Water Resources:
Problems and Solutions

Edited by

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Preface

Water is one of the most important resources for humans. In particular, freshwater is extremely precious on the Earth, but it is heavily used for agricultural and industrial purposes. It is estimated that water scarcity will be more prevalent in the poor countries in view of population growth and environmental pollution. This problem will inevitably impact economy and human health in future. Compared to freshwater, seawater is much more abundant and numerous resources (e.g. seafood and minerals) can be found in the ocean. Over the last few decades, however, marine pollution has been recognized as a global problem, especially in the developing countries, due to rapid urbanization and industrialization. Marine pollution can be caused by various sources, such as agricultural runoff, sewage discharge from factories, oil spills in shipping industry and even atmospheric deposition of pollutants. Given the high nutrient content in agricultural runoff, algal blooms are usually triggered following eutrophication in coastal waters, culminating in mass mortality of marine organisms and economic losses. Industrial sewage contains a variety of chemicals, including heavy metals and organic pollutants, which can pose noxious effects on public health and marine ecosystems due to their toxicity, persistence and bioavailability. The biomagnification of toxic pollutants along the food chain can have serious repercussions on marine ecosystems. It is noteworthy that marine pollution is not a local problem, but regional problem due to the dispersal of pollutants via water current. As such, water quality monitoring is indispensable to elucidate the potential impacts of pollutants on humans and marine ecosystems. Apart from regular monitoring, water treatment technologies should be applied to improve water quality and avoid the dispersal of pollutants so that water resources, public health and marine ecosystems are protected. Despite the benefits of these technologies, many developing counties cannot afford their high operating cost and maintenance cost (e.g. sewage treatment plants using the most innovative technologies). Green technology, such as phytoremediation, could be a possible option for these countries to improve water quality. In this eBook, the water resource issues are generally addressed. The technical details and procedures of how to conduct environmental monitoring and risk assessment of pollutants are reviewed and illustrated by a case study. Regarding the possible solutions to the issues, different water treatment technologies are discussed in detail with respect to their principles, effectiveness and limitations. I hope that this eBook can raise public awareness about the current issues of our water resources.

Thank you

About Editor

Jonathan Y.S. Leung earned his bachelor degree (BSc, 1st class honours) and master degree (MPhil) at City University of Hong Kong. He was awarded International Postgraduate Research Scholarship (IPRS) and Australian Postgraduate Award (APA), and then studied for his doctorate degree (PhD) at the University of Adelaide, Australia. He is a marine ecologist with broad research interests. In particular, he is interested in how environmental factors, especially pollution and climate change, influence marine invertebrates from physiological level to community level. Apart from marine ecology, he is collaborating with Guangzhou University in China to study environmental chemistry and pollution caused by anthropogenic activities. Over the last few years, his research areas have been focusing on: (1) Impacts of hypoxia, ocean acidification and warming on the fitness and survival of marine invertebrates (e.g. polychaetes and molluscs), (2) Ecological functions of macrobenthic community in mangrove ecosystems following habitat modifications, (3) Environmental monitoring and risk assessment of pollutants (e.g. heavy metals, PAHs, PBDEs, etc.) in different environmental media, and (4) sewage treatment technology.

Acknowledgement

Environmental Monitoring and Risk Assessment of Contaminants

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Introduction

Water is considered as one of the most important natural resource. Water is the most essential asset of our day-to-day life as it is used for drinking, in agricultural and industrial processes. Consequently, it plays a significant role in sustainable development processes. It is considered that, in the world, the total volume of water available is constant and is adequate to meet all the necessities of manhood, but its quantity and quality is uneven in different parts of the world and thus causes the problems of scarcity and suitability. Today, a number of factors are contributing to degradation of water quality. Key factors include discharge of toxic chemicals and contamination of water bodies by substances that promote to algal growth. On the other side, aquatic ecosystems are being threatened by a variety of pollutants on a world-wide scale [1]. Enhancement of nutrients from various origins, principally by domestic sewage, industrial and agricultural run-off, results into acceleration of eutrophication. Surface water is being contaminated directly with metals discharged from mining, industrial manufacturing and smelting. Likewise, when fossil fuels are burned, the atmospheric moisture fuses with the gases produced and, falls as acid rain, and thus leads to acidification of surface waters. In the time of the past few years, the human actions have been increased dangerously, thus influencing the environment; and due to this, ecological systems and the atmosphere are all critically affected.

Therefore, man is using and managing this scarce asset as judiciously and efficiently as possible and for this task to be executed; we must have precise and satisfactory information about the quality of water under constantly changing human activities. Water quality monitoring is essential for protection of environment, management of waterways and in identification of pollution events. Monitoring is done to provide information about water-systems by taking measurements. This chapter begins with an introduction of water quality which is followed by an explanation of what is environmental monitoring, a discussion of the steps involved in water quality monitoring, and finally, the assessment of risk contaminants with respect to human health and ecological systems has been discussed.

Water Quality

The term "water quality" is defined as "those physical, biological or chemical characteristics

of water by which the user assesses the appropriateness of water". For example, limitations are made on the concentrations of toxic substances for the purpose of drinking water, or restrictions on pH and temperature ranges for invertebrate populations leaving in water. Many factors, such as, turbidity, colour, odour, and taste of water, whether of natural or other origin, affect consumer behavior and perceptions [2]. Industries such as irrigation, paper, textiles and brewing, that use water, have their own particular water quality requirements. For an instance, textile industry uses vast amount of water for cleaning the raw material and to meet this requirement, we use water of low quality. To indicate the quality of water, we determine the presence of contaminants as well as the characteristics of water. The water quality indicators can be categorized as given in Table 1.

Physical	Chemical	Biological	Radioactive	Aesthetic
a) Turbidity and clarity b) Temperature c) Suspended solids d) Dissolved solids	a) Colour b) pH c) Biological Oxygen Demand d) Dissolved Oxygen e) Organic and inorganic compounds	a) Algae b) Bacteria (*E.coli* and *fecal coliform*)	alpha, beta and gamma radiation emitters	a) Odour b) Colour

Table 1: Different water quality indicators.

In order to determine whether water is suitable for use for which it is required and to monitor the changes in water quality, these above indicators are measured. Suspended solids are those solids which cannot be pass through a filter with a pore size of 2 micron(0.002cm) . This includes algae, silt and clay particles, fine organic debris, and other particulate matters.While, on the other hand, dissolved solids can be pass through a 2 micron filter and it includes ions of chlorides, calcium, nitrate, sulphur, iron, phosphorous, etc. Designing of water quality monitoring programs is a specialized field. The cost of a monitoring program to assess all these indicators would be unaffordable; hence resources are typically focused towards assessing those contaminants that are significant for the local environment or else for a particular use of water. For example, for the purpose of drinking, we analyze pH, odour, colour, turbidity and the presence of biological entities in the water. Human interference has major effects on water quality [3]. More noticeable are the polluting actions, such as the ejection of domestic, agricultural, industrial, urban and other wastewaters into the watercourse. Water pollution is also caused by human faeces. Faecal pollution may take place in underdeveloped and developing countries since there are no public facilities for waste disposal, collection and management facilities are insufficient, or on-site sanitation facilities drain into aquifers directly. Similarly, water quality is being affected by a wide range of natural influences and the most significant of them are geological and climatic influences, since these affect the quantity and the quality of water available [4]. Their impact is usually greatest when water is available in low quantities and maximum use of it must be made by the limited resources. For instance, high salinity of water is a recurrent problem in coastal areas, but it is not feasible to desalinize sea-water or saline groundwater when considering financial and technical resources. Natural happenings such as heavy rainfall and storms lead to excessive erosion and landslides, resulting into the increase the content of suspended solids in affected lakes and rivers. Fortunately, the use of water that has the highest demands for quantity often requires the lowest demands for quality. For instance, drinking water requires water with the highest quality but in comparatively small quantities.

Environmental Monitoring

Monitoring is defined by the International Organization for Standardization (ISO 5667) as: "the programmed process of sampling, measurement and subsequent recording or signaling, or both, of various water characteristics, often with the aim of assessing conformity to specified objectives". This common definition can be distinguished into three types of monitoring activities as:

- **Monitoring** is the long-term, homogeneous measurement and observation of the environment in order to define status and developments.

- **Surveys** are the short-term, concentrated programmes to measure and notice the quality of the environment for a definite purpose.

- **Surveillance** is continuous, definite measurement and surveillance for the purpose of water quality management and functioning activities.

Water quality management is based on the foundation of water quality monitoring [5]. Monitoring delivers the information on the following matters:

a) Describe water resources.

b) Developing and applying water quality management programmes.

c) Identification of real and developing problems of water pollution.

d) Construction of plans and setting importance for water quality management.

e) Evaluation of the usefulness of management activities.

Environmental Monitoring Strategy

The foundation of the whole water quality monitoring programme is the scoping and the network designing step. Scoping and network designing of monitoring programme is based on rich scientific understanding of monitoring objectives, related background information, suitable methods and the characteristics of water systems. The key objective of the network design should be to minimize the cost of environmental monitoring without surrendering the desired data and statistics to the level of accuracy. It is also imperative that the planned monitoring activities should be practicable so that the objectives of the programme will be met. Because of economic and practical considerations; sampling frequencies, monitoring network design and rate of laboratory analysis should be determined on the basis of the requirement of the information [6]. Moreover, it is also imperative to improve the amount of efforts required and its significance to achieve the set objectives. Hence, to execute this, it is mandatory to prepare a study plan that consists of the objectives of the monitoring programme and a complete explanation of the monitoring area. The study plan should include the localities and sampling frequency and the variables required for analysis.The key components of a study plan include a clear declaration of scopes and objectives, a description of the concerned study area, an explanation of the sampling locations, a list of the water quality variables which will be measured, recommended timing and frequency of sampling, an estimation of the assets that are required to implement the network design, and a proposal for quality control and quality assurance. The principal reason behind the execution of water quality monitoring is to verify whether the observed water quality is appropriate or not for proposed uses. However, monitoring is done toexamine how the environment is being affected by the discharge of contaminants, by waste treatment procedures or by human actions.

The monitoring and valuation of water quality is based primarily upon the fundamental physical, biological and chemical properties of water [7]. On the other hand, water quality monitoring and its assessment are a method of analysis, clarification and communication of assets in context of human activity and use, and the safeguarding of the natural environment. Although it is not a stable process, yet it is adapted for native, national or international requirements. The absolute aim of this is to provide information which is suitable for management. Depending upon institutions, assets and importance, strategies of management varies.

Steps Involved in Water Quality Monitoring

Water quality monitoring objectives

It is imperative to have rich understanding on the monitoring objectives before formulation of any monitoring programme [8]. Therefore, it is mandatory that every person who is involved in the programme team have to be completely aware of the monitoring objectives, methodology, quality control and assurance, and other aspects of the monitoring programme. Moreover, environmental monitoring must have an important role as well as a clear purpose in the procedure of risk assessment and in control of pollution. The most significant objectives of water quality monitoring programs may be as follows:

a) To detect any signs of deterioration in water quality.

b) To identify any water-body that does not meet the necessities of desired water quality criteria.

c) To evaluate efficacy of pollution control efforts that are already in existence.

d) To recognize any zone that is contaminated.

e) To identify nature and magnitude of pollution control which is has to be required.

f) To identify the mass flow of contaminants.

g) To determine the degree and effects of particular waste discharges.

h) To evaluate the efficiency of a water quality management interference.

i) To formulate water quality guidelines as well as standards for particular water uses.

j) To develop water pollution control programme.

Evaluation of resource availability

After knowing the monitoring objectives, it is imperative to evaluate the availability of resources required for monitoring. Hence, it is important to make sure that following resources are available before designing water quality monitoring programme:

a) Laboratory amenities

b) Sampling tools

c) Funds to carry out the procedure of monitoring and for maintenance of laboratory

d) Transportation facility for sampling

e) Ample number of trained manpower

f) Equipment required to study desired parameters

g) Chemicals,glassware and other appliances required for investigation of desired parameters

Area exploration

A monitoring programme generally covers the water-course system of a catchment area (i.e. a main river, lakes, ponds, canals or streams, etc.). Thus the catchment area is defined as the area through which water runs to the water-course. A few days consumed to go through all accessible reports and records regarding the water quality of all waste discharges might save numerous days of field work as well as may avoid the collection of unusable data. Hence, it is significant to make a survey of the river in the course of the planning stage and to note all sources of wastes, all incoming rivers or streams that might

be a source of a potential pollutant. This act will also include a survey of geography, land use, topography, hydrology, climate, weather, hydrogeology, urbanization, industrialization and agriculture of the water course system. This information will help in network designing and in planning the schedule for taking sampling.

This survey will give an overview of the geographical location of the water body to be monitored, its accessibility all kind of human influences to decide appropriate sampling location and also appropriate number of sampling locations. The survey may include acquisition of information about location map, background information on water body, human activities around the water body, identification of potential polluting sources, water abstraction-quantity and uses, water flow regulation - schedule, quantity etc.

Network designing

In network designing, it is significant to examine the ideal number of sampling locations and sampling frequency to achieve the desired objectives.

Sampling frequency: The frequency of a sample is based on the level of dissimilarity in quality of water of a water-course. If there are large variations in a short interval of time, a more sampling frequency is compulsory, and, if there is minor variation in the quality of water, repeated collection of water sample is not required.

Criteria for selection of sampling site: The selection of sampling site is usually related with the objectives of water quality monitoring. For instance, to carry out the appropriateness of water for drinking water source, then the site of monitoring should be nearby to the intake point. Some common criteria for selecting suitable sampling sites are:

i. Locations such as drinking water intake points, irrigation canal off-take points should be considered for water quality monitoring.

ii. Sampling sites should be situated both at upstream and downstream of major pollution outfalls; for instance, sewage drains of a particular city.

iii. All water samples must have the identical value of determinants as the water body at the specific place and time of sampling.

iv. It is crucial that all sampling stations should be sampled almost at the same time in order to enable comparisons among different sampling stations. Thus, in the period of two weeks, all sampling should be done.

v. Sites for biological sampling and chemical sampling should be matched with each other.

vi. For the assessment of the oxygen exchange rate of a particular river, a measurement of cross section is mandatory.

vii. Select those sites that are easily accessible as the sampling team has to carry sampling tools with them.

viii. Avoid those sites where the collection of samples can be dangerous in bad weather (such as high flow).

ix. Accessibility of sampling facilities such as bridges, water-boats, and opportunities for walking is essential criteria while selecting the sites for sampling.

x. It is impossible to monitor the quality of groundwater of a specific area entirely as there is large variation in its quality.

Water Sampling

Planning for sampling

Checklist for sampling includes travel plan for the trip (route, locations which are to be covered), Map of area and sampling site and other equipments e.g , Weighted bottle sampler, BOD bottles, Sample preservatives etc. Labeling of the sample container should be done accurately, by attaching an appropriately labeledtag. On the other hand, a water-proof marker can be used to mark a bottle. Information on the sample container or the tag should include information about code of sample number, source and type of sample, date and time of sampling, and sampler's name.

Preservation, transportation and contamination control of the sample

samples should be preserved at a temperature of 4°C or below for Biological Oxygen Demand (BOD) and bacteriological analyses and in the dark as soon as possible after sampling. This means, they are usually placed in an insulated box consists of ice packs in the field. These insulated ice boxes are used for transportation of samples after proper labeling and preservation. Samples must be transported to the concerned laboratory and in the laboratory; they should be transferred to a refrigerator as soon as possible. Analysis of bacteriological samples should be done within 24 hours of collection. For the analysis of Chemical Oxygen Demand (COD), it should be analyzed on the same day as of collection, and if it is not possible, then preserve the sample below pH 2 by the addition of concentrated sulphuric acid. For the detection of the presence of metals, samples should be acidified to pH below 2 through concentrated nitric acid. Global Positioning Systems (GPS) is being used to obtain data regarding accurate sample position [9]. On the other hand, it is equally important to give special attention for the minimization of contamination. Therefore, for this, experiments must be carried out in sterilized conditions to avoid contaminations. Sampling bottles must be autoclaved, pipette tips should be used once, etc.

Instruments

Instruments and equipment that play an important role in field analyses is a thermometer (such as gas thermometer, liquid-crystal thermometer, infrared thermometer, mercury-filled thermometer, thermocouple, etc.), a conductivity meter, and a pH meter. Observation of colour, odour, temperature, pH, electrical conductivity and dissolved oxygen should be done as soon as possible after collecting a particular sample. In the recent years, with the development of biosensors, it has opened a great perspectives to the onsite, simplified and cost-effective monitoring of water quality [10].

Colour

For the determination of the colour of a sample, pour an aliquot of about 10mL of the sample into a glass test tube and observe the colour. Options for colour are: brown, dark brown, green, dark green, light brown, light green or clear.

Odour

Determination of the odour should be done as soon as possible after collecting a sample in the field. For this, pour an aliquot of approximately 5mL of the sample into a glass test tube and smell the odour. Odour may be of one of the following options: odour free, soapy, rotten eggs,fishy, septic,chlorinous, aromatic,alcoholic or asunpleasant.

pH

The three different methods for pH measurement are; pH indicator paper, electronic meters and liquid colorimetric indicators. The best accurate method for measuring water pH is through electronic meter. These meters are capable of measuring pH to the nearest 0.05 of a pH unit by using a 'glass' and a 'reference' electrode. It is essential to calibrate the pH meter before measuring. After the calibration, the pH meter can be used to measure the pH by placing the electrodes in water sample. The electrodes should be rinsed each time with distilled water while determining the pH.

Temperature

Temperature should be measured in °C (degree Celsius), using a glass thermometer which is mercury-filled or a thermistor [11]. Every time, the temperature should be measured directly by dipping the thermometer in the water. If it is not possible, take about 500 mL of sample in a glass container and measure temperature by the thermometer. Record the temperature in degrees Celsius with 1 digit after the decimal point, for e.g. 16.2 °C.

Electrical conductivity (EC)

The capability of water to conduct an electric current is known as electrical conductivity or specific conductance and it depends upon the concentration of ions in a solution. Conductivity is measured in millisiemens per metre. EC can be measured with a conductivity meter. Before measuring conductivity, it is essential to calibrate the meter. After the calibration, the conductivity can be measured by immersing electrode in a sample of water immediately as it is taken. The reading must be taken after the stabilization.

Laboratory work

The in-charge of the laboratory should maintain a register forwork assignment. An approximation of time required for performing the analyses (such as pH, EC, BOD, etc.) should be entered in the register [12]. Each analyst should have his/her own specific register, where all laboratory analyses and calculations should be entered. After the required analysis and calculations; the results must be recorded in the register having sheets of data record.

Laboratory analysis

It is the duty of laboratory staff to perform the laboratory analysis within the specified time and with accuracy. Table 2 describes the different measurement techniques used to analyze parameters in the laboratory.

Parameters	Unit	Measurement Methods	Significant figures after Decimal
Colour	-	Visual method	
Odour	-	Manual	
Temperature	°C	Thermometer	1
pH	-	pH meter	1
Electrical Conductivity	µS/cm	Conductivity meter	0
Dissolved Oxygen	mg/L	DO Meter or Winkler modified method	1
Turbidity	NTU	Nephelometer	1
Total Dissolved Solids	mg/L	Gravimetry	0
Ammonical Nitrogen (NH_4-N)	mgN/L	Colorimetry	1
Nitrite + Nitrate-N	mgN/L	Colorimetry	1
Total Phosphate	mg/L	Colorimery	4
Orthophosphate	mg/L	Colorimetry	4

Biochemical Oxygen Demand (BOD)	mg/L	DO consumption in 3 days at 27 °C	1
Chemical Oxygen Demand (COD)	mg/L	Potassium dichromate method	1
Sodium	mg/L	Flame photometry	1
Potassium	mg/L	Flame photometry	1
Calcium	mgCaCO$_3$/L	EDTA Titrimetric	1
Magnesium	mg CaCO$_3$/L	EDTA Titrimetric	1
Carbonate as CaCO$_3$	mg CaCO$_3$/L	Titrimetric	1
Bicarbonate, as CaCO$_3$	mg CaCO$_3$/L	Titrimetric	1
Chloride	mg/L	Argentometric titration	1
Sulphate	mg/L	Turbidimetry	1
Fluoride	mg/L	Ion meter, Colorimetry	2
Boron	mg/L	Ion meter, curcumin method	2
Total Coliform	No./100Ml	MPN or MF method	0
Fecal Coliform	No/100mL	MPN or MF method	0
Arsenic	µg/L	Cold vapour AAS	1
Mercury	µg/L	Cold vapour AAS	1
All other heavy metals	µg/L	AAS	1
Pesticides and other organics	µg/L	GC, GC-MS	1

Source: www.cpcb.nic.in

Table 2: Measurement methods, units and significant figures for different parameters used in water quality monitoring.

Data Management and Quality Assurance

In the process of data management, data storage as well as data validation is done. Data analysis and data interpretation are also carried out in this step of water quality monitoring.

Data storage

It comprises all the parameters that may be analysed in the water quality monitoring programme.

Data validation

Data validation is done to check the following things regarding the data obtained:

   i.   Entry of data

   ii.   To check whether data is scientifically possible or not

   iii.   To check whether the data is within the estimated ranges for a parameter or not

   iv.   To check whether the data is within the detection limits of a specific method or not

   v.   To check how many significant digits have been reported

   vi.   To check correlation between the different parameters

   vii.   Checking of cation/anion balance

Data analysis and interpretation

Data analysis is a process of examining, altering and modelling data for discovering useful information to propose conclusions and support decision-making [13]. The data can also be concise in form of index. The data can be presented in different formats after the analysis has been done. The data interpretation includes the understanding of chemistry, biology and hydrology of water. Therefore, data is analyzed and interpreted in terms of

quality of water, variations in water quality and their probable effects on ecosystem. For this, a comparison is made with the predefined criteria that have been set for protection of the ecosystem.

Graphical presentation of data

The data can be presented in the form of graphs. The different forms of graphs are: Time Series Graphs, Histograms, Pie Charts, Profile Plots and Geographical Plots.

Quality assurance

According to ISO 9000, quality assurance is defined as the "part of quality management focused on providing confidence that quality requirements will be fulfilled". Quality assurance is done to cross-check the different management procedures of the laboratory. For the QA programme of a laboratory; it should contain a set of operating principles that have been noted down and agreed by the organization.

Analytical quality control: This includes both Internal QC (IQC) and External QC (EQC). Internal Quality Control (IQC) involves the operative techniques that are used for continuous valuation of the quality results of distinct analytical procedures carried out by the laboratory staff. Thus, the focus is given mainly on monitoring precision as well as on accuracy. Hence, IQC stressesmainly on the specific method and examines its performance against the set criteria of quality which is derived mathematically. On the other hand, External Quality Control (EQC) is done to establish the accurateness of analytical methods and techniques by comparing the results of analyses done in one laboratory with the results of others that conduct the similar analysis on the identical material. Thus, EQC programmes are considered to evaluate bias between the different laboratories.

Internal quality control (IQC)

Internal Quality Control (IQC) can be done with the help of control charts. Shewhart is commonly used control chart in IQC.

Shewhart control chart

It is a graph of time (x-axis) versus the concentration of the variable in the reference material (y-axis). Lines of target, warning and action should be marked parallel to the x-axis. On a Shewhart Chart, data obtained from precision control using reference materials are usually plotted. The target line is at the mean concentration of the variable for that specific pool of material, warning lines are placed at either side of the target line with two standard deviations and action lines are placed at either side of the target line with three standard deviations. Result, which is outside the limits of action lines, leads to the rejection of the data obtained during assay.

External quality control (EQC)

The key objectives of EQC programme are:

1. To examine probable unfairness in measurements in a laboratory.
2. To compare the results obtained in different laboratories in a mutual water quality monitoring programme.

The main objectives of EQC are to evaluate the status of analytical facilities of contributing laboratories, to improve the internal and external quality control of the concerned laboratories, to provide essential support to the concerned laboratories so that they overcome the short comings in the analysis of the parameters, and to promote the scientific competency among the concerned laboratories for the better output.

Human Health Risk Assessment

In context to the risk assessment, EPA defines risk as "the chance of harmful effects to human health or to ecological systems resulting from exposure to an environmental stressor". Any physical, chemical, or biological object that can cause a negative effect to human health or to ecological system is called a stressor. Thus, whole ecosystems, such as plants and animals, and the environment by which the stressors interact, are being affected unfavorably. Risk assessment has been carried out to illustrate the nature and extent of health risks to humans and ecological receptors from contaminants and other stressors that may be present in the environment [14]. Risk assessment is performed principally into two areas: Human Health and Ecological System.

The risk assessment procedure is usually initiated by collecting measurements that illustrate the nature and extent of chemical contamination in the environment, as well as information required to predict how the contaminants will act in the future. Based on this, the occurrence and extent of human and ecological exposures that may occur as a consequence of interaction with the contaminated medium, both now and in the future, is evaluated by the risk assessor. This evaluation of exposure is then shared with information on the in-built toxicity of the chemical to predict the possibility, nature and degree of the adverse health effects that may occur. Thus, through the use of a comprehensive risk assessment and risk management approach, we can consistently ensure the safety of a drinking - water supply from catchment to consumer [15]. In actual life, information regarding key data, needed for risk assessment calculations, is usually limited. This means that risk assessors have to make estimations while carrying out risk calculations, and therefore all risk estimations are undetermined to some extent.It is an iterative process to develop a risk assessment in which researchers identify and fill data gaps to make a more sophisticated assessment of the risk.

A human health risk assessment is the procedure for estimation the type and probability of harmful health effects in humans when they are exposed to stressors.

A human health risk assessment answers the many questions , for instance; What are different types of health problems that may be caused by environmental stressors?; What is the probability of causing health problems to people when they are exposed to different levels of stressors?; To what level some chemicals cause a risk to human health?; What are different stressors that are exposed to people and at what levels?; What are different factors, such as where people work, where people play, etc., that are responsible for causing risk when exposed to stressors?; etc. The patterns of human health, international health care, and public health activities are being influenced fundamentally by environmental and social changes [16].

Phases involved in human health risk assessment

Risk assessment of human health generally includes following 3 phases:

Documentation of hazards: To investigate whether an environmental stressor has the possibility to cause harmful effects to human health.

Dose-response assessment: To study the statistical relationship between an exposure and effects and to observe what we have known about the occurrence and levels of contact with a specific stressor.

Risk depiction: To check how the data support results about the quality and degree of the risk that are aroused due to exposure to stressors.

There are many environmental hazards; chemicals, radiation, biological, and physical. The sources of environmental hazards are:

- Point sources (for instance, industrial effluents)

- Non-point sources (for instance, agricultural runoff; exhaust from automobiles)

- Natural sources

These environmental hazards can be exposed to humans by a number of ways such as through air, food, solid waste, soil, surface water or ground water, or by contact with skin, by breathing, etc. Cancer, heart disease, liver disease and nerve disease are examples of health effects that are caused due to these environmental hazards.

Documentation of hazards*:* To recognize the various types of harmful health effects that are caused by exposing to few agents as well as to illustrate the value of data that support this description. It is the procedure to determine if a stressor is exposed to a human, then whether there is a possibility to cause harmful effects to the human health. In the process of determining the harmful effects caused by chemical hazards, there is need to study the data which is available scientifically for a particular given chemical and thus drawing the relationship between the stressor and the negative effects caused by it. Exposure to a chemical stressor can results in the formation of tumors and other many diseases causing even death. Scientific studies performed on human beings yield the information regarding the resulting effects caused by a stressor. However, due to many ethical concerns, these studies are not available. Thus, experiments are being carried out on animals such as mice, rats, etc., to obtain results regarding the harmful effects that may be caused by a specific stressor.

Types of analysis that are used for identification of hazards are:

a. Toxicokinetics: It analyzes how the human body ingests, circulates, metabolizes and excludes specific stressors.

b. Toxicodynamics: This study illustrates the mechanisms by which a stressor may cause harmful effects to human health.

Dose-response assessment: To report the relationship between the dose exposed and harmful effects caused and to calculate a numerical value of dose.

A dose-response assessment explains how the responses are related to the volume of the dose provided. Generally, when the dose increases, it also increases the measured response. However, at lower amount of doses, there may be no response generated. The response generated by a dose depends upon a number of factors, such as, route of exposure, types of pollutants; etc.There may be different kinds of responses that can be produced when the doses are provided. The different types of responses may be weight loss or even death in some cases. Therefore, it is impossible to investigate all possible assessments for all available responses. It is a two-step process. In the first step, there is an evaluation of entire data which is present or can be obtained by conducting the experiments. This is done to draw the dose-response assessment for which the doses reported in the collected data. On the other hand, in the second step, estimation of the level of risk below which it doesn't cause any harm to the human health is done.

