table 2. Physical-chemical properties of selected macrolides [34,35,37].

Musk compounds selected for this study are from the group of linear musks produced and marketed in the Czech Republic by Aroma Prague Company. They are used for preparation of various fragrances and perfume compositions. Their structures are given in Figure 3 and physical-chemical properties in Table 3.

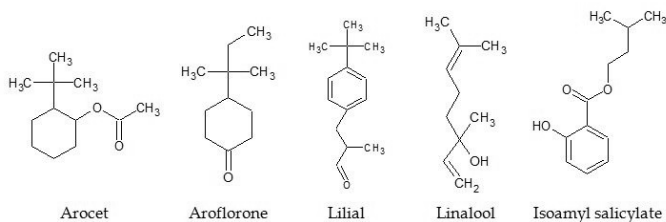


Figure 3. Structures of selected linear musks.

Compound	CAS No.	Molecular mass (g.mol ⁻¹)	log K _{ow}
Aroacet	88-41-5	198.30	4.42
Aroflorone	16587-71-6	168.26	3.40
Lilial	80-54-6	204.31	4.36
Linalool	126-91-0	154.25	3.38
Isoamyl salicylate	87-20-7	208.25	4.49

Table 3. Physical-chemical properties of selected linear musks.

2.2. Sampling locality

The presence of target compounds was monitored in the wastewater from municipal waste water treatment plant (WWTP) Brno – Modřice (catchment region for population of about

500,000 people). This facility was launched in 1961 as classic two-stage plant with anaerobic sludge stabilization. In the period between 2001 – 2003 the overall reconstruction and extension of the WWTP was realized with the main objective to meet the treated wastewater effluent limits set by Czech and European standards and regulations, and to ensure sufficient capacity of the facility to accommodate the growing demand of the city of Brno with almost 500 thousand of inhabitants and several industrial facilities, and also increasing number of the surrounding agglomerations successively connecting to the Brno sewerage system. Nowadays, the technology in WWTP Brno-Modřice corresponds to the EU parameters. Waste water cleaning process includes mechanical removal of rough solid particles – mechanical treatment, which is followed by fat removal. Water is then directed to the sedimentation tanks for removal of fine particles. The next step is biological treatment under anaerobic conditions where dephosphatation and denitrification occurs, followed by biological degradation under aerobic conditions. The rest of the non-biodegradable phosphorus is subsequently removed by chemical precipitation with ferric sulphate. Activated sludge is removed from the water in sedimentation tank, water is then discharged into the recipient and sludge is thickened and decayed. Produced bio-gas is used for the combined generation of heat and electricity. The residence time (technological delay) between inlet and comparable outlet in Brno WWTP is 24 hours.



Figure 4. Sampling locality – waste water treatment plant Brno - Modřice.

Composite 24-hour samples were collected at inflow and outflow of the WWTP by automatic sampling device in 2-hours intervals. Individual portions were collected in the dark glass sample containers with a capacity of 1 L. Samples for analysis of NSAIDs were collected at inflow and outflow of WWTP during July and August 2011, for determination of macrolides

and musk compounds from 11th to 20th of April 2011. Samples were picked up from the WWTP daily and transported to laboratory, where they were either analysed immediately or stored in a refrigerator at 5 °C and analysis was initiated within 24 hours.

2.3. Analysis of Pharmaceuticals

Solid phase extraction (SPE) was applied for the isolation of target compounds from waste water. The suspended particles were removed by filtration using Büchner funnel and filter paper Munktell Filtrak No 388 and No 390 for inflow samples and 390 for outflow samples and pH of the samples was adjusted to a value of 2 by addition of hydrochloric acid (NSAIDs) or formic acid (antibiotics). 300 mL of waste water was then subjected to solid phase extraction using Oasis HLB cartridges (volume 3 mL, 60 mg of sorbent, Waters, USA), which were previously activated by 6 mL of methanol and washed with 6 mL Milli-Q water at pH = 2. After loading of sample the cartridge was again washed by 6 mL Milli-Q water at pH = 2, dried for 5 minutes under flow of nitrogen and then the target compounds were eluted by 6 mL (NSAIDs) or 10 mL (antibiotics) of methanol. The eluate was then evaporated to dryness under gentle stream of nitrogen. For the analysis of NSAIDs the residue was dissolved in 300 µL of BGE and analysed by capillary zone electrophoresis with UV detection. For analysis of macrolides the residue was dissolved in 1 mL of acetonitrile and analysed by HPLC/MS.

2.3.1. Analysis of NSAIDs by capillary zone electrophoresis:

Agilent CE instrument equipped with UV-VIS detector of DAD type was used. Analytical conditions were as follows.

- Separation capillary: fused silica uncoated, ID = 75 µm, L = 83.5 cm, l = 75.4 cm
- Background electrolyte (BGE): 25 mmol.L⁻¹ Na₂B₄O₇ in Milli-Q water (before each injection, the capillary was treated successively with alkaline solution of 0.1 M NaOH, water and BGE)
- Separation voltage: 30 kV, positive polarity
- Temperature of separation capillary: 25 °C
- Detection: 210 nm (bandwidth of 40 nm), 200 nm (bandwidth of 20 nm), 230 nm (bandwidth of 10 nm)
- Sample injection: hydrodynamic, pressure pulse at capillary inlet 5 kPa for 5 s
- Analysis time: 25 min

Fig. 5 shows an example of electrophoregram.

Obtained results together with removal efficiency and limits of detection are presented in Table 4.

Compound	Concentration		Removal efficiency (%)	LOD [$\mu\text{g.L}^{-1}$]
	influent [$\mu\text{g.L}^{-1}$]	effluent [$\mu\text{g.L}^{-1}$]		
Salicylic acid	5.58–44.15	0.47–3.53	97	0.46
Ibuprofen	10.94–42.32	1.18–2.75	96	1.17
Paracetamol	1.00–14.61	0.52–1.65	97	0.46
Naproxen	0.61–14.48	0.51–2.35	78	0.50
Ketoprofen	2.15–28.21	1.34–6.46	92	1.28
Diclofenac	1.09–9.46	1.02–2.17	92	0.98

Table 4. Concentrations of NSAIDs at inflow and outflow, removal efficiency and limits of detection.

The ranges of concentrations of selected drugs in the influent and effluent and average removal efficiency of the WWTP for each drug are listed in Table 4. All selected drugs were detected in analysed samples of wastewater. Salicylic acid (average concentration $28.21 \mu\text{g.L}^{-1}$) and ibuprofen (average concentration $23.11 \mu\text{g.L}^{-1}$), were detected at highest concentrations and almost in all samples. It is caused by the fact, that these compounds are contained in the majority of the most frequently used drugs in the Czech Republic. The levels of other monitored analgesics were below $10 \mu\text{g.L}^{-1}$. Relatively low concentration of favourite painkiller – paracetamol – was surprising, but the reason could be partial decomposition of this compound in waste water before the inflow to the WWTP. Ketoprofen, diclofenac and naproxen were detected in wastewater only in some cases.

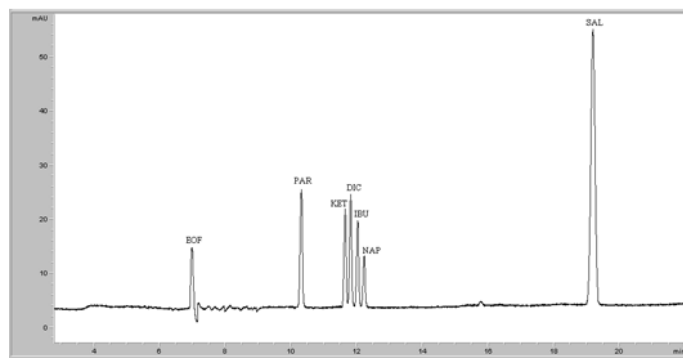


Figure 5. Electrophoregram of NSAIDs standards: EOF – Mesityl oxid (marker of electroosmotic flow); PAR – paracetamol; KET – ketoprofen; DIC – diclofenac; IBU – ibuprofen; NAP – naproxen; SAL – salicylic acid.

Average removal efficiency of all analysed compounds was above 90 %, except for naproxen with an average removal efficiency of 78 %.

2.3.2. Analysis of antibiotics by HPLC/MS

Analysis of samples was performed using high performance liquid chromatography with mass spectrometric detection (HPLC/MS). Agilent 1100 Series liquid chromatograph with Agilent 6320 spherical ion trap mass spectrometer and electrospray ionization were employed. Zorbax Eclipse XDB - C18 column (2.1 x 150 mm, particles 3.5 μm) protected by Zorbax Eclipse XDB - C18 precolumn (2.1 x 20 mm, particles 3.5 μm) was used for separation, binary mobile phase consists from 10mM ammonium acetate (A) and acetonitrile (B), gradient started from 25 % B to 55 % B in 3 min, then 90 % B in 10 min. Flow rate was 150 $\mu\text{L}.\text{min}^{-1}$. Conditions for electrospray: pressure of nebulizing gas (N_2) 20 psi, flow and temperature of drying gas (N_2) 10 $\text{L}.\text{min}^{-1}$ and 350 $^{\circ}\text{C}$, respectively. Positive ions were scanned within the range m/z 100 – 900. Individual compounds were identified by the combination of retention time and quasi-molecular ion detection (erythromycin: t_{R} = 11.2 min, m/z = 734.8; clarithromycin: t_{R} = 13.0 min, m/z = 748.3; roxithromycin: t_{R} = 13.4 min, m/z = 837.4), external standard method based on the response on fragmentograms corresponding to the quasi-molecular peaks of individual compounds was used. Metrological parameters of used analytical method are presented in Table 5.

Parameter	Compound		
	Erythromycin	Clarithromycin	Roxithromycin
Coefficient of determination (R^2)	0.9962	0.9993	0.9971
LOD [$\mu\text{g}.\text{L}^{-1}$]	0.1440	0.2428	0.0970
LOQ [$\mu\text{g}.\text{L}^{-1}$]	0.4305	0.7251	0.2903

Table 5. Metrological parameters of HPLC/MS method.

In real samples the presence of macrolide antibiotics was proved only exceptionally and at levels close to limits of detection (erythromycin 17., 18. and 19. 4. 2011 at inflow at levels of 0.274 $\mu\text{g}.\text{L}^{-1}$, roxithromycin 12.4.2011 at outflow 0.1 $\mu\text{g}.\text{L}^{-1}$). Clarithromycin was not detected at concentrations exceeding LOD at all. Therefore it could be concluded that macrolide antibiotics don't represent any serious risk for the receiving water.

2.4. Analysis of musk compounds

Solid Phase Microextraction (SPME) in head-space mode was used for the isolation of target analytes from waste water. Fibre with 65 μm mixed layer polydimethylsiloxane – divinylbenzene was selected as optimal on the base of previous studies realized in our laboratory. 22 mL glass vials closed with Teflon-lined silicon septum were used. 14 mL of raw sample was placed into the vial, 3.75 g NaCl was added, after inserting of magnetic stirrer vial was closed and heated up to the temperature of 80 $^{\circ}\text{C}$ in water bath. Magnetic stirrer was set to 900 rpm. Equilibration time was 5 minutes, followed by 40 minute sorption. Blank samples were treated by the same method using de-ionized water.

Compound	Quantification ion (m/z)	Qualifier ions (m/z)		t_R (min)	
Linalool	93	71	121	9.12	
Arocet (2 isomers)	82	123	57	13.483	14.044
Aroflorone	98	168	71	15.330	
Lilial	189	204	147	20.675	
Isoamyl salicylate	120	138	208	20.825	

Table 6. Experimental parameters for the GC/MS analysis of linear musks.

Isolated compounds were analysed by GC/MS using Agilent 6890N GC and Agilent 5973 MS equipped with quadrupole analyser and electron ionization @ 70 eV. Separation column was DB-5MS (20 m x 0.18 mm x 0.18 μ m) (J&W), helium 6.0 (SIAD, Czech Republic) at a flow rate of 0.8 mL.min⁻¹ (constant flow mode) was the carrier gas. Desorption from SPME fibre was realized in split/splitless injector of the GC in splitless mode for 3 min at a temperature of 250 °C. Column temperature program was as follows: 50 °C for 3 min, then 10°/min to 90 °C, then 5°/min to 120 °C, hold 4 min, then 10°/min to 160 °C, 5°/min to 185 °C, 20°/min to 285 °C, final isotherm 2 min. GC/MS interface temperature was set to 285 °C, temperature of ion source was 250 °C. Mass spectrometer was operated in SIM mode; parameters are summarized in Table 6.

Date	Linalool [μ g.L ⁻¹]		Arocet [μ g.L ⁻¹]		Aroflorone [μ g.L ⁻¹]		Lilial [μ g.L ⁻¹]		Isoamyl salicylate [μ g.L ⁻¹]	
	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow	Inflow	Outflow
11.4.11	61.31	ND	2.633	ND	3.442	ND	1.222	0.049	0.975	NQ
12.4.11	42.33	NQ	2.406	ND	1.342	ND	0.406	0.049	0.922	ND
13.4.11	33.28	NQ	2.847	ND	1.413	ND	0.439	0.017	0.328	ND
14.4.11	36.75	ND	1.388	ND	0.809	NQ	0.429	0.060	0.589	NQ
15.4.11	25.92	0.199	0.473	ND	0.369	ND	0.197	0.042	0.121	NQ
16.4.11	66.72	0.139	1.399	ND	1.427	ND	0.404	0.049	0.403	NQ
17.4.11	39.57	NQ	0.546	ND	0.727	ND	0.307	0.033	0.202	ND
18.4.11	90.81	0.114	3.223	ND	5.336	ND	0.391	0.058	0.492	NQ
19.4.11	75.67	ND	4.294	ND	2.419	NQ	0.684	0.065	0.734	NQ
20.4.11	84.79	ND	4.406	ND	0.925	ND	0.433	0.047	0.495	ND
Average	55.72	0.046	2.361	0.0002	1.821	0.0007	0.491	0.047	0.526	0.0003
LOD	0.0012		0.0004		0.0011		0.0002		0.0004	
LOQ	0.0041		0.0014		0.0037		0.0008		0.0012	

Table 7. Concentrations of selected linear musks in waste water. For the calculation of average compound concentrations following values were used: ND = 0.5 • LOD and NQ = LOD.

Table 7 presents the concentrations of selected linear musks in raw and cleaned waste water. Linalool was found in highest concentrations at inflow ranging from 33 to 91 $\mu\text{g.L}^{-1}$, followed by aroclor and aroclorone with levels in low units of $\mu\text{g.L}^{-1}$. Inflow concentrations of linal and isoamyl acetate were in tenths of $\mu\text{g.L}^{-1}$. These concentrations are lower than that of polycyclic musks at the same locality – levels found for galaxolide and tonalide were in hundreds and tens of $\mu\text{g.L}^{-1}$, respectively [38]. For all linear musks except of linal, high removal efficiencies were attained, usually more than 99.5 %. Linal removal efficiency was between 78.68 and 96.13 % (average 88.7 %). These results are very satisfactory.

3. Ecotoxicology

Our generation has recently stepped over a threshold of the new millennium. The growth of the human population coupled with increasing consumption and overuse of natural resources brings with it also growing impact on the total environment. The human activities that have accelerated since the 18th century with the beginning of the industrial revolution led in many cases to long-term consequences which disturbed the natural balance and gathered an irreversible and uncontrollable character [39]. Effects of above mentioned human activities, mainly uncontrolled release of various manmade chemicals, is not without adverse consequences. These negative effects are studied within the discipline of ecotoxicology, which was firstly defined around 1969 by Dr. René Truhaut, a member of the French Academy of Sciences. This new field of science "Ecotoxicology" he defined as "the study of adverse effects of chemicals with the aim of protecting natural species and populations." Thus ecotoxicology deals with potentially harmful effects of countless man-made chemicals and wastes released into biosphere on organisms. Ecotoxicity involves the identification of chemical hazards to the environment. "Ecotoxicity studies measure the effects of chemicals on fish, wildlife, plants, and other wild organisms" [40,41]. Bioassays are one of the main tools in ecotoxicological assessments. Ecotoxicology has the task to examine effects of chemicals or environmental samples on species, biocenoses and ecosystems. Results of ecotoxicological research constitute the main scientific background for setting immission standards for the protection of the environment. The Water Policy Directive [2] of the European Union (EU) strives for a good ecological and chemical status for surface waters. This Directive is to contribute to the progressive reduction of emissions of hazardous substances to water. However, the Directive is aimed especially at a monitoring of the state of the waters and is based on a combined approach using control of pollution at source (substance-specific assessment) through the setting of emission limit values and of environmental quality standards instead of an assessing threats to the waters from effluent discharges [2,42]. The solution is the whole effluent assessment (WEA), which can be defined as the assessment of the whole effluents by using a range of biological methods or techniques in order to reveal (potential) effects. It focuses on toxicity (acute and chronic), genotoxicity (including mutagenicity), bioaccumulation and persistence. Therefore WEA increases the understanding of the combined effect of all known and unknown substances, especially in complex mixtures [43]. Global evaluation of wastewaters should include ecotoxicological tests to complete the chemical

characterization. The integrated assessment of biological effects of wastewater discharges in the ecosystems is relevant and ecotoxicity tests are referred as extremely useful tools for the identification of environmental impacts [44]. On the other hand there exist some ways how to partially prevent environment and water ecosystem. On 1st June 2007 EU regulation REACH entered into force. The law is the European Community Regulation on chemicals and their safe use [45]. It deals with the Registration, Evaluation, Authorisation and Restriction of Chemical substances. The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. Three specific properties of a chemical are used to describe its potential hazard to the aquatic environment [46,47]:

- Aquatic toxicity: The hazard of a substance to living organisms, based on toxicity tests to aquatic animals and plants.
- Degradability: The persistence of the substance in the environment, based on molecular structure or analytical testing.
- Bioaccumulation/bioconcentration: The accumulation of a substance in living organisms (from water sources for bioconcentration), which may or may not lead to a toxic effect; based on calculations or bioconcentration factor (BCF) studies using fish.

Aquatic toxicity is determined using internationally harmonized test methods, which are preferred; in practice, data from national methods may also be used where they are considered as equivalent. Data are preferably to be derived using OECD Test Guidelines, US Environmental Protection Agency (EPA) or equivalent according to the principles of Good Laboratory Practices (GLP). For ecotoxicity evaluation of chemicals fish, crustacean, algae and freshwater plant (*Lemna minor*) are used. On the base of obtained results from tests the hazards to the aquatic environment which they present is identified and chemical substances are classified into categories and they are assigned risk phrases [46,48,49].

3.1. Ecotoxicity testing of chemical compounds

To assess the effect of chemical compounds on various aquatic organisms the ecotoxicity tests, biotests, bioassays using organisms from various trophic levels are used. The goal of the ecotoxicological tests is the determination of effective concentration (EC), eventually lethal concentration (LC) or inhibition concentrations (IC) [40]. These parameters refer to the concentration of toxic substance that results in 50% reduction of end-point relative to control at a given period of time [50]. These concentrations of tested compounds cause the mortality of 50 % testing organisms or 50% inhibition growth rate in relation to control group. Lower values of LC (EC, IC)50 means higher toxicity of the tested chemical compounds. In accordance with testing regulation the limit test, preliminary tests and definitive test were conducted with single compounds. In limit test concentration 100 mg.L⁻¹ of tested compound is used. Preliminary tests (range finding test) are used to find approximate toxicity of the chemical compounds if it is unknown. In this case the dilution series is following: 100 mg.L⁻¹, 10 mg.L⁻¹, 1 mg.L⁻¹, 0.1 mg.L⁻¹ and 0.01 mg.L⁻¹. The results of preliminary tests are

used to determine the range of dilution series of the final test. From obtained experimental endpoints (mortality, immobility, growth inhibition etc.) in ecotoxicity tests the ecotoxicological values EC50, IC50, LC50 are calculated

3.1.1. *Daphnia magna* – acute toxicity test

Daphnia magna is a common component of freshwater zooplankton. It refers to the group of *Arthropoda*, *Branchiopoda*, *Daphnidae*. *Daphnia* are small arthropods of 1–5 mm in size. They live in various aquatic environments. Ontogenesis of individual is direct without larval stages. During the year there is one or several biological cycles in which parthenogenetic generations are alternated by bisexual generations which enclose the cycle. Species *D. magna* is the largest species of *Daphnia* group. Thus it is vulnerable to fish predation that it is excluded from fish-inhabiting lakes. It occurs mainly in ephemeral habitats like small ponds and rockpools where vertebrate predators are rare. *D. magna* is most commonly used species in aquatic toxicity testing because of many characters that make it easy and economical to culture it in the laboratory. It is relatively small but bigger than other daphnids, thus manipulation with it is easy. It has short life cycle, high fecundity, and parthenogenetic reproduction. On the other hand in a few comparative studies *D. magna* tended to be less sensitive to toxic substances than other cladocerans, and this may be due in part to life-history and size differences [51,52]. *Daphnids* are integral part of water biocenosis and food chain; this is the reason why their using in ecotoxicity testing is important. There exist many national and international standard methods which use this organism for acute or chronic ecotoxicity assessment [53-59].

Alternative small scale method Daphtoxkit FTM (purchased from MicroBioTests Inc., Gent, Belgium) for the determination of EC50 value was used for our purposes. The Standard Operational Procedure of the Daphtoxkit FTM is in accordance with the OECD and ISO test protocols for the acute *Daphnia magna* toxicity tests [54,55]. Standard Freshwater was prepared with the concentrated salt solutions included in the kit. This medium, which has the composition recommended by the ISO for acute toxicity tests with *D. magna*, is used as a hatching medium and as a dilution medium for the preparation of the toxicant dilution series. Because of low water solubility of tested substances DMSO as solvent for preparation of 100 mg.L⁻¹ stock solutions of tested compounds was used. Maximal concentration of DMSO used for dilution series preparation in tests was 3 %. This concentration doesn't exhibit any negative influence on testing organisms in control group. *Ephippia* were hatched in Petri dishes with Standard Freshwater (ISO) medium three days before test at temperature 20 - 22 °C under continuous illumination of 6 000 lux. Pre-feeding of neonate with suspension of spirulina powder was done two hours before the test to prove them energetic reserve. *Daphnids* (aged less than 24 hours) were exposed to dilution series of tested compounds in preliminary and final tests. Experiments were conducted at temperature 20 °C in darkness incubator. After 24 and 48 h the endpoint - immobility was observed. The values of 24hEC50 and 48hEC50 were calculated by probit analysis. The test was considered valid if the number of dead organisms in the control did not exceeded 10 %.

3.1.2. *Thamnocephalus platyurus* - acute toxicity test

Ecotoxicological evaluation of selected musk substances was done also via freshwater crustaceans *Thamnocephalus platyurus*. It refers to class *Branchiopoda* orders *Anostraca*, originated from North America. For calculation value of 24LC50 alternative test Thamnotoxkit FTM was used (purchased from MicroBioTests Inc., Gent, Belgium). The *T. platyurus* assay has already been incorporated in some countries in regional or national regulations for toxicity testing but requests have also been formulated from various sides to propose this micro-biotest to “international” organisations for endorsement as a “standard toxicity test”, for specific applications in a regulatory framework. On the base of proposal to the International Standardisation Organisation (ISO) for consideration the *T. platyurus* micro-biotest as a new ISO standard ecotoxicological test committee draft ISO/CD 14380 was in 2010 prepared. This test is often used to toxicity assessing in freshwater, waste water and determination of acute toxicity of chemicals [60-62]. Thamnotoxkit FTM is similar to Daphtoxkit FTM - it also contains all the materials to perform six complete acute (24-hour) toxicity tests (range-finding or definitive) based on mortality of testing organisms. Larvae of the fairy shrimp *T. platyurus* hatched from cysts are used. The test procedure followed the Standard Operational Procedure manual of the Thamnotoxkit FTM micro-biotest. Standard freshwater was prepared by diluting of the concentrated salt solutions included in the kit to obtain 1 L of medium, which served for hatching of the cysts and for preparation of the toxicant dilution series. In case of organisms *T. platyurus* acetone as solvent for preparation of 100 mg.L⁻¹ stock solution of tested compounds was used. Maximal concentration of acetone used for dilution series preparation in tests was 3 %, which have no negative effect on testing organisms in control group. Before testing the eggs of *T. platyurus* were hatched 24 hours at a temperature of 25 °C under continuous illumination at 4 000 lux. The assays were carried out in the multiwell test plates provided in the kits in the darkness at temperature of 25 °C. Larvae were exposed to dilution series of tested compounds in preliminary and final tests. Lethality (endpoint for effect calculation) was observed after 24 h. The values of 24hLC50 were calculated by probit analysis. The test was considered valid if the number of dead organisms in the control did not exceed 10 %.

3.2. Ecotoxicity of linear musk compounds

In our study four selected synthetic linear musk compounds were evaluated via alternative ecotoxicity tests on freshwater crustaceans *T. platyurus* and *D. magna*: Arocet (2-*tert*-butylcyclohexylacetate, Aroflorone (4-*tert*-amylcyclohexanone), Lilial [3-(4-*tert*-butylphenyl)-2-methylpropanal] and Linalool (3,7-dimethylocta-1,6-diene-3-ol). All substances were obtained from their producer Aroma Praha Company Ltd. Information on the occurrence of these substances in waste water and surface water as well as information concerning their ecotoxicity is absent in scientific literature. Material safety data sheet (MSDS), if available, gives only data concerning their toxicity. The Globally Harmonized System for Classification and Labelling of Chemicals (GHS) describes testing for hazards to the aquatic environment in Part 4, Chapter 4.1 [47]. The purpose of obtaining aquatic toxicity data for chemicals

is to classify them to their acute or chronic toxicity in the hazard classification in different classes. Ecotoxicological values obtained on the most sensitive of testing organisms (fish, crustacean algae or other aquatic plant) in acute toxicity tests serve to classification in three acute classification categories; ecotoxicological value $< 1 \text{ mg.L}^{-1}$, (class I-very toxic to aquatic organisms); $1 - 10 \text{ mg.L}^{-1}$ (class II-toxic to aquatic organisms); $10 - 100 \text{ mg.L}^{-1}$ (class III-harmful to aquatic organisms). Substances with value EC₅₀ above 100 mg.L^{-1} would not be classified. Results obtained in test of acute toxicity on *D. magna* and *T. platyurus* are summarized in Table 8. To compare toxicity of linear musk compounds with other musks in Table 9 are summarized results obtained in our laboratory on the same testing organisms via the same testing procedure [38].

Tested compounds	<i>Thamnocephalus platyurus</i>	<i>Daphnia magna</i>	
	24hLC50 [mg.L ⁻¹]	24EC50 [mg.L ⁻¹]	48EC50[mg.L ⁻¹]
Lilial	11.98	4.4	2.13
Arocet	54.52	63.68	40.23
Arofloron	68.34	53.63	40.42
Linalool	53.94	156.26	124.59

Table 8. Results of acute toxicity tests of linear musks on *Thamnocephalus platyurus* and *Daphnia magna*.

Group	Compound	<i>Thamnocephalus platyurus</i>	<i>Daphnia magna</i>	
		24h LC50 [mg.L ⁻¹]	24h EC50 [mg.L ⁻¹]	48h EC50 [mg.L ⁻¹]
Nitromusks	Musk xylene	6.15	2.39	2.22
	Musk ketone	6.14	2.33	2.13
Polycyclic musks	Galaxolide (HHCB)	1.14	1.22	1.12
	Tonalide (AHTN)	1.58	1.51	1.33

Table 9. Results of acute toxicity tests of nitromusks and polycyclic musks on *Thamnocephalus platyurus* and *Daphnia magna*.

From compounds tested in our study lilial was found as the most toxic to testing organisms. Although we have ecotoxicological values only on one organism defined for chemicals water ecotoxicity assessment, on the base of 48EC₅₀ values obtained for *D. magna* we could try to classify them as follows: all substances except linalool and lilial were harmful to aquatic organisms (class-III). Lilial was found to be toxic to aquatic organisms (class-II). From results obtained on a limited number of species it seems that linalool is not hazardous to aquatic environment. In comparison with results obtained in our similar study on the same testing organism for polycyclic and nitro musk (see Table 9) we can conclude that linear

musk compounds are more friendly to the environment than polycyclic and nitro musks. The 48EC50 values for tonalide, galaxolide, musk ketone and musk xylene on *D. magna* were 1.33 mg.L⁻¹, 1.12 mg.L⁻¹, 2.13 mg.L⁻¹ and 2.22 mg.L⁻¹, respectively. In this case they could be classified as toxic to aquatic organisms (II-class). As seems the linear musk compounds (exception lilial) are in our case in the order of ten times less toxic to the testing organism *T. platyurus* and *D. magna* than polycyclic and nitro musks. As mentioned above this finding is very positive in view of prevention of environmental pollution because the production of linear musk compounds in the Czech Republic is on the rise and replaces the use polycyclic and nitro musk compounds. Equally important is the finding that the concentration at the outlet of the WWTP was mostly below the detection limit as in this article published. Exception is only lilial, but its levels detected at the WWTP outflow (mean value 0.047 µg.L⁻¹, see Table 7), are much lower than in our case the value of 24LC50 found in our experiments.

4. Conclusions

As a consequence of increasing living standard of mankind the environment is loaded with increasing number of various chemicals. Pharmaceuticals and personal care products (PPCPs) belong to the group with increasing use, but these compounds also attract increasing interest as new or emerging environmental contaminants. Negative effects of these compounds or formulations are caused not only by parent compounds, but also their degradation or transformation products could show in some cases even stronger negative effects than their precursors.