Risk depiction: To compile and assimilate information from the previous steps so as to make conclusions about risks. In this phase of human health risk assessment, judgment of risk assessor conveys the quality of the risks. It also conveys whether the risk is present or absent and the information regarding how the risk assessment has been done. Moreover, risk depiction phase occurs in risk assessments of both human healths as well as in ecological system. Each phase of the human health risk assessment has particular depiction of risks having main findings; assumptions and limitations related to the risks and this information provide a basis to compose an integrative analysis for risk depiction. Thus, particular risk depiction and an integrative analysis are the main components of entire risk depiction process.

Ecological Risk Assessment

An ecological risk assessment is the procedure to determine how the environment may be affected when exposing to environmental stressors [17]. Thus, ecological risk assessment answer the many questions, such as, how the dams affect the aquatic environment or how the fertilizers in the agricultural run-off affect the water bodies, etc.

Phases involved in ecological risk assessment: Ecological risk assessment includes following three phases:

Problem designing: To determine which ecosystem is at risk and what are the requirements to protect them.

Analysis: This phase determines which plants and animals are being exposed to stressors and at what level.

Characterization of risks: It consists of estimation of risks and risk depiction.

Management of hazardous waste locations, industrial chemicals, and insecticides is done through the risk assessment of ecological system.

Problem designing: This phase defines endpoint of assessment to decide which ecological entity is crucial to protect. An ecological entity can be a species (e.g. Hooded merganser), a functional group of species (e.g. carnivores), a community (for example: benthic micro-invertebrates), an ecosystem (e.g. lake, river), a specific valued habitat (e.g. wetlands) and another ecological entity of concern. After the identification of the identity, the next step is to determine which specific attribute of the entity is at risk and essential to protect. This information provides a basis for measurement in the assessment of risk. Professional judgment based on preliminary surveys, site-specific information, or other available information is required in determining ecological importance in specific cases. Ecological importance is linked to nature and strength of effects, potential for recovery, spatial and sequential scales of effects, level of organization possibly affected and the role of entity in the ecosystem. It is hardly clear which of these ecosystem components are most valuable or which are most critical to ecosystem function, and thus increases the task in choosing which ecosystem component have to be protected. We can execute this task by following three principal criteria i.e. by knowing ecological importance of the ecosystem components, and by defining their relevance to management goals.

The main challenge is to find ecological values that are scientifically rigorous and are also acknowledged as valuable by the risk managers as well as by the public. Possible effective examples include endangered species or ecosystems, commercially or recreationally important species, ecosystem functions or services such as food supply, flood control, or nutrient cycling, aesthetic values such as clean air in national parks and existence of charismatic species such as eagles or whales. Once endpoints of assessments are chosen, a conceptual model is developed to provide a visual representation (a map, flow chart, or schematic) of hypothesized relationships between ecological entities and the stressors to which they may be exposed, accompanied by a written description of this process and of the risk questions. These models include information about source, stressors, receptors, potential exposure and predicted effects on an ecological entity.

Analysis: The main aim of this phase is to provide the components that are necessary for determination or prediction of ecological responses to stressors under the circumstances of exposure of interest. It is the examination of what type of plants and animals are exposed and to what amount they are exposed to risks and to know whether that level of exposure have the possibility to cause harmful ecological effects or not. These calculations may consist of hazard quotient which equals to the ratio of concentration of chemical contaminant to a particular screening benchmark; and numerous parameters used to determine the different levels of exposure to a stressor by a designated receptor.

Characterization of risks: It is the concluding phase of an ecological risk assessment and in this; we make conclusions of all the work done during the previous phases. During characterization of risk, in order to estimate the risk that can be posed to ecological entities, the assessor uses the results of analysis done in the previous phase. After this, the assessor explains the risk, indicates the degree of assurance in the risk estimation, summarizes uncertainties, cites evidence that supports the risk estimation, and interprets the difficulty of ecological effects. The key factors that are considered while estimating ecological risk include whether the risk is acute or chronic, what is the time for which risks occurrence, how many organisms are vulnerable to risk, whether the risk corresponds to one species or many species, what is the harshness of ecological effects etc. Many approaches can be used to answer these questions and to construct the estimate of risk that consists of surveys, procedure simulations that depend on theoretical calculations of exposure and effects, and comparisons between exposure and effects data.

Conclusion

Water is required for our existence on this planet. To do any activity we need water with desired quality, for instance, for drinking we need potable water. But water with undesired quality possesses a great impact on human health as well as threatens ecological systems. Due to contaminated water by a number of factors, such as by discharge of chemical toxins through mining or by inappropriate treatment of human faces, we are suffering from a number of diseases like cholera, typhoid, etc. On the other hand, aquatic ecosystems are also being affected due to various pollutants or by improper water management practices. Water of good quality is crucial for social and economic development processes. Thus there is an urgent need to monitor the various factors that contribute to water pollution and to do risk assessments of those contaminants in order to study their effects on human health as well as on ecological system at each level, starting from local to national level. Therefore, government organizationsalong with local natives must take efforts for the preservation of this valuable entity.

References

1. Chapman D [Ed.] (1996) Water Quality Assessments. A Guide to the Use of Biota, Sediments and Water in Environmental Monitoring (2nd edition). Chapman & Hall, London. Chelsea, MI: Lewis Publishers.

2. WHO (1997) Guidelines for Drinking-Water Quality. Volume 3, Surveillance and Control of Community Supplies. World Health Organization, Geneva.

3. Serruya C and Pollingher U (1983) Lakes of the Warm Belt. Cambridge University Press, Cambridge.

4. Foster SSD and Gomes DC (1989) Groundwater Quality Monitoring: An Appraisal of Practices and Costs. Pan American Centre for Sanitary Engineering and Environmental Science (CEPIS), Lima.

5. Hem JD (1984) Study and Interpretation of the Chemical Characteristics of Natural Water (3rd edition). Water Supply Paper 2254, United States Geological Survey, Washington, DC.

6. Hach Company (1989) Hach Water Analysis Handbook. Hach Company, Loveland, CO.

7. Chaplin, Mark (2004) Water Structure and Behavior, London South Bank University, London , England.

8. ISO (1990) Water Quality Sampling. Part 2: Guidelines on Sampling Techniques. International Standard ISO 5667-2, International Organization for Standardization, Geneva.

9. Nash H and McCall JGH (1994) Groundwater Quality. Chapman & Hall, London.

10. Jon Chouler and Mirella Di Lorenzo (2015) Water Quality Monitoring in Developing Countries; Can Microbial Fuel Cells be the Answer? Biosensors 5(3), 450-470.

11. APHA (1992) Standard Methods for the Examination of Water and Wastewater (18th edition). American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), Washington, DC.s

12. Lloyd B and Helmer R (1991) Surveillance of Drinking-Water Quality in Rural Areas. Longman, Harlow.

13. APHA (2012) Standard Methods for the Examination of Water and Wastewater(20th edition). American Public Health Association (APHA), Washington, DC.

14. Foster SSD and Hirata R (1988) Groundwater Pollution Risk Assessment: A Method Using Available Data. Pan American Centre for Sanitary Engineering and Environmental Science (CEPIS), Lima.

15. WHO (2011) Guidelines for Drinking-water Quality. (4thedition), World Health Organization, Geneva.

16. Labonte R, Mohindra K, Schrecker T (2011) The growing impact of globalization on health and public health practice. Annu Rev Public Health32:263-283.

17. Bartell SM, Gardner RH and O'Neill RV (1992) Ecological Risk Estimation. Lewis Publishers, Chelsea, MI, USA.

Water Quality in Urban Rivers: A Case Study for the Hawkesbury-Nepean River System in Australia

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Abstract

Rivers are the main water sources for drinking, irrigation, recreational and industrial uses in many inland areas around the globe. Although river water accounts for only 0.0001% of the total water on earth, this is one of the main sources of fresh water for human consumption. Rivers are major carriers of nutrients from catchments to sea. In many countries around the globe, river water quality has been threatened by anthropogenic activities (e.g. urbanisation, intensive agriculture and industrialisation) as well as by the changes in climatic condition. A comprehensive assessment of river water quality is essential to safeguard river health. In this chapter, water quality of the Hawkesbury Nepean River System (HNRS) in New South Wales, Australia is investigated. The HNRS is one of the most important river systems in Australia, which provides drinking water to over 4.8 million people in Sydney. Water quality data from 9 monitoring stations are used in this study. It is found that water quality at all the 9 stations fall under either 'poor' or 'marginal' states based on the Canadian Water Quality Index (CWQI). None of the stations fall in the category of 'good quality' water. Further studies are recommended to investigate the underlying causes of the pollution and formulate management strategies to improve the water quality of the HNRS in near future.

Keywords: Australia; Hawkesbury; Nepean River; Pollution; Urban River; Water Quality Index

Introduction

River is regarded as an integral part of eco-system. It is the primary sources of water for drinking, irrigation and industrial purposes for many localities around the globe. It also supports various recreational activities such as boating and fishing and serves as inland transport route. Rivers carry pollutants to the nearby sea, which affects sea ecology by endangering sea plants, fish and other habitats. It supports the lives of many people living in their catchments by providing fresh water. Rivers are 'comfort of eyes' and are regarded

as holy by many societies. On the other hand, rivers sometimes cause devastating floods resulting loss of human lives, livestock and crops.

Many rivers around the globe have been affected over the past decades by anthropogenic activities (e.g. urbanisation, intensive agriculture and industrialisation) as well as by the changes in climatic and natural conditions (e.g. changes in rainfall increase in droughts and floods, and bank erosion) [1]. Quality of river water is being degraded continuously at many locations around the globe, which has significant ecological, health and economic implications. For example, over the past few decades, water quality in many Australian peri-urban rivers (e.g. Mary River and Albert River in Queensland and Ord River in Western Australia) has been degraded due to extensive urban and agricultural activities [2]. About 180 to 240 Million Australian Dollars (AUD) are spent every year to deal with algal blooms in Australian rivers [3]. Therefore, a comprehensive assessment of river water quality is essential to devise strategies for effective management of river health, and issuing short- and long-term advisories to the stakeholders of a river system.

River water quality generally depends on various factors such as geologic, climatic, catchment and land use characteristics, and greatly varies over space and time. Among the factors, climate and land use characteristics are considered to be the key drivers of water quality in a river system [4]. Several studies have assessed the land use impact on river water quality and found that land use has a notable impact on river water quality [e.g. 5-7]. In addition, various point sources related to industries and mining activities can have significant impacts on a river system [8,9]. When water travels over the land to the rivers, it picks up different residues/contaminants from the land which negatively affect the water quality. For example, water from agricultural lands may contain nutrients and sediments, and water from highly urban areas may contain rubber fragments and heavy metals. Surface runoff during the first flush is also an important cause of water pollution that is generally considered as nonpoint source pollution [10]. As there is a growing concern of the impact of anthropogenic activities on water quality, an increasing awareness has been noticed in recent years in different countries to assess the impacts of anthropogenic activities on river water quantity and quality [11-13]. In addition, pollutant build up and wash off in connection with urban catchments have become a focus of current research in many countries [14-17].

Status of the physical (e.g. temperature and turbidity), biological (e.g. E.coli and coliform) and chemical properties/conditions (e.g. pH, dissolved oxygen and nutrients) in the water body generally represent the quality of a river. River water quality is assessed mainly based on measurements of water quality variables. The observed data are compared against the recommended guidelines/standards to benchmark a river [18]. Several guidelines have been developed internationally to assess the health of freshwater for biotic species and humans; for example, IUCN Global Freshwater Initiative (International Union for Conservation of Nature and Natural Resources), Healthy Watershed Initiative in the US [19], Pressure, State, Response model in Australia [20], EU Water Framework Directive in Europe [21] and Australian and New Zealand guidelines for fresh and marine water quality [22].

Water quality monitoring programs have been established in many countries with the primary aim to monitor and evaluate the river water quality [23-25]. These monitoring programs generally collect water samples from the rivers and evaluate the physical, chemical and bio-logical parameters to identify the states of river water quality. Having reliable information on water quality is vital for effective and efficient river management, as it provides important information regarding the states of a river and its adjacent landscapes, as well as it provides the means to diagnose the causes of water quality degradation. This information on water quality is useful to develop restoration plan, estimate the ecological

risks associated with land use plans in a watershed and to select alternative development plans to minimise overall degradation of a river.

This chapter presents a case study on the assessment of water quality in the Hawkesbury-Nepean River System (HNRS) in Australia. The HNRS is one of the most important rivers in Australia as it provides drinking water to over 4.8 million people in Sydney, the largest city in Australia. This study uses measured water quality data, and water quality index method to make a statement on the overall quality of the HNRS.

Water Quality Index

Water Quality Index (WQI) is a mathematical representation, adopted to transform a set of large water quality data matrix into a single number [26], which provides a simple and convenient tool for the water authorities and policy makers to evaluate the overall health of a river [27]. The concept of WQI is based on the principle of comparing water quality parameters with respective regulatory standards [28]. WQI has several benefits, such as it improves the understanding of the state of water quality to the public and policy makers, which is important in shaping public opinion on certain aspects of river water quality. Furthermore, it assists evaluating the changes in water quality and identifying the spatial and temporal trends in water quality. River water can be classified based on the identified single value of WQI, which is useful to stakeholders e.g. farmers, water supply authorities, environmentalists and government agencies.

The first study on WQI was done by Horton [29]; since then, several WQIs have been developed based on different types and numbers of water quality parameters. The following five WQI are commonly adopted to assess the river water quality [30]:

(a) US National Sanitation Foundation Water Quality Index, NSFWQI [31];

(b) Canadian Water Quality Index [32];

(c) British Columbia Water Quality Index, BCWQI [33];

(d) Oregon Water Quality Index, OWQI [34]; and

(e) Florida Stream Water Quality Index, FWQI [35].

Dede et al., [36] used 5 WQI methods (Oregon WQI, Aquatic toxicity index, overall index of pollution, universal water quality index and CCME WQI) to evaluate surface water quality, and concluded that CCME WQI was the only method that allowed utilization of all the available parameters in the calculation of an overall index value. Based on the recommendation of Dede et al., [36], Canadian Water Quality Index (CWQI) has been adopted in this study to derive an overall and easily understood description of water quality status in the HNRS. The index has been calculated based on three variables: exceedances, frequency of exceedances and magnitude of exceedances of regulatory standards for specific parameters. The variable "exceedances" is generally termed as "Scope (F_1)", whereas the other two variables "frequency of exceedances" and "magnitudes of exceedances" are termed as "Frequency (F_2)" and "Amplitude (F_3)", respectively. Table 1 presents the descriptions and formulae for the scope, frequency and amplitude.

Variable in WQI	Variable description	Equation
Scope (F_1)	Number of variables not meeting the water quality standards	$$F_1 = \frac{Total\ number\ of\ failed\ variables}{Tatal\ number\ of\ variables} \times 100$$
Frequency (F_2)	Number of times these standards are not met	$$F_2 = \frac{Number\ of\ failed\ tests}{Total\ number\ of\ variables} \times 100$$
Amplitude (F_3)	Amount/deviation of the quality parameters from the standards	$$F_3 = \left(\frac{nse}{0.01nse + 0.01} \right) \ Where$$ $$nse = \frac{\sum_{t-1}^{n} \left(\frac{failed\ test\ value)}{Objective_t} \right)}{Number\ of\ tests} - 1$$

Table 1: Definition for the scope, frequency and amplitude in water quality index.

The CWQI is calculated by Equation 1:

$$CWQI = 100 - \left(\frac{F_1^2 + F_2^2 + F_3^2}{1.732} \right) \tag{1}$$

Factor 1.732 in Equation 1 scales the index from 0 to 100. The index is categorised into five divisions (Table 2) to represent the overall water quality [37].

CWQI	Water Quality	Description
0 - 44	Poor	Water quality is almost always threatened or impaired and conditions usually depart from natural or desirable levels
45 - 64	Marginal	Water quality is frequently threatened or impaired and conditions often depart from natural or desirable levels
65 - 79	Fair	Water quality is usually protected, but occasionally threatened or impaired and conditions sometimes depart from natural or desirable levels
80 - 94	Good	Water quality is protected with only a minor degree of threat or impairment and conditions rarely depart from natural or desirable levels
95 - 100	Excellent	Water quality is protected with a virtual absence of threat or impairment and conditions very close to natural or pristine levels

Table 2: Five descriptive categories of CWQI [36].

Hawkesbury-Nepean River System

Hawkesbury Nepean River System (HNRS) is the major source of fresh drinking water supply to more than 4.8 million people living in and around Sydney, the largest city in Australia. The HNRS system (shown in Figure 1) is a combination of two major rivers, the Nepean River (155 km long) and the Hawkesbury River (145 km long) [38]. The average annual discharge of the HNRS is 2,765,000 ML [39]. This river system has multiple geologic and land use characteristics, the upper part contains poorly accessible gorges, the middle part runs through irrigated farm lands, and the lower part has tidal slopes with deposited soil pockets [40]. The middle part of the river is being continuously influenced by increasing population growth, urbanization, industrialization and other anthropogenic activities, which cause contamination of the river from different sources (e.g. sewage, stormwater, runoff from disused mines, toxic forms of blue-green algae, and waste from domestic and native animals). Land use in the HNRS catchment includes regions that are heavily peri-

urbanised and industrialised. Agricultural runoff contributes approximately 40% to 50% of phosphorus loads and 25 % of nitrate loads into the HNRS, which are believed to have mainly originated from agricultural and animal farms [37].

Figure 1: Hawkesbury Nepean River System in Australia.

Unlike other natural rivers where flow is dominated by rainfall events, flow of the HNRS is highly regulated by impoundments and treated effluent discharge from multiple sewage treatment plants. There are some 22 dams and 15 weirs situated along the HNRS. The major dam on this river is at Warragamba, which holds about 2.057×109 m^3 of water captured from a 9,000 km^2 catchment area [41]. There are 18 sewage treatment plants along the HNRS discharging significant volumes of treated municipal wastewater into the river. Table 3 presents the discharge volumes from the Sewage Treatment Plants (STP) to the HNRS.

STP location	Treatment level	Discharge (ML/day)
Picton	Tertiary (includes additional Phosphorus removal and disinfection)	1.5
West Camden	Tertiary (includes additional Phosphorus removal and disinfection)	10.7
Wallacia	Tertiary (includes additional Phosphorus and nitrogen removal and disinfection)	0.8
Penrith	Tertiary (includes additional Phosphorus and Nitrogen removal and disinfection)	22.4
St. Marys	Tertiary (includes ultrafiltration, reverse osmosis, de-carbonation, additional Phosphorous and Nitrogen removal and disinfection)	33.5
Winmalee	Tertiary(includes additional Phosphorus and nitrogen removal and disinfection)	16.5
North Richmond	Tertiary (includes additional Phosphorus removal and disinfection)	0.9
Riverstone	Tertiary(includes additional Phosphorus removal and disinfection)	1.8
Quakers Hill	Tertiary (includes additional Phosphorus and Nitrogen removal and disinfection)	31.1
Rouse Hill	Tertiary (includes additional Phosphorus and Nitrogen removal and disinfection) also includes ultra-violet irradiation and super-chlorination for reuse water	15.3
Castle Hill	Tertiary (includes additional Phosphorus removal and disinfection)	6.5

Table 3: Sewage Treatment Plants (STP) along the HNRS.

Water Quality Assessment in the Hawkesbury-Nepean River System

Water quality data, collected fortnightly, from 9 sampling stations (N14, N21, N35, N42, N44, N57, N67, N75 and N92), as shown in Figure 2 along the HNRS during the last 21 years (1993 to 2014) were used to identify changes in water quality at different sampling stations over time, and for comparisons of the water quality status among the stations in the HNRS. A schematic diagram of the monitoring stations along the HNRS with different inflows is presented in Figure 3.

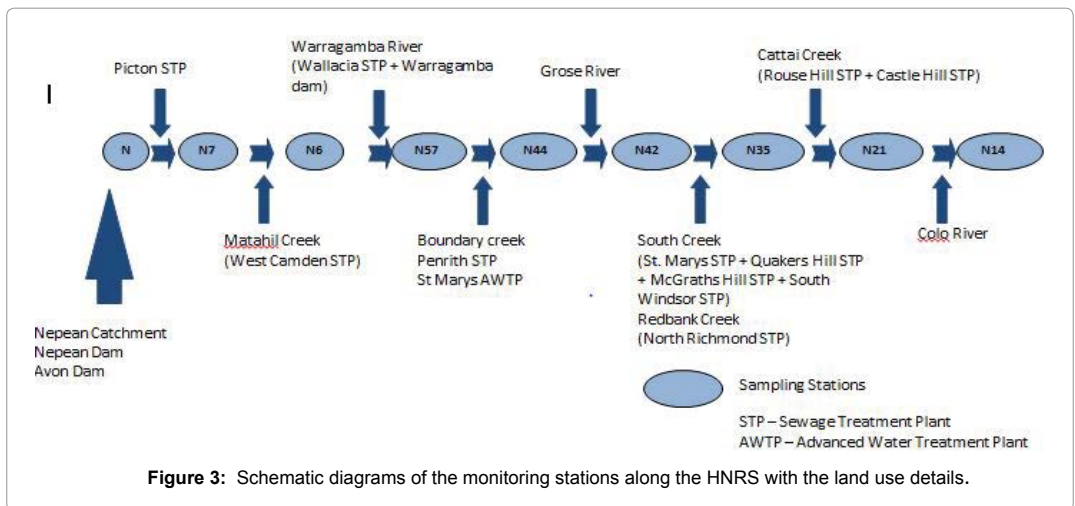**Figure 2:** Nine sampling locations along the HNRS.

Figure 3: Schematic diagrams of the monitoring stations along the HNRS with the land use details.

This study provides a measure of the overall state of water quality in the HNRS against the Australian and New Zealand water quality guidelines, which is known as ANZECC 2000 [22]. Table 4 presents the descriptive statistics of 12 water quality parameters in the HNRS considering the 9 sampling stations, and their respective ANZECC trigger values for safe use of river water. In the "ANZECC trigger values" column (Table 4) represents the recommended value corresponding to 'good water condition'; for example, pH value should remain in between 6 to 8 and iron total should be less than 0.3 in the river system to satisfy acceptable water quality status. Some 12 water quality parameters were selected according to the availability of water quality data; all the parameters were considered equally important in deriving the CWQI. The bold marked values in Table 4 represent the non-compliance of the ANZECC 2000 recommended thresholds for the average value of a parameter. As can be seen that average values of 3 parameters (Chlorophyll-a, Alkalinity and Nitrogen Total) are above the ANZECC 2000 limit, indicating that the river water is not in 'good condition' with respect to these 3 parameters. However, the other 9 parameters have been found to be within the recommended range including parameters such as pH, colour, turbidity and suspended solids. To get the overall water quality status of an individual sampling station, CWQI has been calculated for all the stations, and the stations are then ranked based on the derived CWQI values.

Water quality parameter	Unit	Min	Max	Median	ANZECC trigger value
pH		5.78	9.94	7.63	6< pH < 8
Iron Total	mg/L	0.04	5.62	0.29	< 0.3
Chlorophyll-a	ug/L	0.20	253.10	**5.10**	< 5
True Colour		1.00	93.00	11.00	< 15
Nitrogen Total	mg/L	0.08	5.90	**0.45**	< 0.35
Turbidity	NTU	-0.60	380.00	3.85	< 20
Alkalinity	mgCaCO3/L	1.00	298.00	**40.00**	< 20
Aluminium Total	mg/L	0.01	3.97	0.08	< 0.2
Dissolved Oxygen	mg/L	1.50	16.20	9.10	> 5
Phosphorus Total	mg/L	0.01	0.18	0.01	< 0.05
Suspended Solids	mg/L	1.00	105.00	3.00	< 20
Conductivity Field	mS/cm	0.01	48.40	0.30	< 0.35

Table 4: Descriptive statistics of water quality parameters and ANZECC trigger values.

Scope, frequency and amplitude values at 9 monitoring stations were calculated based on the equations shown in Table 1. The calculated values are presented in Figure 4, where it can be seen that the scope values were within the range of 66% to 88% indicating a notable percentage of water quality values falling byound the recommend values by the ANZECC 2000 guideline. The mean frequency and amplitude values were found to be around 36%, which indicates that around 36% of time, the variables were failed, and the failed deviation was also around 36%. Among all the 9 stations, the scope and frequency values were found to be the highest for the station, N35, which indicated that most of the water quality values for N35 were beyond the guidelines and the deviation was the highest among all the selected stations. The obtained results are not surprising as the upstream of the station N35 is affected by quality and magnitude of flows coming from the South Creek (which carries discharge from St Marys Sewage Treatment Plant (STP), Riverstone STP, Quakers Hill STP, McGraths Hill STP and South Windsor STP) and North Richmond STP). Moreover, the dominant land use in this part of the catchment includes rural, grazing, commercial gardening, intensive agriculture and scattered urban and industrial activities.
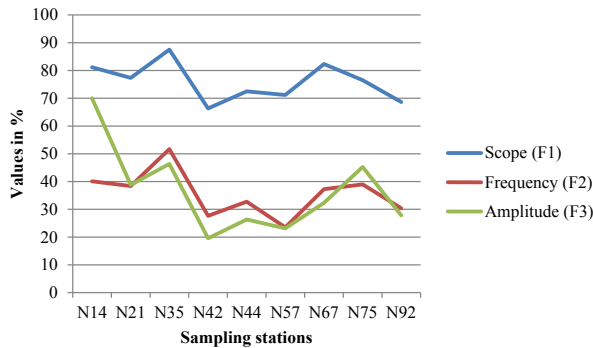
Figure 4: Scope, frequency and amplitude values at 9 monitoring stations in the HNRS during 1993 to 2014.

From the calculated CWQI values (Table 5) for all the 9 stations, it can be seen that the CWQI values were in the range of 33 to 57, indicating that the quality of the HNRS water falls under the category of 'poor' and 'marginal' based on the categorisation in Table 2. Water quality status at the stations N21, N42, N44, N57 and N92 were found to be marginal, which demonstrated that the water of these stations are subject to frequent threatening, whereas water quality at the stations N14, N35, N67 and N75 are always under threat as their water quality was categorised as poor based on the calculated

Water quality monitoring station in the HNRS	Average CWQI value
N14	33.37
N21	45.02
N35	35.27
N42	56.77
N44	51.12
N57	53.73
N67	44.21
N75	43.41
N92	53.09

Table 5: Average CWQI for 9 sampling stations in the HNRS.

CQWI. Among the 9 sampling stations, station N14 showed the poorest water quality as CWQI was found to be the lowest, which was mainly due to the higher scope and amplitude values.
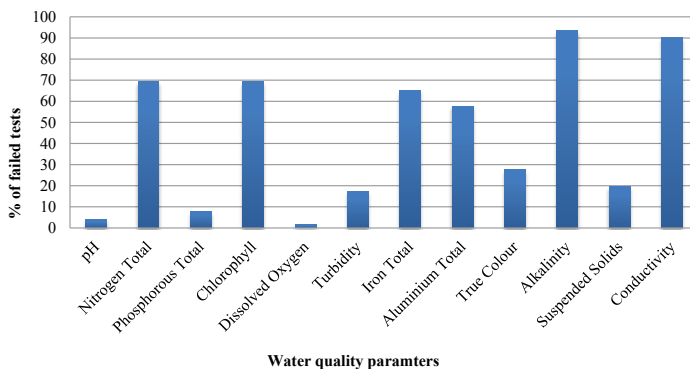

Figure 5: Percentage of failed tests of the water quality parameters at station N14 in HNRS.

As station N14 exhibited the most deteriorated water quality condition, further data exploration was undertaken to identify the water quality parameters which contributed to the overall water quality deterioration at this station. Figure 5 presents the details of average percentage failed tests for different water quality parameter at station N14. It can be seen in Figure 5 that percentage of failed tests of the Nitrogen, Chlorophyll-a, Iron, Aluminium, Alkalinity and Conductivity were found to be relatively higher compared with the other parameters indicating that these parameters were mainly responsible for the poor water quality at station N14. Nitrogen concentrations in rivers and streams generally increase due to factors such as discharge of sewage water, pollutant wash off from urban and agricultural land, and atmospheric deposition. Increased nitrogen may result in overgrowth of algae, which can decrease the dissolved oxygen content of the water, thereby harming or killing fish and other aquatic species. The HNRS has seen a number of episodes of algal blooms in the past causing public concern and serious threat to Sydney water supply. For examples, the shallow mid Nepean River section was affected heavily by aquatic weed Egeria Densa [42], and the Berowra Creek estuarine section of the river was infested by toxic dinoflagellate algal blooms [43]. When considering the median values of Chlorophyll-a (Figure 6), there are 6 stations (out of 9) where values have exceeded the ANZECC trigger threshold value. The high Chlorophyll-a level at many stations warrants further investigation to identify the underlying reasons and to recommend necessary controlling measures. The long-term persistence of elevated levels of Chlorophyll-a is a major concern to water authorities. An excessive growth often leads to poor water quality, noxious odours, oxygen depletion, and human health problems. It may also be linked to harmful (toxic) algal blooms. Observed increases in the concentrations of chlorophyll may be related to increased nutrient concentrations, decreased flow/changed hydrodynamics (increased residence times) and/ or decreased turbidity.
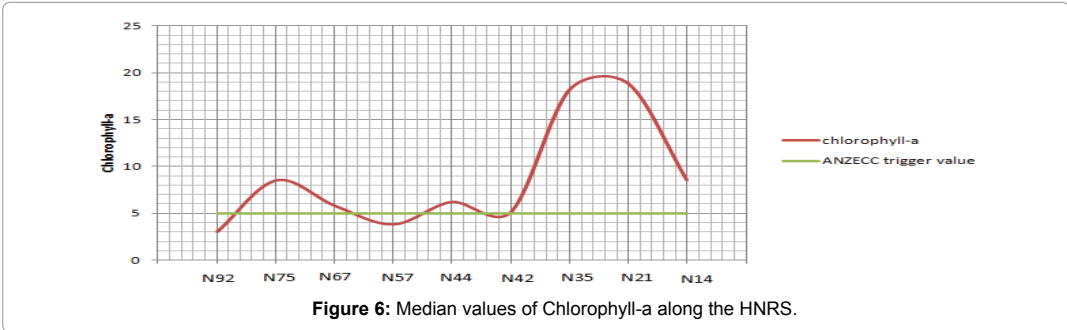

Figure 6: Median values of Chlorophyll-a along the HNRS.