This study was focused on three groups of chemicals belonging to PPCPs: non-steroid anti-inflammatory drugs, which are used widely, macrolide antibiotics which gain wider importance due to their therapeutical properties, and linear musk compounds which represent the most modern synthetic fragrances with great perspectives. The levels of these compounds at the inflow and outflow of waste water in municipal waste water treatment plant in Brno-Modřice were determined. From the group of non-steroid anti-inflammatory drugs ibuprofen was the compound with the highest concentration in the raw waste water reaching more than 40 µg.L⁻¹, followed by salicylic acid and ketoprofen. The removal efficiency of the cleaning process was found to be very good for all compounds under study with the exception of naproxen – its removal efficiency was 78 %, in all other cases it was better than 90 %.

The levels of macrolide antibiotics (erythromycin, clarithromycin and roxithromycin) were found to be very low in raw waste water (in several samples erythromycin and roxithromycin were found in sub- µg.L⁻¹, their levels in cleaned waste water were below the limits of detection of used analytical procedure. It could be stated that these compounds due to low concentrations don't represent any serious risk for the receiving water.

The concentrations of linear musks produced in the Czech Republic in the raw waste water ranged from tens of µg.L⁻¹ for linalool, units of µg.L⁻¹ for aroclor and aroclorone to sub- µg.L⁻¹ levels for lilial and isoamylacetate. Removal efficiencies were in common better than 99.5 % with exception of lilial with average removal efficiency of 88.7 %. The last compound also

exhibited the highest ecotoxicity from all tested linear musk compounds with 24EC50 value 4.4 mg.L⁻¹. Nevertheless, this value significantly exceeds the concentrations found in real samples.

Acknowledgements

Authors acknowledge the financial support from the project No. FCH-S-12-4 from the Ministry of Education, Youth and Sports of the Czech Republic.

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Determination of Trace Metals in Waste Water and Their Removal Processes

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/52025>

1. Introduction

Since the second part of 20th century, there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. Environmental impact of heavy metals was earlier mostly attributed to industrial sources. In recent years, metal production emissions have decreased in many countries due to strict legislation, improved cleaning/purification technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, regulations for heavy metal containing waste disposal have been tightened [1].

A significant part of the anthropogenic emissions of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe and Ni, as well as industrial products that, at the end of their life, are discharged in wastes. Major urban inputs to sewage water include household effluents, drainage water, business effluents (e.g. car washes, dental uses, other enterprises, etc.), atmospheric deposition, and traffic related emissions (vehicle exhaust, brake linings, tires, asphalt wear, gasoline/oil leakage, etc.) transported with storm water into the sewerage system. For most applications of heavy metals, the applications are estimated to be the same in nearly all countries, but the consumption pattern may be different. For some applications which during the last decade has been phased out in some countries, there may, however, today be significant differences in uses [2-4].

Most common sources of heavy metals to waste and/or waste water are [1]; (i) Mining and extraction; by mining and extraction a part of the heavy metals will end up in tailings and other waste products. A significant part of the turn over of the four heavy metals with mining waste actually concerns the presence of the heavy metals in waste from extraction of other metals like zinc, copper and nickel. It should, however, be kept in mind that mining waste is generated in-

dependent of the subsequent application of the heavy metal. (ii) Primary smelting and processing; a minor part of the heavy metals will end up in waste from the further processing of the metals. (iii) Use phase; a small part of the heavy metals may be lost from the products during use by corrosion and wear. The lost material may be discharged to the environment or end up in solid waste either as dust or indirectly via sewage sludge. (iv) Waste disposal; the main part of the heavy metals will still be present when the discarded products are disposed off. The heavy metals will either be collected for recycling or disposed of to municipal solid waste incinerators (MSWI) or landfills or liquid waste. A minor part will be disposed of as chemical waste and recycled or landfilled via chemical waste treatment. (v) volcanic eruptions. (vi) fossil fuel combustion. (vii) agriculture (viii) erosions (ix) metallurgical industries. Actually metal pollutants are neither generated nor completely eliminated; they are only transferred from one source to another. Their chemical forms may be changed or they are collected and immobilized not to reach the human, animals or plants.

The term *heavy metal* has never been defined by any authoritative body such as The International Union of Pure and Applied Chemistry (IUPAC). It has been given such a wide range of meanings by different authors that it is effectively meaningless. No relationship can be found between density (specific gravity) and any of the various physicochemical concepts that have been used to define "heavy metals" and the toxicity or ecotoxicity attributed to *heavy metals*. The term bioavailability is more appropriate to define the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters as well as the physicochemical properties of metallic elements, their ions, and compounds. These in turn depend upon the atomic structure of the metallic elements. Thus, any classification of the metallic elements to be used in scientifically based legislation must itself be based on the periodic table or some subdivision of it. In conclusion, heavy metals commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but all of them are not dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn. All of them pose a number of undesired properties that affect humans and the environment [5].

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large-scale sector contain considerable amounts of toxic metal ions [4]. The toxic metals and their ions are not only potential human health hazards but also to another life forms. Toxic metal ions cause physical discomfort and sometimes life-threatening illness including irreversible damage to vital body system [6]. From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium(VI). In many instances, the effect of heavy metals on human is not well understood. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels. Mine tailing and effluents from non-ferrous metals industry are the major sources of heavy metals in the environment. Among commonly used heavy metals, Cr(III), Cu, Zn, Ni and V are comparatively less toxic than Fe and Al. Cu is mainly employed in electric goods industry and brass production. Major applications for Zn are galvanization and production of alloys. Cadmium has a half-life of 10–30 years and its accumulation in human body affects kidney, bone and also causes cancer and its use is increasing in industrial applica-

tions such as electroplating and making pigments and batteries. Chromium compounds are nephrotoxic and carcinogenic in nature. As a result of increasing awareness about the toxicity of Hg and Pb, their large-scale use by various industries has been either curtailed or eliminated. An effluent treatment facility within the industry discharging heavy metals contaminated effluent will be more efficient than treating large volumes of mixed wastewater in a general sewage treatment plant. Thus it is beneficial to devise separate treatment procedures for scavenging heavy metals from the industrial wastewater [4,6,7].

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to heavy legislation, improved production and cleaning technology. A variety of inorganic techniques can be used to measure trace elements in waste water including flame atomic absorption spectrometry (FAAS) and graphite furnace (or electrothermal) atomic absorption spectrometry (GFAAS or ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Depending upon the number of elements to be determined, expected concentration range of analytes and the number of samples to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. Among the various treatment methods applied to remove heavy or trace metals, chemical precipitation process has been the most common technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes such as bio-sorption, neutralization, precipitation, ion exchange, adsorption etc. have been developed and extensively used for the heavy metal removal from wastewater.

In this chapter the novel and common methods for the determination of trace heavy metals in waste water and their removal processes are explained.

2. Toxicity effects of some heavy metals in the wastewater [1,3,5]

All heavy metals are effected to human and environment by different ways. For example; lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Of particular concern for the general population is the effect of lead on the central nervous system. Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 µg/dl. Lead is known to cause kidney damage. Some of the effects are reversible, whereas chronic exposure to high lead levels may result in continued decreased kidney function and possible renal failure. The evidence for carcinogenici-

ty of lead and several inorganic lead compounds in humans is inadequate. Classification of The International Agency for Research on Cancer (IARC) is class 2B which is the agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans. In the environment, lead binds strongly to particles, such as soil, sediment and sewage sludge. Because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. It does not bioaccumulate in most organisms, but can accumulate in biota feeding primarily on particles, e.g. mussels and worms. These organisms often possess special metal binding proteins that removes the metals from general distribution in their organism. Like in humans, lead may accumulate in the bones. One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment.

Mercury is a peculiar metal. Most conspicuous is its fluidity at room temperature, but more important for the possible exposure of man and the environment to mercury are two other properties:

1. Under reducing conditions in the environment, ionic mercury changes to the uncharged elemental mercury which is volatile and may be transported over long distances by air.
2. Mercury may be chemically or biologically transformed to methylmercury and dimethylmercury, of which the former is bioaccumulative and the latter is also volatile and may be transported over long distances. Mercury is not essential for plant or animal life. The organic forms of mercury are generally more toxic to aquatic organisms than the inorganic forms. Aquatic plants are affected by mercury in the water at concentrations approaching 1 mg/litre for inorganic mercury, but at much lower concentrations of organic mercury.

Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tends to bioaccumulate. Cadmium is not essential for plant or animal life. Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II). The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth.

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) and Cr(VI) (hexavalent chromium) are of main biological relevance. There is a great difference between Cr(III) and Cr(VI) with respect to toxicological and environmental properties, and they must always be considered separately. Chromium is similar to lead typically found bound to particles. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains. Contrary to the three other mentioned heavy metals, Cr(III) is an essential nutrient for man in amounts of 50 - 200 µg/day. Chromium is nec-

essary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element. In general, Cr(III) is considerably less toxic than Cr(VI). Cr(VI) has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer. Hexavalent chromium is in general more toxic to organisms in the environment than the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities. Chromium can make fish more susceptible to infection; high concentrations can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms. Reproduction of the water flea *Daphnia* was affected by exposure to 0.01 mg hexavalent chromium/litre. Hexavalent chromium is accumulated by aquatic species by passive diffusion. In general, invertebrate species, such as polychaete worms, insects, and crustaceans are more sensitive to the toxic effects of chromium than vertebrates such as some fish. The lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre.

Copper can be found in many wastewater sources including, printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 ppm from copper cleaning operations. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions [8].

Nickel is a naturally occurring element widely used in many industrial applications for the shipbuilding, automobile, electrical, oil, food and chemical industries. Although it is not harmful in low quantities, nickel is toxic to humans and animals when in high concentrations. Nickel can be present in wastewater as a result of human activities. Sources of nickel in wastewater include ship cruise effluents, industrial applications and the chemical industry [9].

Arsenic is found in wastewater from electronic manufactures making gallium arsenide wafers and electronic devices. It also can be found in silicon semiconductor operations that use high dose arsenic implants. Other sources of arsenic are ground water in agricultural areas where arsenic was once used as an insecticide. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic exists in the -3, 0, +3 and +5 oxidation states. Each of them have different toxic effect both human and environment.

Actually all chemicals, including even essential elements, drugs and in fact water, are toxic above (and below) their limiting values. However, some elements such as arsenic, lead, cadmium, mercury, described as toxic, are known to be toxic for living beings at any concentration and they are not asked to be taken in to the body even in ultratrace levels.

3. Determination Techniques of Heavy Metals in Waste Water Samples

In order to determine the heavy trace metals, there are many inorganic techniques such as FAAS, ETAAS, ICP-OES, ICP-MS as well as anodic stripping and recently laser induced breakdown spectroscopy (LIBS). Each technique has its own advantages and disadvantages which will be discussed in this chapter.

Actually all the steps of an analysis, namely (i) representative sampling, (ii) to prevent analyte loss e.g. its sorption on vessel wall, (iii) contamination from the environment, wares, chemicals added to the sample, (iv) transfer the sample to the lab, (v) treatment of sample prior to analysis (leaching, extraction, preconcentration/separation of the analytes, (vi) choose of the method considering its limitations, (vii) calibration of the vessels, instrument etc, (viii) preparation of sample, all solutions, standards correctly and appropriately, (ix) to test the accuracy of the method using Certified Reference Materials (CRM), (x) evaluation of results statistically and reporting are all the rings of a chain. Each step is important and potential source of error if not applied conveniently. The weakest ring of the chain limits the accuracy and quality of the results. If it is broken, the analysis collapses. Therefore, all the steps of an analysis should be performed with caution. A problem or error even in one of those steps causes the result to be wrong. As in all analyses, sample preparation step is the most important one which should be completed quickly, easy and safely. Waste water samples may contain particulates or organic materials which may require pretreatment before spectrometric analysis. In order to analyze total metal content of a sample, concentration of metals inorganically and organically bound, dissolved or particulated materials should be found.

As stated in Standard Methods, samples which are colorless and transparent, having a turbidity of <1 NTU (Nephelometric Turbidity Unit), no odor and single phase may be analyzed directly or, if necessary, after enrichment by atomic absorption spectrometry (flame or electro thermal vaporization) or inductively coupled plasma spectrometry (atomic emission or mass spectrometry) for metals without digestion. For further verification or if changes in existing matrices are encountered, comparison of digested and undigested samples should be done [10].

If samples have particulates and only the dissolved metals will be analyzed, filtration of sample and analyzing of filtrate will be enough. To be on the safe side, if particulates involved, convenient digestion procedures are suggested. Since different filtration procedures produce different blank values, it is always suggested to study with a blank solution. If only the metal contents of particulates are asked to be determined, then the sample is filtered and the filter is digested and analyzed.

In order to reduce interferences, organic matrix of the sample should be destroyed by digestion as well as metal containing compounds are decomposed to obtain free metal ions which can be determined by atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) more conveniently. The procedures for destroying organic material and dissolving heavy metals fall into three groups; wet digestion by acid mixtures prior to elemental analysis, dry ashing, followed by acid dissolution of the ash and microwave assisted digestion

[11]. In Standard Methods if metal concentration is around 10-100, it is advised to digest 10 mL of sample. For less metal concentrations, sample volume could be around 100 mL for subsequent enrichment [10]. For most digestion procedures, nitric acid is used which is an acceptable matrix for both flame and electrothermal atomic absorption and ICP-MS [12]. For nitric acid digestion, 100 mL of sample is heated in a beaker with 5 mL concentrated nitric acid. Boiling should be prevented and addition of acid should be repeated til a light colored, clear solution is obtained [10]. Sometimes, if the samples involve readily oxidisable organic matters, mixtures of HNO_3 - H_2SO_4 or HNO_3 - HCl may be used. Samples with high organic contents, mixtures of HNO_3 - HClO_4 or HNO_3 - H_2O_2 or HNO_3 - HClO_4 - HF can be used. The latter is especially important for the dissolution of particulate matter. For samples which have high organic content, dry ashing may be favored. Wet digestion systems are performed either with a reflux or in a beaker on a laboratory hot plate. These methods are temperature limited because of the risk of contaminants from the air, laboratory equipment etc. Also there may be lost of volatile elements (As, Cd, Pb, Se, Zn and Hg etc.). Temperature limitation can be overcome by closed pressure vessels, i.e. microwave digestion. Closed systems allow high pressures above atmosphere to be used. This allows boiling at higher temperatures and often leads to complete dissolution of most samples [13]. In the American Society for Testing and Materials (ASTM) Standards (D1971-11) 'Standard practices for digestion of water samples for determination of metals by FAAS, ETAAS, ICP-OES or ICP-MS' for waste water samples it is advised to use, 100 volume of sample: 5 volume HCl : 1 volume HNO_3 is put to microwave digestion vessels for 30 minutes at 121°C and 15 psig [14]. A comparison of digestion techniques is given in Table 1.

	Wet Ashing	Microwave Digestion
Time Consumption	Slow	Rapid
Temperature	Low	High
Pressure	Atmospheric	Above Atmospheric
Operator Skills	High	Moderate
Safety	Corrosive-explosive reagents	Corrosive-explosive reagents
Operating Cost	Low	High
Environmental Effect	High	Low
Analyte Loss&Contamination	High	Low

Table 1. Comparison of Digestion Techniques.

After choosing the effective sample preparation step, most useful techniques were explained below, like atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), laser induced breakdown spectroscopy (LIBS) and anodic stripping.

3.1. Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is an analytical method for quantification of over 70 different elements in solution or directly in solid samples. Procedure depends on atomization of elements by different atomization techniques like flame (FAAS), electrothermal (ETAAS), hydride or cold vapor. Each atomization technique has its advantages and limitations or drawbacks. A comparison of several AAS techniques is given in Table 2.

Two types of flame are used in FAAS: (i) air/acetylene flame, (ii) nitrous oxide/acetylene flame. Flame type depends on thermal stability of the analyte and its possible compounds formed with flame concomitants. Temperature formed in air-acetylene flame is around 2300°C whereas acetylene-nitrous oxide (dinitrogen oxide) flame is around 3000°C [15]. Generally with air/acetylene flame antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin and zinc can be determined. On the other hand for refractory elements such as aluminium, barium, molybdenum, osmium, rhenium, silicon, thorium, titanium and vanadium, nitrous oxide/acetylene flame should be used [10]. But some elements like vanadium, zirconium, molybdenum and boron has lower sensitivity in the determination by FAAS because the temperature is insufficient to break down compounds of these elements. Samples should be in solution form, or digested to be detected by FAAS. Typical detection limits are around ppm range and sample analysis took 10-15 seconds per element [16]. The block diagram of FAAS and GFAAS is depicted in Figure 1. Generally, hollow cathode lamps as source, flame or graphite furnace as an atomizer, grating as a wavelength selector and photomultiplier as a detector are used.

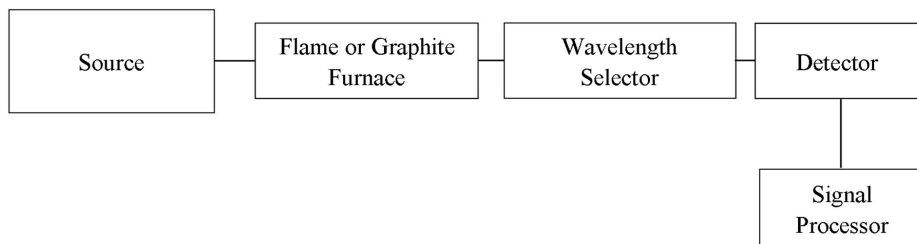


Figure 1. Block Diagram for FAAS and GFAAS.

Mahmoud et al. determined Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb by FAAS after enrichment with chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine (SiG-CHBPA) [16]. Afkhami et al. determined Cd in water samples after cloud point extraction in Triton X-114 without adding chelating agents [18]. Mohamed et al. determined chromium species based on the catalytic effect of Cr(III) and/or Cr(VI) on the oxidation of 2-amino-5-methylphenol (AMP) with H_2O_2 by FAAS [19]. Mahmoud et al. pre-concentrated Pb(II) by newly modified three alumina-physically loaded-dithizone adsorbents then determined by FAAS [20]. Cassella et al. prepared a minicolumn packed with a styrene-divinylbenzene resin func-

tionalized with (S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]-pyrrolidine-1-carboxylic acid ethyl ester to determine Cu in water samples [21]. Carletto et al. used 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of Zn(II) by FAAS [22]. Gunduz et al. preconcentrated Cu and Cd using TiO₂ core-Au shell nanoparticles modified with 11-mercaptopundecanoic acid and analysed their slurry [23].

ETAAS is basically same as FAAS; the only difference is flame is replaced by graphite tube which can be heated up to 3000 °C for atomization. Since sample is atomized in a much smaller volume the atoms density will be higher, its detection limit is much more than FAAS, around ppb range. Graphite furnace program typically consists of four stages; drying for evaporation of solvent; pyrolysis for removal of matrix constituents; atomization for generation of free gaseous atoms of the analyte; cleaning for removal of residuals in high temperature. Generally samples are liquids, but there are some commercial solid sampling instruments also. Analyze took 3-4 minutes per element. 50 and more elements can be analyzed by GFAAS [15].

Burguera et al. determined beryllium in natural and waste waters using on-line flow-injection preconcentration by precipitation dissolution for electrothermal atomic absorption spectrometry. They used a precipitation method quantitatively with NH₄OH-NH₄Cl and collected in a knotted tube of Tygon without using a filter then the precipitate was dissolved with nitric acid injected to graphite furnace [24]. Baysal et al. accomplished to preconcentrate Pb by cobalt/pyrrolidine dithiocarbamate complex (Co(PDC)₂). For this purpose, at first, lead was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex formed using ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent and cobalt as a carrier element. The supernatant was then separated and the slurry of the precipitate prepared in Triton X-100 was directly analyzed [25].

Hydride generation atomic absorption spectrometry is a technique for some metalloid elements such as arsenic, antimony, selenium as well as tin, bismuth and lead which are introduced to instrument in gas phase. Hydride is generated mostly by adding sodium borohydride to the sample in acidic media in a generator chamber. The volatile hydride of the analyte generated is transferred to the atomizer by inert gas where it is atomized. The oxidation state of the metalloid is very important so before introducing to the hydride system, specific metalloid oxidation state should be produced. This method lowers limit of detection (LOD) 10-100 times [15,27]

Coelho et al, presented a simple procedure was developed for the direct determination of As(III) and As(V) in water samples by flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS), without pre-reduction of As(V) [24]. Cabon and Madec determined antimony in sea water samples by continuous flow injection hydride generation atomic absorption spectrometry. After continuous flow injection hydride generation and collection onto a graphite tube coated with iridium, antimony was determined by graphite furnace atomic absorption spectrometry [28]. Yersel et al. developed a separation method with a synthetic zeolite (mordenite) was developed in order to eliminate the gas phase interference of Sb(III) on As(III) during quartz furnace hydride generation atomic absorption spectrometric determination [29]. Anthemidis et al. determined arsenic (III) and total arsenic in water by using an on-line sequential insertion system and hydride generation atomic ab-

sorption spectrometry [31]. Erdogan et al. determined inorganic arsenic species by hydride generation atomic absorption spectrometry in water samples after preconcentration/separation on nano $\text{ZrO}_2/\text{B}_2\text{O}_3$ by solid phase extraction [31]. Korkmaz et al. developed a novel silica trap for lead determination by hydride generation atomic absorption spectrometry. The device consists of a 7.0cm silica tubing which is externally heated to a desired temperature. The lead hydride vapor is generated by a conventional hydride-generation flow system. The trap is placed between the gas-liquid separator and silica T-tube; the device traps analyte species at 500 °C and releases them when heated further to 750 °C. The presence of hydrogen gas is required for revolatilization; O_2 gas must also be present [32].

Cold vapour atomization technique is used for the determination of mercury which is the only element to have enough vapour pressure at room temperature. Method is based on converting mercury into Hg^{+2} , followed by reduction of Hg^{+2} with tin(II)chloride or borohydride. Then produced elemental mercury swept into a long-pass absorption tube along with an inert gas. Absorbance of this gas at 253.7 nm determines the concentration. Detection limit is around ppb range. Beside to inorganic mercury compounds, organic mercury compounds are problematic as they cannot be reduced to the element by sodium tetrahydroborate, and particularly not by stannous chloride. So it is advised to apply an appropriate digestion method prior to the actual determination [15].

Kagaya et al. managed to determine organic mercury, including methylmercury and phenylmercury, as well as inorganic mercury by cold vapor atomic absorption spectrometry (CV-AAS) by adding sodium hypochloride solution [33]. Pourreza and Ghanemi developed a novel solid phase extraction for the determination of mercury. The Hg(II) ions were retained on a mini-column packed with agar powder modified with 2-mercaptobenzimidazole. The retained Hg(II) ions were eluted and analysed by CV-AAS [34]. Sahan and Sahin developed for on-line solid phase preconcentration and cold vapour atomic absorption spectrometric determination of Cd(II) in aqueous samples. Lewatit Monoplus TP207 iminodiacetate chelating resin was used for the separation and preconcentration of Cd(II) ions at pH 4.0 [35].

However, qualitative analysis cannot be made by AAS because a specific hollow cathode lamp (HCL) is used for each element. Therefore, elements should be determined one by one which make a qualitative analysis almost impossible. In addition, non-metals cannot be determined because their atomic absorption wavelengths are in far UV range which is not suitable for analysis due to absorption of air components.

Since 2004, new generation high resolution continuum source atomic absorption spectrometer (HR-CS-AAS) which is equipped with high intensity xenon short-arc lamp, high resolution double monochromator, CCD detector are produced. The continuous source lamp emits radiation of intensity at least an order of magnitude above that of a typical hollow cathode lamp (HCL) over the entire wavelength range from 190 nm to 900 nm. With these instruments, aside from the analysis line, the spectral environment is also recorded simultaneously, which shows noises and interferences effecting analysis. Improved simultaneous background correction and capabilities to correct spectral interferences, increase the accuracy of analytical results. With high resolution detector, interferences are minimized through optimum line separation. With these instruments, not only metals and non-metals e.g. F, Cl, Br, I, S, P can be determined

by their hyperfine structured diatomic molecular absorbances. There are various papers for fluoride determination by GaF [36], SrF [37], AlF [38], CaF [39], chloride by AlCl [40], InCl [41], bromide by AlBr [42], CaBr [43], sulfur by CS [44], phosphorus by PO [45].

	FAAS	GFAAS	Hydride Generation AAS	Cold Vapour AAS
Elements	68	50	As, Se, Sb, Bi, Pb, Sn	Hg
Limit of Detection	+	++++	++++	++++
Precision	++++	+	+	+
Interferences	+++	+	++++	++++
Analysis Time	++++	+	++	++
Sample Preparation	+++	+++	++	++
Operation Skills	+++	++	++	++
Operation Costs	++++	++	++	++

+Bad, ++:Moderate, +++:Good, ++++:Very Good

Table 2. Comparison of AAS techniques.

3.2. Inductively Coupled Plasma Optical Emission Spectrometry

Inductively coupled plasma-optical (or atomic) emission spectrometry (ICP-OES or ICP-AES) is an analytical technique used for determination of trace metals. This is a multi-element technique which uses a plasma source to excite the atoms in samples. These excited atoms emit light of a characteristic wavelength, and a detector measures the intensity of the emitted light, which is related with the concentration. Samples are heated through 10000 °C to atomize effectively which is an important advantage for ICP technique. Another advantage is multi element analysis. With ICP technique, 60 elements can be analysed in single sample run less than a minute simultaneously, or in a few minutes sequentially. Besides instrument is only optimized for one time for a set of metal analysis. High operating temperature lowers the interferences. Determinations can be accomplished in wide linear range and refractory elements can be determined at low concentrations (B, P, W, Zr, U). On the other hand consumption of inert gas is very much higher than AAS techniques which cause high operating costs.

ICP instruments can be 'axial' and 'radial' according to their plasma configuration. In radial configuration, the plasma source is viewed from the side. Emissions from axial plasma are viewed from horizontally along its length, which reduces background signals resulting in lower detection limits. Some instruments have both viewing modes [46]. The block diagram of ICP-OES is depicted in Figure 2. Generally, radio frequency (RF) powered torch as a source, polychromators as a wavelength selector, photomultiplier (PMT) or charge capacitive discharged arrays (CCD) as detectors are used.

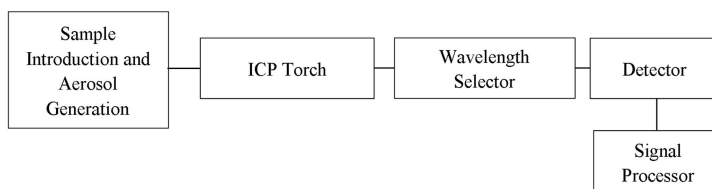


Figure 2. Block Diagram of ICP-OES.

Enrichment/separation procedures have been applied prior to ICP analyses as well. Atanasove et al. used sodium diethyldithiocarbamate to co-precipitate for the pre-concentration of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd to detect by ICP-AES [47]. Zougagh et al. determined Cd in water ICP-AES with on-line adsorption preconcentration using DPTH-gel and TS-gel microcolumns [48]. Zougagh et al. developed a simple, sensitive, low-cost and rapid, flow injection system for the on-line preconcentration of lead by sorption on a microcolumn packed with silica gel functionalized with methylthiosalicylate (TS-gel) then the metal is directly retained on the sorbent column and subsequently then eluted from it by EDTA and elution determined by ICP-AES [49].

3.3. Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique which uses plasma source to atomize the sample, and then ions are detected by mass spectrometer. Mass spectrometer separate ions according to their mass to charge ratio. This technique has excellent detection limits, in ppt (part per thousand) range. Samples generally introduced as an aerosol, liquid or solid. Solid samples are dissolved prior to analysis or by a laser solid samples are converted directly to aerosol. All elements can analyze in a minute, simultaneously. But it needs high skilled operator, because method development is moderately difficult from other techniques. There are various types of ICP-MS instruments; HR-ICP-MS (high resolution inductively coupled plasma mass spectrometry and MC-ICP-MS (multi collector inductively coupled plasma mass spectrometry). HR-ICP-MS, has both magnetic sector and electric sector to separate and focus ions. By these instruments elimination or reduction of the effect of interferences due to mass overlap is accomplished but operation cost, time and complexity will increase. MC-ICP-MS, are designed to perform high-precision isotope ratio analysis. They have multiple detectors to collect every isotope of a single element but the major disadvantage of system is that all the isotopes should be in a narrow mass range which eliminates these instruments from routine analysis [46]. The block diagram of ICP-MS is depicted in Figure 3. The main difference from ICP-OES is that quadrupole mass spectrometers are used instead of wavelength selectors to detect the analytes.

Krishna et al. used moss (*Funaria hygrometrica*), immobilized in a polysilicate matrix as substrate for speciation of Cr(III) and Cr(VI) in various water samples and determined by ICP-MS and FAAS [41]. Hu et al. simultaneously separated and speciated inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters by capillary microextraction with mesoporous Al_2O_3 before de-

termination with ICP-MS [51]. Chen et al. speciated of chromium in waste water using ion chromatography coupled inductively coupled plasma mass spectrometry [52].

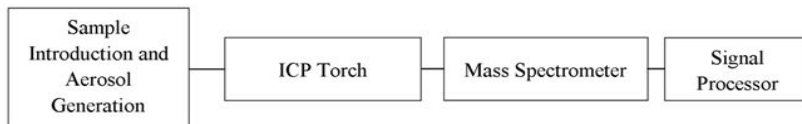


Figure 3. Block diagram of ICP-MS instrument.

Both ICP-OES and ICP-MS are not free of interferences. ICP-OES suffers from spectral interferences due to wavelength overlap of different elements. Similarly, in ICP-MS, the combination of different elements forms diatomic molecules which give the same (or indistinguishable) signal as that the analyte. In Table 3, a comparison of AAS and ICP techniques is given.