Figure 6: Median values of Chlorophyll-a along the HNRS.

If the alkalinity level is too high, the water can be cloudy, which inhibits the growth of underwater plants. A higher alkalinity may raise the pH level, which in turn can harm or kill fish and other aquatic organisms, which are too sensitive to higher pH level. High alkalinity may result from the presence of the bicarbonate ion, which is derived from the dissolution of carbonates by carbonic acids due to factors such as weathering of limestone and dolomite rocks mainly composed of calcite.

There are number of factors that can lead to high conductivity level. For examples, streams that run through clay catchments may have higher conductivity level as the presence of clay particles that ionize when enter into the river system. Groundwater inflows can have the same effects if it contains clay particles. An underperforming sewage treatment plant could raise the conductivity level in the effluent because of the presence of chloride,

phosphate and nitrate. Further studies are recommended to identify the causes of poor water quality identified in this study and devise strategies to improve the overall water quality of the HNRS in future.

Conclusion

In this chapter, water quality of the Hawkesbury Nepean River System (HNRS) in New South Wales, Australia has been investigated. It is found that water quality at 9 stations fall under either poor or marginal category based on the Canadian Water Quality Index (CWQI) categorisation where the CWQI values are found to be in the range of 33 to 57. Marginal water quality is found for 5 stations, and poor water quality is found for the remaining 4 stations. None of the stations is found to have good quality water as per CWQI criteria. Stations N14 and N35 are found to be the most polluted stations in the HNRS among the 9 selected stations. With detailed investigation at the station N14, it is found that the higher values of water quality parameters: Nitrogen, Chlorophyll-a, Iron, Aluminium, Alkalinity and Conductivity have contributed to the poor water quality condition at N14. Further studies are recommended to investigate the underlying causes of the elevated pollution and to formulate management strategies to improve the overall water quality of the HNRS in near future.

References

1. Simeonov V, Stratis JA, Samara C, Zachariadis G, Voutsa D (2003) Assessment of the surface water quality in Northern Greece. See comment in PubMed Commons below Water Res 37: 4119-4124.

2. Pinto U, Maheshwari BL (2011) River health assessment in peri-urban landscapes: an application of multivariate analysis to identify the key variables. See comment in PubMed Commons below Water Res 45: 3915-3924.

3. Atech (2000) Cost of algal blooms. LWRRDC Occasional paper 26/99. Land and Water Resources Research and Development Corporation, Canberra, ACT, Australia. 42 pp.

4. Interlandi SJ, Crockett CS (2003) Recent water quality trends in the Schuylkill River, Pennsylvania, USA: a preliminary assessment of the relative influences of climate, river discharge and suburban development. See comment in PubMed Commons below Water Res 37: 1737-1748.

5. Wang X (2001) Integrating water-quality management and land-use planning in a watershed context. See comment in PubMed Commons below J Environ Manage 61: 25-36.

6. Tong ST, Chen W (2002) Modeling the relationship between land use and surface water quality. See comment in PubMed Commons below J Environ Manage 66: 377-393.

7. Lee JY, Yang JS, Kim DK, Han MY (2010) Relationship between land use and water quality in a small watershed in South Korea. See comment in PubMed Commons below Water Sci Technol 62: 2607-2615.

8. Tian J, Fernandez G (2000) Seasonal trend analysis of monthly water quality data. Doctoral dissertation, University of Nevada, Reno.

9. Kendall C A R O L, Elliott EM, Wankel SD (2007) Tracing anthropogenic inputs of nitrogen to ecosystems. Stable Isotopes in Ecology and Environmental Science 2: 375-449.

10. Yu J, Yu H, Fang H, Lei M, Li S (2014) Pollution characteristics of lead, zinc, arsenic, and cadmium in short-term storm water roof runoff in a suburban area. Toxicological and Environmental Chemistry 96(7): 1034-1046.

11. Ma J, Ding Z, Wei G, Zhao H, Huang T (2009) Sources of water pollution and evolution of water quality in the Wuwei basin of Shiyang river, Northwest China. See comment in PubMed Commons below J Environ Manage 90: 1168-1177.

12. Erturk A, Gurel M, Ekdal A, Tavsan C, Ugurluoglu A (2010) Water quality assessment and meta model development in Melen watershed - Turkey. See comment in PubMed Commons below J Environ Manage 91: 1526-1545.

13. Tabari, Hossein, Somee BS, Zadeh MR (2011) Testing for long-term trends in climatic variables in Iran. Atmospheric Research 100(1): 132-140.

14. Rahman A, Thomas E, Bhuiyan S, Goonetilleke A (2002) Modelling pollutant washoff from south-east Queensland catchments Australia. Proc. Enviro 2002 and International Water Association 3rd World Water Congress, A unique approach to a unique environment, Melbourne, 7-12 April 2002 .

15. Egodawatta P, Thomas E, Goonetilleke A (2009) Understanding the physical processes of pollutant build-up and wash-off on roof surfaces. See comment in PubMed Commons below Sci Total Environ 407: 1834-1841.

16. Van der Sterren M, Rahman A, Dennis G (2013) Quality and quantity monitoring of five rainwater tanks in Western Sydney, Australia. Journal of Environmental Engineering 139: 332-340.

17. Haddad K, Egodawatta P, Rahman A, Goonetilleke A (2013) Uncertainty analysis of pollutant build-up modelling based on a Bayesian weighted least squares approach. See comment in PubMed Commons below Sci Total Environ 449: 410-417.

18. de Rosemond S, Duro DC, Dubé M (2009) Comparative analysis of regional water quality in Canada using the Water Quality Index. See comment in PubMed Commons below Environ Monit Assess 156: 223-240.

19. Young TF, Sanzone S (2002) A Framework for Assessing and Reporting on Ecological Condition. US Environmental Protection Agency, EPA Science Advisory Board.

20. Commonwealth of Australia (1996) Australia. State of the Environment. CSIRO Publishing, Collingwood, Victoria.

21. Kaika M (2003) The water framework directive: A new directive for a changing social, political and economic European framework. European Planning Studies 11: 299-316.

22. Hong SH, Yim UH, Shim WJ, Oh JR, Viet PH (2008) Persistent organochlorine residues in estuarine and marine sediments from Ha Long Bay, Hai Phong Bay, and Ba Lat Estuary, Vietnam. See comment in PubMed Commons below Chemosphere 72: 1193-1202.

23. Bartram, Jamie, Balance R (1996) Water quality monitoring: a practical guide to the design and implementation of freshwater quality studies and monitoring programmes. CRC Press.

24. Yang W, Nan J, Sun D (2008) An online water quality monitoring and management system developed for the Liming River basin in Daqing, China. See comment in PubMed Commons below J Environ Manage 88: 318-325.

25. Singh KP, Malik A, Mohan D, Sinha S (2004) Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India)--a case study. See comment in PubMed Commons below Water Res 38: 3980-3992.

26. Štambuk-Giljanovic, Nives (1999) Water quality evaluation by index in Dalmatia. Water Research 33(16): 3423-3440.

27. Bordalo AA, Nilsumranchit W, Chalermwat K (2001) Water quality and uses of the Bangpakong River (eastern Thailand). See comment in PubMed Commons below Water Res 35: 3635-3642.

28. Boyacioglu H (2010) Utilization of the water quality index method as a classification tool. See comment in PubMed Commons below Environ Monit Assess 167: 115-124.

29. Horton RK (1965) An index-number system for rating water quality. Journal of Water Pollution Control Federation 37(3): 300-306.

30. Said A, Stevens DK, Sehlke G (2004) An innovative index for evaluating water quality in streams. See comment in PubMed Commons below Environ Manage 34: 406-414.

31. Brown, Robert M, McClelland N I, Deininger R A, Tozer R G (1970) A water quality index – do we dare.

32. Canadian Council of Ministers of the Environment (CCME) (2001) Canadian water quality guidelines for the protection of aquatic life: CCME Water Quality Index 1.0.

33. Zandbergen PA, Hall KJ (1998) Analysis of the British Columbia water quality index for watershed managers: A case study of two small watersheds. Water Quality Research Journal of Canada 33: 519–549.

34. Cude CG (2001) Oregon water quality index: A tool for evaluating water quality management effectiveness. Journal of American Water Resources Association 37(1): 125–137.

35. SAFE (1995) Strategic assessment of Florida's environment, Florida stream water quality index, statewide summary. online: http://www.pepps.fsu.edu/safe/environ/swq1.html.

36. Dede OT, Telci IT & Aral MM (2013) The use of water quality index models for the evaluation of surface water quality: a case study for Kirmir Basin, Ankara, Turkey, Water Quality. Exposure and Health 5(1): 41-56.

37. Technical Report. In: Canadian environmental quality guidelines (1999). Winnipeg: Canadian Council of Ministers of the Environment..

38. http://realtimedata.water.nsw.gov.au/water.stm?ppbm=212_hawkesbury&rs&2&rsvm_org

39. Markich SJ, Brown PL (1998) Relative importance of natural and anthropogenic influences on the fresh surface water chemistry of the Hawkesbury-Nepean River, south-eastern Australia. See comment in PubMed Commons below Sci Total Environ 217: 201-230.

40. Diamond R (2004) Water and Sydney's Future – Balancing the Value of Our Rivers and Economy. Final Report of the Hawkesbury-Nepean River Management Forum NSW: Department of Infrastructure, Planning and Natural Resources, Sydney.

41. Turner L, Erskine W D (2005) Variability in the development, persistence and breakdown of thermal, oxygen and salt stratification on regulated rivers of southeastern Australia. River Research and Applications 21(2-3): 151-168.

42. Roberts DE, Church AG, Cummins SP (1999) Invasion of Egeria into the Hawkesbury-Nepean River, Australia, Aquatic Plant Management 37: 31-34.

43. SMEC (1997) Options for sewage treatment and effluent disposal for west Hornsby and Hornsby Heights Sewage Treatment Plants, Prepared for Sydney Water, SMEC Australia.

Sewage Treatment Technology (E.G. Physical, Chemical and Biological Processes)

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Pollution of the aquatic environment and ubiquitous water quality deterioration is of major concern. Modern wastewater treatment systems include a complex of different physical, chemical and biological processes, which allow not just minimizing deterioration of water quality, but can also make possible the water reuse. Pollutants removal from wastewater can be achieved using different conventional treatment processes such as coagulation-flocculation, adsorption, ion exchange, precipitation, etc. However, in recent years biological methods of wastewater treatment have become increasingly popular. In the present chapter, the physical, chemical and biological techniques widely applied in wastewater treatment are discussed. Their advantages and limitations in application are also evaluated.
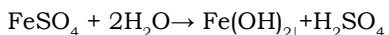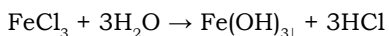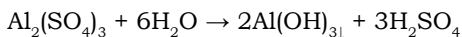
Introduction

The quality of the life is largely determined by the quality of the water. Today, in the epoch of the rapid industrialization and urbanizations, every day thousands of different chemicals are introduced in bodies of water. Natural water pollution is primarily caused by the discharge of insufficient treated or untreated industrial, domestic, and agricultural wastewater, which contain different inorganic, organic substances, solid suspended particles and microorganisms. Almost all countries worldwide have elaborated law and regulations for wastewater treatment in order to prevent natural water pollution and environmental damage. These legislative documents determine the maximal permissible concentration for different groups of specific chemicals. Unfortunately, current laws do not cover the entire spectrum of harmful substances as their quantities grow day to day. To remove pollutants from wastewater different physical, chemical and biological techniques are applied. Some of these methods have a wide application while other are applicable just for certain type of wastewater. The degree of wastewater treatment must be enough not just for its discharge in water body, but also for preparation of potable water and its repeated use in industrial processes. The correct combination of methods allows reducing the concentration of pollutants in treated wastewater to µg/L or mg/L. The common applied methods for wastewater treatment include coagulation-flocculation, adsorption, ion exchange, chemical precipitation, electrochemical treatment technologies membrane filtration, etc. The special place belongs to biological processes of wastewater treatment, as they are cost effective in

terms of energy consumption and chemical usage. The objective of the chapter is to provide an overview of physical, chemical and biological techniques widely applied for wastewater treatment.

Coagulation-Flocculation

Coagulation-flocculation is a well-known and widely applied method of removing particles, inorganic and organic matter, from wastewater [1,2]. The process can be divided in two distinct procedures: coagulation and flocculation. The process of coagulation consists of the introduction of a coagulant in water, which neutralizes the surface charge of suspended particles or colloidal systems, and facilitates particle aggregation and precipitation [3]. Coagulation is a short process, which occurs in period of about 120s [4]. The most commonly used coagulants are alum $Al_2(SO_4)_3 \cdot 14H_2O$ and ferric chloride ($FeCl_3 \cdot 6H_2O$) [1,4,5]. Their effectiveness is determined by the ability to form multi-charged polynuclear complexes with good adsorption characteristics. Colloidal, finely divided and suspended particles are adsorbed on the flocculated surface and form precipitates.

$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_{3\downarrow} + 3H_2SO_4$

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_{3\downarrow} + 3HCl$

$FeSO_4 + 2H_2O \rightarrow Fe(OH)_{2\downarrow} + H_2SO_4$

In order to reduce the consumption of coagulants coagulation process should be carried out in the range of optimal pH. The optimal pH value for $Al(OH)_3$- is 4.5-7 and 8-10 for $Fe(OH)_3$. The amount of coagulant necessary for the realization of a process depends also of coagulant type, wastewater composition and required level of wastewater purification. All this parameters are usually determined experimentally. Wide application of metal coagulants can be explained by relatively low cost and simple application route [4]. At the same time metal coagulant have a number of disadvantages, such as the need for pH control, the sensitivity to temperature changes, excessive sludge production, necessity of acid neutralization, and increasing of mineralization of treated wastewater [4,6]. At the low pH value mainly the colloidal substances with negative charges can be coagulated, for effective metal cations removal the pH need to be increased, however at high pH values the turbidity removal decreases [6] Nowadays, traditional inorganic agents have been largely replaced by organic coagulants, such as polyaluminum chloride, polyaluminium sulfates, polyaluminum sulfate chloride and forms of polyaluminum chloride with organic polimers [1,2,4].

The second sub-process flocculation involves the addition of floc-forming chemical reagents usually after coagulation to agglomerate non-settable and slow-settling colloidal solids, which thereby forms large agglomerates in the presence of polymeric materials, that can be easily separated through gravity settling [3,4]. In contrast to coagulation, flocculation occurs over a period of 20 to 45 min [4].

In dependence of polar group composition flocculants can be divided in:

- non-ionic – polymers, containing non-ionic groups: - OH, >CO (starch, hydroxyethyl cellulose, etc);
- anionic - polymers, containing anionic groups: -COOH, -SO₃H, OSO₃H (sodium polyacrylate, sodium alginate, ect);
- cationic - polymers, containing cationic groups: -NH₂, =NH (polyethylene imine, etc);
- amfoteric, containing both anionic and cationic groups (proteins, polyacrylamide, ect.) [7].

According to their origin, flocculants can be classified into two main categories: natural

and synthetic polymers. Natural polymers (biopolymers) have long been used as flocculants. Typical examples of bioflocculants are starch derivatives, guar gums, tannins, chitosan and the alginates. Despite the fact that bioflocculants are non-toxic flocculants, synthetic polymers have been found to be more widely applicable. Their applicability can be explained by their low price and the possibility of controlling their properties, such as the number and type of charged units and the molecular weight [4]. The continuous search of new materials with better characteristics compared to that of conventional coagulants and flocculants has led to the production of hybrid materials, with combined properties. Application of these materials allows conducting wastewater treatment with the addition of one chemical in one procedure instead of two-step conventional coagulation–flocculation process [3].

Adsorption

Adsorption is recognized as a cost effective and efficient method for wastewater treatment [8,9]. The process of adsorption can be described in three steps; (1) the transport of the pollutant from the bulk solution to the sorbent surface; (2) adsorption on the particle surface; (3) transport within the sorbent particle [8,10,11]. Adsorption can be of two types: physical and chemical. Physical adsorption appears due to relatively weak Van der Waal's forces. It is a reversible process, which take place on all sorbent surfaces and adsorption energy usually does not exceed 80 kJ/mol. Chemical adsorption (chemisorption) occurs by the way of chemical interaction of sorbent molecules and sorbate. It is irreversible, highly selective, single-layer process. In comparison to physical sorption chemisorption is localized, *i.e.* adsorbate molecule cannot move over the surface of the adsorbent. Since chemisorption is the chemical process it requires the activation energy of the order of 40 - 120 kJ/mol. Physical and chemical adsorption may occur on the surface at the same time [12].

Sorbents usually have a complex porous structure that consists of pores of different sizes and shapes. According to pores width they can be classified in three groups: micropores (< 2 nm), mesopores (2 -50 nm), and macropores (≥ 50 nm) [13]. The adsorbent may be of mineral, organic or biological origin. Activated carbon is one of the commonly used sorbents for removing a wide variety of pollutants from wastewater due to its large surface area and high adsorption capacity [14-16]. However, wide application of activated carbon produced on industrial scale is limited by its high price [10]. Agricultural wastes are one of the richest sources of relatively inexpensive sorbents [9,11]. Some studies have shown that activated carbon produced from agricultural wastes can be efficiently applied for the removal of pollutants from wastewater [9,17,18]. Frequently agricultural wastes can be used as biosorbents directly without any pretreatment [10,19,20]. Beside agricultural waste, an interesting and attractive alternative as adsorbents represent the biopolymers as starch, chitin, chitosan, etc. [8]. Furthermore, it is important to understand that during adsorption of the organic substances, they are simply transferred from one phase to another without destruction. It is therefore better to combine adsorption with biological treatment [15]. In case of heavy metals, they can be removed through the adsorption process and then further regeneration of the sorbent is necessary.

Ion-exchange

Ion exchange is another method, which is successfully used for removing pollutants such as metals, phosphate, nitrate, ammonia from wastewater. Ion exchange includes two stages: saturation and regeneration. During the first stage, wastewater passes through the column and the effluent free of the polluting ion is withdrawn at the column outlet. During this process the interchange of ions between a solution and an insoluble solid, which can be of natural or synthetic origin, takes place. The saturation is considered complete after the concentration of the pollutants in the outlet solution exceeds allowable concentration. Ion exchange is a reversible process and therefore after saturation, the resins can be regenerated by replacing the retained ions with ions of the regenerant [11,21].

In ion exchange systems, polymeric resins are usually employed, capable of exchanging either cation or anion forms of pollutants. Ion-exchanging resins can be generally divided in four groups: strongly acidic ($-SO_3H$), weakly acidic ($-COOH$), strongly basic ($-N^+R_3$) and weakly basic (amine $-N^+R_2H$ and $-N^+RH_2$) [22]. The performance of the cation exchange resins IRN77 and SKN1 in removing chromium from wastewater was investigated by Rengaraj et al., [23]. Obtained results have shown that IRN77 and SKN1 were capable of removing 100 mg/L chromium from aqueous solution to the extent of 98%. Two ion exchange resins Duolite ES 467 and a chelating ion-exchange resin (containing hydroxamic acid functional groups) were used for treatment of wastewater containing lead and iron [24]. Extraction of Cr (III) from a model solution and from a tannery waste solution was studied by ion exchange using Indion 790 resin, which is a macro-porous strongly acidic cation exchange resin of sulfonated polystyrene group [25]. Beside synthetic resins, natural materials (zeolites, clay, and soil humus) also can be used as ion-exchanger. The most frequently applied ion-exchangers are zeolites, which are naturally occurring hydrated aluminosilicate minerals. They have shown to have high affinity for several heavy metals such as lead, cadmium [26], copper, cobalt, zinc, manganese [27], and chromium [28].

The advantages of ion exchange processes are the low: process and regenerate cost, energy requirement, volume of sludge [23]. There are, however, a number of limitations as mechanical and chemical durability of the exchanger material, formation of highly concentrated sludge, which requires careful disposal and presence of competitive ions requiring more frequent resins regeneration [11,24].

Precipitation

Chemical precipitation is widely used and proven technique to remove heavy metals from wastewater. Metals can be removed by precipitation as metal oxides, hydroxides, sulfides, carbonates, and phosphates. Hydroxide treatment is based on reaction between the metal cations and alkaline reagents (CaO, $Ca(OH)_2$, $Mg(OH)_2$, $NaOH$, NH_4OH) [29-31] resulting in the formation of insoluble hydroxides [6]. The reaction takes place through the following mechanism:

$$M^{2+} + 2OH^- \leftrightarrow M(OH)_2\downarrow$$
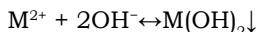
Viadero and co-authors [31] have shown that is more cost effective to use $NaOH$ and NH_4OH for metal precipitation, which form soluble by-products and further recovery of metals is possible. Since use of $Ca(OH)_2$ for acidic effluents leads to the formation of $CaSO_4 \cdot 2H_2O$, the quantity of sludge and the cost of their disposal is increased [30]. Hydroxide precipitation does not allow decreasing of the concentration of all metals presented in wastewater to the permissible levels because they do not precipitate at the same pH. Sulfide precipitation in contrast to hydroxide treatment offers some advantages, among them lower residual metal concentrations, high selectivity, and possibility of metal recovery. The process can be described by the reaction:

$$M^{2+} + S^{2-} \leftrightarrow MS\downarrow$$
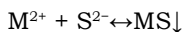
As precipitating agent substances like Na_2S, $NaHS$, H_2S, and FeS can be used. Disadvantages of this method can include the possibility of H_2S formation, high price of the process, and necessity of water pre- and post-treatment. In some studies sodium phosphate was used as precipitating agent but use of phosphate salts lead to the increase of the residual phosphorus concentration in the treated wastewater [6,32]. To improve the quality of wastewater treatment a two-step precipitation process can be applied. On the first stage as precipitating agent hydroxides are used followed by sulfide precipitation and solid sludge removal by physical methods. Marchioretto and co-workers [29] have shown that the addition of $NaOH$ as first precipitating agent reduced the addition of Na_2S by almost 200 times. The process of pollutant precipitation in some cases can be facilitated by the

addition of coagulants, which gather the insoluble metal compound particles into flocs that can settle rapidly by gravity. The drawbacks of all types of chemical precipitation processes can be considered to be the high amount of used chemicals and their cost, formation of a large volume of sludge, waste disposal, high cost of the equipment, work with corrosive chemicals, and increasing operator safety concerns [6,29,30].

Electrochemical methods

Various electrochemical methods such as electrocoagulation, electroflotation, electrochemical oxidation, electrochemical reduction, electrodeposition and electrodisinfection can be used for removal of pollutants from wastewater. In electrochemical methods the main role belongs to the electron. Electrochemical methods possess several benefits including environmental compatibility, adaptability, energy efficiency, safety, selectivity, possibility of complete automation, and cost effectiveness, less retention time, rapid sedimentation of the electrogenerated flocculants, less sludge production, and smaller space requirements and capital costs [33-36]. The main drawbacks of these methods are their high operating cost due to high-energy consumption, necessity of electrolyte addition in case of sewage with low conductivity, and the possibility of the formation of chlorine organic substances [37].

Electrocoagulation

Electrocoagulation is the process of colloidal system coagulation due to the action of direct current, which causes electrolytic dissociation of salts present in the system [33,38]. The metal ion generation takes place at the anode; hydrogen gas and hydroxide ions as well hydrogen gas are released from the cathode.

The electrocoagulation process includes three main stages:

(i)   Formation of coagulants by electrolytic oxidation of the electrode;

(ii)   Destabilization of the contaminant;

(i)   Flocs formation [34].

As an example the process on aluminum electrode can be seen in the following equations:

$Al \leftrightarrow Al^{3+} + 3e^-$ (anode)

$3H_2O + 3e^- \leftrightarrow 1.5H_2 + 3OH^-$ (catode) [33]
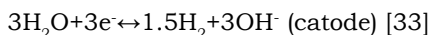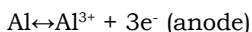
Aluminum ions and hydroxide ions form aluminum hydroxide flocs, which have large surface area and contribute to rapid sorption of organic/inorganic pollutants and colloidal particles [39].

$Al^{3+} + 3OH \rightarrow Al(OH)_3 \downarrow$
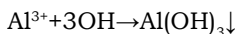
The hydrogen gas helps to remove the aluminum hydroxide flocs. The electrocoagulation is highly dependent on the sewage parameters as conductivity, pH, particle size, and pollutants concentration [38].

Electroflotation

Electroflotation is a process in which pollutants float to the surface of wastewater by bubbles generated from wastewater electrolysis according to the following reactions:

Anode reaction: water oxidation

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
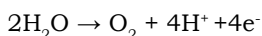
* Cathode reaction: water reduction

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [40,41]

Electrooxidation

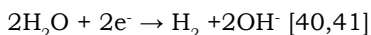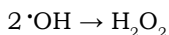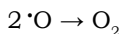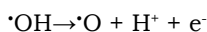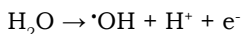Electrochemical oxidation of pollutants can take place through direct or indirect oxidation and can lead to the conversion of organic pollutants to CO_2, H_2O and other inorganic components. Direct oxidation occurs at anodes through the generation of physically adsorbed "active oxygen" and usually includes two steps (i) diffusion of pollutants from the bulk solution to the anode surface and (ii) the oxidation of pollutants at the anode surface [37,42,43]. Indirect electrochemical oxidation consists in the generation of a strong oxidizing agent at the anode surface followed by the destruction of the pollutants. The most used electrochemical oxidant is chlorine formed by the oxidation of chloride at the anode. In addition to chlorine, peroxide, Fenton's reagent, Cl_2, hypochlorite, peroxodisulfate and ozone can be used as oxidizing agents [37,42]. A key element of this technology is the anode material. In scientific reports the use of anode materials Pt, PbO_2, IrO_2 and SnO_2 has been reported. At the present, an attractive anode material for electrooxidation process is considered to be boron-doped diamond [43].

Electrodisinfection

Electrochemical wastewater disinfection is a process of eradication of microorganisms by using an electric current passed through the wastewater under treatment. Microorganisms can be electrochemically inactivated either directly or via the generation of active chemical species, such as $^\bullet OH$ radicals or OCl^- ions. In many cases is difficult to distinguish this processes, as both of them play significant role in microorganisms inactivation. Direct inactivation consists in the electrosorption of bacteria on the electrode surface and their subsequent destruction. The process can be applied for disease-related microorganism removal and prevention of infection-related problems [42,44]. Between processes with participation of active chemical species, the most popular is electrochlorination, characterized by on-site generation of disinfectants. The active chlorine species responsible for microorganisms inactivating can be produced by the following reactions:

$2Cl^- \rightarrow Cl_2 + 2e^-$

$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^-$

$Cl_2 + 4H_2O \rightarrow 2ClO_2 + 8H^+ + 8e^-$
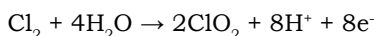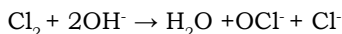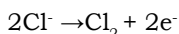
Together with electrochlorination high disinfecting power possesses reactive oxygen species: hydroxyl radical, atomic oxygen, hydrogen peroxide, and ozone, which can be generated in the following way:

$H_2O \rightarrow {}^\bullet OH + H^+ + e^-$

${}^\bullet OH \rightarrow {}^\bullet O + H^+ + e^-$

$2\, {}^\bullet O \rightarrow O_2$

$2\, {}^\bullet OH \rightarrow H_2O_2$

$O_2 + {}^\bullet O \rightarrow O_3$ [42,44]
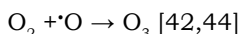
Efficiency of the disinfection process is strongly dependent of electrode material. Anode materials include platinised titanium or niobium, tantalum, graphite, carbon, metal oxides, silver, copper, and nickel, etc. [44]. In comparison with other electrode materials, conductive-diamond has shown a higher chemical and electrochemical stability, and also a higher current efficiency in many oxidative processes [45]. As material for cathode mainly stainless steel, copper, graphite, and carbon are used [44]. The main mechanisms of microorganism inactivation can be considered: oxidative stress caused by electrochemically generated oxidants, permeabilization of cell membranes and oxidation of vital cellular constituents due to exposure to electric current [44].