	FAAS	GFAAS	ICP-OES	ICP-MS
Analysis Time	++	+	+++	+++
Cost of Instrument	+++	++	++	+
Solid Sample Analysis	-	+++	-	-
Operating Cost	+	++	++	++
LOD	+	++	++	+++
Lineer Range	+	+	+++	+++
Precision	+++	+	++	++

-: Cannot Accomplished, +: Bad, ++: Medium, +++: Good

Table 3. Comparison of AAS and ICP Techniques.

3.4. Laser Induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. It is based on analysing of atomic emission lines close to the surface of sample generated by laser pulse where the very high field intensity initiates an avalenche ionisation of the sample elements, giving rise to the breakdown effect. Spectral and time-resolved analysis of this emission are suitable to identify atomic species originally present at the sample surface [53]. It can determine various metals but only limitation is the power of laser, sensitivity and wavelength range of the spectrometer. Generally this technique is used for solid samples because there are many accurate methods for liquid samples which does not require preparatory steps. Addition to

this, using LIBS for liquid samples may cause many problems due to the complex laser-plasma generation mechanisms in liquids [54]. Also splashing, waves, bubbles and aerosols caused by the shockwave accompanying the plasma formation effects precision and analytical performance. In order to overcome these problems, there are various procedures for liquid samples like analysing the surface of a static liquid body, the surface of a vertical flow of a liquid, the surface of a vertical flow of a liquid or of infalling droplets, the bulk of a liquid or dried sample of the liquid deposited on a solid substrate [55]. Though the results obtained were satisfactory, but it is obvious that such experimental tricks contradict with one of the most attractive advantages of LIBS, namely working on an unprepared sample, which facilitate in-situ and real-time measurements [56]. The block diagram of LIBS is depicted in Figure 4. Laser generates spark and plasma light is collected by a fiber optic and directed into a spectrograph. A sample output spectrum can be seen from figure 4.

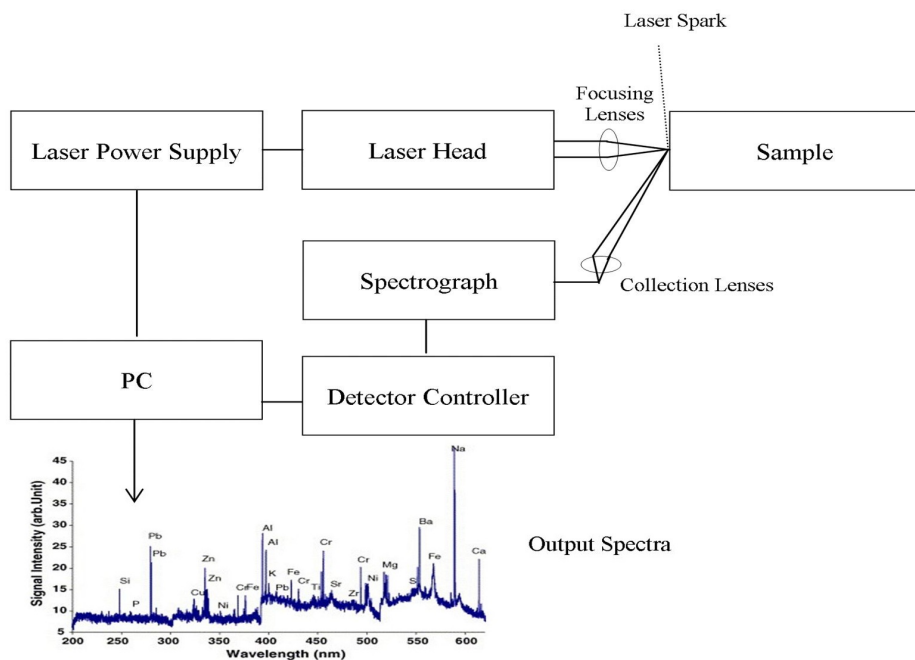


Figure 4. Scheme of an LIBS instrument (Spectra from Reference 48).

Gondal and Hussain, accomplished to determine many toxic trace elements in paint manufacturing plant waste water by LIBS. The results of LIBS method showed accuracy with the results found by ICP in the range of 0.03-0.6 %, which shows that this method can easily be used for trace element analysis [57]. Rai and Rai have also determined Cr in waste water collected from Cr-electroplating industry [58].

3.5. Anodic Stripping Voltammetry (ASV)

Anodic Stripping Voltammetry (ASV) is an analytical technique that specifically detects heavy metals in various matrices. Its sensitivity is 10 to 100 times more than ETAAS for some metals. Since its limit of detection is low, it may not require any preconcentration step. It also allows determining 4 to 6 metals simultaneously with inexpensive instrumentation. ASV technique consists of three steps. First step is electroplating of certain metals in solution onto an electrode which concentrates the metal. Second, stirring is stopped and then finally metals on the electrode are stripped off which generates a current that can be measured. This current is characteristic for each metal and by its magnitude quantification can be done. The stripping step can be either linear, staircase, square wave, or pulse [59].

Sonthalia et al. used anodic stripping for determination of various metals (Ag, Cu, Pb, Cd and Zn) in several waste water samples. Boron-doped diamond thin film is used [60]. McGaw and Swain compared the performance of boron-doped diamond (BDD) with Hg-coated glassy carbon (Hg-GC) electrode for the anodic stripping voltammetry (ASV) for determination of heavy metal ions (Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Ag^{+}). Generally Hg has been used as the electrode for ASV but there is an ongoing search for alternate electrodes and diamond is one of these. Produced BDD showed comparable results with Hg electrodes [61]. Bernalte et al. determined mercury by screen-printed gold electrodes with anodic stripping voltammetry [62]. Mousavi et al. developed a sensitive and selective method for the determination of lead (II) with a 1,4-bis(prop-2-enyloxy)-9,10-anthraquinone (AQ) modified carbon paste electrode [63]. Kong et al. produced a method for the simultaneous determination of cadmium (II) and copper (II) during the adsorption process onto *Pseudomonas aeruginosa* was developed. The concentration of the free metal ions was successfully detected by square wave anodic stripping voltammetry (SWASV) on the mercaptoethane sulfonate (MES) modified gold electrode, while the *P. aeruginosa* was efficiently avoided approaching to the electrode surface by the MES monolayer [64]. Giacomino et al. investigated parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode. Potential wave forms (linear sweep, differential pulse, square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedures were examined for their effect on the mercury peak shape and intensity and five supporting electrolytes were tested. The best responses were obtained with square wave potential wave form and diluted HCl as supporting electrolyte [65].

The literature is full of papers on the application of various methods for the determination of metals in waste water. Innumerable procedures, preconcentration/separation techniques, digestion techniques for several samples have been proposed.

4. Removal of heavy metals from waste water

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture,

printing and photographic industries, etc. The toxic metals, probably existing in high concentrations (even up to 500 mg/L), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment [66].

In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption, coagulation, cementation, electro-dialysis, electro-winning, electro-coagulation and reverse osmosis (See in Figure 5) [4, 67-70].

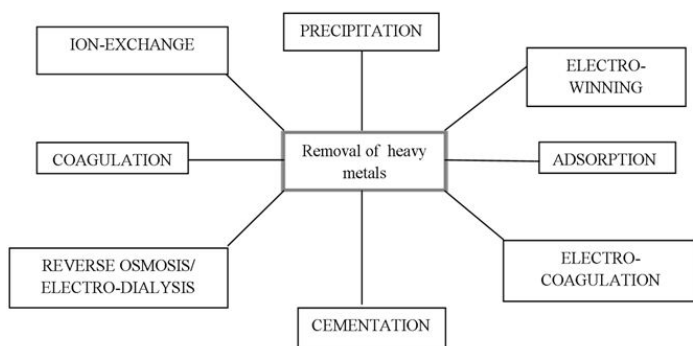


Figure 5. Some conventional methods for the removal of heavy metals.

Some conventional methods are explained below [4, 71-76];

1. Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Since some metal salts are insoluble in water and which get precipitated when correct anion is added. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, bisulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration.
2. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the sur-

rounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.

3. Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes.
4. Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.
5. Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe(0) to ferrous Fe(II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.
6. Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated.

Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ionexchange is feasible when an exchanger has a high selectivity for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. Cost effective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, a sorbent can be assumed as 'low cost' if it requires little processing, is abundant in nature, or is a by-product or waste material from another in-

dusty. Of course improved sorption capacity may compensate the cost of additional processing. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals. Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance.

In light of the above, biological materials and some adsorption materials have emerged as an economic and eco-friendly option. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. According to literature, an adsorbent (sorbent) can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry [66-68, 76-78].

Of course improved sorption capacity may compensate the cost of additional processing. Some of the reported low-cost sorbents such as bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton. Important parameters for the sorbent effectiveness are effected by pH, metal concentration, ligand concentration, competing ions, and particle size [4, 66-68].

Another type of sorbent is plant waste [68]. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood, maize leaf, teak leaf powder, lalang (*Imperata cylindrica*) leaf powder, rubber (*Hevea brasiliensis*) leaf powder, *Coriandrum sativum*, peanut hull pellets, sago waste, saltbush (*Atriplex canescens*) leaves, tree fern, rice husk ash and neem bark, grape stalk wastes, etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration. However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents was also reported in literature [67].

In a conclusion, a wide range of low-cost adsorbents obtained from naturel and chemical sorbent or chemically modified plant wastes has been studied and most studies were focused on the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr(VI) ions. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal up-

take. Although chemically modified plant wastes can enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce 'low-cost' adsorbents.

Another option is using biological materials [4, 66-68, 76, 77]. Biomaterials of microbial and plant origin interact effectively with heavy metals. Metabolically inactive dead biomass due to their unique chemical composition sequesters metal ions and metal complexes from solution, which obviates the necessity to maintain special growth-supporting conditions. Metal-sorption by various types of biomaterials can find enormous applications for removing metals from solution and their recovery. Rather than searching thousands of microbial species for particular metal sequestering features, it is beneficial to look for biomasses that are readily available in large quantities to support potential demand. While choosing biomaterial for metal sorption, its origin is a major factor to be taken into account, which can come from (a) microorganisms as a by-product of fermentation industry, (b) organisms naturally available in large quantities in nature and (c) organisms cultivated or propagated for biosorption purposes using inexpensive media. Different non-living biomass types have been used to adsorb heavy metal ions from the environment. Seaweed, mold, bacteria, crab shells and yeast are among the different kinds of biomass, which have been tested for metal biosorption or removal. Advantages and disadvantages of biosorption by non-living biomass are as follows [67, 75-77]:

Advantages of biosorption;

1. Growth-independent, non-living biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present.
2. Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation.
3. The process is not governed by the physiological constraint of living microbial cells.
4. Because of non-living biomass behave as an ion exchanger; the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake.
5. Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process.
6. Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment.

Disadvantages of biosorption;

1. Early saturation can be problem i.e. when metal interactive sites are occupied, metal desorption is necessary prior to further use, irrespective of the metal value.

2. The potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing. Because production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized.
3. There is no potential for biologically altering the metal valency state. For example less soluble forms or even for degradation of organometallic complexes.

Metabolic independent processes can mediate the biological uptake of heavy metal cations. Biosorption offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solution. The process of biosorption has many attractive features including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biosorbent can easily be produced using inexpensive growth media or obtained as a by-product from industry. It is desirable to develop biosorbents with a wide range of metal affinities that can remove a variety of metal cations. These will be particularly useful for industrial effluents, which carry more than one type of metals. Alternatively a mixture of non-living biomass consisting of more than one type of microorganisms can be employed as biosorbents. Bacterial biomass, algal biomass, fungal biomass were applied to removal of metals in the waste waters. The use of immobilized biomass rather than native biomass has been recommended for large-scale application but various immobilization techniques have yet to be thoroughly investigated for ease, efficiency and cost effectivity [67, 77].

Biosorption processes are applicable to effluents containing low concentrations of heavy metals for an extended period. This aspect makes it even more attractive for treatment of dilute effluent that originates either from an industrial plant or from the primary wastewater treatment facility. Thus biomass-based technologies need not necessarily replace the conventional treatment routes but may complement them. At present, information on different biosorbent materials is inadequate to accurately define the parameters for process scale up and design perfection including reliability and economic feasibility. To provide an economically viable treatment, the appropriate choice of biomass and proper operational conditions has to be identified. To predict the difference between the uptake capacities of the biomass, the experimental results should be tested against an adsorption model. The development of a packed bed or fluidized-bed biosorption model would be helpful for evaluating industrial-scale biosorption column performance, based on laboratory scale experiments and to understand the basic mechanism involved in order to develop better and effective biosorbent.

5. Conclusion

An unfortunate consequence of industrialization and industrial production is the generation and release of toxic waste products which are polluting our environment. Many trace and heavy metals (Cd, Pb, Mn, Cu, Zn, Cr, Fe and Ni) and their compounds have been found that are toxic. Many of them are used in several industrial activities including metallurgy,

tanneries, petroleum refining, electroplating, textiles and in pigments. Their presence in environment has been responsible for several types of health problems in animals, plants and human beings. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively.

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to legislation, improved cleaning technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, wastewater may need to be measured for a variety of metals at different concentrations, in different wastewater matrices. A variety of inorganic techniques can be used to measure trace elements in waste water including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP mass spectrometry (ICP-MS). Depending upon the number of elements that need to be determined and the number of samples that need to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Cd, Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, probably existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. The various treatment methods employed to remove heavy or trace metals, adsorption and chemical precipitation process is the most common treatment technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes have been developed for the heavy metal removal from wastewater, like biosorption, neutralization, precipitation, ion exchange etc. The use of all these techniques for removal of the heavy metals offers several advantages and limitations compared to each other. The important parameters for the selection of removal technique of heavy metal from waste water are waste type, the growth of the wastewater field, cheap or low-cost removal material, operational costs and problem of disposal of residual metal sludge. The significance of developing new treatment/removal methods for heavy metal from waste or waste water samples has been widely recognized especially in the fields of environmental sciences.

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Nutrient Fluxes and Their Dynamics in the Inner Izmir Bay Sediments (Eastern Aegean Sea)

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51546>

1. Introduction

Nitrogen, which is the most limiting nutrient for marine productivity of the ecosystem, is an essential element contributing to the biological process of all organisms (Capone and Knapp 2007; Bertics et al. 2012). Nitrification, the sequential oxidation of ammonia to nitrite and then nitrate by nitrifiers, is also a critical step in the biological removal of nitrogen from the wastewater treatment process. In coastal ecosystems, nitrification is often coupled to denitrification (Jenkins and Kemp 1984; Sebilo et al. 2006), ultimately resulting in nitrogen being returned to the atmosphere (Bernhard and Bollmann 2010). Most transformation reactions recognized so far in the benthic N cycle are catalyzed by a suite of bacteria and include the release of ammonium during the degradation of organic matter, the aerobic oxidation of ammonium to nitrite and nitrate (nitrification) and the bacterial denitrification of nitrite and nitrate to N_2 under anaerobic conditions. Denitrification and nitrification are two of the main bacterial pathways responsible for inorganic nitrogen removal and speciation in estuaries (Rao et al. 2007). Denitrification, dissimilatory reduction of NO_3^- and NO_2^- to N_2 and N_2O , is recognized as the key process to maintain nitrogen limitation for primary production in marine environments. As a consequence, denitrification is important in controlling the eutrophication level in coastal environments that are increasingly affected by nutrient inputs (Cloern 2001; Poulin et al. 2007). The exposure of nutrient inputs removed by denitrification in sediments of continental margins leads to high bacterial mineralization. In addition, microbially mediated nitrogen transformations have a potential impact on coastal eutrophication and estuarine oxygen status (Balls et al. 1996; Sanders et al. 1997; Barnes and Owens 1998).

Sediments play a key role in the global N cycle, especially in regard to the sinks and sources of fixed N (Capone and Knapp 2007; Carpenter and Capone 2008), is incomplete and often debated (Bertics et al. 2012). In sediments impacted by bioturbation, nitrification and denitrification are closely coupled yet spatially separated by the oxic/anoxic interface, and the interactions of aerobic and anaerobic processes lead to a relatively complex overall regulation of N_2 formation (Nishio et al. 1983; Jenkins and Kemp 1984; Seitzinger 1988; Christensen et al. 1989, Rysgaard et al. 1994; Thamdrup and Dalsgaard 2000).

The dependence of benthic denitrification derived from in situ nitrification and nutrient fluxes from overlying water into sediments may be controlled by several factors such as temperature, salinity, pH, dissolved oxygen and mineralization. Additionally, burrowing sediment infauna can also greatly influence the oxic conditions of surface sediments, especially by transporting oxygen down into the sediment, otherwise anoxic zones can develop in the sediment (Christensen et al. 2003). Several studies have stressed the important role of nitrification, denitrification and nutrient flux in coastal marine sediments (Jenkins and Kemp 1984; Rysgaard et al. 1994; Christensen et al. 2003; Capone and Knapp 2007), but this study is the first report on İzmir Bay. This paper was,

1. To measure sediment-water fluxes of nitrogen and phosphorus at sites sampled
2. To quantify nutrient fluxes across the sediment-water interface in order to assess the relative importance of benthic nutrient recycling
3. To compare fluxes and denitrification measurements among the sampling sites.

2. Materials and methods

2.1. Study area

İzmir Bay is one of the great natural bays of the Mediterranean. It is divided into three sections (outer, middle and inner) according to topographic points of view (Figure 1). It is an important semi-enclosed basin and has been increasingly polluted with massive loads of contaminants discharged from various anthropogenic sources.

This research was conducted in the inner İzmir Bay which is located 38° 20N and 38° 40N latitude and 26° 30E and 27° 10E longitude. Inner İzmir Bay is a shallow estuarine with a surface area of 66,68 km² located in the eastern Aegean Sea. Fine-grained sediments with high values of water content are the characteristics of the inner bay. It is suggested that the eastern Aegean Sea acts as an effective trap for nutrients and autochthonous particulate organic matter. The quality of the water and sediment in the inner İzmir Bay is seriously affected by pollutants which enter through drains that bring domestic as well as industrial effluents and discharge into the river and also from the sewage system that pumps treated effluent into the bay water. The main industries in the city include food processing, beverage manufac-

turing and bottling, tanneries, oil soap and paint production, chemical industries, paper and pulp factories, textile industries, metal and timber processing (Küçüksezgin 2001). The inner part of the Izmir Bay, has an average depth of 15 m, a small volume relative to the other parts of the Bay. The main fresh water sources of the bay are Melez, Bayraklı, Bostanlı and Poligon rivers. The rivers' flow typically peaks in late winter and early spring and is at a minimum in the summer to fall months.

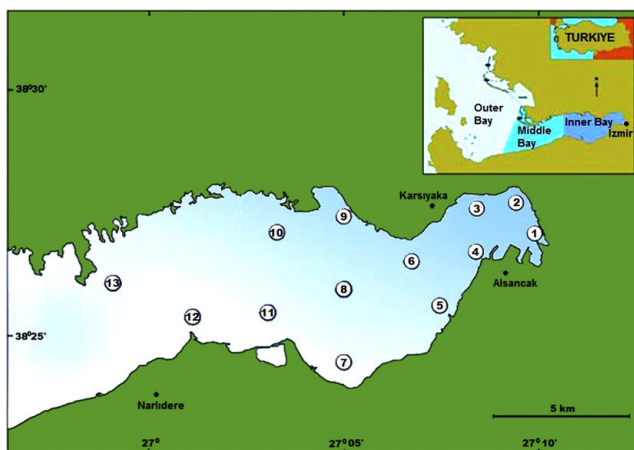


Figure 1. Map of inner İzmir Bay and the sampling stations.

2.2. Analytical procedure

The sediment samples used in this study were taken by a 4.0 cm ID gravity corer with removable acrylic liners. In addition, water samples were collected vertically and temperature, salinity, pH and dissolved oxygen content were measured. Based on the knowledge gained from a full seasonal study in the inner bay, sampling was chosen at 13 stations in three sampling seasons (summer, autumn and summer) during 2007-2008. Every trial has been replicated. After the lower lids of the cores were closed, they were filled with bottom water. Each of the water levels over the sediment in the acrylic cores was measured in millimeter (mm). Surface water was passed from the two incubation tanks by a submerged pump to stabilize water temperature. Each of the sediment cores was placed in two tanks, where nutrient fluxes were measured in the dark condition (Figure 2). As a starting process ($t=0$), 50 ml HDPE (high density polyethylene) bottles were filled with water and then put into an ice bag at -78°C . The reduced water level in the cores was compensated by bottom water. All the sediment cores taken from the 13 stations were coated with dark acetate papers. Starting and finishing times were noted and incubation times of the cores were around 24 hours. Control incubations were made with cores including only bottom water. The core tubes were closed by their lids with two Luer lock injectors on, one of which was filled with bottom water and the other pressed empty.



Figure 2. The incubation of core liners in the constant temperature tank on the vessel.

When the injector filled with bottom water was pushed to homogenize the overlying water in the core tube, the water was elevated in the other injector to stabilize pressure. This process was repeated prior to both starting and finishing trials. After 24 hours the lids were removed and the 50 ml sample was siphoned out of the core and frozen on dry ice until further analysis (Ozkan and Buyukisik 2012).

2.3. Nutrients and flux measurements

The pore waters were obtained after the incubation experiments. The first 10 cm part of the sediment from the core samples was put into a sediment pore water squeezer system and compressed through a two-layer Whattman GF/C glass filter paper to obtain clear water. The water samples were diluted 10-100 fold prior to nutrient analysis. The nutrient concentrations (NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-}) were measured according to Strickland and Parsons (1972).

Seawater temperature was recorded by an electronic thermometer, the pH of the samples was measured on-site using a pH-meter, and also dissolved oxygen was determined by using the Winkler method immediately after sampling.

The nutrient fluxes were measured from both the controls and experimental series calculated as $\mu\text{mol}/\text{m}^2$ day. Flux measurements were made by formula,

$$J_{\text{gross}} = V_t (C_t - C_0) / \Delta t A \quad (1)$$

where J_{gross} : gross nutrient flux ($\mu\text{mol}/\text{m}^2$ day), V_t : water volume on the core surface at time (t), C_t : solute concentration at time (t), C_0 : initial solute concentration in the experiment, Δt : time of sampling (day with the beginning of the experiment being 0), A : core surface area (cm^2).

The rate of flux measured was regarded as the gross flux. In addition, it measured only nutrient flux of overlying water as a control (C_{cont}). The net flux was calculated from the difference between solute concentration at time (t) and solute concentration in control at time (t). So net flux was calculated by

$$J_{\text{net}} = (C_t - C_{\text{cont}}) \cdot 24 \cdot h \cdot 10000 / \Delta t \cdot A \quad (2)$$

where J_{net} : net nutrient flux ($\mu\text{mol}/\text{m}^2$ day), V_t : water volume on the core surface at time (t), C_t : solute concentration at time (t), C_{cont} : solute concentration at time (t) in control cores, Δt : time of sampling (day with the beginning of the experiment being 0), A : core surface area (cm^2), h : height of overlying water (m).

2.4. Statistical analysis

The data set has been subjected to factor analysis for elucidating the relationships between nutrient fluxes and physicochemical parameters such as temperature, pH, dissolved oxygen and salinity.

3. Results

The results from incubation tests were classified as three groups. The first one of them is measurement of flux from processes at overlying water (control). The second one is measurement of gross flux. The third one is calculated as net flux from sediment. NO_3^- contribution of overlying water via nitrification was seen at most of the stations (Figure 5). In the bottom water, negative flux values for NO_3^- can be assumed as dark uptake for phytoplankton if dissolved oxygen is sufficient. The values of gross fluxes from direct measurements of incubations show that there is a NO_3^- flux directed from sediment to water at most of the stations in winter. The highest values of gross fluxes were observed in stations 2 and 9 (Figure 6). In summer and autumn, gross flux values are lower than they are in winter. Net NO_3^- fluxes from sediment to overlying water were given in Figure 5. Negative values were seen at many stations. The loss of nitrate by denitrification in sediment was at a maximum at stations 6 and 12 in winter and at station 3 in summer. In Figure 6, the NH_4^+ flux values of overlying water were generally negative, indicating a nitrification process. Positive values at station 6 in summer, and at station 7 and 12 in winter were observed indicating mineralization of organic matter. Many of the core samples were showed positive gross NH_4^+ fluxes, explaining the mineralization of organic matter (Figure 5). The negative values of net NH_4^+

fluxes were relatively lower at stations 6 and 7 and higher at station 12, indicating nitrification in sediment (Figure 6). In Figure 3 and 4, controls and net fluxes were plotted for ammonium and nitrate. The first 10 stations showed that mineralization and nitrification processes had been taken place in sediment and overlying water respectively. A denitrification process was taking place in sediment. Negative nitrate fluxes in overlying water can be explained by diffusive processes to sediment for denitrifying. The general trend in changing fluxes from summer to winter was a decreasing of nitrification in overlying water and mineralization in sediment. Convective water mixing in winter caused increased diffusive transport of the dissolved species and increased denitrification. Also nitrification is taking place in sediment and overlying water.

In winter, net 289 kg NH_4^+ per day nitrified in sediment of the complete Inner Bay area when 643 kg per day is nitrified in overlying water. 1135 kg $\text{NH}_4^+\text{-N}$ per day is produced in sediment of the Inner Bay area. 45% of total $\text{NH}_4^+\text{-N}$ flux is nitrified in overlying water. In summer, 4147 kg $\text{NH}_4^+\text{-N}$ loading from sediment was found. 50% of ammonium loading is nitrified in overlying water.

In summer, 479 kg $\text{NO}_3^+\text{-N}$ per day is produced by nitrification in water. 574 kg per day is removed by denitrification when 856 kg/day is released to water. Net nitrate loading is 282 kg/day. 67% of nitrate loading is removed by the denitrification process. In winter, 2583 kg nitrate per day is produced in overlying water. 2145 kg nitrate per day is produced by nitrification in sediment while 1398 kg /day is removed by denitrification. 65% of nitrate loading is removed by denitrification.

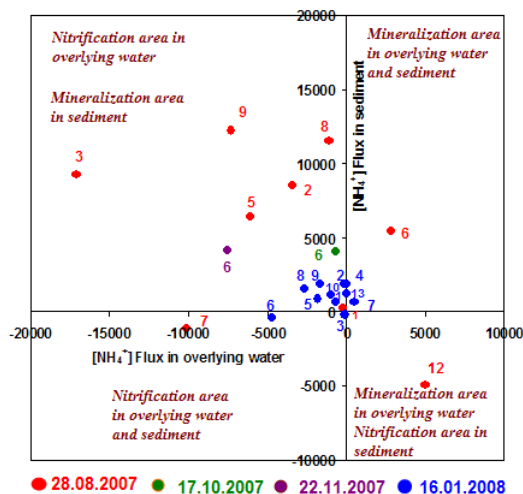


Figure 3. The plot of NH_4^+ fluxes of overlying water against net NH_4^+ fluxes in sediment.

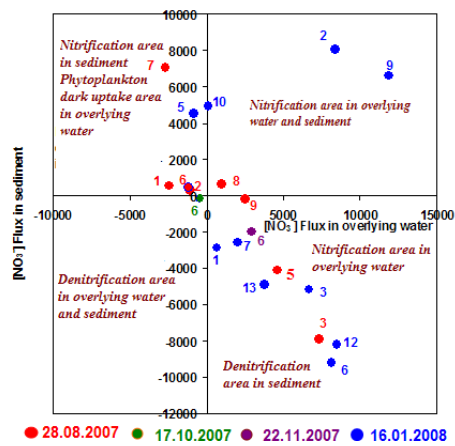


Figure 4. The plot of NO_3^- fluxes of overlying water against net NO_3^- fluxes in sediment ($\mu\text{molN}/\text{m}^2\text{day}$).

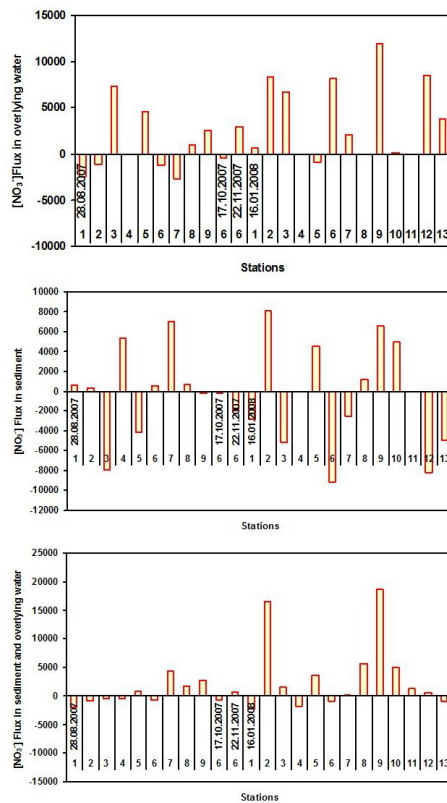


Figure 5. Control, gross and net NO_3^- fluxes of experimental core samples ($\mu\text{mol}/\text{m}^2\text{ day}$).

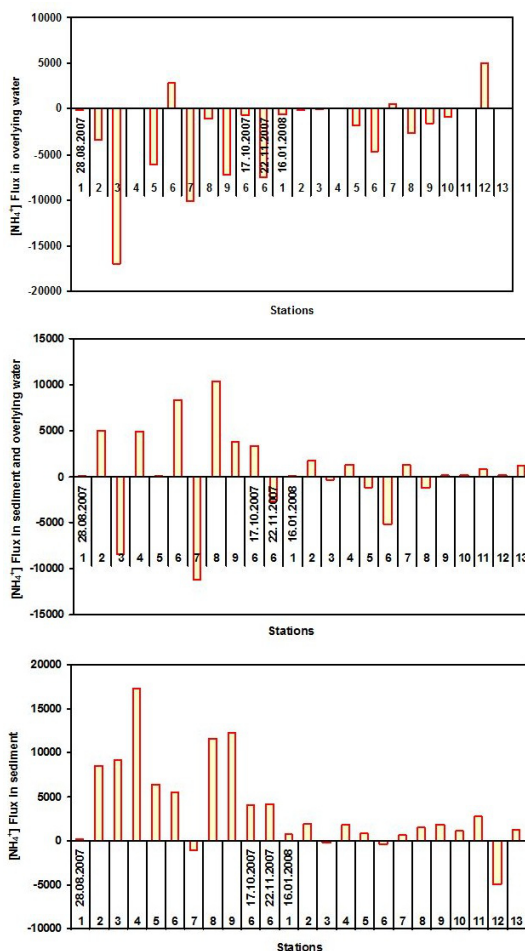


Figure 6. Control, gross and net NH_4^+ fluxes of experimental core samples ($\mu\text{mol}/\text{m}^2$ day).