Membrane Processes

Reverse osmosis, ultrafiltration, microfiltration, and nanofiltration are the most commonly applied membrane techniques for wastewater treatment.

Reverse osmosis

In comparison with traditional techniques, reverse osmosis is considered as highly efficient technique for pollutants removal [46]. The principle of reverse osmosis consists of the separation of solutions with different concentrations by a semipermeable membrane at high pressures (2,000–10,000 kPa). Pressure is applied on the side of the concentrated solution to reverse the natural osmotic flow. Membranes used in reverse osmosis are semipermeable allowing fluid that is being purified to pass through them and preventing the passage of solutes (such as salt ions) [46-48]. The retention of ions is typically in the range 95–99.9% depending on the ions and the membrane. The reverse osmosis process is used for the production of pure water for industrial, medical and pharmaceutical purposes. The reverse osmosis technique is applicable for separation, concentration and fractionation of organic as well as or inorganic substances [46,49]. However, reverse osmosis systems have some limitations. The operating range of reverse osmosis falls in the order of a nanometer and method is not very efficient for solutions of high contaminant concentration. A polyamide thin-film composite membrane TW30-181 2-50 has been showed to be efficient for $Cu(NO_3)_2$, $CuSO_4$, $ZnSO_4$ and $Ni(NO_3)_2$ removal [48]. Reverse osmosis membrane modules (Module no. 1 and Module no.2) were applied for rejection of all forms of arsenic present in the feedwater [49]. A thin film composite spiral wound type membrane was studied for its ability to reject the Cu^{2+} and Ni^{2+} from single-salt and mixed-salt systems. The experimental results indicated that due to larger ionic size Cu^{2+} removal from the model solutions was more than Ni^{2+}. Addition of chelating agent disodium salt ethylene diamine tetraacetic acid (Na_2EDTA) significantly increased the ions rejection efficiency in the removal process by the used membrane [46]. Ultra-low pressure reverse osmosis membrane (ES20) was applied for divalent and hexavalent heavy metals ions extraction from solution at different operating parameters: pressure, feed concentration, pH, and effect of other ions. The rejection of heavy metal found to be greater than 95% for the tested membrane [50]. In Ujang et al., work [51] the efficiency of Zn^{2+} and Cu^{2+} removal by low-pressure composite membranes achieved up to 99% removal.

Nanofiltration

In nanofiltration process, solute separation through membranes takes place mainly due to electro-static interaction of membrane and solutes on the membrane surface and size exclusion [52]. In comparison with reverse osmosis, nanofiltration membranes are operated at lower pressure values 700-3,000 kPa. Pores of size 2-5 nm lead monovalent ions and low-molecular-weight organic molecules to pass through the membrane [47]. A series of experiments was carried out for the separation of hexavalent chromium by nanofiltration membranes by adding cationic, anionic and non-ionic surfactants. Results showed enhancement in the separation of chromium from 97 to 99.5%, even with a very low concentration of cationic surfactant additions and no change in the permeate flux was observed for anionic and non-ionic surfactants [53]. Retention of five metal solutions (Cd(II), As(III), Cu(II), Mn(II), Pb(II)) was investigated using the nanofiltration membrane NF270 by Al-Rashdi et al., [54]. The effect of the pressure, initial metal concentration and pH was studied. The NF270 membrane rejected almost 100% of copper ions at low copper concentrations in solution. However, with the increase of copper concentrations in solution the membrane rejection effectiveness decreased. For cadmium, manganese and lead at their concentrations in solution 1000 mg/L degree of purification was 99%, 89% and 74%, respectively. The lowest removal efficiency for the NF270 membrane was shown to be for arsenic. Reverse osmosis and nanofiltration technologies were applied for copper

and cadmium removal from wastewater [55]. Comparison of two techniques showed that reverse osmosis was more efficient for the studied metals removal. Beside single-metal systems, studied techniques can be applied for complex systems as well. The degree of sewage purification in case of reverse osmosis achieved 99.4% removal of pollutants, and for nanofiltration it was 97%.

Ultrafiltration

Ultrafiltration allows for the separation of macromolecules and suspended solids with molecular weights from 1000 to 100,000 Da from solutions using membranes with pores sizes of 1 to 100 nm [47,52]. During the process of utrafiltration, lower-molecular-weight compounds and water pass through the membrane while higher-molecular-weight compounds remain on the membrane. The copolymer of maleic acid and acrylic acid (PMA-100), combined with a Polyvinyl Butyral (PVB) hollow fiber ultrafiltration membrane was applied in a complexation–ultrafiltration process for the removal of heavy metal ions Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}, from an aqueous solution [56]. For the solution with metal ion concentrations of 10 mg/L, at pH 6.0, a dosage of 60-70 mg/L with the copolymer could ensure removal efficiency above 98.8%.

Polyethersulfone (FUS 0181) was used as an ultrafiltration membrane and carboxy methyl cellulose as a metal complexing agent for the removal of Cu (II), Ni(II), and Cr III) ions from synthetic wastewater solutions in a study by Barakat and E. Schmidt [57]. It was found that the complexation and filtration processes are pH dependent; the metal rejection was more efficient at neutral and alkaline conditions than at acidic ones. The metal rejection efficiency values, with initial metal ion concentration of 10 mg/L, were 97.6, 99.5 and 99.1% for Cu (II), Cr (III), and Ni (II), ions, respectively at pH 7. The membrane had worked efficiently on a wide range of concentrations up to 100 mg/L for both Cu (II) and Cr (III) ions, while the Ni (II) ions' rejection efficiency decreased to 57%.

In a study by Vieira et al., [58], metal removal from pulp and paper industry wastewater was conducted by coupling complexation with water-soluble polymeric ligands and an ultrafiltration process. Metal retention was not significant when only ultrafiltration (polyvinilidene fluoride membrane) was used. To increase the efficiency of the process, polyethyleneimine and polyvinylalcohol were used as water-soluble polymeric macroligands.

Microfiltration

Microfiltration is the membrane process, which is more comparable to both ultrafiltration and conventional coarse filtration. The pore size of a microfiltration membranes ranges between 0.02 and 10 µm. [47,59]. Microfiltration is applied when pollutant removal by sedimentation, centrifugation, and/or depth filtration is difficult or not cost efficient. Herzberg et al., [60] showed what microfiltration could be used as pretreatment step to reduce the fouling of reverse osmosis membranes due to the removal of particulate/colloidal matter. The microfiltration process using ceramic membrane (α-Al_2O_3) with pore size 50 nm was successfully applied for the oily wastewater treatment by Hua et al., [61]. The influence of parameters such as transmembrane pressure, cross-flow velocity, oil concentration in feed, as well as pH and salt concentrations on separation behaviors were studied. The high degree of sewage purification was achieved under high trans membrane pressure and cross-flow velocity and low oil concentration.

Zeolite microfiltration membranes NaA/α-Al_2O_3 with pore sizes of 1.2 µm, 0.4 µm and 0.2 µm were applied for the oily water treatment. Better than 99% oil rejection was obtained for oil-in-water emulsion containing 100 mg/L oil using membranes with pore sizes of 1.2 µm and 0.4 µm [62].

Advanced oxidation

Advanced oxidation is a process of hydroxyl radical generation for the oxidation of chemicals presented in wastewater. Hydroxyl radicals are; very reactive short-lived oxidants with an oxidation potential of 2.33V, able to oxidize pollutants into mineral products, and yield CO_2 and inorganic ions [63,64]. Hydroxyl radicals react mostly with organic and partially with inorganic solutes with high rate constants, and have been shown to be more effective than oxidizing agents such as ozone and hydrogen peroxide [65].

Hydroxyl radicals (OH·) may be produced in systems using: cavitation, photochemical initiation (homogenous photochemical degradation, Fenton-based reactions, titanium dioxide/ultraviolet radiation) [63,65]. Cavitation is the phenomena of the formation, growth and subsequent "clapping" of microbubbles occurring in an extremely small interval of time (milliseconds), and subsequently releasing large magnitudes of energy [65]. In the clapping moment, several processes take place: electric discharge, particle ionization and chemical bond breakage. The size of bubbles is between 1-10 μ, when its surface is covered with surfactant [7]. There is practically no water in the nature without such bubbles. The photo-activated chemical reactions are based on the interaction of photons of a proper energy level with the molecules of chemicals presented in sewage, in the presence or absence of a catalyst. The radicals can be easily produced using UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone.

$$H_2O_2 + h^\nu \rightarrow 2\,^\cdot OH$$
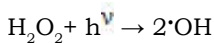
The rate of H_2O_2 photolysis is pH dependent and increases in alkaline conditions [64].

Free radicals can be obtained by heterogeneous photocatalysis, and can be accelerated by the action of a catalyst like TiO_2. Light irradiation of the catalyst leads to transition of electrons from the valence to the conduction band. In particular, both migrating electrons and the holes created in the valence band can participate in redox reactions with compounds absorbed on the photocatalyst [64].

$$TiO_2 \rightarrow TiO_2{}^* + e_{aq}^- \,[\rightarrow O_2^-]$$
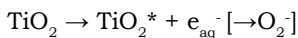
The use of Fenton's reagent (hydrogen peroxide in the presence of a ferrous salt) allows for the obtainment of reactive oxidizing species, which possess the ability to destroy pollutants from sewage [65].

$$FeOH^{2+} + h^\nu \rightarrow Fe^{2+} + OH^-$$

$$FeOR^{2+} + h^\nu \rightarrow Fe^{2+} + RO \; [7]$$
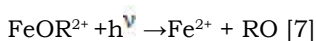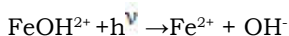
Advanced oxidation processes are more efficient, cheap, and ecofriendly in the degradation of any kind of toxic pollutants and can be used in the pre- and/or post-treatment of biological systems. In general, all conventional methods of pollutants removal suffer from a few major disadvantages such as high-energy requirements, generation of toxic sludge, incomplete metal removal and low efficiency at pollutant concentrations less than 10-100 mg/L. There is thereby a growing interest in biological methods of wastewater treatment, which require less energy and are considered environmentally friendly.

Biological Methods

Biological methods are an important and integral part of any wastewater treatment plant and can be divided into aerobic and anaerobic ones. There are multitudes of aerobic and anaerobic biological treatment processes mainly applied for organic substances mineralization. The most used installation for aerobic wastewater treatment are aeration tanks. Aeration tank represents a reservoir equipped with aeration device where wastewater is mixed with activated sludge. Aeration is carried out with the scope to saturate wastewater

with oxygen necessary for active sludge microorganisms activity. The activated sludge of the aeration basin of a wastewater treatment plant is a complex ecosystem of competing organisms (actinomycetes, alga, viruses and other aerobic microorganisms) [7,66]. In aeration tank, the bacteria or other microorganisms are concentrated in the flocculent material of the activated sludge. The flocs of porous structure are formed from aggregates of organic polymers which are supposed to be secreted by bacteria. The microorganisms are adsorbed on to the internal and external surfaces of the floc. Immediately after the wastewater enters the aeration tank the fine particulates, colloidal particles and large molecules, are adsorbed on the floc material [67]. The efficiency of wastewater treatment is mainly determined by the microorganism's type. The main role in wastewater treatment is played by bacteria. During the microbial degradation, pollutants are transformed to non-toxic or less toxic compounds since microorganisms use organic compounds as source of nutrients and energy [68,69]. Mono- di- and tri-atomic alcohols, organic acids, hydrocarbons, aldehydes are easily subjected to biochemical oxidation, more difficult aromatic compounds and surfactants [7]. However, in case of some substances, for example polycyclic aromatic hydrocarbons they could be transformed into compounds that are more toxic. The biodegradation is a complex process, which depends on the organic compounds' chemical structure, physical state, and toxicity. With the time activated sludge becomes used to environmental conditions and wastewater composition, and change of parameters as: decrease of oxygen concentration, high amount of toxic compounds, and lack in nitrogen and phosphorus lead to the sludge disease and the need of sludge replacement arises. Usually the time of wastewater contact with activated sludge is 12-24 h [7]. Anaerobic wastewater treatment is an energy-efficient process that is typically utilized to treat wastewaters with high concentrations of biodegradable organic matter. In contrast to aerobic treatment, anaerobic treatment does not require oxygen input and is characterized by generation of small amount of sludge [70], which can be used as fertilizer.

Anaerobic wastewater treatment includes three stages:

- Hydrolysis of organic compounds;

- Acetogenesis and acids formation – formation of organic acids, alcohols, aldehides, etc.;

- Methanogenesis -fermentation of organic compounds, resulting in methane production.

$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ [7,71].}$$

During the fermentation process, energy-rich organic compounds are oxidized while other organic and inorganic compounds are used as the electron acceptors. Despite the high efficiency of organic pollutants biodegradation the anaerobic water treatment process has some disadvantages such as low rate of microorganisms growth, formation of ammonium ion and hydrogen sulfide, need of purified effluents aerobic post-treatment [71]. For this reason is better to use multi-unit anaerobic–aerobic systems for wastewater treatment.

Biological methods are often applied for purification of wastewater containing nitrogen compounds by mean of nitrification and dynitrification. Usually nitrogen is presented in the wastewater in the form of ammonium and organic compounds, containing nitrogen in the ratio 1:5.

Nitrification is the aerobic biological process of ammonia conversion to nitrite and then to nitrate. Nitrification can be achieved at low organic loadings and where suitable environmental conditions are provided: temperature,C:N:P ratio, oxygen supply, pH. Microbial strains Nitrosomonas and Nitrobacter are responsible for nitrification process, which can be described by the following reactions:

$NH_4^+ + 1.5O_2 \rightarrow NO_2 + 2H^+ + H_2O$ (I)

$NO_2^- + 0.5O_2 \rightarrow NO_3^-$ (II) [7,72]
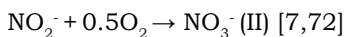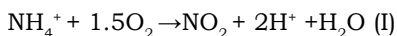
Under anaerobic conditions, microbiological reduction of nitrates take place via denitrification process. For denitrification process very important is the presence of biodegradable carbon in the medium.

$NO_3^- + CH_3OH \rightarrow N_2 + CO_2 + H_2O$ [7,72]
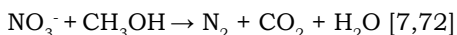
Depending of the level of wastewater pollution with nitrogen compounds different installations are used for its purification [7]. In case of metal removal from wastewater using biological objects the special emphasis is given to biosorption and bioaccumulation processes.

Biosorption

Biosorption is relatively rapid, simple, cost-efficient and environmentally friendly technique for pollutant removal, especially from diluted solutions, and carries the possibility of metal recovery. The principle of method consists of the interaction of metal ions with functional groups present on the cell surface (biosorbent). As biosorbents naturally abundant biomass, residual biomass of different industry or biomass grown on the cheap cultivation media can be used. Use of different techniques, especially FT-IR spectroscopy, have shown that carboxyl, hydroxyl, sulfate, sulfhydryl (thiol), phosphate, amino, amide, imine, thioether, phenol, carbonyl (ketone), imidazole, phosphonate groups are the main site of metal binding on the microbial surface [73-75]. The process of biosorption is strongly influenced by temperature, type and concentration, and oxidation state of metal, composition and pH of sewage, type of microorganisms and mechanism of metal removal, concentration of biosorbent, etc. Metal ions capture in biosorption processes can take place through several mechanisms, such as: adsorption, ion exchange; metal ion complexation with biomass components, electrostatic attraction or microprecipitation. Biosorption is a metabolically-passive process and can be carried out using dead biomass [68,74].

Bioaccumulation

Bioaccumulation is the irreversible process of pollutant uptake by living biomass and the subsequent incorporation of the pollutants within the inner cellular structures. Bioaccumulation can be described as two-step process. In the first stage, pollutants are bound to the functional groups on the cell surface. The second stage consists of pollutants penetrating inside the cell [74,76]. Microorganisms have developed several mechanisms of resistance to pollutant action, such as: metal enzymatic reduction to less toxic forms; excretion of organic acids and proteins with the ability of pollutants immobilization; microprecipitation, and intracellular chelation by metallothionein proteins and glutathione-derived-peptides called phytochelatins. An important role in the bioaccumulation process plays low molecular weight proteins, called metallothioneins, which are rich in thiol groups. These molecules can exclude metals from metabolic reactions though binding them in non-biologically active forms [77]. As well as biosorption, bioaccumulation process depends on many factors, which include: temperature, pollutant form and concentration, characteristics of the organism, and substrate composition [68,74]. Bioaccumulation processes require high expenditure for the maintenance of the microorganism's vitality during the contact with pollutants, thus for large-scale applications, it is more preferable to use biosorption processes.

Conclusion

The wastewater treatment is a complex process. There is no unique technique that can be used for pollutants removal. Some methods like precipitation, ion exchange are

applicable for metal removal while other e.g. biological methods are more suitable for organic compounds biodegradation. For highly polluted wastewater, it is recommended to use coagulation–flocculation, precipitation techniques and biological purification. Ion exchange and adsorption techniques show the best efficacy at pollutants concentration in the range of <10–100 mg/L. High cost techniques such as advance oxidation, electrochemical and membrane methods are suitable for special technological tasks. Considering the energy consumption and cost of physical and chemical methods recently a growing interest represents biological methods of wastewater treatment.

Acknowledgment

References

1. Dovletoglou O, Philippopoulos C, Grigoropoulou H (2002) Coagulation for treatment of paint industry wastewater. See comment in PubMed Commons below J Environ Sci Health A Tox Hazard Subst Environ Eng 37: 1361-1377.

2. Sinha S, Yoon Y, Amy G, Yoon J (2004) Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. See comment in PubMed Commons below Chemosphere 57: 1115-1122.

3. Lee KE, Morad N, Teng TT, Poh BT (2012) Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review. Chem Eng J 203:370–386.

4. Tzoupanos ND, Zouboulis AI (2008) Coagulation-flocculation processes in water/wastewater treatment: the application of new generation of chemical reagents. Proceedings of the 6th IASME/WSEAS International Conference on Heat Transfer, Thermal Ingineering and Environment (HTE'08), 309-317.

5. van Benschoten JE, Edzwald JK (1990) chemical aspects of coagulation using aluminum salts I. Hydrolytic reactions of alum and polyaluminum chloride. War Res 24:1519-1526.

6. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. See comment in PubMed Commons below J Environ Manage 92: 407-418.

7. Duca G, Scurlatov Yu (2002) Ecological chemistry. Publishing Center M.S.U., Chisinau.

8. Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog Polym Sci 30:38-70.

9. Chiban M, Soudani A, Sinan F, Persin M (2012) Wastewater treatment by batch adsorption method onto micro-particles of dried Withania frutescens plant as a new adsorbent. See comment in PubMed Commons below J Environ Manage 95 Suppl: S61-65.

10. Berrios M, Martin MA, Martin A (2012) Treatment of pollutants in wastewater: Adsorption of methylene blue onto olive-based activated carbon. J Ind Eng Chem 18:780-784.

11. Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arabian J Chem 4: 361–377.

12. Webb PA (2003) Introduction to Chemical Adsorption Analytical Techniques and their Applications to Catalysis. MIC Technical Publications 1-12.

13. Dabrowski A (2001) Adsorption--from theory to practice. See comment in PubMed Commons below Adv Colloid Interface Sci 93: 135-224.

14. Pereira MFR, Soares SF, Órfão JJM, Figueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon 4:811–821.

15. Shen L, Liu Y, Xu HL (2010) Treatment of ampicillin-loaded wastewater by combined adsorption and biodegradation. J Chem Technol Biotechnol 85: 814–820.

16. Hu Zh, Lei L, Li Y, Ni Y (2003) Chromium adsorption on high-performance activated carbons from aqueous solution. Sep Purif Technol 31:13–18.

17. Abdel Salam OE, Reiad NA, ElShafei MM (2011) A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J Adv Res 2: 297–303.

18. Singh KP, Malik A, Sinha S, Ojha P (2008) Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material. See comment in PubMed Commons below J Hazard Mater 150: 626-641.

19. Bulut Y, Tez Z (2007) Removal of heavy metals from aqueous solution by sawdust adsorption. See comment in PubMed Commons below J Environ Sci (China) 19: 160-166.

20. Nurchi VM, Villaescusa I (2008) Agricultural biomasses as sorbents of some trace metals. Coord Chem Rev 252:1178–1188.

21. Bochenek R, Sitarz R, Antos D (2011) Design of continuous ion exchange process for the wastewater treatment. Chem Eng Sci 66:6209-6219.

22. Hubicki Z, Kolodyn´ska D (2012) Selective removal of heavy metal ions from waters and waste waters using ion exchange methods. In Kilisliog?lu A (ed), Ion Exchange Technologies. InTech, ISBN 978-953-51-0836-8

23. Rengaraj S, Yeon KH, Moon SH (2001) Removal of chromium from water and wastewater by ion exchange resins. See comment in PubMed Commons below J Hazard Mater 87: 273-287.

24. Srinivasa Rao K, Dash PK, Sarangi D, Chaudhury GR, Misra VN (2005) Treatment of wastewater containing Pb and Fe using ion-exchange techniques. J Chem Technol Biotechnol 80:892–898.

25. Sahu SK, Meshram P, Pandey BD, Kumar V, Mankhand TR (2009) Removal of chromium(III) by cation exchange resin, Indion 790 for tannery waste treatment. Hydrometallurgy 99:170-174.

26. Curkovic L, Cerjan-Stefanovic S, Filipan T (1997) Metal ion exchange by natural and modified zeolites. War Res 31:1379-1382.

27. Erdem E, Karapinar N, Donat R (2004) The removal of heavy metal cations by natural zeolites. See comment in PubMed Commons below J Colloid Interface Sci 280: 309-314.

28. de Barros MASD, Machado NRCF, Alves FV, Sousa-Aguiar EF (1997). Ion exchange mechanism of Cr+3 on naturally occurring clinoptilolite. Braz J Chem Eng 14:

29. Marchioretto MM, Bruning H, Rulkens W (2005) Heavy metals precipitation in sewage sludge. Separ Sci Technol 40: 3393-3405.

30. Blais JF, Djedidi Z, Ben Cheikh R, Tyagi RD, Mercier G (2008) Metals Precipitation from Effluents: Review. Pract Period Hazard Toxic Radioact Waste Manage 12:135-149.

31. Viadero RC, Wei XC, Buzby KM (2006) Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization. Environ Eng Sci 23:734-743.

32. López-Maldonado EA, Oropeza-Guzman MT, Jurado-Baizaval JL, Ochoa-Terán A (2014) Coagulation-flocculation mechanisms in wastewater treatment plants through zeta potential measurements. See comment in PubMed Commons below J Hazard Mater 279: 1-10.

33. Bazrafshan E, Kord Mostafapour F, Farzadkia M, Ownagh KA, Mahvi AH (2012) Slaughterhouse wastewater treatment by combined chemical coagulation and electrocoagulation process. See comment in PubMed Commons below PLoS One 7: e40108.

34. Al Aji B, Yavuz Y, Koparal AS (2012) Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes Separ Purif Technol 86:248-254.

35. Qin X, Yang B, Gao F, Chen G (2013) Treatment of restaurant wastewater by pilot-scale electrocoagulation-electroflotation: optimization of operating conditions. J Environ Eng 139: 1004-1016.

36. Karichappan T, Venkatachalam S, Jeganathan PM (2014) Optimization of electrocoagulation process to treat grey wastewater in batch mode using response surface methodology. See comment in PubMed Commons below J Environ Health Sci Eng 12: 29.

37. Anglada A, Urtiag A, Ortiz I (2009) Contributions of electrochemical oxidation to wastewater treatment: fundamentals and review of applications. J Chem Technol Biotechnol 84:1747–1755.

38. Yavuz Y (2007) EC and EF processes for the treatment of alcohol distillery wastewater. Sep Purif Technol 53:135-140.

39. Dermentzis K, Valsamidou E, Lazaridou A (2011) Nickel removal from wastewater by electrocoagulation with aluminum electrodes. J Eng Sci Technol. Review 4:188-192.

40. Ksentini I, Ben Mansour L (2014) Modeling the hydrodynamic of an electroflotation column for the treatment of industrial wastewaters. Desalin Water Treat 1-6, doi: 10.1080/19443994.2014.950989.

41. Chen G, Hung YT (2007) Electrochemical Wastewater Treatment Processes. Advanced Physicochemical Treatment Technologies, Handbook of Environmental Engineering, pp 57-106.

42. Martínez-Huitle CA, Ferro S (2006) Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. See comment in PubMed Commons below Chem Soc Rev 35: 1324-1340.

43. Dimitrijevic SB, Dimitrijevic SP, Vukovic MD (2013) modern water treatment by electrochemical oxidation - a review. Proceedings of International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2013.

44. Ghernaouta D, Ghernaoutb B (2010) From chemical disinfection to electrodisinfection: The obligatory itinerary? Desalin Water Treat 16:156–175.

45. Canizares P, Saez C, Sanchez-Carretero A, Rodrigo MA (2009) Synthesis of novel oxidants by electrochemical technology. J Appl Electrochem 39:2143-2149.

46. Mohsen-Nia M, Montazeri P, Modarress H (2007) Removal of Cu^{2+} and Ni^{2+} from wastewater with a chelating agent and reverse osmosis processes. Desalination 217:276-281.

47. Vigneswaran S, Ngo HH, Chaudhary DS, Hung YT (2004) Physico–chemical treatment processes for water reuse. In: Wang LK, Hung YT, Shammas NK (Eds.), Physicochemical Treatment Processes. Humana Press, New Jersey, pp. 635-676.

48. Bakalár T, Búgel M, Gajdošová L (2009) Heavy metal removal using reverse osmosis Acta Montanistica Slovaca 14:250-253.

49. Pawlak Z, Zak S, Zablocki L (2006) Removal of Hazardous Metals from Groundwater by Reverse Osmosis. Polish J Environ Stud 15:579-583.

50. Ozaki H, Sharmab K, Saktaywirf W (2002) Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters. Desalination 144:287-294.

51. Ujang Z, Anderson GK (1996) Application of low-pressure reverse osmosis membrane for Zn^{2+} and Cu^{2+} removal form wastewater. War Sci Tech. 34:247-253.

52. Kurniawan TA, Chan GYS, Lo WH, Babel S (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals. Chem Eng J 118: 83-98.

53. Muthukrishnan M, Guha BK (2006) Heavy metal separation by using surface modified nanofiltration membrane. Desalination 200:351-353.

54. Al-Rashdi BAM, Johnson DJ, Hilal N (2012) Removal of heavy metal ions by nanofiltration. Desalination 315: 2-17.

55. Abu Qdaisa H (2004) Removal of heavy metals from wastewater by membrane processes: a comparative study. Hassan Moussa. Desalination 164:105-110.

56. Qiu YR, Mao LJ (2013) Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid. Desalination 329:78-85.

57. Barakat MA, Schmidt E (2010) Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. Desalination 256:90-93.

58. Vieira M, Tavares CR, Bergamasco R, Petrus JCC (2001) Application of ultrafiltration-complexation process for metal removal from pulp and paper industry wastewater. J Membr Sci 194: 273-276.

59. Al-Malack MH, Anderson GK (1997) Use of crossflow microfiltration in wastewater treatment. War Res 31:3064-3072.

60. Herzberg M, Berry D, Raskin L (2010) Impact of microfiltration treatment of secondary wastewater effluent on biofouling of reverse osmosis membranes. See comment in PubMed Commons below Water Res 44: 167-176.

61. Hua FL, Tsang YF, Wang YJ, Chan SY, Chua H, et al. (2007) Performance study of ceramic microfiltration membrane for oily wastewater treatment. Chem Eng J 128:169-175.

62. Cui J, Zhang X, Liu H, Liu S, Yeung KL (2008) Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water. J Membr Sci 325:420-426.

63. Swaminathan M, Muruganandham M, Sillanpaa M (2013) Advanced oxidation processes for wastewater treatment. Int J Photoenergy ID 683682, 3 pages.

64. Cesaro A, Naddeo V, Belgiorno V (2013) Wastewater treatment by combination of advanced oxidation processes and conventional biological systems. J Bioremed Biodeg 4:8.

65. Gogate PR, Pandit AB (2004) A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. Adv Environ Res 8:501–551.

66. Mittal A (2011) Biological Wastewater Treatment. Water Today 32-44.

67. Spencer Davies P (2004) The Biological Basis of Wastewater Treatment. Strathkelvin Instruments Ltd, 20 p.

68. Wu Y, Li T, Yang L (2012) Mechanisms of removing pollutants from aqueous solutions by microorganisms and their aggregates: a review. See comment in PubMed Commons below Bioresour Technol 107: 10-18.