3.1. Factor Analysis

Factor analysis is a powerful statistical technique, which delineates simple patterns distributed among complex data by evaluating the structure of the variance-covariance matrix and extracting a small number of independent hypothetical variables (R mode) or sample (Q mode) referred to as factors (Klovan and Imbrie 1971, Duman et al. 2006). Principal component analysis (PCA) were used as type of factory. PCA seeks a linear combination of variables such that the maximum variance is extracted from the variables. It then removes this variance and seeks a second linear combination which explains the maximum proportion at the remaining variance, and soon. This method results in uncorrelated factors.

Data variables were chosen as: $\text{NH}_4\text{FluxGross}$ (sediment+water), $\text{NH}_4\text{FluxWater}$, $\text{NH}_4\text{FluxSediment}$, $\text{NO}_3\text{FluxGross}$ (sediment+water), $\text{NO}_3\text{FluxWater}$, $\text{NO}_3\text{FluxSediment}$, RP, NO_3 , TIN (total inorganic nitrogen), pH, DO (dissolved oxygen), T (temperature), S (salinity). The factor analysis results for the raw data show that five factors extracted account for 86,99% of the total variance. Remaining variance was assumed to be random. In Table 1, eigen values, percentage of variances and cumulative variances were given. The eigen value for a given factor measures the variance in all the variables which is accounted for by that factor. Kaiser criterion was chosen for dropping all components with eigen values under 1.0 as usual in most statistical software. The factor analysis results for the raw data show that five factors account for a total of 86.98% of the total variance. Remaining 13.02% of the variance cannot be explained by factor analysis and is assumed to be random. Factor loading matrix after varimax rotation was also given in Table 2. Factor loadings are the correlation coefficients between the variables and factors.

Factor Number	Eigenvalue	Percent of Variance	Cumulative Percentage
1	4,2628	32,791	32791
2	2,48938	19,149	51940
3	1,92521	14,809	66,749
4	1,61264	12,405	79,154
5	1,01821	7,832	86,986
6	0,838686	6,451	93,438
7	0,402971	3,100	96,538
8	0,275157	2,117	98,654
9	0,0934268	0,719	99,373

Table 1. The eigen values and variances and extracted factors.

The 3D plot and 2D plot of factor loadings were seen in Figure 7. Factor 1 explains 32,79% of total variance and includes the mineralization and nitrification processes in the overlying water and the related variables as pH, DO and temperature. Factor 1 can be described as “overlying water factor”. Factor 2 explains 19,15% of total variance and includes bottom water nitrate concentrations, total inorganic nitrogen (TIN) and the bottom water salinity. In Figure 8a, inverse relationships were found between sediment pore water NH_4^+ concentrations and bottom water salinity. NH_4^+ release from clay minerals in high salinities can be important. This explains the decreased NH_4^+ pore water concentrations in high salinity bottom waters because of the obtaining of pore water samples after the core incubation ex-

periments. Factor 2 can be described as “anthropogenic factor “. Factor 3 accounts for 14,81% of total variance and includes gross and net sediment fluxes and overlying water processes for NO_3^- . The nitrification process in overlying water has a negative effect. Factor 3 can be described as “ NO_3^- flux factor “. Factor 4 accounts for 12,41% of total variance and includes gross fluxes in nitrogen species, mineralization in overlying water and sediment, nitrification in overlying water and denitrification in sediment. Factor 4 can be described as “ biological processes on nitrogen species “. Factor 5 explains 7,8% of total variance and includes reactive phosphorus (RP) in bottom water. Ammonium and RP releases from decomposition of organic matter in 16:1 ratio and ammonium is consumed and oxidized to nitrate in the same N:P ratio. In denitrification, this ratio was reported as 104:1 and inorganic nitrogen distributions are effected. Nitrate deficite values ($=16 \times \text{RP} - \text{NO}_3^-$) do not reflect the truth. The second term in the right hand side of the equation for inner Izmir Bay waters was much lower than the first term. This situation has been explained by Ozkan and Buyukisik (2012) by means of RP release from sediment via Fe mobilization. Factor 5 can be described as “iron and RP mobilization factor“.

	<i>Factor</i>	<i>Factor</i>	<i>Factor</i>	<i>Factor</i>	<i>Factor</i>
	1	2	3	4	5
NH4FluxGross	-0,215254	-0,194004	0,00849782	0,845738	0,104213
NH4FluxW	0,484817	-0,0461229	0,0452335	0,840061	0,0817993
NH4FluxSed	-0,778075	-0,168951	-0,0475222	0,00121901	0,0257112
NO3FluxGross	0,262306	-0,120293	0,737525	-0,417474	0,0243472
NO3FluxW	0,453693	-0,162346	-0,719379	-0,34443	0,0872775
NO3FluxSed	-0,190756	0,0252568	0,973636	0,091898	-0,0353923
RP	-0,0563268	-0,0754223	-0,0494444	0,135157	0,965347
NO3	0,109249	0,901002	0,00312072	0,183428	-0,132118
TIN	0,0905194	0,892973	0,0267146	-0,329392	-0,174481
pH	0,917485	0,148011	-0,189637	0,0547122	-0,10158
DO	0,879905	0,0185277	-0,092712	-0,127195	0,183948
T	-0,913059	-0,210555	0,068695	-0,0684956	0,159605
S	-0,259059	-0,815551	-0,0017208	0,173195	-0,184399

Table 2. Factor Loading Matrix After Varimax Rotation.

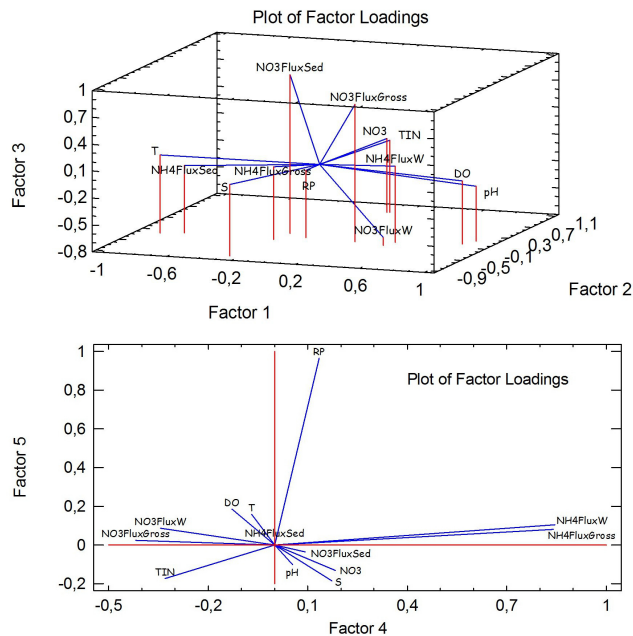


Figure 7. and 2D representation of factor loadings.

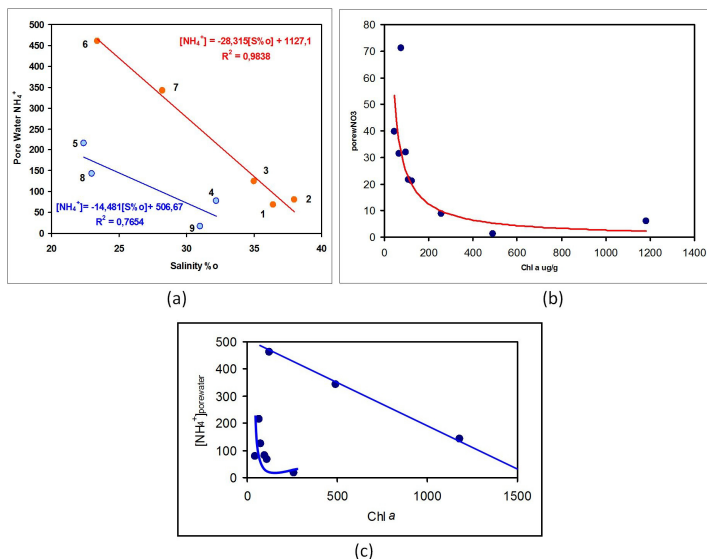


Figure 8. a) The relationships of salinity against the pore water NH_4^+ concentration in sediment samples after the incubation experiments. The plot of surface sediment Chl a ($\mu\text{g/g}$) values against pore water NO_3^- concentrations (b) and pore water ammonium concentrations (c).

Relative importance of ANAMMOX for dinitrogen producing inversely related with remineralized solute (NH_4^+) production, benthic oxygen demand and surface sediment chlorophyll *a* values (Engström et al. 2005). In Figure 8 b and 8c, Chl-*a* values in sediment surfaces at stations 1 to 9 changed in the range of 43.9 - 1180.9 $\mu\text{g/g}$. Anammox process is not expected as an important process in stations 1 to 9. Pore water nitrate and ammonium concentrations decreased hyperbolically/linearly with increasing Chl *a* values in sediment (Figure 8b, 8c).

4. Conclusion

Although the waste water treatment plant reduces ammonia inputs, creeks have high ammonium concentrations (Ozkan et al. 2008) and enrich increasingly the surface waters via rainfall. In the bottom waters, another ammonium sources results from the sinking of organic matter produced by primary production of phytoplankton in the surface waters and mineralization of it in sediment by bacteria. NH_4^+ production is released to bottom water in relation to bottom water salinity and contributed to bottom water reserves. Nitrification in the bottom water is the dominant process except at station 12. Nitrate is produced by this process and diffused in to the sediment. A denitrification process is taking place in suboxic sediments and produces dinitrogen gas as a loss process of nitrogen. Some of the mineralized ammonium in sediment is oxidized to N_2 gas by the anammox process if the sediment contains MnO_2 and it does not reach to $\geq 1 \mu\text{gChl-a/g}$ sediment and $\geq 2 \mu\text{MNH}_4^+/\text{h}$ (Engström et al. 2005) in the bay. Only in station 12 at the boundary of inner Izmir Bay, ammonia and nitrate loss can be attributed to anammox and the denitrification process. Creeks provide MnO_2 to stations 1,2,3,4 and 9 upto $1,5 \mu\text{MMnO}_2/\text{g}$ sediment. Sediments of other stations (except station 12) do not have Mn because hypereutrophication caused anoxia in the bottom waters before the wastewater treatment plant and mobilization of reduced Fe and Mn may have been transported out of the inner Izmir Bay (Ozkan and Buyukisik 2012). Natural treatment of nutrients in the benthic area can contribute to reduced nitrogen levels in the inner Izmir Bay after the enrichment of sediments with Mn and Fe, but it will take some time.

Factor analysis discriminates five factors with a low number of variables. Mineralization and nitrification in the overlying water is affected by pH, DO and temperature (factor 1:overlying water factor). Bottom water nitrate and TIN is negatively effected by salinity (factor 2: anthropogenic factor). Factor 3 was described as " NO_3^- flux factor". The nitrification process in overlying water affects the factor 3. Factor 4 explains the biological process on nitrogen species (TIN). Factor 5 clarifies the RP does not statistically effect on the other variables and supports that RP fluxes are related with Fe and RP mobilization from sediment. RP coming from mineralization of organic matter comprises 0.3-6.9 % of bottom water. RP concentrations cannot be used for the evaluation of denitrification, nitrification and N_2 fixation processes (Tyrell and Lucas, 2002).

Acknowledgements

We would like to thank the municipality of Izmir for the kind support to this project.

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Effects of Sewage Pollution on Water Quality of Samaru Stream, Zaria, Nigeria

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/51597>

1. Introduction

Water bodies are important economically, aesthetically and intellectually. The livelihood of many communities is hinged to the water bodies around them. Water bodies mirror the environment in which they are found and accumulate substances generated in their catchment (Yongendra and Puttaiah, 2008).

Assessment of water quality is very important for knowing its suitability for different uses (Choubey *et al.*, 2008). Urbanization and rapidly growing human population results in an increase in waste water discharge into fresh water ecosystems, thus impairing water quality, sometimes to unacceptable levels, thereby, limiting its beneficial use (Tanimu *et al.*, 2011).

The contaminants in domestic sewage have been categorized by Wang *et al.* (2007) into Suspended Solids (SS) and dissolved solids (DS), organic matter (Chemical Oxygen Demand and Biochemical Oxygen Demand) and nutrients (nitrogen and phosphorus). Raw sewage can carry a number of pathogens including bacteria, viruses, protozoa, helminths (intestinal worms) and fungi (RMCG, Chigoret *et al.*, 2011).

The Samaru stream is the major drain of domestic waste of Samaru village, several researchers have lamented the poor state of water quality in the stream Smith (1975), Tiseer *et al.* (2008 and 2008b), Olubgenga (2009), and Chigor *et al.* (2011). During a field visit to the Samaru stream in May 2010, the water in the stream was observed to be blackish in colour with an offensive odour due to sewage pollution. Therefore this study was carried out to evaluate water quality characteristics of the stream.

2. Materials and Methods

Study Area and Sampling Sites: The Samaru stream is a seasonal stream with its head waters in the Samaru village, a suburban settlement that hosts the main campus of the Ahmadu Bello University, Zaria. The stream is a tributary of the River Kubanni on which the Ahmadu Bello University (Kubanni) Dam is built. The stream flows from Samaru village through a gully into the University community to the reservoir of the Ahmadu Bello University reservoir, which is the major source of water (for drinking, domestic and other uses) to the University community. The Samaru stream receives sewage from the Samaru village and student hostels (UsmanDanfodio, Sassakawa and Icsa/Ramat Halls).

Sample Collection and Analysis: Samples were collected during a field survey at the onset of the wet season (May 2010). Surface Water Temperature, pH, Electrical Conductivity, Total Dissolved Solids were determined in situ with the aid of a portable HANNA instrument (pH/Electrical Conductivity/Temperature/TDS meter model 210).

Samples of water were collected in prewashed sample bottles and transported to the laboratory for analysis of other parameters. Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) were determined using the Azide Modification of the Winkler method, Nitrate-Nitrogen ($\text{NO}_3\text{-N}$) was determined using the phenoldisulphonic acid method, Phosphate-Phosphorus using the Stannous Chloride method (all as described by APHA, 1998).

Sample for metal analysis were digested by Nitric acid (HNO_3) and the concentration of metals in the samples was determined by Atomic Absorption spectrophotometry (AAS) (APHA 1998).

3. Data Analysis

Water Quality Index (WQI) was determined by methods described by Yogendra and Puttaiah (2008).

The WQI of a water sample in which n number of parameters (characteristics) have been determined is expressed as a summation of the product of quality rating for the n^{th} Water quality parameter (q_n) and the unit weight of each parameter (W_n) divided by sum of the unit weights of all the (n) parameters ($\sum W_n$).

Mathematically:
$$WQI = \frac{\sum (q_n W_n)}{\sum W_n}$$

q_n = quality rating for the n^{th} Water quality parameter, corresponding to the nth parameter is a number reflecting the relative value of this parameter in the polluted water with respect to its standard permissible value and is given by $= 100(V_n - V_{io}) / (S_n - V_{io})$

V_n = Estimated value of the nth parameter at a given sampling station.

S_n = standard permissible value of the nth parameter.

V_{io} = ideal value of the n th parameter in pure water (i.e. 0, for all parameters except pH, 7.0 and Dissolved Oxygen, 14.6 mg/L).

W_n = unit weight of n th parameter = K/S_n

Metal Index (MI) for the concentration of n number of metals determined in a water sample is given by the summation of the observed concentration of each metal divided by its Maximum Allowable Concentration (MAC).

Mathematically $MI = \sum_{i=1}^n \left(\frac{C_i}{MAC_i} \right)$ (Karami and Bahmani, 2008)

C = the concentration of each element in solution,

MAC is maximum allowed concentration for each element

i = the i th sample.

The higher the concentration of a metal compared to its respective MAC value, the worse the quality of the water.

Pearson Correlation Coefficient was used to determine the relationships between observed water quality characteristics.

4. Results

The mean pH of the water in the stream was found to be 7.68, with a maximum value of 8, minimum of 7.30 and a standard deviation 0.12 (Table 1). EC and TDS showed a similar trend across the stream cross, increasing from concentrations of 1000 to 1049 and 500 mg/L to 525 mg/L in stations 1 and 2, respectively and then decreasing steadily across stations 3, 4 and 5 (Fig 1). The mean EC was 816.20 μ S/cm with a standard Error of 134.71 μ S/cm while a mean of 409.80 mg/L was recorded for TDS with a Standard Error of 134.71 mg/L (Table 1).

Dissolved Oxygen decreased from station 1 (0.85 mg/L) to station 2 (0.25 mg/L) and then increased steadily in stations 3 (0.3 mg/L), 4 (0.4 mg/L) and 5 (0.85 mg/L) (Fig 2). Biochemical Oxygen Demand declined from station 1 (0.4 mg/L), 2 (0.25 mg/L), 3 and 4 (0.05 mg/L) and then a slight increase in station 5 (0.1 mg/L) (Fig 2). Table 1 shows mean and standard errors for DO and BOD of 0.53, 0.13 and 0.17, 0.07 respectively.

$\text{NO}_3\text{-N}$ increased from station 1 to 2, decreased in 3 and then increased and decreased in stations 4 and 5 in a zigzag manner giving a similar trend with $\text{PO}_4\text{-P}$ concentration in the five (5) stations. (Fig.2). the maximum $\text{NO}_3\text{-N}$ concentration observed was 3.80 mg/L and a lowest of 0.90 mg/L. $\text{PO}_4\text{-P}$ mean concentration observed in the stream was 0.44 mg/L with a standard error of 0.17.

Surface Water Temperature had the highest value of 31°C and lowest of 27°C, Cu and Cr had concentrations below detectable limits (Table 1). Zn, Ni and Cd showed a similar concentrations gradient from station 1 to 5 while Fe showed an opposite trend with the other

metals, decreasing in concentration were the others increase and increasing where they decrease (Fig 3). Among the four (4) metals, only Zn concentration was within the acceptable limits (Table 1).

Parameter	Mean	Standard Error	Minimum	Maximum	Standard	Recommending Agency
pH	7.68	0.12	7.30	8.00	< 8	WHO
EC ($\mu\text{S}/\text{cm}$)	816.20	134.71	298.00	1049.00	1000.00	WHO
TDS (mg/L)	409.80	67.55	149.00	525.00	500.00	WHO
DO (mg/L)	0.53	0.13	0.25	0.85	5.00	WHO
BOD (mg/L)	0.17	0.07	0.05	0.40	5.00	WHO
NO ₃ -N (mg/L)	2.58	0.55	0.90	3.80	10.00	WHO
PO ₄ -P (mg/L)	0.44	0.17	0.02	1.00	5.00	WHO
Temp. (°C)	29.20	0.66	27.00	31.00	NA	NA
Fe (mg/L)	0.47	0.12	0.29	0.89	0.30	SON
Cu (mg/L)	BDL	BDL	BDL	BDL	1.00	SON
Cr (mg/L)	BDL	BDL	BDL	BDL	0.05	SON
Zn (mg/L)	0.39	0.05	0.25	0.56	3.00	SON
Ni (mg/L)	0.40	0.04	0.33	0.50	0.02	SON
Cd (mg/L)	0.09	0.02	0.06	0.16	0.003	SON

EC= Electrical Conductivity, TDS= Total Dissolved Solids, DO= Dissolved Oxygen, BOD= NO₃-N= Nitrate-Nitrogen, PO₄-P= Phosphate-Phosphorus, Temp.= Temperature, BDL= Below Detectable Limit, SON= Standard Organisation of Nigeria, NA= not available

Table 1. Summary Statistic of Water quality characteristics of Samaru stream and standard values for water quality.

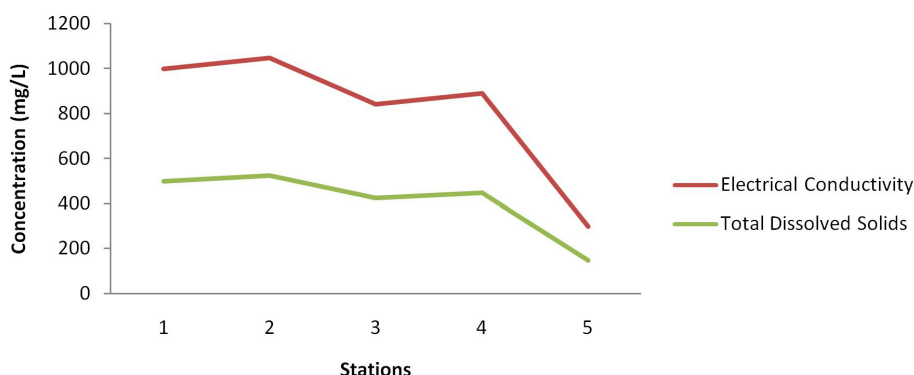


Figure 1. Variation of Electrical Conductivity and Total Dissolved Solids in Samaru stream.

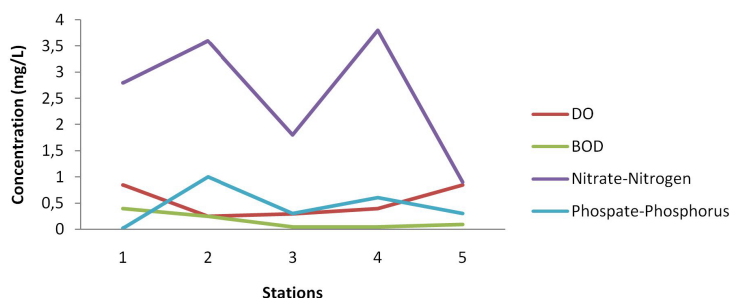


Figure 2. Variation of concentration of Dissolved Oxygen, Biochemical Oxygen Demand, Nitrate-Nitrogen and Phosphate-Phosphorus in Samaru stream.

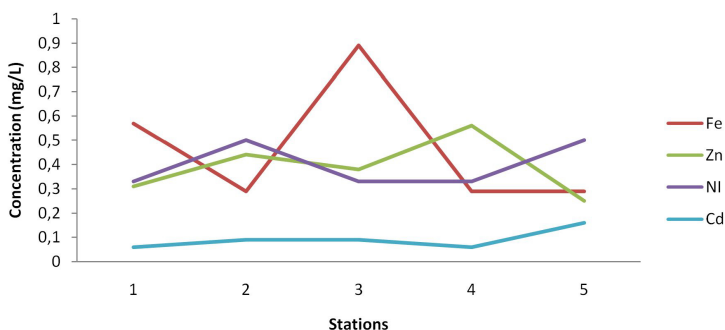


Figure 3. Variation of concentration of Fe, Zn, Ni and Cd in Samaru stream.

The Water quality index and Metal Index showed a similar pattern of distribution in Stations 1 to 4, increasing from 52.45 and 38.1 (station 1) to 58.95 and 56.11 (station 2) decreasing to 55.25 and 49.51 (station 3) and, 48.31 and 37.65 (station 4). In station 5, the lowest WQI of 45.03 was observed while in contrast station 5 recorded the highest MI value of 79.38 (Table 2).

Station	Water Quality Index	Metal Index
1	52.45	38.5
2	58.95	56.11
3	55.25	49.51
4	48.31	37.65
5	45.03	79.38

Table 2. Water Quality and Metal Indices of the five sampling stations in Samaru stream.

Water Quality Index Level	Water Quality Status
0-25	Excellent water quality
26-50	Good water quality
51-75	Poor water quality
76-100	Very Poor Water quality
>100	Unsuitable for drinking

Table 3. Water Quality Index and water quality status (Yogendra and Puttaiah 2008).

Significant positive correlation was observed between Fe concentration and pH ($r=0.76$) ($P<0.01$); Electrical Conductivity and BOD ($r=0.46$) ($P<0.05$), $\text{NO}_3\text{-N}$ ($r=0.83$) ($P<0.01$), Surface Water Temperature (0.68) ($P<0.05$) and Zn (0.57) ($P<0.05$); TDS with BOD ($r=0.45$) ($P<0.05$) and $\text{NO}_3\text{-N}$ ($r=0.83$) ($P<0.01$), Surface Water Temperature (0.69) ($P<0.01$) and Zn ($r=0.58$) ($P<0.01$); DO with BOD ($r=0.40$) ($P<0.05$); $\text{NO}_3\text{-N}$ with $\text{PO}_4\text{-P}$ ($r=0.56$), Temperature ($r=0.69$) ($P<0.01$) and Zn ($r=0.82$) ($P<0.01$); $\text{PO}_4\text{-P}$ with Zn ($r=0.62$) ($P<0.01$) and Ni ($r=0.50$) ($P<0.05$); Temperature with Zn ($r=0.86$) ($P<0.01$); and Ni with Cd ($r=0.74$) ($P<0.01$) (Table 4).

Significant negative correlation was observed between EC and DO ($r=-0.53$) ($P<0.05$), Ni ($r=-0.43$) ($P<0.05$) and Cd ($r=0.89$) ($P<0.01$); TDS with DO ($r=-0.53$) ($P<0.05$), Ni ($r=-0.44$) ($P<0.05$) and Cd ($r=-0.89$) ($P<0.01$); DO with $\text{NO}_3\text{-N}$ ($r=-0.50$) ($P<0.05$), $\text{PO}_4\text{-P}$ ($r=-0.73$) ($P<0.01$), Surface Water Temperature ($r=-0.64$) ($P<0.01$) and Zn ($r=-0.73$) ($P<0.01$); $\text{NO}_3\text{-N}$ with Cd ($r=-0.80$) ($P<0.01$); $\text{PO}_4\text{-P}$ and Fe ($r=-0.52$) ($P<0.05$); Surface Water Temperature with Ni ($r=-0.74$) ($P<0.01$) and Cd ($r=-0.83$) ($P<0.01$); Fe with Ni ($r=-0.60$) ($P<0.01$); and Zn with Cd ($r=-0.64$) ($P<0.01$) (Table 4).

	pH	EC	TDS	DO	BOD	$\text{NO}_3\text{-N}$	$\text{PO}_4\text{-P}$	Temp.	Fe	Zn	Ni	Cd
pH	1.00											
EC	0.37	1.00										
TDS	0.36	1.00	1.00									
DO	-0.23	-0.53*	-0.53*	1.00								
BOD	0.34	0.46*	0.45*	0.40*	1.00							
$\text{NO}_3\text{-N}$	-0.19	0.83**	0.83**	-0.50*	0.26	1.00						
$\text{PO}_4\text{-P}$	-0.15	0.30	0.30	-0.73**	-0.20	0.56*	1.00					
Temp.	-0.05	0.68*	0.69**	-0.64**	-0.24	0.69**	0.21	1.00				
Fe	0.76**	0.21	0.21	-0.15	-0.05	-0.31	-0.52*	0.27	1.00			
Zn	-0.35	0.57*	0.58*	-0.73**	-0.33	0.82**	0.62**	0.86**	-0.21	1.00		
Ni	-0.10	-0.43*	-0.44*	0.06	0.03	-0.25	0.50*	-0.74**	-0.60**	-0.33	1.00	
Cd	-0.11	-0.89**	-0.90**	0.34	-0.33	-0.80**	-0.03	-0.83**	-0.23	-0.64**	0.74**	1.00

EC= Electrical Conductivity, TDS= Total Dissolved Solids, Temp.= Surface Water Temperature, DO= Dissolved Oxygen, BOD= Biochemical

Oxygen Demand, $\text{PO}_4\text{-P}$ = Phosphate-Phosphorus, $\text{NO}_3\text{-N}$ = Nitrate-Nitrogen, *Significant $P<0.05$, **Significant $P<0.01$

Table 4. Pearson Correlation Coefficient of physicochemical characteristics of water of Samaru stream.

5. Discussion

On the basis of water Quality Index, stations 1, 2 and 3 (upstream stations) may be classified to be of poor water quality, whereas stations 4 and 5 may be classified to be of good water quality. The trend where downstream stations are of a better water quality when the source of pollution is upstream may be explained by the role bacteria, algae and aquatic macrophytes play in ultra filtration of polluted water as it flows from upstream-down stream. Similar results have been reported Tiseer *et al.*, (2008a) and Taurai (2012).

The mean metal concentration of Fe, Ni and Cd observed were above the permissible limit in drinking water (SON, 2007), while the high metal index observed in the stream may be a great indication that the sewage entering the stream contains a high concentration of heavy metals. The higher MI observed in station 5 may be as a result of pollution from the University Press and/or the dumpsite behind Icsa/Ramat Halls.

Abolude *et al.*, (2009) reported that concentrations of seven (7) out of the nine (9) studied trace elements (including Fe, Ni and Cd) in the Kubanni reservoir were above the recommended levels for drinking water, the present study implicates the Samaru stream to be an important contributor to the problem.

The significant relationships observed between pH and Surface Water Temperature and parameters such as DO, $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, EC, TDS, Fe, Zn, Ni, Cd may be attributed to the reason that the solubility of this chemical substances in water is affected by pH and Temperature.

5.1. Recommendations

Measures are required to be taken to halt the continuous inflow of sewage into the Samaru stream from the Samaru village and the some student hostels (Danfodio, Sasakawa and Icsa/Ramat) of the Ahmadu Bello University, Zaria to reduce or totally eliminate the continuous pollution of water in the Samaru stream and the University reservoir by extension.

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