69. Zeyaullah M., Abdelkafe AS, Zabya WB, Arif Ali (2009) Biodegradation of catechols by microorganisms – A short review. Afr J Biotechnol 8:2916-2922.

70. van Lier JB, Mahmoud N, Zeeman G (2008) Anaerobic Wastewater Treatment: Henze M, van Loosdrecht MCM, Ekama GA, Brdjanovic D (eds). Biological water treatment.Principles Modelling and Design. IWA Publishing, London, UK, pp. 401-439.

71. Chan YJ, Chong MF, Law CL, Hassell DG (2009) A review on anaerobic–aerobic treatment of industrial and municipal wastewater. Chem Eng J 155:1-18.

72. Breisha GZ (2010) Bio-removal of nitrogen from wastewaters-A review. Nature and Science 8:210-228.

73. Javanbakht V, Alavi SA, Zilouei H (2014) Mechanisms of heavy metal removal using microorganisms as biosorbent. See comment in PubMed Commons below Water Sci Technol 69: 1775-1787.

74. Chojnacka K (2009) Biosorption and bioaccumulation in Practice. Nova Science Publishers, Inc, New York. ISBN: 978-1-60876-408-2 (e-book).

75. Zinicovscaia I, Cepoi L, Chiriac T, Rudi L, Culicov OA, et al. (2015) Spirulina platensis as biosorbent of chromium and nickel from wastewaters. Desalin Water Treat doi: 10.1080/19443994.2015.1042061.

76. Das K, et al. (2008) Biosorption of heavy metals-An overview. Indian J Biotechnol 7:159-169.

77. Mishra A, Malik A (2013) Recent Advances in Microbial Metal Bioaccumulation. Crit Rev Environ Sci Technol 43:1162–1222.

Water Treatment Technologies: Principles, Applications, Successes and Limitations of Bioremediation, Membrane Bioreactor and the Advanced Oxidation Processes

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Abstract

The release and accumulation of organic and inorganic pollutants in the environment by natural and anthropogenic sources have led to serious environmental problems; this subsequently results to adverse effects on human health and wildlife. Therefore, to prevent the harmful effects of environmental contaminants, the development of newer and/or combined technologies for the remediation of contaminated water and wastewaters has been of great importance. This chapter presents bioremediation, membrane bioreactor and the Advanced Oxidation Processes (AOPs) as other forms of water and wastewater treatment technologies. Bioremediation and membrane bioreactor are ecofriendly, effective and cheap methods of detoxification. The AOPs have also emerged as a set of versatile water and wastewater treatment techniques. AOPs have been widely applied for the removal of a wide range of contaminants including pharmaceuticals, dyes, surfactants, pesticides, herbicides, disinfection by-products, endocrine disrupting chemicals etc. However, there are still ongoing investigation on the impact of the oxidants used, nanoparticles/catalysts, and resultant metabolites on human health and the environment.

Keywords: Advanced Oxidation Processes; Bioremediation; Catalysis; Membrane Bioreactor; Nanotechnology; Phytoremediation; Sonolysis

Introduction

In the last three decades, concerns about environmental pollution have increased around the world and this has resulted in the promulgation of more restrictive environmental laws.

With the development of more advanced analytical techniques for the identification and quantification of pollutants, there is the tendency to continue expanding those restrictions to protect the environment with special focus on the regulation of toxic substances, mutagens and carcinogenic precursors and carcinogenic substances. Especially important are the regulations placed on water from water purification plants, industrial and municipal wastewater/sewage treatment plants. Recently, there has been an increased concern about the quality of water discharged from industrial/sewage plants and from water purification plants as certain recalcitrant xenobiotic organic compounds have been detected in surface water, ground water systems, and in drinking water. A vast number of pharmaceuticals and Endocrine Disrupting Chemicals (EDCs) have been detected in effluents from sewage treatment plants [1], surface water [2,3] and less frequently in drinking water [4]. These pharmaceuticals range from simple antibiotics to anticonvulsants, beta-blockers, cytostatic drugs and x-ray contrasting media [5,6]. The intrinsic design of these chemicals prevents their attack by the microbes used in the biological treatment of municipal sewage and therefore they persist in the effluent during discharge of treated wastewater. Natural water and treated wastewater represent the most significant exposure pathways for EDCs to biota as they are only partially removed by wastewater treatment processes [7]. A review of their potential environmental impact has been presented [8,9]. Xenobiotic end products such as dyes [10], pesticides, herbicides and insecticides [11], and other precursor chemicals such as nitro- and chloro- benzenes [12] have also been detected in water samples.

From the foregoing, it is apparent that the present conventional techniques such as flocculation, coagulation, adsorption on activated carbon, biological treatment and membrane processes for the purification of drinking water and the treatment of wastewater are ineffective for the removal of certain recalcitrant organics in water [13]. One major disadvantage of some of these techniques is the concentration of pollutant on a secondary medium or in solution and hence the generation of sludge which is more concentrated and more acutely toxic than the individual pollutant. The proper disposal of this secondary generated pollutant therefore offers another problem. At present, membrane waste sludge which contains several stabilized xenobiotic compounds [14] is emptied into sewers and surface waters where they pose further environmental threat [15]. Also, while adsorption on activated carbon shows promise for removal of organics, reports on application in real wastewater revealed that adsorption of certain organics was reduced by as much as 1000 times when compared to results from laboratory scale experiments [16]. Coupled with this fact is that the reuse of activated carbon is limited to a specific number of cycles [17], and the generated spent carbon requires proper treatment. This poses a major disadvantage to this technology. Biological degradation and photo-degradation are few of the major technologies applied for removal of toxic chemicals such as chlorinated phenols, aromatics and pesticides [18]. However, in the context of remediation described by the European Commission Joint Center [19], these conventional technologies have been regarded as unsatisfactory for treatment of industrial wastewater since many of the organics present are resistant to biological treatment. Arguably, some of these techniques including adsorption when carried out in the biosorption mode utilize inexpensive adsorbents and as such the reduction in running cost may become an advantage. Presently, there is still no report of a single material capable of total pollutants removal from wastewater.

Thus, this chapter presents bioremediation, membrane bioreactor and the Advanced Oxidation Processes (AOPs) as other forms of water and wastewater treatment technologies. The basic principles, applications, successes and limitations of these treatment technologies were presented and discussed.

Bioremediation

Bioremediation involves the use of living organisms such as microorganisms, fungi, algae, enzymes and plants to degrade/breakdown complex materials (pollutants) into simple end

products. It can also be described as the addition of biological materials to contaminated environments to cause an acceleration of the natural biodegradation processes [20], the addition of terminal electron acceptor/donor or control of moisture and temperature conditions to establish microbial consortia [21]. It is a proficient technique of removing contaminants from water and wastewater. It is a simple and inexpensive method of water and wastewater treatment which results to nontoxic by-product.

There are two main approaches to bioremediation:

Bio augmentation: This is the process in which microbes are added to supplement the existing microbial population.

Bio stimulation: It involves the addition of nutrients or other growth-limiting co-substrates to stimulate the growth of indigenous degraders.

Some microbes and fungi that are commonly used in bioremediation include *Pseudomonas sp, Bacillus sp, Klebsiella sp, Pandoraea sp, Phanerochaete chrysosporium, Mycobacterium sp, Agrocybe semiorbicularis, Auricularia auricula, Coriolus versicolor, Dichomitus squalens, Flammulina velupites, Hypholoma fasciculare, Pleurotus ostreatus, Stereum hirsutum,* and *Avatha discolor,* the genera *Flavobacterium, Arthrobacter, Azotobacter* and *Burkholderia* are the most commonly used bacterial species, while *P. putida* theortical oxygen demand enzyme and fungal enzymes oxidoreductases, laccase and peroxidases have been reported to have prominent application in the removal of contaminants in the environment [22,23].

Recent studies have shown that bioremediation using algae can increase biomass by utilizing waste as nutrients and can help in solving problems created by effluents [24,25]. Hence, microalgae cultures have been applied by several authors for the treatment of contaminated soils, water and wastewater [25]. Chekroun *et al.,* [26] gave an overview of the mechanisms used by microalgae for the bioremediation of organic pollutants in aquatic ecosystems and the impact of genetically modified microalgae on xenobiotic degradation to minimize their impact on the environment. Chekroun et al., [26] concluded that the application of microalgae in biomonitoring and restoration of aquatic systems favour the phytoextraction and biodegradation of organic pollutants, however, there are still some persistent organic pollutants that are difficult to break down by microalgae. They opined that genetic engineering can be employed to improve the absorption and bioremediation of many organic pollutants and increase microalgal tolerance to these pollutants. In Egypt, the bioremediation of Al-Sayyadin lagoon polluted water using wild and mutant strains of microalgae (*Chlamydomonas reinhardtii CC1021 and Parachlorella kessleri PC*) was assessed by Zayadan *et al.,* [25]. They reported that the wild and mutant strains of *P. kessleri* had higher efficiency in phytoremediation than the wild and mutant strains of *C. reinhardtii CC1021*, and that the mutant algae of *P kessleri PC* exhibited higher growth rate and removal efficiency than the wild type.

Sheela and Khasim [27] carried out a detailed review of the bioremediation of ammonia from polluted waste waters. They discussed the biological processes for ammonia-nitrogen removal; which includes nitrification/denitrification, simultaneous nitrification and denitrification, autotrophic nitrification/denitrification, nitrification/denitrification via nitrite pathway, anammox process, and partial nitrification/anammox. The factors affecting the efficiency of ammonia bioremediation were also discussed. Finally, they argue that the anammox system was found to be feasible and extremely suitable for the treatment of high concentrated ammonia containing industrial effluents, and that the major drawbacks for anammox bacteria are their isolation in pure form and slow growth rate. Olawale [28] investigated the bioremediation potential of *Pseudomonas aeruginosa* (a common Gram-negative bacterium) in removing heavy metals from industrial effluent wastewater. Olawale reported that the wastewater treated with *P. aeruginosa* shows that the concentrations of Pb, Se, As and Cd degraded by 96.43%, 99.94%, 99.80% and 90.38%, respectively, at the end of fifteen experimental days.

In addition, bioremediation has been reported as a new method of oil spill clean-up that is more effective than chemical and mechanical methods [28].

Phytoremediation

Phytoremediation is a promising technology that uses green plants to assimilate or detoxify organic and inorganic pollutants from contaminated soils, water and wastewater. Plants possess a natural ability to eliminate, detoxify or immobilize environmental contaminants in a growth matrix by means of various biological processes [22], thus phytoremediation can be applied to a broad range of contaminants, including: heavy metals, radionuclides, chemicals, organics etc. This technology conserves the environment in a natural state, improves soil quality, it is relatively cheap and harmless, the plants can be monitored, and valuable contaminants can easily be recovered and re-used. However, it is limited to the following: surface area and depth occupied by the roots, slow plant growth and several growing seasons required to achieve the desired level of decontamination, leaching of contaminants into groundwater which may not be totally prevented, toxicity of the contaminated land and the general condition of the soil that affects the survival of the plants, and bio-accumulation of contaminants which may pass into the food chain. Thus, the plant species used in phytoremediation are selected based on ability to extract or degrade the contaminants of concern, adaptation to local climates, high biomass, depth root structure, compatibility with soils, growth rate, ease of planting and maintenance, and the ability of the plant to take up large quantities of water through the roots (http://www.epa.gov/superfund/accomp/news/phyto.htm). Moreover, the efficiency of phytoremediation is determined by the biomass production and the bioconcentration factor. The bioconcentration factor is a measure of the ability of a plant to take up and transport contaminants to the shoots, which are the plant parts that can be easily harvested [29].

Mechanism of phytoremediation

Pirzadah *et al.,* [22] and Favas *et al.,* [30] presented the mechanisms and factors affecting phytoremediation. These essential mechanisms (Figure 1) include: phytoextraction, phytostabilisation, phytodegradation (phytotransformation), phytostimulation, phytovolatilization and rhizofiltration.
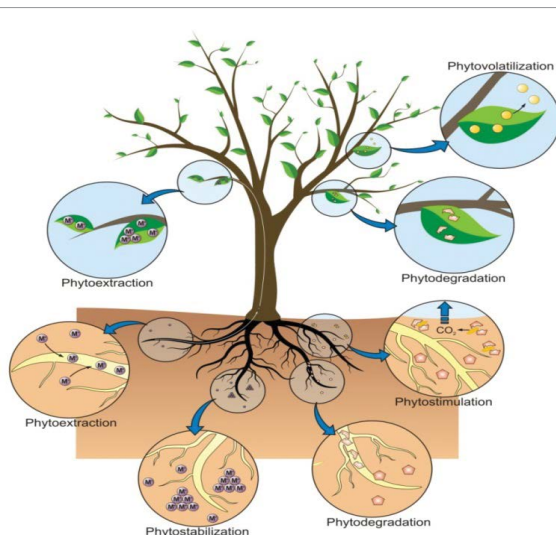

Figure 1: Mechanism of phytoremediation [30].

Phytoextraction: This is the process by which plants (hyperaccumulators) actively eliminate contaminants from soil or water, and translocate them to higher tissues where they are accumulated. Plants are thus harvested as required and managed accordingly i.e. the plants could be incinerated, composted or used as firewood, etc. Proper disposal is essential for the plant biomass that accumulates the contaminants, whereas, ash must be disposed of in hazardous waste landfill if the plants are incinerated. For a successful phytoextraction, the contaminant needs to dissolve into what the plant roots can absorb, the plant roots need to absorb and transport the contaminants, the plant should be able to safely store the contaminants, and lastly, the plant must adjust to any damages the contaminants might have caused during transportation and storage.

Phytostabilisation: This is the interaction between the plants' rhizosphere, the contaminants and the substrate in order to reduce the mobility of contaminants in the environment. This process is used to restrain contaminants in the soil and groundwater through absorption, adsorption and accumulation by the roots, or precipitation within the rhizosphere (a process in which plant roots release plant exudates such as phosphate, which may result to the formation of insoluble precipitate of the contaminants, thus removing the contaminant from solution without having it taken up into the plant). Phytostabilisation minimizes the mobility of contaminants, prevents movement to the groundwater or air, and also decreases bioavailability for entry into the food chain.

Phytodegradation or phytotransformation: The phenomenon by which the plants metabolize or transform the contaminants to less harmful products through the effect of enzymes produced by the plants. The contaminants are broken down into simpler molecules and are integrated into the plant tissues to aid the plants rapid growth.

Phytostimulation or rhizosphere degradation: This is the enhancement of soil microbial activity for the degradation of contaminants, typically by organisms that associate with roots. Rhizosphere degradation occurs mainly in soil, yet, stimulation of microbial activities in the root zone of aquatic plants could possibly occur.

Phytovolatilization: The use of plants to take up contaminants from soil, water or wastewater and translocate them into the shoots, where the contaminants or a modified form of the contaminants may be volatilized.

Rhizofiltration: This is the filtration of water through a mass of roots to remove toxic substances or excess nutrients. The pollutants remain absorbed in or adsorbed to the roots. Examples of plants known to remove pollutants through rhizofiltration are duckweed, water spinach, calamus etc. Ndimele *et al.,* [31] reported the ability of water hyacinth (*Eichhornia crassipes* (*Mart.*) *Solms.*) to absorb and translocate Fe and Cu. Their investigation revealed that Cu had better translocation capacity than Fe, while the accumulation potential of Fe by water hyacinth is higher than Cu. They concluded that *Eichhornia crassipes* can be effectively utilized for the phytoremediation and adequate for biomonitoring programmes for contaminated water. Syuhaida *et al.,* [32] carried out the comparison of the phytoremediation abilities of water mimosa (*Neptunia oleracea*) and *Eichhornia crassipes*. Their results indicated that *Neptunia oleracea* has lower heavy metals uptake and bioconcentration factor value compared to *Eichhornia crassipes*. However, it was reported that both plants accumulate high heavy metals in the roots compared to stems and leaves and that both plants use rhizofiltration process to remove heavy metals. Pedro *et al.,*[33] evaluated the capacity of *Salicornia ramosissima* (*S. ramosissima*) on Cd phytoremediation under different salinities and Cd concentrations in a greenhouse experiment. They reported that the highest Cd accumulation was detected in the roots, and decreased with increase salinity and Cd concentration. They suggested *S. ramosissima* as a potential candidate for Cd phytoremediation at salinities close to 0 and that the ability of *S. ramosissima* in Cd phytoaccumulation and phytostabilization was found to be remarkable. The phytoremediation of water polluted by thallium, cadmium, zinc, and lead with the use

of *Callitriche cophocarpa* (*C. cophocarpa*) was reported by Augustynowicz *et al.,* [34]. After a 10-day incubation period, shoots of *C. cophocarpa* were found to effectively biofiltrated the water so that it met (for Cd, Zn and Pb) appropriate quality standards. They reported that the *C. cophocarpa* significantly eradicated polluted water toxicity according to the Microtox bioassay and that *C. cophocarpa* exposed to metallic pollution did not exhibit significant changes in its physiological status compared with the control. Marrugo-Negrete *et al.,* [35] investigated the the phytoremediation of mercury-contaminated soils by *Jatropha curcas (J. curcas)*. The authors assessed the growth behavior, mercury accumulation, translocation and bioconcentration factors of *J. curcas* and reported that the different tissues in *J. curcas* was in order of decreasing accumulation Hg as: roots > leaves > stems, and that *J. curcas* species showed high bioconcentration factor and low translocation factor, and their use could be a promising approach to remediating mercury-contaminated soils. The uptake and biotransformation of Trichloroethylene (TCE) by hybrid poplars in artificial aquifer was reported by Newman *et al.*, [36]. They reported that nearly one to two percent of the applied TCE was completely mineralized to carbon dioxide by the poplar cell cultures and that unaltered TCE and TCE metabolites (trichloroethanol, trichloroacetic acid, dichloroacetic acid and reductive dechlorination products) were detected in the aboveground portion of the hybrid poplars.

Membrane bioreactors

Membrane Bioreactors (MBRs) are systems integrating biological degradation of pollutants with membrane filtration (Figure 2). MBR is an emerging advanced wastewater treatment technology that has been successfully applied in municipal and industrial wastewater treatment, groundwater and drinking water abatement, solid waste digestion and odor control. Cicek [37] presented a critical review of MBRs and their potential application in agricultural wastewater treatment. Studies have also shown that certain configurations of MBRs would retain, concentrate, and consequently break down hormones, industrial chemicals, pesticides, herbicides, pharmaceuticals etc. without requiring sophisticated tertiary treatment processes.
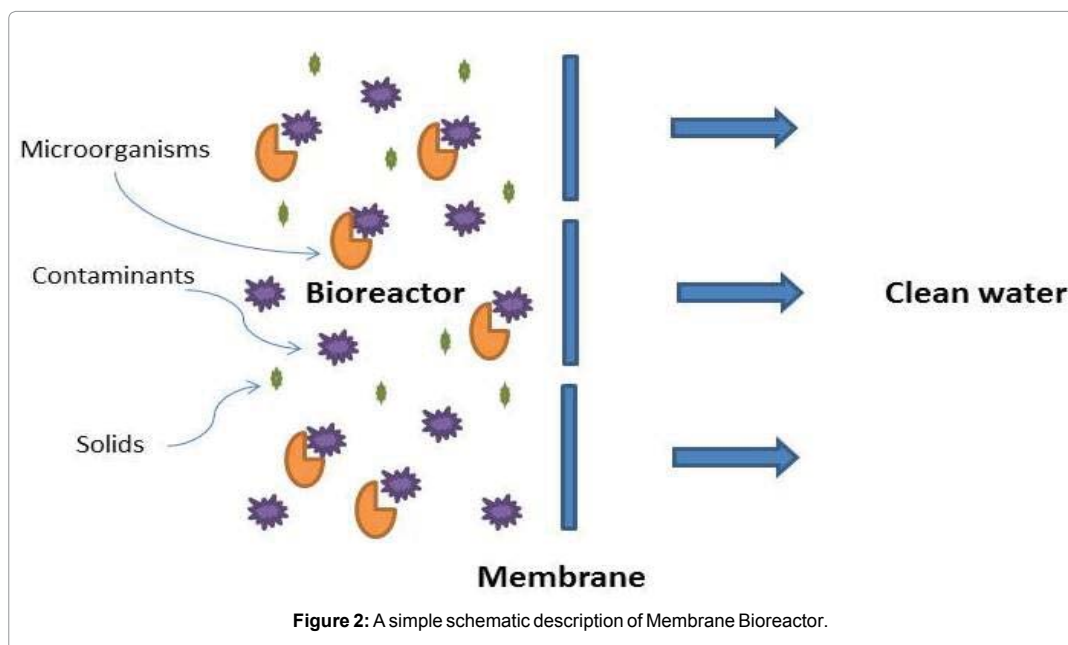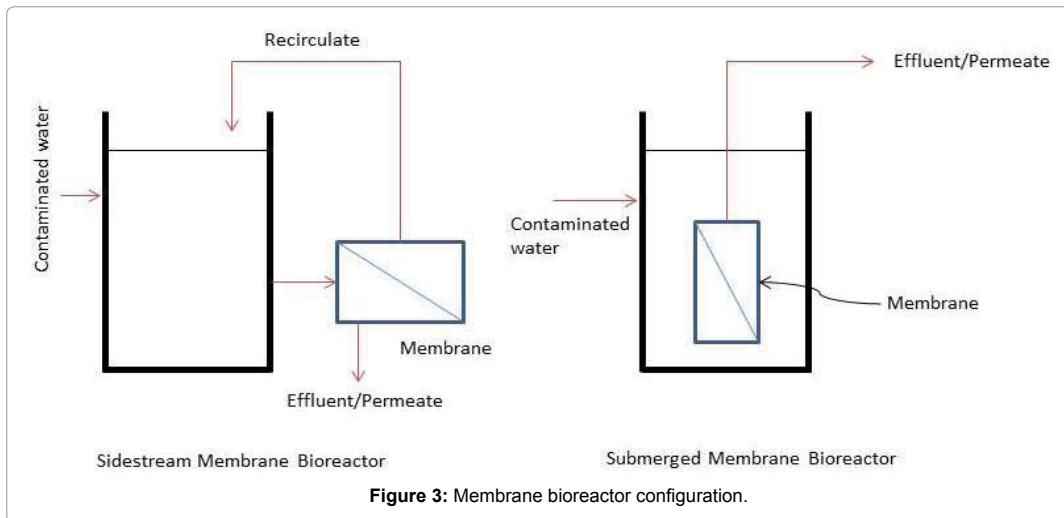

Figure 2: A simple schematic description of Membrane Bioreactor.

Figure 3: Membrane bioreactor configuration.

The membrane unit can either be constructed side stream (external or cross flow) or submerged in the bioreactor (Figure 3). The submerged is the most common type of MBR due to its compactness and low energy requirement. In the submerged MBR, the membrane segments are directly installed in the activated sludge reactor vessel, with the effluent sucked out of the membrane segments by the aid of a permeate pump and the suspended solids fall back into the basin. In the sidestream MBR, the membrane segments are located outside the reactor basin, thus, the mixed liquor from the reactor is pumped into the external membrane segments. This makes the sidestream MBR configuration to consume more energy and it also requires additional space. However, it should be noted that the choice of any of the configurations depends on application requirements.

The major advantages of MBRs water and wastewater treatments include high quality effluent free of bacteria and pathogens, good control of the biological activity, smaller plant size and higher organic loading rates. However, high capital costs due to expensive membrane units and high energy costs, membrane fouling, and sludge disposal problems constitute major setbacks. Furthermore, contaminants accumulating in the bioreactor can reach concentration levels that can be detrimental to the microbial population or membrane structure [37].

Advanced Oxidation Processes

AOPs were defined in 1987 by Glaze [38] as "near ambient temperature and pressure treatment processes which involve the generation of hydroxyl radicals in sufficient quantities to effect water purification". Hydroxyl radical is traditionally thought to be the active species responsible for the destruction of pollutants. In the light of recent evidence, this definition may require a revision as several publications have reported the use of other radicals such as the sulfate radical [39-41] and azide radical [39] generated in-situ for the degradation of organic pollutants in wastewater. The use of the AOPs also referred to as the Advanced Oxidation Technologies (AOTs) have been reported to bring about complete mineralization of toxic xenobiotic organics frequently detected in water and wastewater. AOPs have also been successfully applied to the removal of disease causing pathogens in water [42]. Several workers have reported the use of AOPs for removal of pharmaceuticals [43,44], endocrine disruptors [45], pesticides [46-48], surfactants [49] and a wide range of other industrial toxicants such as phenols [50,51], humic acids and benzene derivatives [52,53] commonly detected in surface, ground and wastewaters. These techniques are superior to the conventional chlorination of water as they can be optimized to also oxidize disinfection

by-products such as the halomethanes and haloacetic acids associated with chlorination of water [54]. Since the end products of complete mineralization are carbon dioxide and water, the AOPs offer another significant advantage in avoiding the production of a secondary pollutant encountered when using other conventional techniques. Furthermore, the AOPs have been applied to several real waste scenarios such as dye effluents from dye industry [55], pulp mill effluents high in phenolics [56,57], land fill leachates [58] and drinking water [59,60]. These have shown better treatment efficiency when compared with conventional processes. In combined mode with other techniques, they have also been used as pre-treatment or post-treatment unit operations as part of the multiple barrier approach for water purification [55,61, 62]. The possible application of AOPs in hybrid water treatment processes based on adsorption and catalytic wet air oxidation has recently been proposed [63].

Although the AOPs use different reagent systems, which include photochemical degradation processes (UV/O_3, UV/H_2O_2), photo-catalysis (TiO_2/UV, photo-Fenton), and chemical oxidation processes (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}), they all produce hydroxyl radicals (OH^-) which are highly reactive and non-selective [64,65]. Sulphate radicals (SO_4^{--}) produced using oxone is more selective than hydroxyl radical [40]. A schematic classification of the advanced oxidation processes is presented in Figure 4.

Figure 4: A schematic classification of the advanced oxidation processes. Abbreviations: O_3 ozonation; H_2O_2 peroxide; AC activated carbon; UV ultraviolet; TiO_2 titanium oxide; WO wet oxidation; WPO wet peroxide oxidation; SCWO supercritical wet oxidation.
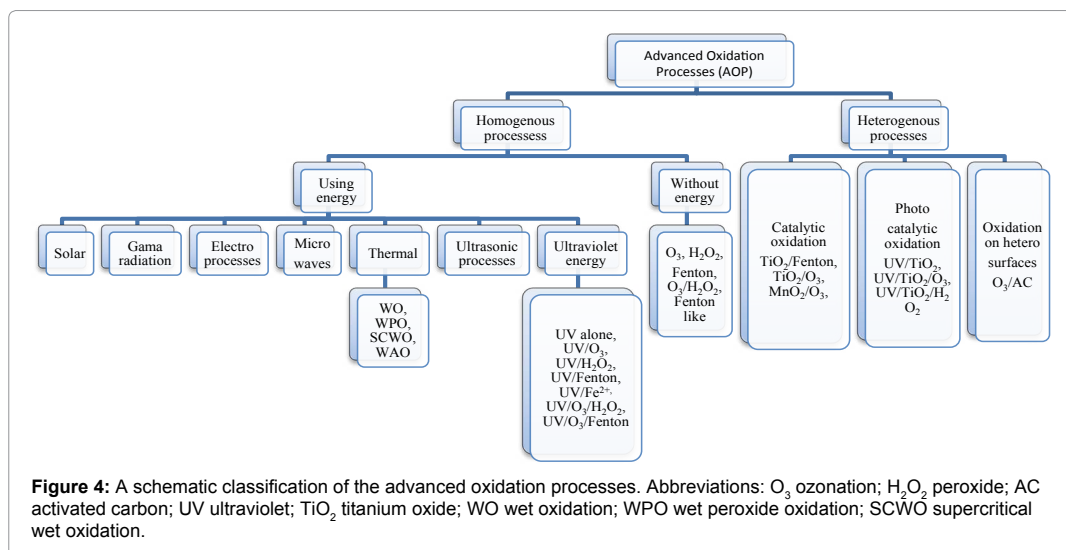
These AOPs summarized in Figure 4 may be classified as homogeneous or heterogeneous [66]. The major distinguishing factor between these two broad classes is the absence of a solid phase catalyst or promoter in the homogeneous process. In homogeneous processes, reagents such as H_2O_2, soluble O_3 and/or aqueous metals are used to generate OH radicals in aqueous phase for oxidizing dissolved organics. Energy sources such as solar, microwave, thermal and others presented in figure 4 are not considered as a separate phase from the aqueous medium. On the other hand, heterogeneous processes utilize a solid catalyst phase or surface upon which radicals are generated. The generation of radicals by UV generated holes on TiO_2 solids dispersed in an aqueous medium is a typical example. Others such as O_3 break down on solid metal oxides may be specifically regarded as catalytic processes and are broadly classified under heterogeneous processes. Homogeneous processes can be further subdivided into processes that are driven by external energy and processes that do not operate on external energy sources. These energy sources include UV light, solar energy, electrochemical, ultrasonic (sonolysis), microwave, thermal and gamma radiation.

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Homogeneous Aops without Energy

Ozonation in alkaline medium

Ozone is unstable in aqueous medium, decomposing spontaneously by a complex mechanism that involves the generation of hydroxyl radicals. The degradation of organic compounds occur through the action of O_3 itself as well as through the radicals generated in alkaline medium. The scheme for the radical generation has been extensively argued [67]. Hoigne [67] showed that ozone decomposition in aqueous solution proceeds via the formation of hydroxyl radicals as shown in the Equations 1-8. In the reaction mechanism, hydroxyl ion (OH⁻) has the role of initiator.

$$OH^- + O_3 \rightarrow O_2 + HO_2^- \tag{1}$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \, (acidic \, medium) \tag{2}$$

$$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{-\cdot} \tag{3}$$

$$HO_2^{\cdot} \leftrightharpoons H^+ + O_2^{-\cdot} \tag{4}$$

$$O_2^{-\cdot} + O_3 \rightarrow O_2 + O_3^{-\cdot} \tag{5}$$

$$O_3^{-\cdot} + H^+ \rightarrow HO_3^{\cdot} \tag{6}$$

$$HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2 \tag{7}$$

$$HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2 \tag{8}$$

$$HO^{\cdot} + O_3 \rightarrow HO_2^{\cdot} + O_2 \tag{9}$$

The mechanism also elucidates the role exerted by H_2O_2 since it is formed during the decomposition of ozone as shown in Equation 2. It is therefore clear that the addition of H_2O_2 to O_3 aqueous solution would enhance the O_3 decomposition, with the formation of OH radicals. This forms the basis for the use of another process based on O_3 and H_2O_2: the peroxone process (O_3/H_2O_2). A less complex scheme for decomposition of O_3 to radicals was proposed by Alaton and co-workers [68]. The use of ozonation has been extensively applied for the decomposition of organics in water and wastewater. The effluents from pulp and paper industry contain a number of toxic compounds especially phenols and its chlorinated derivatives. The paper making process utilizes a large amount of water and their effluents laden with xenobiotic organics are directly discharged into surface water streams, posing deleterious effects to aquatic life. Catalkaya and Kargi [56] utilized the ozonation process as a pretreatment operation for effluents from a pulp mill in Turkey. The method was regarded as effective for the removal of colour from the effluent. Chelme-Ayala and co-workers utilized the ozonation process for the treatment of pesticides present in a membrane concentrate from a membrane plant in Alberta, Canada [69]. The workers recorded removal efficiency of 87% for bromoxynil and 63% for trifluralin from the concentrates. A good number of articles published on the application of ozonation for the treatment of various organics in wastewater can be found in the literature [70-75]. The major limitation to the use of O_3 for water treatment lies with the operational cost of the process itself. O_3 is an unstable gas with a lifetime spanning only a few minutes when in water. It therefore has to be produced in-situ when required. Also, its application requires well-designed gas-liquid contacting devices to bring about effective mass transfer of O_3 from the gas phase to liquid phase.

Oxidation using H_2O_2

Oxidation by peroxide (H_2O_2) alone is not regarded as an AOP because H_2O_2 is not a radical. It is stable in water and oxidation is based on the intrinsic oxidative power of the peroxide molecule being a natural oxidizing agent. However, in practical applications, H_2O_2 undergoes solar photolysis, providing radicals in a way similar to UV photolysis of H_2O_2 and

as such the participation of the OH$^\bullet$ during H_2O_2 oxidation cannot be ruled out. The process of H_2O_2 breakdown without a catalyst is slow and has been largely regarded as ineffective for the treatment of organics in wastewater. In a study by Coca *et al.*, [76], peroxide alone added to brown coloured molasses obtained from a fermentation factory in Spain, did not bring about any change in colour of the wastewater even after 18 hr of contact. Continued stepwise addition of peroxide (0.02 M) up until 23 hr also did not lead to a significant change in the brown colour of the syrupy wastewater. The use of UV combined separately with chlorine and H_2O_2 as a novel AOP for the treatment of trichloroethylene in drinking water was evaluated by Wang *et al.*, [77]. In their study, the rate of trichloroethylene decay by UV, UV/chlorine and UV/H_2O_2 at different pH values were studied and compared. They reported that the UV/chlorine process was more efficient than the UV/H_2O_2 process at pH 5, but in the neutral and alkaline pH range, the UV/H_2O_2 process became more efficient. An earlier article published by Prado and Esplugas [78] had shown that the formation of hydroxyl radical by hydrogen peroxide in the absence of UV light was only favorable at high pH. They reported the effect of varying pH on the oxidation of atrazine (a pesticide) by H_2O_2. At pH 4.8 and 6.8, atrazine removal of 4% and 9% (respectively) was observed over a 24 hr period. However, at higher basic pH (11.4), a 100% removal of the pesticide was achieved within 180 min. The mechanism of generation of the radicals suspected to be involved in the oxidation process at high pH has however not been investigated. In another study, Yasar and co-workers in Pakistan [42] studied the use of H_2O_2 (a well-known disinfectant) for the immobilization of pathogens in industrial effluents. Results obtained under optimized oxidant dose of 170 mg/L showed that the oxidant was capable of removing 99% of the pathogens present in the wastewater. As a drawback to its use the authors highlighted that pathogens immobilized by H_2O_2 were reactivated after an incubation period, which varied depending on the reaction condition. This problem was overcome when H_2O_2 was used in combination with other processes such as UV and O_3. Base on the findings of the referenced literature, we may infer that the use of H_2O_2 for water treatment is significantly affected by pH and only effective at alkaline pH. Also, when applied as a disinfectant for living cells (pathogens), colony regrowth is only suppressed when H_2O_2 is used in conjunction with other processes. Another disadvantage of this process is the presence of residual peroxide, which may require further attention after the water treatment itself. Some other researchers have reported the use of peroxide as an oxidant for organics [53,79].

Fenton and fenton-like processes

More than a century ago, HJ Fenton described the oxidation power of H_2O_2 on certain organic molecules in which OH radicals are produced from H_2O_2 in the presence of Fe(II) as catalyst. Later on, a reaction mechanism was proposed by Walling [80] and is illustrated by Equations 10-12.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{10}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \tag{11}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{12}$$

The renewed interest of researchers for this classic old reactive system is today underscored by a significant number of investigations devoted to its application in wastewater treatment. Due to its simplicity (requiring neither special apparatus nor reactants), the Fenton process is one of the most widely applied and researched processes for treatment of recalcitrant compounds. Mandal *et al.*, [62] investigated the use of Fenton reagent for the degradation of wastewater collected from industrial effluent plants in India. They investigated the effect of operating variables such as pH, temperature, peroxide and Fe(II) dose for the reduction of Chemical Oxygen Demand (COD) in the wastewater sample. The Fenton process requires strict pH control and several published data places optimum pH for the process in the range: 2.5-3.5. The authors observed that at optimized conditions of pH 3, Fe(II) 6 mg/L,

and peroxide dose of 220 mg/L, the COD removal after 30 min was 90%. Extending the time to 24 hr only increased the COD removal by an additional 5%. It was therefore suggested that the process be used in combination with biological treatments for total removal of organics in the wastewater, as it was ineffective for low concentrations of the organic in their study. Chen *et al.,* [81] also utilized the Fenton process for the degradation of model pollutant (salicyclic acid) in aqueous solution. Salicyclic acid removal efficiency under optimized conditions was 96% after 150 min, and COD reduction was 80%. As shown by the results, the Fenton process was effective for the degradation of salicyclic acid. The complete mineralization was however not as efficient as the degradation of the pollutant. Several other reports concerned with the application of Fenton process for the amelioration of organics in wastewater abound in the literature [15,82-85]. All processes which involve the use of Fe^{3+} ions (either as hydroxyl complexes or as oxalate complexes) or oxidizing metals such as manganese (as permanganate) are referred to as Fenton-like processes. Especially important amongst them is the ferrioxalate complex which has a strong absorption at wavelengths above 400 nm and therefore undergoes reactions that can be photo-catalyzed by visible light. The photo degradation of hydroxyl and oxalate complexes of Fe(III) generate Fe^{2+} ions which catalyses the decomposition of H_2O_2 to OH radicals. Equations 12-16 shows the participation of Fe as oxalate in the production of hydroxyl radical.

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \tag{13}$$

$$Fe(C_2O_4) + H_2O_2 \rightarrow Fe(C_2O_4)^{+} + OH^{\bullet} + OH^{-} \tag{14}$$

$$Fe(C_2O_4)_3^{3-} + hv \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \tag{15}$$

$$Fe(C_2O_4)_3^{3-} + C_2O_4^{-\bullet} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \tag{16}$$

$$C_2O_4^{-\bullet} \rightarrow CO_2 + CO_2^{-\bullet} \tag{17}$$
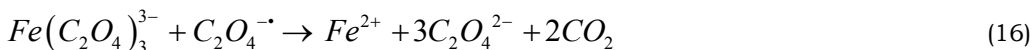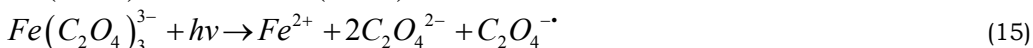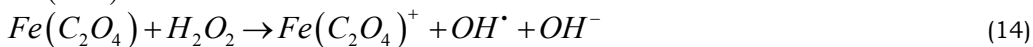
Additionally, other free radicals and active species are generated as shown by Equation 16. A significant advantage of the Fenton-like process is the avoidance of Fe^{3+} sludge associated with the classical Fenton process.

Ozone/H_2O_2 (peroxone) process

H_2O_2 in an aqueous solution is partially dissociated to hydro-peroxide ion (HO_2^{-}), which reacts with ozone giving rise to a series of chain reactions involving OH radicals [86]. Equations 17 and 18 illustrate the direct attack of O_3 by H_2O_2 and hydro-peroxide ion to give OH radicals and HO_2 radicals, respectively. The efficiency of the peroxone process is based on the generation of these radicals.

$$H_2O_2 + 2O_3 \rightarrow 2OH^{\bullet} + 3O_2 \tag{18}$$

$$HO_2^{-} + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet} \tag{19}$$

The hydro-peroxide ion produced by the decomposition of H_2O_2 reversibly recombines with hydrogen ions in solution to give H_2O_2 (Equation 18)

$$HO_2^{-} + H^{+} \rightleftharpoons H_2O_2 \tag{20}$$

Indeed the decomposition of ozone at high pH also produces the hydro-peroxide ion which reversibly produces peroxide as shown by Equation 2. The external addition of H_2O_2 to aqueous solution of ozone would therefore enhance the decomposition of ozone to give OH radicals according to the Le' Chatelier principle. The influence of pH is also evident since in the ozone decomposition mechanism the active species is the conjugate base OH_2^{-} whose concentration is strictly dependent on pH. An increase in pH and addition of H_2O_2 to an aqueous solution of ozone would thus result in higher hydroxyl radical production and the attainment of a higher steady state concentration of OH in the radical chain decomposition

process. It is worthy to note that the adoption of this AOP does not bring about a significant change in the apparatus or industrial reactor since it is only necessary to add an H_2O_2 dosing system. Cortez and co-workers applied the peroxone system for the treatment of landfill leachates in Portugal with the aim of increasing the biodegradability of the treated leachate in a combined chemical/biological process [58]. While both ozonation and peroxone process significantly improved the Biochemical and Chemical Oxygen Demand Ratios (BOD/COD), implying improved biodegradability, the peroxone process presented higher ratios and hence higher biodegradability of the treated leachates. The application of one process over the other would therefore depend on the running cost of chemicals weighed against the desired quality of effluent required for subsequent biological treatment. The use of ozone in combination with H_2O_2 has been widely accepted to increase the generation of the non-selective OH⋅ during ozonation, leading to improved elimination of refractory organic compounds [60,76,87].

Homogeneous Aops Using UV

Homogeneous AOPs using UV radiation are generally applied for the degradation of compounds that adsorb UV radiation. These are usually dyes and aromatic hydrocarbons capable of absorbing UV energy. As previously mentioned, the UV is not considered a separate phase from the aqueous medium to which it is applied.

UV/ozone

AOPs using ozone and UV proceeds via the photolysis of aqueous ozone to produce hydroxyl radicals as shown by the reaction presented in the Equations 20-21. The aqueous solution is irradiated with UV light at a wavelength of 254 nm for ozone absorption. At this wavelength, the extinction coefficient of ozone is 177 times greater than that of peroxide.

$$H_2O + O_3 + UV \rightarrow 2OH^{\cdot} + O_2 \tag{21}$$

$$2OH^{\cdot} \rightarrow H_2O_2 \tag{22}$$

This method has been used for the degradation of phenol [88]. Results were compared with processes run without the use of UV radiation. The comparison showed the effect of UV radiation on the oxidation process. The UV/O_3 process was capable of 99.2% removal of dissolved organic carbon as compared to O_3 alone (58.2%). Some researchers have equally applied this method for the degradation of carbamazepine, clofibric acid, diazepam and diclofenae, and monitored the degradation products by Liquid Chromatography-Mass Spectrometry (LC-MS) [89]. They reported a complete removal (100%) of these recalcitrant pharmaceuticals (except for diazepam) under optimized conditions of ozonation by UV photolysis. Haloacetic acid and trihalomethanes are a major group of disinfection by-products and have been identified as carcinogens. The UV/O_3 was reported to have been suitable for the mineralization of trichloro- and dichloroacetic acids [90] which are classical haloacetic acids produced during disinfection of water by chlorination.

UV/ H_2O_2

The use of UV to bring about photolysis of hydrogen peroxide has also been adopted for the treatment of wastewater contaminated with a wide range of organics. This process entails the photolytic symmetrical splitting of a molecule of peroxide to give two hydroxyl radicals as shown by Equation 22. Typical UV absorption of H_2O_2 is 257 nm.

$$H_2O_2 + UV \rightarrow 2OH^{\cdot} \tag{23}$$

UV/H_2O_2 system can totally mineralize any organic compound reducing it to CO_2 and water. However, in real-life scenarios, such a drastic process is not necessary. The toxicity of oxidation products is not a problem since they are easily biodegraded [91]. The major

drawback of this process is the smaller extinction coefficient of H_2O_2 which is 18.6 $M^{-1}cm^{-1}$ at 257 nm, thus only a relatively small fraction of the incident UV light is exploited for AOP. Nevertheless, several studies have been carried out to optimize this process for purification of water. This is justified by the relative ease of handling H_2O_2 and the cost of chemicals. The use of UV/H_2O_2 for the detoxification of raw textile wastewater prior to biological treatment with dehydrogenase has been reported [92]. The decrease in inhibitory effect from 30% when UV was used alone to 26% for UV/ H_2O_2 was attributed to the synergistic effect of the combined treatment. The raw wastewater inhibited the enzyme activity by 47%. They concluded that the AOP was an effective method for detoxification of textile wastewater. The positive impact has been demonstrated by a significant decrease of inhibitory action of microbial growth on activated sludge during subsequent biodegradation. Kestioglu and co-workers have applied the UV/ H_2O_2 process for the treatment of raw effluent from an olive mill treatment plant in Turkey [93]. The effluent was characterized by a very low pH (<2), high COD (10, 240 mg/L) and total phenol (975 mg/L). Treatment periods of 400 and 1440 min reduced the COD to 3060 and 3650 mg/L, respectively. The total phenol for optimized peroxide dose was also reduced to 22 and 10 mg/L, respectively, accounting for 99% of COD and phenol removal. The use of this method as an AOP for treating contaminant in wastewater has also been reported in other studies [94-97].

UV/fenton process (Fe^{2+}/UV/ H_2O_2)

The rate of degradation of an organic pollutant with Fenton-Fenton like reagents is strongly accelerated by irradiation with UV-vis light [94,98-99]. This is an extension of the Fenton process which takes advantage of energy derived from photons in UV-vis irradiation at wavelength values higher than 300 nm. In these conditions, the photolysis of iron (III) hydroxide complex, that is, the product of Fenton process (Equation 12) allows for the regeneration of Fe^{2+} as given by Equation 23.

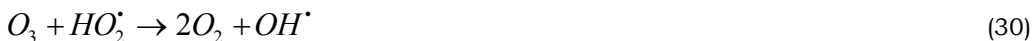$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + OH^{\cdot} \tag{24}$$

In this scheme using UV radiation, Fe^{2+} acts as a real catalyst as it is regenerated and recycled during the production of radicals after reaction with H_2O_2. Another advantage of this process is the reduction in the formation of Fe^{3+} sludge which is associated with the conventional Fenton process. Despite the great deal of work devoted by researchers to these processes, scanty indications have been found about their industrial application. This is not surprising since the application of the Fenton processes requires strict pH control. Generally, pH range between 2.5 and 3.0 are regarded as the best for this system. Huang *et al.,* [100] studied the oxidation of dye-reactive black-B using the UV/Fenton process and compared the results with experiments run for the Fenton and an electro-Fenton process. UV light source was from a UV-A lamp, wavelength 365 nm, with dye concentration 10,000 mg/L. Optimum pH for the process was established as 2.5 and mineralization was found to be 98%. The synergistic effect of the UV light was apparent when compared to the Fenton process which brought about a 78% mineralization. They also identified two degradation intermediates i.e. oxalic acid and formic acid. While the process readily mineralized the formic acid, the oxalic acid intermediate was more persistent to the chemical treatment. The degradation mechanism of carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methylcarbamate), a frequently used carbamate derivative pesticide considered to be a priority pollutant, using the UV/Fenton process, was reported by Javier Benitez and co-workers [84]. The carbamate concentration was 4.52 x 10^{-4} M, temperature 20°C and pH 3. At H_2O_2 and Fe^{2+} concentrations 50 x 10^4 and 5 x 10^{-4}M, respectively, the process brought about a complete mineralization of carbofuran in 5 min, with a rate constant 30 times higher than a similar experiment conducted in the absence of UV radiation. The authors concluded that the synergic effect observed in the photo-Fenton system was due to the generation of OH radicals in several reactions and to the catalytic character of the Fenton's reaction in

the presence of UV radiation. Other relevant discussions on the use of this process are well presented in the literature [56, 101-104].

Homogeneous AOP using ultrasound (Sonolysis)

The formation of OH radicals when ultrasounds are used is caused by high temperature and pressure conditions that are reached inside the bubbles generated by the ultrasounds. The process is based on the 'hot-spot' theory (localized generation of extreme conditions of temperature and pressure). According to the theory, sonolysis causes liquid cavitation given rise to energy bubble which collapse generating radicals. In the case of reactions where the controlling mechanism is the radical attack, the use of hydrogen peroxide and ozone enhances the degradation due to generation of additional free radicals. Generally, this type of AOP reduces cost since no radiation is needed, and can be readily combined with other methods. Sonolysis has been reported to be safe, sludge free and without the generation of secondary pollutant. It has the ability to penetrate cloudy waters and presents better energy conservation schemes. Despite its advantages, there are technical and economic challenges limiting the scale-up and adoption of this technology for industrial wastewater treatment. The technology necessary is still in its budding stage, and not well developed as other options.

The reactions that occur in the presence of ozone and ultrasound (represented as ')))') are shown in the Equations 24-31 [105].

$$H_2O \xrightarrow{)))} H^\bullet + OH^\bullet \tag{25}$$

$$O_3 \xrightarrow{)))} O_2 + O \tag{26}$$

$$O + H_2O \rightarrow 2OH^\bullet \tag{27}$$

$$O_3 + OH^\bullet \rightarrow O_2 + HO_2^\bullet \tag{28}$$

$$O_2 + H^\bullet \rightarrow HO_2^\bullet \tag{29}$$

$$O_3 + HO_2^\bullet \rightarrow 2O_2 + OH^\bullet \tag{30}$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{31}$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2 \tag{32}$$

He *et al.,* [105] used this ultrasound method to achieve effective degradation of p-aminophenol, an intermediate in the production of paracetamol. For an initial p-aminophenol concentration of 10 mmol/L, a degradation efficiency of 99% was achieved within 30 min. Mineralization of the p-aminophenol was 77% at this time. Ozone dose was at 5.3 g/h at 25°C with a pH of 11 and an ultrasonic energy density of 0.3 W/mL. It was observed that the degradation was influenced by the pH, temperature and ozone dose, but unaffected by an increase in energy density per unit volume of the ultrasound energy. By combining ultrasounds and H_2O_2, it was possible to achieve the formation of free radicals in gaseous phase of the cavitation bubbles formed during the sonication. Proposed mechanism for the production of free radicals was given by Shemer and Narkis [106] and is shown in Equations 32-34.

$$H_2O_2 \xrightarrow{)))} OH^\bullet + OH^\bullet \tag{33}$$

$$H_2O_2 + O_2 \xrightarrow{)))} 2HO_2^\bullet \tag{34}$$

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{35}$$

Homogeneous process using solar energy

The current trend in energy management is to develop technologies that run on renewable energies. Especially important in this regard are those that run on the universally abundant solar energy. The radiant energy from the sun consists of a wide band of energized photons capable of generating hydroxyl radicals via the photolysis of peroxide in a manner similar to the use of UV-vis light source. The non-selective radical generated then degrades the organics. The use of solar energy as source of energy to drive the photolytic cleavage of H_2O_2 and the Fenton process was adopted by Muruganandham and Swaminathan [107] for the de-colorization of reactive yellow-14 (dye) in heterogeneous and homogeneous media. The experiments were carried out under sunny conditions in borosilicate glass tubes with solar irradiation out in open air condition. Solar intensity was measured every 30 min using a LT Lutron LX-10/A (digital Lux meter) and the average light intensity over the duration of the experiment was calculated. They reported that the use of solar irradiation in the presence of H_2O_2 enhanced the de-colorization of the dye solution resulting in an increase in the percentage removal from 12.7% to 71.2%. The reaction has been more favorable at lower pH. The percentage removal of the dye using the Fenton process in the presence of solar energy also rose from 73.7% to 80.3%. In another experiment using solar energy and TiO_2, the dye removal after 80 min was 82.1%. In a solar/TiO_2 process, TiO_2 utilizes UV part of the solar spectrum (wavelength shorter than 380 nm) to produce e- and h+. The highly oxidative h+ (E^o = 2.7 eV) directly reacts with the surface adsorbed dye molecule or directly oxidizes the organic compounds via formation of OH radical. Studies on the effect of solar light intensity on the de-colorization showed that an increase of the solar light intensity from 700 to 1250 Lux increases the decolorization from 73.2% to 91.25, 85.3 to 93.4% and 28.7 to 42.1% for solar/TiO_2, solar/H_2O_2/Fe^{2+} and solar/H_2O_2 processes, respectively. The enhancement of removal rate is due to increase in hydroxyl radical production. Light intensity determines the amount of photons adsorbed by the catalyst. With the increase in the solar power, the catalyst absorbs more photons and produces more hydroxyl radicals. The removal of *p*-nitroaniline from aqueous solution using solar/Fenton process was studied by Sun and coworkers [85]. Solar experiments were carried out on sunny days in water cooled double glass cylindrical jacket reactors. The results for degradation of *p*-nitroaniline in water showed that *p*-nitroaniline is hardly decomposed by solar/H_2O_2. However, in both Fenton and solar/Fenton process, *p*-nitroaniline could be degraded effectively with degradation efficiency of 90.72 and 99.59%, respectively.

Wet oxidation process using thermal energy

The Wet Oxidation (WO) also referred to as Wet-Air Oxidation (WAO) or subcritical oxidation process is another effective method extensively used in industrial oxidation to treat hazardous waste and heavily polluted effluents. The process was pioneered by Strehlenert in 1911 [108]. It differs from the rest of the other conventional AOPs not only in terms of operating conditions but also in the concentration of the pollutant present in the wastewater. They are mainly used for concentrated wastewaters in order to allow auto-thermal operation and thus reduction in operating cost. The basic idea of WO is the oxygenation of organic and/or oxidizable inorganic-containing matters in fluid phase to inorganic or smaller molecular organic matter using air or pure oxygen as oxidant at upper temperatures (125-350°C) and pressures (0.5-20 MPa). In WO processes, elevated temperatures and pressure increase the concentration of dissolved oxygen and enhance the contact between molecular oxygen and organic matter [109] and thus the oxidation rate. Although the degree of oxidation in the process is dependent on the process conditions, retention time and feed composition, WO can treat varieties of organic waste, domestic sludge, and even those produced by various branches of industrial activity.

The process can be coupled with a biological treatment facility, and unlike incineration, is not handicapped by a bad ecological image. The technique, however, requires a high first

investment capital, but the operating cost is moderate as compared to other AOPs. Other variants of this technique are the Supercritical Water Oxidation (SCWO), which operates at T ≥ 375°C and P ≥ 22.1 MPa, and the Wet Peroxide Oxidation (WPO) which substitutes hydrogen peroxide for oxygen as the active oxidant, efficiently reducing the running cost. Hydroxyl radicals are formed when hydrogen peroxide decomposes on heterogeneous surface of the reactor or on other heterogeneous species present. Garcìa-Molina et al., [110] applied the wet peroxide oxidation for the treatment of solutions containing 4-Chlorophenol (4-CP) and 2,4-Dichlorophenol (2,4-DCP). At the three tested temperatures of 100, 130 and 160°C, the percentage removal of 4-CP was 100% using 2.5 mL and 5 mL of H_2O_2 in 200 mL solution of 4-CP (1000 mg/L). The total mineralization was however not complete as TOC values for 4-CP were as low as 70%. 2,4-DCP was tested at two temperatures (100 and 130°C) owing to its volatility to the gas phase at 160°C. At 5 mL H_2O_2, again a complete removal (100%) was reported with TOC values of 72.1 and 75.5% for the two temperatures, respectively. Lower concentrations of H_2O_2 had TOC values as low as 58.5%. Identified intermediates include phenol, hydroquinone and benzoquinone. Kusvuran et al., [108] also employed the WO process for decolorization of a solution of reactive red-120 (azo dye) in aqueous solution. Reactor operating temperature was varied between 200 and 300°C with a constant pressure of 17 bar. The degradation of the dye was markedly improved by increasing temperature from 200 to 300 °C. At 250°C and 17 bar, the substrate was completely removed after 20 min treatment. The temperature had the major effect on the reaction rate and the half-life of the organics.

Oxidation using microwave energy

Microwave technology has emerged as a promising technique based on physical, chemical and biological methods for the treatment of wastewater and waste activated sludge. When applied as an energy source for AOPs, the microwave radiation provides not only a heat source (the thermal effect) but also a specific effect (the non-thermal effect). Marken and co-workers [111] suggested that this effect leads to an enhanced photo-assisted degradation of several substrates. The non-thermal effect can lead to an increased number of charge on a metal oxide such ad TiO_2, as well as induce formation of traps that can prolong carrier lifetimes and lead to additional quantities of $OH^{\bullet}$ produced in TiO_2 photo-assisted oxidations in water. This secondary non-thermal effect of microwave on nanoparticles would prove useful in the fields of environmental management and pollution control.

In order to investigate the non-thermal effect of microwave in AOP, Horikoshi and co-workers [112] developed and applied a Microwave Discharge Electrodeless Lamp (MDEL) an AOP for the degradation of 0.05 M 2,4-dichlorophenoxyacetic acid (a herbicide: 2,4-D). Degradation of the herbicide was monitored spectrophotometrically by the loss of UV absorption at 204 nm and also by reduction in Total Organic Carbon (TOC). Efficiency of the MDEL was compared with those for Conventional Microwave (MW) energy source and UV lamp (Hg source). The authors observed That Microwave Discharge Electrodeless Lamp (MDEL) gave superior results when compared to the conventional UV lamp or the microwave source. The workers identified lamp proximity to substrate solution as an important variable for the reaction process. This is expected since heat transfer from the lamp (thermal effect) would be greatly reduced with increasing distance of the lamp from the reactor setup. TiO_2 was also tested with success as a potential catalyst for sequestering microwave energy generated from the MDEL. They went on to conclude that the MDEL electrodeless lamp introduced a non-thermal effect into the microwave technique which would prove to be an attractive innovative when developed for attenuation and disposal of environmental contaminants.

In another experiment utilizing the microwave technique, Wang and co-workers [113] applied the microwave–H_2O_2 AOP for the pretreatment of sewage sludge obtained from Gaobeidian municipal sludge process plant in Beijing, China. The effect of catalase on the

efficiency of the process was investigated. Catalase present as a biological component of the sludge is a terminal respiratory enzyme which attacks H_2O_2, breaking it to molecular O_2 and 2 electrons [114-115]. By monitoring the reduction of residual H_2O_2 with increasing temperatures, the workers were able to establish that the activity of the catalyst was significantly reduced above 45°C. Compared to control experiments, a considerable increase in sludge solubilization with increasing temperatures was also observed. The degree of sludge solubilization was strongly affected by H_2O_2 ratios with increasing amounts of soluble COD and TOC been released into the supernatant as H_2O_2 dosing ration increased. Although the AOP (microwave/H_2O_2) was effective for sludge pretreatment in the study, there were still high concentrations of residual H_2O_2 in the sludge, ranging 436-18773 mg H_2O_2/L. The higher the H_2O_2/TCOD dosing ratio was, the lesser the amount of consumed H_2O_2 that was consumed by the process. The proper evaluation of residual H_2O_2 would therefore prove crucial in the practical application of this AOP.

Heterogeneous Catalytic Oxidation

In recent years, there has been an enormous amount of research and development in the area of heterogeneous catalytic and photo-catalytic water purification processes due to their effectiveness in degrading and mineralizing recalcitrant organic compounds as well as the possibility of utilizing solar, UV and visible spectrum. Applied catalysts include activated carbon, tempered metals, and metal oxide nanoparticles [116]. Several research projects have been directed at advancing the synthesis and functionality of various sizes and shapes of semi-conductor and metal nanoparticles. The objectives of these projects are mainly to improve the performance and utilization of nanoparticles in various applications which include the AOPs. While the mechanism of mineralization using activated carbon in AOP is by adsorption on the carbon surface followed by rapid oxidation of concentrated pollutant on the carbon interface, the mechanism for metals and nanoparticles in AOP is by complex photo- or thermal- initiated redox reactions which lead either to direct mineralization of the organics or the generation of free radicals with subsequent mineralization. Heterogeneous catalyst utilized in AOP may be applied in one of three modes. (1) as hetero-catalyst at ambient temperatures and pressure to catalyze an optimized AOP such as ozonation, Fenton or peroxone processes; (2) as hetero-catalyst at elevated temperatures to catalyze wet oxidation processes and (3) as catalyst applied in photo-processes to bring about photo-catalytic degradation of an organic substrate (when used alone with UV light) or with other AOP such as UV/ozonation or UV/Fenton.

Heterogeneous catalysis at ambient conditions

Materials applied as catalyst at ambient conditions include Activated Carbon (GAC), metals supported on metal oxide surfaces (TiO_2, Al_2O_3, ZrO_3, CeO_2, $FeOOH$, MnO_2, $Cu-Al_2O_3$, and $Cu-TiO_2$) or supported on activated carbon. The catalyst support serves to increase the surface area of the catalyst, decrease sintering and improve hydrophobicity as well as the thermal and chemical stability of the material [117]. Heterogeneous catalytic ozonation is an AOP in which the oxidative property of ozone is improved by adding solid catalytic materials. The process is potentially a low cost AOP which has been operated successfully at ambient conditions by several workers and may be relatively easier to apply in a water treatment plant [118]. It has been demonstrated that GAC can enhance ozone transformation into OH radicals [87,118-120]. Electrons in the graphenic layers and basic surface groups on GAC are the main factors responsible for the decomposition of O_3 into $OH^•$ [119,121-122]. These generated hydroxyl radicals are responsible for the oxidation of organics using O_3/ GAC process. Besides the catalytic role, GAC also serves as an important adsorbent for the organics been treated and would be effective for the removal of hydrophobic micro-pollutants that cannot be oxidized by ozone. Sanchez-Polo *et al.,* [87] applied the O_3/GAC AOP for the treatment of para-chlorobenzoate (pCBA) and compared the efficiency of this

process with the conventional homogeneous ozonation in alkaline medium (pH 7 and 9) and peroxone processes (O_3/H_2O_2). pCBA was selected for the study because of its low reactivity with O_3 (K_{O3}= 0.15 $M^{-1}s^{-1}$) and slow adsorption kinetics on GAC. Their report showed that the O_3/GAC system was inferior to the homogeneous processes. Radical generation in the heterogeneous system involved the adsorption of ozone onto the activated carbon and its subsequent breakdown to radicals. Since this process requires more than one phase, it is therefore more slower compared to the system where O_3 and the species (OH, H_2O_2 or soluble metals) initiating its breakdown are in the same phase. Despite this disadvantage, the use of heterogeneous catalyst for ozone breakdown is gathering interest. This is because the possibility of catalyst regeneration and reuse out ways the inefficiency of the heterogeneous process. More so, the use of metals in homogeneous process poses another problem as these metals whether toxic or not would require removal after the treatment process.

In a recent work, Oputu and co-workers applied FeOOH as potential catalyst for removal of 4-chlorophenol from aqueous medium. While the catalyst showed potential, reducing reaction time by one-third, the possibility of metal leaching was of concern. Further work by the group was centered on supporting the catalyst on support NiO to eliminate the catalyst breakdown and increase possibility of reuse. The uses of catalyst supports have become the trend of heterogeneous catalysis.

Heterogeneous wet oxidation

The application of heterogeneous catalyst to either the wet air oxidation (WAO, subsequently referred to as Catalytic Wet Air Oxidation, CWAO) or the Wet Peroxide (WPO, subsequently referred to as catalytic wet peroxide oxidation, CWPO) AOP (both described in section 5.5), have been reported [123-129]. The application of proper catalysts for CWAO, not only reduces the severity of the reaction conditions but also more easily decomposes even refractory pollutants, thereby reducing capital and operational cost [130-131]. Heterogeneous catalysts applied in these processes possess high temperature, physical, chemical and mechanical stability. They would also possess a high resistance to attrition over a wide pressure and temperature range.

Catalytic Wet Air Oxidation

Various heterogeneous catalyst including noble metals, metal oxides and mixed metal oxides have been extensively studied to enhance the efficiency of CWAO. In the three phase CWAO process, organic pollutants are oxidized by activated O_2 species in the presence of a solid catalyst, forming biodegradable intermediates (such as low molecular weight carboxylic acids), or are mineralized to CO_2, water and associated inorganic salts. Several recently developed heterogeneous catalysts, including transition metal oxides and noble metals deposited on different supports, have shown good catalytic activity in CWAO of organic pollutants present in drinking and wastewater [132-134]. The use of mixed metal oxides for CWAO of phenol in water was reported [123]. Batch experiments were run using varying combinations of copper, zinc and aluminum oxides in an autoclave and a paar reactor. The effect of operating variables such as catalyst loading, catalyst composition, temperature, oxygen partial pressure, initial phenol concentration and stirring speed was reported. The time required for total phenol conversion ranged from 0.5-2 hr and was dependent on the experimental conditions. When the reaction between oxygen species and phenol was started from room temperature, the degradation was observed to proceed via two regimes. Firstly, an induction period, after which there was a transition to a much higher activity regime. However, when the phenol was introduced after a preheating period of a solution saturated with oxygen, no induction period was observed.

An overview of the catalytic pattern of homogeneous (Cu^{2+}, Fe^{3+}, Mn^{2+}) and ceria-supported ($CuCeO_x$, $MnCeO_x$) transition metals in the CWAO of phenol has been reported [124]. Catalyst test were carried out at 150°C and 1.4 MPa using a PTF-lined autoclave

containing 0.25 mL, 1000 mg/L phenol and operated in a semi-batch mode. The catalytic homogeneous wet air oxidations were observed to proceed via an unselective autocatalytic free-radical path leading to refractory C1-C2 acids, while the CWAO on heterogeneous ceria gave superior efficiency and was accounted for by the Langmuir-Hinshekwood (L-H) mechanism. In a recent study, Yu and co-workers applied Ru supported on γ-Al$_2$O$_3$ and Ce/γ-Al$_2$O$_3$ for CWAO of isopropyl alcohol, phenol, acetic acid and N,N- dimethylformamide [128]. The efficiency of the catalyst was observed to increase with increasing temperature. The Ru-Ce/γ-Al$_2$O$_3$ catalyst produced superior removal efficiency compared to the Ru-γ-Al$_2$O$_3$ for all the substrates studied and ascribed to the better dispersion of the Ru particles on the Ce/γ-Al$_2$O$_3$ surface as well as increase in number of effectively active sites on the cluster-derived catalyst surface. The efficiency of Platinum (Pt) supported on activated carbon and on multi-walled Carbon Nano-Tubes (CNT), as heterogeneous catalyst in CWAO of selected pharmaceuticals was investigated by Benitez and coworkers [125]. Supported platinum catalyst has been reported to be highly effective in the oxidation of organic compounds [135-136]. Operating variables such as catalyst type, dose, temperature (120-140°C), and oxygen pressure (20-40 bar) were considered. There was significant enhancement in the removal of the pharmaceuticals using CWAO relative to WAO. Pt supported on activated carbon gave greater removal efficiency compared to Pt supported on CNT under the same conditions, reflecting the contribution of adsorption effects in addition to oxidation pathways for the removal of the pharmaceuticals under study.

A recent review by Kim and Ihm [50] summarizes heterogeneous catalysts applied in wet air oxidation systems for the removal of refractory organic pollutants in industrial wastewater. The review covers earlier application of CWAO to pollutants such as phenol and phenolic compounds, carboxylic acids, dyes, ammonia, and industrial waters. Also discussed in the review are reaction mechanisms and kinetics of CWAO and catalyst deactivation processes. Catalyst metals covered in the review include noble metals such as Ru, Rh, Pd, Ir and Pt as well as oxides of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo and Ce.

Catalytic wet peroxide oxidation

The mechanistic pathway for the generation of hydroxyl radicals from the decomposition of hydrogen peroxide proposed by Li *et al.,* [137] involves the initiation of a chain reaction by the reaction of hydrogen peroxide with homogeneous or heterogeneous species present in the reactor system. According to this suggested pathway, one way of improving the efficiency and yield of hydroxyl radicals, and thus lowering operating cost would be to introduce a heterogeneous catalyst into the reactor system. In view of this, several workers have applied various catalysts to WPO processes. Doocey and Sharratt [126] applied iron-loaded zeolite for the removal of chlorinated phenolic waste from aqueous waste. The efficient use of generated hydroxyl radicals is sustained by selective adsorption of the phenolic waste onto the iron-loaded zeolite followed, by in-situ Fenton oxidation by the hydroxyl radicals on the catalyst surface. This Fenton-type oxidation using iron supported on alumina and activated carbon has also been reported for the CWPO of halogenated organic compounds in ground water [127]. Over the last decade, hydrotalcite-like compounds (HT), otherwise referred to as Layered Double Hydroxide (LDHs) have received increasing attention owing to their diverse application especially in catalysis [138-139]. These compounds based on the mineral hydrotalcite have been synthesized and employed as catalyst in WPO processes [140-142]. The CWPO of phenol by Cu-Ni-Al hydrotalcite was recently reported [143]. There was a synergistic effect when the catalyst was applied in the presence of hydrogen peroxide, bringing about a complete (100%) removal of phenol within 2 hr when the system was operated at 30°C. When applied alone, the metal HT and hydrogen peroxide only brought about 15.7% and 39.7% removal of phenol, respectively. The effect of operating variables such as catalyst dose, temperature and oxidant/phenol ratio was also reported.

Heterogeneous Photocatalysis

The most common nanoparticle applied as a heterogeneous photo-catalyst in AOP is TiO_2. To this end, a vast number of articles have been devoted to studies of the application of this oxide to various pollutants, and in combination with other processes such as the ozonation and ultrasound-assisted-photolytic processes [96,108,144-150,151-152]. Others heterogeneous catalyst applied in AOP include: ZnO, SnO_2, Al_2O_3, In_2O_3, ZnS, Fe_2O_3, CeO_2, ZrO_2, SiO_2, CuO, MnO_2 and CdS [50,123,146-148]. While the physical, chemical and catalytic properties of these catalysts vary markedly, the principle of operation as photo-catalysts remains the same. The adsorption of electromagnetic energy (in the UV or visible region) by electrons on the surface of a photo-catalyst brings about an excitation of these surface electrons. When the energy absorbed is greater than the band-gap energy (ΔE), the excited electrons move from the valence-band to the conduction-band. This mechanism generates active species which promotes redox reactions. The absorption of photons with energy lower than ΔE or longer wavelengths usually causes energy dissipation in the forms of heat. A good schematic diagram illustrating the principle of TiO_2 photo-catalysis leading to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band has been described by Ahmed and co-authors [146-147].
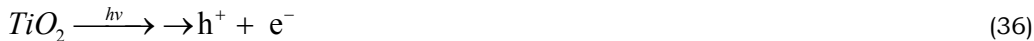
Photo-catalytic oxidation

Early applications of photo-catalyst include coating of self-cleaning windows and windshields, and floor-tiles which have been used in hospitals to reduce the density of colonies of microorganisms in hospital walls and floors. They have also been applied in architectural constructions, producing deodorizing, mold-preventing and self-cleaning surfaces [149]. In recent times, the application has extended to water purification for removal of organics in water. The use of UV/TiO_2 for the treatment of dye solutions and other refractory organic pollutants in water has been reported [96,108,151-152]. Mascolo and co-workers [152] applied the UV/TiO_2 process for the removal of Methyl-Tert-Butyl-Ether (MTBE) from (I) laboratory prepared solutions containing MTBE and (II) ground water samples containing MTBE collected from a petrochemical site in Southern Italy. The workers reported that the process was most suitable for the simulated wastewater and recommended that particular care should be taken when extrapolating organic degradation results obtained from synthetic aqueous solutions.

Saritha and co-workers [104] applied the UV/TiO_2 process for the removal of 4-chloro-2-nitrophenol, a USEPA listed pollutant, widely available in bulk drug and pesticide wastes. Under similar operating conditions, results for the UV/TiO_2 process were superior to the UV/H_2O_2, Fenton, peroxide and UV processes. The UV/TiO_2 process brought about an 85% mineralization of the pollutant in 120 min. In the absence of TiO_2, UV mineralization was very slow because 4-chloro-2-nitrophenol undergoes light absorptions which do not contribute to the removal of the compound. Due to surface are limitations and poor adsorption capacity of TiO_2 (resulting from its non-porous nature), present research is directed towards incorporating photo-catalysts on porous supports which would absorb target environmental pollutants more efficiently prior to subsequent oxidation by the photo-catalyst [153-155].

Recently, Chen and co-workers prepared and successfully applied TiO_2 co-pillared with SiO_2 on montmorillonite for the adsorption and photo-catalytic degradation of 2,4,6-trichlorophenol in water [156]. The application of TiO_2 on sepiolite for the degradation of pollutants has also been reported [157]. A recent review highlights the roles of titanium and ion-doped titanium oxide on photo-catalytic degradation of pollutants in aqueous solutions [158]. Other reviews covering a wide range of catalyst including ZnO, TiO_2, SnO_2, and doped metal oxides which incorporate noble and precious metals such as Au, Ag, Pt and Zr have been recently published [146,147].

Photo-catalytic ozonation

The basic mechanism of photo-catalytic ozonation may be represented by Equations 35-38;

$$TiO_2 \xrightarrow{\ hv\ } \rightarrow h^+ + e^- \tag{36}$$

$$O_3 + e^- \rightarrow O_3^- \tag{37}$$

$$O_3^- \rightarrow O_2 + O^- \tag{38}$$

$$H_2O + O^- \rightarrow OH^- + OH^{\bullet} \tag{39}$$

Even though the actual mechanism may be more complicated [159], the principle has been widely applied for the treatment of environmental pollutants in water [160-166]. The UV/TiO$_2$/O$_3$ process was reported to be superior to O$_3$, UV/O$_3$, and UV/TiO$_2$/O$_2$ process for the degradation of neonicotinoid insecticide in water [162]. The synergistic effect of O$_3$ on TiO$_2$ was evident at neutral and acidic pH. At basic pH, decomposition of O$_3$ by reaction with OH$^-$ was the prevailing mechanism for OH radical production [162,164]. A similar synergistic effect was also reported for the photo-catalytic ozonation of dimethyl phthalate using laboratory prepared TiO$_2$ [163]. The rate constants for the UV/TiO$_2$/O$_3$ process was 2.5(5.2) times more than that in UV/TiO$_2$/O$_2$ (UV/O$_3$) process. The TOC removal of the photo-catalytic ozonation process increased with increasing ozone dosage and was describe by the Langmuir-Hinshelwood model.

Conclusion

Protecting the integrity of our water resources is one of the most essential environmental issues of the 21st century. With the continued persistence of several toxic recalcitrant contaminants in ground and drinking water systems, it is evident that the currently employed treatment technologies are inadequate for removing certain contaminants currently detected in water. Nevertheless, bioremediation, MBRs and the AOPs treatment technologies have been reported to bring about commendable removal.

Bioremediation employ the use of microorganisms, fungi, algae, and enzymes to degrade or detoxify substances hazardous to human health or environment [165-167,168]. Phytoremediation is a specific type of bioremediation technology in which accumulator plants effective for the uptake of target pollutants are applied to the remediation of contaminated soil, water and wastewater. In bioremediation, microorganisms with the ability to transform toxic matters in their normal biological activities to yield non-toxic by-products are used. Thus, attention is currently drawn towards genetically engineered microorganisms to increase their ability to metabolize specific pollutants. The use of plants and microbes to detoxify and clean up contaminated sites is safe, cost-effective, less intrusive to the contaminated site, and more environmental friendly in terms of its end products.

MBRs, a combination of membrane technology (microfiltration or ultrafiltration) and biological treatment process have also proven very effective in removing organic, inorganic and biological contaminants from wastewater.

The AOP treatments in some cases have been reported to bring about complete mineralization of xenobiotic organic pollutants in water. AOPs have emerged as versatile technologies for the treatment of contaminated water and wastewater, however, many articles have only reported the efficiency of AOPs without necessarily identifying the reaction intermediates or characterizing the final end products left in solution. It is important to note that the complete removal of a pollutant from matrix may not bring about a cleaner water stream as the end product water may contain more toxic organics which are resistant to the applied AOP. It is therefore recommended that analytical techniques for determinations

be combined with other methods to monitor the complete mineralization of pollutants and their intermediates. More work is also needed to be done in the area of catalyst development in photolytic systems with interest being on visible light application, and in developing catalysts capable of operating at near ambient conditions in wet oxidation processes. Also the application of AOP to composite mixture of pollutants requires further study as rates and mechanisms for single and mixed systems would vary markedly. Furthermore, the development and application of catalysts to ozonation processes which would improve efficiency of the process or limit restrictions from operating variables such as pH would also be of interest.

In conclusion, many of the applications of water and wastewater treatment technologies reported to date are usually limited to single modeled pollutants. A few other articles have extended developed methods to real wastewater scenarios. While it is impractical to monitor all the pollutants individually/simultaneously in a real wastewater, it is important to study the effect these technologies have on groups of chemicals which are found together in real contaminated water and wastewater.

References

1. Andreozzi R, Caprio V, Marotta R, Radovnikovic A (2003) Ozonation and H2O2/UV treatment of clofibric acid in water: a kinetic investigation. See comment in PubMed Commons below J Hazard Mater 103: 233-246.

2. Castiglioni SR, Fanelli D, Calamari R, Bagnati ZE (2004) Methodological approaches for studying pharmaceuticals in the environment by comparing predicted and measured concentrations in river Po, Italy. Regul Toxicol Pharmacol 39(1): 25-32.

3. Brown KD, Kulis J, Thomson B, Chapman TH, Mawhinney DB (2006) Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico. See comment in PubMed Commons below Sci Total Environ 366: 772-783.

4. Stackelberg PE, Gibs J, Furlong ET, Meyer MT, Zaugg SD, et al. (2007) Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. See comment in PubMed Commons below Sci Total Environ 377: 255-272.

5. Focazio MJ, Kolpin DW, Barnes KK, Furlong ET, Meyer MT, et al. (2008) A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States--II) untreated drinking water sources. See comment in PubMed Commons below Sci Total Environ 402: 201-216.

6. Wang C, Shi H, Adams CD, Gamagedara S, Stayton I, et al. (2011) Investigation of pharmaceuticals in Missouri natural and drinking water using high performance liquid chromatography-tandem mass spectrometry. See comment in PubMed Commons below Water Res 45: 1818-1828.

7. Daughton CG, Ternes TA (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? See comment in PubMed Commons below Environ Health Perspect 107 Suppl 6: 907-938.

8. Ikehata K, El-Din MG (2005) Aqueous pesticide degradation by ozonation and ozone-based advanced oxidation processes: A review (Part II). Ozone: Sci Eng 27(3): 173-202.

9. Ikehata K, Gamal El-Din M (2005) Aqueous Pesticide Degradation by Ozonation and Ozone-Based Advanced Oxidation Processes: A Review (Part I). Ozone: Sci Eng 27(2): 83-114.

10. Correia A, Galesio M, Santos H, Rial-Otero R, Lodeiro C (2007) Can sample treatments based on advanced oxidation processes assisted by high-intensity focused ultrasound be used for toxic arsenic determination in human urine by flow-injection hydride-generation atomic absorption spectrometry. Talanta 72(3): 968-975.

11. Gilliom RJ, Barbash JE, Kolpin DW, Larson SJ (1999) Peer reviewed: testing water quality for pesticide pollution. See comment in PubMed Commons below Environ Sci Technol 33: 164A-9A.

12. Cortés S, Sarasa J, Ormad P, Gracia R, Ovelleiro JL (2000) Comparative Efficiency of the Systems O3/High pH And 03/catalyst for the Oxidation of Chlorobenzenes in Water. Ozone: Sci Eng 22(4): 415-426.

13. Gültekin I, Ince NH (2007) Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes. See comment in PubMed Commons below J Environ Manage 85: 816-832.

14. Erickson BE (2002) Analyzing the ignored environmental contaminants. See comment in PubMed Commons below Environ Sci Technol 36: 140A-145A.

15. Tambosi JL, de Sena RF, Gebhardt W, Moreira RFPM, José HJ (2009) Physicochemical and Advanced Oxidation Processes – A Comparison of Elimination Results of Antibiotic Compounds Following an MBR Treatment. Ozone: Sci Eng 31(6): 428-435.

16. Fukuhara T, Iwasaki S, Kawashima M, Shinohara O, Abe I (2006) Absorbability of estrone and 17beta-estradiol in water onto activated carbon. See comment in PubMed Commons below Water Res 40: 241-248.

17. Choi KJ, Kim SG, Kim CW, Kim SH (2005) Effects of activated carbon types and service life on removal of endocrine disrupting chemicals: amitrol, nonylphenol, and bisphenol-A. See comment in PubMed Commons below Chemosphere 58: 1535-1545.

18. Oller I, Malato S, Sanchez-Perez JA (2010) Combination of advanced oxidation processes and biological treatments for wastewater decontamination- A review. Sci Total Environ Article in press.

19. http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/5619/2/EUR%2020418%20EN-2.pdf

20. Office of Technology Assessment (1991), Bioremediation of marine oil spills: An analysis of oil spill response technologies, OTA-BP-O-70, Washington, DC.

21. Singh R, Singh P, Sharma R (2014) Microorganism as a tool of bioremediation technology for cleaning environment: A review. Proceedings of the International Academy of Ecology and Environmental Sciences 4(1): 1-6.

22. Pirzadah TB, Malik B, Tahir I, Kumar M, Varma A (2015) Chapter 5 - Phytoremediation: An Eco-Friendly Green Technology for Pollution Prevention, Control and Remediation. Soil Remediation and Plants: Prospects and Challenges, pp 107-129.

23. Rani K, Dhania G (2014) Bioremediation and biodegradation of pesticide from contaminated soil and water - A noval approach. Int J Curr Microbiol App Sci 3(10): 23-33.

24. Mehta SK, Gaur JP (2005) Use of algae for removing heavy metal ions from wastewater: progress and prospects. See comment in PubMed Commons below Crit Rev Biotechnol 25: 113-152.

25. Zayadan BK, Gaballah MM, Saleh MM (2014) Bioremediation of Al-Sayyadin lagoon polluted water using wild and mutant strains of microalgae. African Journal of Microbiology Research 8(26): 2522-2533.

26. Chekroun KB, Sánchez E, Baghour M (2014) The role of algae in bioremediation of organic pollutants. International Research Journal of Public and Environmental Health 1(2): 19-32.

27. Sheela B, Khasim Beebi Sk (2014) Bioremediation of ammonia from polluted waste waters – A review. American Journal of Microbiological Res 2.6: 201-210.

28. Olawale AM (2014) Bioremediation of waste water from an industrial effluent system in Nigeria using Pseudomonas aeruginosa: Effectiveness tested on albino rats. J Pet Environ Biotechnol 5: 166. doi: 10.4172/2157-7463.1000167.

29. Dmuchowski W, Gozdowski D, Bragoszewska P, Baczewska AH, Suwara I (2014) hytoremediation of zinc contaminated soils using silver birch (Betula pendula Roth). Ecological Engineering 71: 32–35.

30. Favas PJC, Pratas J, Varun M, D'Souza R, Paul MS (2014) Phytoremediation of soils contaminated with metals and metalloids at mining areas: Potential of native flora. Environmental Risk Assessment of Soil Contamination, Dr. Maria C. Hernandez Soriano (Ed.), ISBN: 978-953-51-1235-8, InTech, DOI: 10.5772/57469.

31. Ndimele PE, Kumolu-Johnson CA, Chukwuka KS, Ndimele CC, Ayorinde OA, et al. (2014) Phytoremediation of Iron (Fe) and Copper (Cu) by Water Hyacinth (Eichhornia crassipes (Mart.) Solms). Trends in Applied Sciences Research 9: 485-493.

32. Syuhaida AWA, Norkhadijah SIS, Praveena SM, Suriyani A (2014) The comparison of phytoremediation abilities of water mimosa and water hyacinth. ARPN Journal of Science and Technology 4(12): 722-731.

33. Pedro CA, Santos MS, Ferreira SM, Gonçalves SC (2013) The influence of cadmium contamination and salinity on the survival, growth and phytoremediation capacity of the saltmarsh plant Salicornia ramosissima. See comment in PubMed Commons below Mar Environ Res 92: 197-205.

34. Augustynowicz J, Tokarz K, Baran A, PÅ‚achno BJ (2014) Phytoremediation of water polluted by thallium,

cadmium, zinc, and lead with the use of macrophyte Callitriche cophocarpa. See comment in PubMed Commons below Arch Environ Contam Toxicol 66: 572-581.

35. Marrugo-Negrete J, Durango-Hernández J, Pinedo-Hernández J, Olivero-Verbel J, Díez S (2015) Phytoremediation of mercury-contaminated soils by Jatropha curcas. See comment in PubMed Commons below Chemosphere 127: 58-63.

36. Newman LA, Wang X, Muiznieks IA, Ekuan G, Ruszaj M, Cortellucci R, Domroes D, Karscig G, Newman T, Crampton RS, Hashmonay RA, Yost MG, Heilman PE, Duffy J, Gordon MP, Strand SE (1999) Remediation of trichloroethylene in an artificial aquifer with trees: A controlled field study. Environ Sci Technol 33(13): 2257-2265.

37. Cicek N (2003) A review of membrane bioreactors and their potential application in the treatment of agricultural wastewater. Canadian Biosystems Engineering 45: 6.37-6.49.

38. Glaze WH, Kang J-W, Chapin DH (1987) The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. Ozone: Sci Eng 9(4): 335-352.

39. An T, Yang H, Li G, Song W, Cooper WJ, et al. (2010) Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. Appl Catal B 94(3-4): 288-294.

40. Sun J, Li X, Feng J, Tian X (2009) Oxone/Co(2+) oxidation as an advanced oxidation process: comparison with traditional Fenton oxidation for treatment of landfill leachate. See comment in PubMed Commons below Water Res 43: 4363-4369.

41. Yang S, Wang P, Yang X, Wei G, Zhang W, et al. (2009) A novel advanced oxidation process to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation. See comment in PubMed Commons below J Environ Sci (China) 21: 1175-1180.

42. Yasar A, Ahmad N, Latif H, Amanat Ali Khan A (2007) Pathogen Re-Growth in UASB Effluent Disinfected By UV, O3, H2O2, and Advanced Oxidation Processes. Ozone: Sci Eng 29(6): 485-492.

43. Klavarioti M, Mantzavinos D, Kassinos D (2009) Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. See comment in PubMed Commons below Environ Int 35: 402-417.

44. Méndez-Arriaga F, Torres-Palma RA, Pétrier C, Esplugas S, Gimenez J (2009) Mineralization enhancement of a recalcitrant pharmaceutical pollutant in water by advanced oxidation hybrid processes. See comment in PubMed Commons below Water Res 43: 3984-3991.

45. Olmez-Hanci T, Dalmaz B, Arslan-Alaton I, Kabdasli I, Tünay O (2010) Kinetic Modeling and Toxicity Assessment of Diethyl Phthalate Treated by H2O2/UV-C Process. Ozone: Sci Eng 32(4): 238-243.

46. Abdessalem AK, Oturan MA, Oturan N, Bellakhal N, Dachraoui M (2010) Treatment of an aqueous pesticides mixture solution by direct and indirect electrochemical advanced oxidation processes. Int J Environ Anal Chem 90(3-6): 468-477.

47. Ballesteros Martín MM, Sánchez Pérez JA, Casas López JL, Oller I, Malato Rodríguez S (2009) Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. See comment in PubMed Commons below Water Res 43: 653-660.

48. Ballesteros Martín MM, Sánchez Pérez JA, García Sánchez JL, Montes de Oca L, Casas López JL, et al. (2008) Degradation of alachlor and pyrimethanil by combined photo-Fenton and biological oxidation. See comment in PubMed Commons below J Hazard Mater 155: 342-349.

49. Bandala ER, Peláez MA, Salgado MJ, Torres L (2008) Degradation of sodium dodecyl sulphate in water using solar driven Fenton-like advanced oxidation processes. See comment in PubMed Commons below J Hazard Mater 151: 578-584.

50. Kim KH, Ihm SK (2011) Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review. See comment in PubMed Commons below J Hazard Mater 186: 16-34.

51. Pimentel M, Oturan N, Dezotti M, Oturan MA (2008) Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode. Appl Catal B 83(1-2): 140-149.

52. Ayoub K, van Hullebusch ED, Cassir M, Bermond A (2010) Application of advanced oxidation processes for TNT removal: A review. See comment in PubMed Commons below J Hazard Mater 178: 10-28.

53. Ikematsu T, Hayashi N, Ihara S, Satoh S, Yamabe C (2004) Advanced oxidation processes (AOPs) assisted by excimer lamp. Vacuum 73(3-4): 579-582.

54. Chin A, Bérubé PR (2005) Removal of disinfection by-product precursors with ozone-UV advanced oxidation process. See comment in PubMed Commons below Water Res 39: 2136-2144.

55. Feng F, Xu Z, Li X, You W, Zhen Y (2010) Advanced treatment of dyeing wastewater towards reuse by the combined Fenton oxidation and membrane bioreactor process. See comment in PubMed Commons below J Environ Sci (China) 22: 1657-1665.

56. Catalkaya EC, Kargi F (2007) Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: a comparative study. See comment in PubMed Commons below J Hazard Mater 139: 244-253.

57. Jamil TS, Ghaly MY, El-Seesy IE, Souaya ER, Nasr RA (2011) A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. See comment in PubMed Commons below J Hazard Mater 185: 353-358.

58. Cortez S, Teixeira P, Oliveira R, Mota M (2011) Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments. See comment in PubMed Commons below J Environ Manage 92: 749-755.

59. Rahman MF, Jasim SY, Yanful EK, Ndiongue S, Borikar D (2010) Advanced Oxidation Treatment of Drinking Water: Part II. Turbidity, Particles and Organics Removal from Lake Huron Water. Ozone: Sci. Eng. 32(5): 295-304.

60. Rahman MF, Yanful EK, Jasim SY, Bragg LM, Servos MR, et al. (2010) Advanced Oxidation Treatment of Drinking Water: Part I. Occurrence and Removal of Pharmaceuticals and Endocrine-Disrupting Compounds from Lake Huron Water. Ozone: Sci Eng 32(4): 217-229.

61. Grafias P, Xekoukoulotakis NP, Mantzavinos D, Diamadopoulos E (2010) Pilot treatment of olive pomace leachate by vertical-flow constructed wetland and electrochemical oxidation: an efficient hybrid process. See comment in PubMed Commons below Water Res 44: 2773-2780.

62. Mandal T, Maity S, Dasgupta D, Datta S (2010) Advanced oxidation process and biotreatment: Their roles in combined industrial wastewater treatment. Desalination 250(1): 87-94.

63. Julcour Lebigue C, Andriantsiferana C, N'Guessan K, Ayral C, Mohamed E, et al. (2010) Application of sludge-based carbonaceous materials in a hybrid water treatment process based on adsorption and catalytic wet air oxidation. J Environ Manage 91(12): 2432-2439.

64. Rosenfeldt EJ, Chen PJ, Kullman S, Linden KG (2007) Destruction of estrogenic activity in water using UV advanced oxidation. See comment in PubMed Commons below Sci Total Environ 377: 105-113.

65. Skoumal M, Cabot PL, Centellas F, Arias C, Rodríguez RM, et al. (2006) Mineralization of paracetamol by ozonation catalyzed with Fe2+, Cu2+ and UVA light. Appl Catal B 66(228-240.

66. Benitez FJ, García J, Acero JL, Real FJ, Roldan G (2015) Non-catalytic and catalytic wet air oxidation of pharmaceuticals in ultra-pure and natural waters. Process Saf Environ Prot. Article in Press.

67. Hoigné J (1997) Inter-calibration of OH radical sources and water quality parameters. Water Sci Technol 35(4): 1-8.

68. Alaton IA, Balcioglu IA, Bahnemann DW (2002) Advanced oxidation of a reactive dyebath effluent: comparison of O3, H2O2/UV-C and TiO2/UV-A processes. See comment in PubMed Commons below Water Res 36: 1143-1154.

69. Chelme-Ayala P, El-Din MG, Smith DW (2010) Treatability Study on Membrane Concentrate Containing Pesticides Using Advanced Oxidation Processes. Ozone: Sci Eng 32(1): 16-24.

70. Consejo C, Ormad MP, Sarasa J, Ovelleiro JL (2005) Treatment of Wastewater Coming from Painting Processes: Application of Conventional and Advanced Oxidation Technologies. Ozone: Sci Eng 27(4): 279-286.

71. Dombi A, Ilisz I, László Z, Wittmann G (2002) Comparison of Ozone-based and other (VUV and TiO2/UV) Radical Generation Methods in Phenol Decomposition. Ozone: Sci Eng 24(1): 49-54.

72. Schröder HF, Meesters RJW (2005) Stability of fluorinated surfactants in advanced oxidation processes--A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. J Chromatogr A 1082(1): 110-119.

73. Wu JJ, Muruganandham M, Chang LT, Yang JS, Chen SH (2007) Ozone-Based Advanced Oxidation Processes for the Decomposition of N-Methyl-2-Pyrolidone in Aqueous Medium. Ozone: Sci Eng 29(3): 177-183.

74. Wu JJ, Muruganandham M, Chen SH (2007) Degradation of DMSO by ozone-based advanced oxidation processes. See comment in PubMed Commons below J Hazard Mater 149: 218-225.

75. Wu JJ, Wu CC, Ma HW, Chang CC (2004) Treatment of landfill leachate by ozone-based advanced oxidation processes. See comment in PubMed Commons below Chemosphere 54: 997-1003.

76. Coca M, Peña M, González G (2005) Chemical Oxidation Processes for Decolorization of Brown-Colored Molasses Wastewater. Ozone: Sci Eng 27(5): 365-369.

77. Wang D, Bolton JR, Hofmann R (2012) Medium pressure UV combined with chlorine advanced oxidation for trichloroethylene destruction in a model water. See comment in PubMed Commons below Water Res 46: 4677-4686.

78. Prado J, Esplugas S (1999) Comparison of Different Advanced Oxidation Processes Involving Ozone to Eliminate Atrazine. Ozone: Sci Eng 21(1): 39-52.

79. Ledakowicz S, Michniewicz M, Jagiella A, Stufka-Olczyk J, Martynelis M (2006) Elimination of resin acids by advanced oxidation processes and their impact on subsequent biodegradation. See comment in PubMed Commons below Water Res 40: 3439-3446.

80. Walling C (1975) Fenton's reagent revisited. Acc Chem Res 8: 125-131.

81. Chen XM, da Silva DR, Martínez-Huitle CA (2010) Application of advanced oxidation processes for removing salicylic acid from synthetic wastewaters. Chin Chem Lett 21(1): 101-104.

82. Faouzi M, Cañizares P, Gadri A, Lobato J, Nasr B, et al. (2006) Advanced oxidation processes for the treatment of wastes polluted with azoic dyes. Electrochim Acta 52(1): 325-331.

83. Javier Benitez F, Acero JL, Real FJ (2002) Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes. See comment in PubMed Commons below J Hazard Mater 89: 51-65.

84. Sun JH, Sun SP, Fan MH, Guo HQ, Lee YF (2008) Oxidative decomposition of p-nitroaniline in water by solar photo-Fenton advanced oxidation process. See comment in PubMed Commons below J Hazard Mater 153: 187-193.

85. Al Momani F (2007) Degradation of cyanobacteria anatoxin-a by advanced oxidation processes. Sep Purif Technol 57(1): 85-93.

86. Sánchez-Polo M, Rivera-Utrilla J, Méndez-Díaz JD, Canonica S, von Gunten U (2007) Photooxidation of naphthalenesulfonic acids: comparison between processes based on O(3), O(3)/activated carbon and UV/H(2)O(2). See comment in PubMed Commons below Chemosphere 68: 1814-1820.

87. Catorceno LLC, Nogueira KRB, Teixeira ACSC (2010) Treatment of Aqueous Effluents Containing Phenol by the O3, O3-UV, and O3-H2O2 Processes: Experimental Study and Neural Network Modeling. Sep Sci Technol 45(11): 1521-1528.

88. José HJ, Gebhardt W, Moreira RFPM, Pinnekamp J, Schröder HF (2010) Advanced Oxidation Processes for the Elimination of Drugs Resisting Biological Membrane Treatment. Ozone: Sci Eng 32(5): 305-312.

89. Wang K, Guo J, Yang M, Junji H, Deng R (2009) Decomposition of two haloacetic acids in water using UV radiation, ozone and advanced oxidation processes. See comment in PubMed Commons below J Hazard Mater 162: 1243-1248.

90. Vogelpohl A (2007) Applications of AOPs in wastewater treatment. See comment in PubMed Commons below Water Sci Technol 55: 207-211.

91. Ledakowicz S, Solecka M, Zylla R (2001) Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes. See comment in PubMed Commons below J Biotechnol 89: 175-184.

92. Kestioglu K, Yonar T, Azbar N (2005) Feasibility of physico-chemical treatment and Advanced Oxidation Processes (AOPs) as a means of pretreatment of olive mill effluent (OME). Process Biochem (Amsterdam, Neth.) 40(7): 2409-2416.

93. Benitez FJ, Beltran-Heredia J, Acero JL, Rubio FJ (2000) Contribution of free radicals to chlorophenols decomposition by several advanced oxidation processes. See comment in PubMed Commons below Chemosphere 41: 1271-1277.

94. Cañizares P, Paz R, Sáez C, Rodrigo MA (2008) Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes: A comparison with other advanced oxidation processes. Electrochim Acta 53(5): 2144-2153.

95. Sauer TP, Casaril L, Oberziner ALB, José HJ, Moreira RdFPM (2006) Advanced oxidation processes applied to tannery wastewater containing Direct Black 38--Elimination and degradation kinetics. J Hazard Mater 135(1-3): 274-279.

96. Thiruvenkatachari R, Kwon TO, Jun JC, Balaji S, Matheswaran M, et al. (2007) Application of several advanced oxidation processes for the destruction of terephthalic acid (TPA). See comment in PubMed Commons below J Hazard Mater 142: 308-314.

97. Catalkaya EC, Sengül F (2006) Application of Box-Wilson experimental design method for the photodegradation of bakery's yeast industry with UV/H2O2 and UV/H2O2/Fe(II) process. See comment in PubMed Commons below J Hazard Mater 128: 201-207.

98. Prato-Garcia D, Vasquez-Medrano R, Hernandez-Esparza M (2009) Solar photoassisted advanced oxidation of synthetic phenolic wastewaters using ferrioxalate complexes. Solar Energy 83(3): 306-315.

99. Huang Y-H, Huang Y-F, Chang P-S, Chen C-Y (2008) Comparative study of oxidation of dye-Reactive Black B by different advanced oxidation processes: Fenton, electro-Fenton and photo-Fenton. J Hazard Mater 154(1-3): 655-662.

100. Kusvuran E, Erbatur O (2004) Degradation of aldrin in adsorbed system using advanced oxidation processes: comparison of the treatment methods. See comment in PubMed Commons below J Hazard Mater 106: 115-125.

101. Liou MJ, Lu MC, Chen JN (2003) Oxidation of explosives by Fenton and photo-Fenton processes. See comment in PubMed Commons below Water Res 37: 3172-3179.

102. Muñoz I, Rieradevall J, Torrades F, Peral J, Domènech X (2006) Environmental assessment of different advanced oxidation processes applied to a bleaching Kraft mill effluent. See comment in PubMed Commons below Chemosphere 62: 9-16.

103. Saritha P, Aparna C, Himabindu V, Anjaneyulu Y (2007) Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol. See comment in PubMed Commons below J Hazard Mater 149: 609-614.

104. He Z, Song S, Xia M, Qiu J, Ying H, et al. (2007) Mineralization of C.I. Reactive Yellow 84 in aqueous solution by sonolytic ozonation. See comment in PubMed Commons below Chemosphere 69: 191-199.

105. Shemer H1, Narkis N (2005) Trihalomethanes aqueous solutions sono-oxidation. See comment in PubMed Commons below Water Res 39: 2704-2710.

106. Muruganandham M, Swaminathan M (2007) Solar driven decolourisation of Reactive Yellow 14 by advanced oxidation processes in heterogeneous and homogeneous media. Dyes Pigm 72(2): 137-143.

107. Kusvuran E, Gulnaz O, Irmak S, Atanur OM, Yavuz HI, et al. (2004) Comparison of several advanced oxidation processes for the decolorization of Reactive Red 120 azo dye in aqueous solution. See comment in PubMed Commons below J Hazard Mater 109: 85-93.

108. Debellefontaine H, Foussard JN (2000) Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. Waste Manage 20(15): 15-25.

109. García-Molina V, López-Arias M, Florczyk M, Chamarro E, Esplugas S (2005) Wet peroxide oxidation of chlorophenols. See comment in PubMed Commons below Water Res 39: 795-802.

110. Marken F, Tsai Y-C, Coles BA, Matthews SL, Compton RG (2000) Microwave activation of electrochemical processes: convection, thermal gradients and hot spot formation at the electrode|solution interface. New J Chem 24(9): 653-658.

111. Horikoshi S, Kajitani M, Sato S, Serpone N (2007) A novel environmental risk-free microwave discharge electrodeless lamp (MDEL) in advanced oxidation processes: Degradation of the 2,4-D herbicide. J Photochem Photobiol A 189(2-3): 355-363.

112. Wang Y, Wei Y, Liu J (2009) Effect of H2O2 dosing strategy on sludge pretreatment by microwave-H2O2 advanced oxidation process. See comment in PubMed Commons below J Hazard Mater 169: 680-684.

113. Guwy AJ, Buckland H, Hawkes FR, Hawkes DL (1998) Active biomass in activated sludge: Comparison of respirometry with catalase activity measured using an on-line monitor. Water Res 32(12): 3705-3709.

114. Guwy AJ, Martin SR, Hawkes FR, Hawkes DL (1999) Catalase activity measurements in suspended aerobic biomass and soil samples. Enzyme Microb Technol 25(8-9): 669-676.

115. Ayanda OS, Petrik LF (2014) Nanotechnology: The Breakthrough in Water and Wastewater Treatment. Int J Chem Mater Environ Res 1 (1): 1-2.

116. Poyatos J, Muñio M, Almecija M, Torres J, Hontoria E, et al. (2010) Advanced Oxidation Processes for Wastewater Treatment: State of the Art. Water, Air, Soil Pollut 205(1): 187-204.

117. Ma J, Sui M-H, Chen Z-L, Wang L-N (2004) Degradation of Refractory Organic Pollutants by Catalytic Ozonation—Activated Carbon and Mn-Loaded Activated Carbon as Catalysts. Ozone: Sci Eng 26(1): 3-10.

118. Rivera-Utrilla J, Sánchez-Polo M, Méndez-Díaz JD, Ferro-García MA, Bautista-Toledo MI (2008) Behavior of two different constituents of natural organic matter in the removal of sodium dodecylbenzenesulfonate by O3 and O3-based advanced oxidation processes. See comment in PubMed Commons below J Colloid Interface Sci 325: 432-439.

119. Bourbigot MM, Hascoet MC, Levi Y, Erb F, Pommery N (1986) Role of ozone and granular activated carbon in the removal of mutagenic compounds. See comment in PubMed Commons below Environ Health Perspect 69: 159-163.

120. Sánchez-Polo M, Salhi E, Rivera-Utrilla J, von Gunten U (2006) Combination of Ozone with Activated Carbon as an Alternative to Conventional Advanced Oxidation Processes. Ozone: Sci Eng 28(4): 237-245.

121. Sánchez-Polo , von Gunten U, Rivera-Utrilla J (2005) Efficiency of activated carbon to transform ozone into *OH radicals: influence of operational parameters. See comment in PubMed Commons below Water Res 39: 3189-3198.

122. Akyurtlu JF, Akyurtlu A, Kovenklioglu S (1998) Catalytic oxidation of phenol in aqueous solutions. Catal Today 40(4): 343-352.

123. Arena F, Italiano C, Raneri A, Saja C (2010) Mechanistic and kinetic insights into the wet air oxidation of phenol with oxygen (CWAO) by homogeneous and heterogeneous transition-metal catalysts. Appl Catal B 99(1-2): 321-328.

124. Benitez FJ, Acero JL, Real FJ, Roldan G, Casas F (2011) Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices. Chem Eng J (Lausanne) 168(3): 1149-1156.

125. Doocey DJ, Sharratt PN (2004) Zeolite-Mediated Advanced Oxidation of Model Chlorinated Phenolic Aqueous Waste: Part 1: Aqueous Phase Fenton Catalysis. Process Saf Environ Prot 82(5): 352-358.

126. Hofmann J, Freier U, Wecks M, Demund A (2005) Degradation of halogenated organic compounds in ground water by heterogeneous catalytic oxidation with hydrogen peroxide. Top Catal 33(1): 243-247.

127. Yu C, Zhao P, Chen G, Hu B (2011) Al2O3 supported Ru catalysts prepared by thermolysis of Ru3(CO)12 for catalytic wet air oxidation. Appl Surf Sci 257(17): 7727-7731.

128. Zhan Y, Li H, Chen Y (2010) Copper hydroxyphosphate as catalyst for the wet hydrogen peroxide oxidation of azo dyes. See comment in PubMed Commons below J Hazard Mater 180: 481-485.

129. Bhargava Sk, Tardio J, Prasad J, Foger K, Akolekar DB, et al. (2006) Wet oxidation and catalytic wet oxidation. Ind Eng Chem Res 45: 1221-1258.

130. Larachi F (2005) Catalytic wet oxidation: micro-meso-macro methodology from catalyst synthesis to reactor design. Top Catal 33: 109-134.

131. Gomes HT, Figueiredo JL, Faria JL, Serp P, Kalck P (2002) Carbon-supported iridium catalysts in the catalytic wet air oxidation of carboxylic acids: kinetics and mechanistic interpretation. J Mol Catal A Chem 182-183:47-60.

132. Levec J, Pintar A (2007) Catalytic wet-air oxidation processes: A review. Catal Today 124(3-4): 172-184.

133. Liu WM, Hu YQ, Tu ST (2010) Active carbon-ceramic sphere as support of ruthenium catalysts for catalytic wet air oxidation (CWAO) of resin effluent. See comment in PubMed Commons below J Hazard Mater 179: 545-551.

134. Garcia J, Gomes HT, Serp P, Kalck P, Figueiredo JL, Faria JL (2005) Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds. Catal Today 102-103: 101-109.

135. Mikulová J, Rossignol S, Barbier Jr J, Mesnard D, Kappenstein C, et al. (2007) Ruthenium and platinum catalysts supported on Ce, Zr, Pr-O mixed oxides prepared by soft chemistry for acetic acid wet air oxidation. Appl Catal B 72(1-2): 1-10.

136. Li L, Chen P, Gloyna EF (1991) Generalized kinetic model for wet oxidation of organic compounds. AIChE J 37: 1687–1697.

137. Centi G, Perathoner S (2008) Catalysis by layered materials: A review. Microporous Mesoporous Mater 107(1-2): 3-15.

138. Debecker DP, Gaigneaux EM, Busca G (2009) Exploring, tuning, and exploiting the basicity of hydrotalcites for applications in heterogeneous catalysis. See comment in PubMed Commons below Chemistry 15: 3920-3935.

139. Dubey A, Kannan S, Velu S, Suzuki K (2003) Catalytic hydroxylation of phenol over CuM(II)M(III) ternary hydrotalcites, where M(II) = Ni or Co and M(III) = Al, Cr or Fe. Appl Catal A 238(2): 319-326.

140. Kannan S, Dubey A, Knozinger H (2005) Synthesis and characterization of CuMgAl ternary hydrotalcites as catalysts for the hydroxylation of phenol. J Catal 231(2): 381-392.

141. Wang H, Xiang X, Li F, Evans DG, Duan X (2009) Investigation of the structure and surface characteristics of Cu-Ni-M(III) mixed oxides (M = Al, Cr and In) prepared from layered double hydroxide precursors. Appl Surf Sci 255(15): 6945-6952.

142. Zhou S, Qian Z, Sun T, Xu J, Xia C (2015) Catalytic wet peroxide oxidation of phenol over Cu-Ni-Al hydrotalcite. Appl Clay Sci. Article in Press.

143. Madhavan J, Grieser F, Ashokkumar M (2010) Degradation of orange-G by advanced oxidation processes. See comment in PubMed Commons below Ultrason Sonochem 17: 338-343.

144. Madhavan J, Kumar PS, Anandan S, Zhou M, Grieser F, et al. (2010) Ultrasound assisted photocatalytic degradation of diclofenac in an aqueous environment. See comment in PubMed Commons below Chemosphere 80: 747-752.

145. Ahmed S, Rasul MG, Brown R, Hashib MA (2011) Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. See comment in PubMed Commons below J Environ Manage 92: 311-330.

146. Ahmed S, Rasul MG, Martens WN, Brown R, Hashib MA (2010) Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments. Desalination 261(1-2): 3-18.

147. Kamat PV, Meisel D (2002) Nanoparticles in advanced oxidation processes. Curr Opin Colloid Interface Sci 7(5-6): 282-287.

148. Heller A (1995) Chemistry and Applications of Photocatalytic Oxidation of Thin Organic Films. Acc Chem Res 28(12): 503-508.

149. Oputu O, Chowdhury M, Nyamayaro K, Fatoki O, Fester V (2015) Catalytic activities of ultra-small β-FeOOH nanorods in ozonation of 4-chlorophenol. See comment in PubMed Commons below J Environ Sci (China) 35: 83-90.

150. Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, et al. (2002) Photocatalytic degradation of various types of dyes (alizarin S, Crocein orange G, methyl red, congo red, methylene blue) in water by UV-irradiated titania. Appl Catal B 39: 75-90.

151. Mascolo G, Ciannarella R, Balest L, Lopez A (2008) Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: a laboratory investigation. See comment in PubMed Commons below J Hazard Mater 152: 1138-1145.

152. Fatimah I, Wang S, Narsito, Wijaya K (2010) Composites of TiO2-aluminum pillared montmorillonite: Synthesis, characterization and photocatalytic degradation of methylene blue. Appl Clay Sci 50(4): 588-593.

153. Ökte AN, Yilmaz Ö (2009) La and Ce loaded TiO2-ZSM-5 catalysts: Comparative characterization and photocatalytic activity investigations. Microporous Mesoporous Mater 126(3): 245-252.

154. Papoulis D, Komarneni S, Nikolopoulou A, Tsolis-Katagas P, Panagiotaras D, et al.(2010) Palygorskite- and Halloysite-TiO2 nanocomposites: Synthesis and photocatalytic activity. Appl Clay Sci 50(1): 118-124.

155. Chen J, Liu X, Li G, Nie X, An T, et al. (2011) Synthesis and characterization of novel SiO2 and TiO2 co-pillared montmorillonite composite for adsorption and photocatalytic degradation of hydrophobic organic pollutants in water. Catal Today 164(1): 364-369.

156. Karamanis D, Ökte AN, Vardoulakis E, Vaimakis T (2011) Water vapor adsorption and photocatalytic pollutant degradation with TiO2-sepiolite nanocomposites. Appl Clay Sci 53(2): 181-187.

157. Teh CM, Mohamed AR (2011) Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: A review. J Alloys Compd 509(5): 1648-1660.

158. Ruppert G, Bauer R, Heisler G (1994) UV-O3, UV-H2O2, UV-TiO2 and the photo-Fenton reaction - comparison of advanced oxidation processes for wastewater treatment. Chemosphere 28(8): 1447-1454.

159. Beltrán F, Aguinaco A, García-Araya JF (2009) Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water. See comment in PubMed Commons below Water Res 43: 1359-1369.

160. Beltrán FJ, Aguinaco A, García-Araya JF (2010) Kinetic modelling of TOC removal in the photocatalytic ozonation of diclofenac aqueous solutions. Appl Catal B 100(1-2): 289-298.

161. Cernigoj U, Stangar UL, Trebse P (2007) Degradation of neonicotinoid insecticides by different advanced oxidation processes and studying the effect of ozone on TiO2 photocatalysis. Appl Catal B 75(3-4): 229-238.

162. Jing Y, Li L, Zhang Q, Lu P, Liu P (2011) Photocatalytic ozonation of dimethyl phthalate with TiO2 prepared by a hydrothermal method. See comment in PubMed Commons below J Hazard Mater 189: 40-47.

163. Rajeswari R, Kanmani S (2009) A study on synergistic effect of photocatalytic ozonation for carbaryl degradation. Desalination 242(1-3): 277-285.

164. Tong S-p, Xie D-m, Wei H, Liu W-p (2005) Degradation of sulfosalicylic acid by O3/UV O3/TiO2/UV, and O3/V-O/TiO2 : A comparative study',. Ozone: Sci Eng 27(3): 233-238.

165. Yu K-P, Lee GWM (2007) Decomposition of gas-phase toluene by the combination of ozone and photocatalytic oxidation process (TiO2/UV, TiO2/UV/O3, and UV/O3). Appl Catal B 75(1-2): 29-38.

166. Balaji V, Arulazhagan P, Ebenezer P (2014) Enzymatic bioremediation of polyaromatic hydrocarbons by fungal consortia enriched from petroleum contaminated soil and oil seeds. See comment in PubMed Commons below J Environ Biol 35: 521-529.

167. Vidali M (2001) Bioremediation. An overview. Pure Appl Chem 73(7): 1163-1172.

168. Radjenovic J, Marin Matosic M, Mijatovic I, Petrovic M, et al. (2008) Membrane bioreactor (MBR) as an advanced wastewater treatment technology. Hdb Env Chem Vol. 5, Part S/2: 37-101.

Chemical Pollutants in Water and Wastewater and Related Eco toxicity: Advanced Developing Technologies for Organic Degradation

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Abstract

Environmental issues nowadays include the presence of contaminants in waters that are increasing in numbers and classes of chemicals. The environmental and human health will always depend on the protection of the air, waters, and soil. The industrial activities are as important as agriculture but a more clean production is imperative. The subject of this chapter is to discuss the xenobiotics contaminants in water and wastewaters and their related toxicity. A second issue is to show some data related to new possible technologies, under development, and their potency for decomposition of organic contaminants. Acute toxicity results evidenced the importance of this tool for assessing the impacts of toxins to living organisms and here they were used for the evaluation of proposed technologies for wastewater improvement. Three treatment technology options were presented (advanced oxidative processes, AOPs; photolysis by UV radiation, also including the Photo-Fenton processes and Ultra-sound; a special biomidia used as an additive effort to enhance biomass in order to treat landfill leachate in a sewage mixture). The last technique and Integrated Fixed-Film Activated Sludge (IFAS) was assessed for also for toxicity removals. *Daphnia similis* water flea and *Vibrio fischeri* bacteria were the target organisms for the evaluation of these processes. Acute effects removal > 20% was achieved for fluoxetine irradiated at 5 kGy. ATZ acute effects were efficiently removed after 60 min of exposure to UV radiation and the combined IFAS processes were the most effective process for toxicity removal.

Introduction

One given pollutant may be considered as a substance or effect that adversely alters the environment by changing the growth rate of species, interferes with the food chain or with health at environment. Once we know the ability of aquatic organisms to adsorb variety of chemicals from water, sediments and food, it is ideal to use such a type of aquatic organisms using the concepts of Ecotoxicology. Pharmaceutical compounds have been reported as emerging pollutants. Are pharmaceuticals in the environment a growing problem? According to Lyons, 2014, a global review of pharmaceuticals in the environment, commissioned by Germany's environment ministry, they found that of the 713 pharmaceuticals tested for, 631 were found above their detection limits (mainly in surface waters, such as lakes and rivers, but also in groundwater, soil, manure and even drinking water) [1].

Some chemicals may be found only at low levels in various tissues, whereas others may builds up to significant concentrations. Accumulation of chemicals by organisms in the aquatic environment is based on the interactions of a variety of physical, chemical and biological characteristics and processes [2]. Pesticides degradation and toxicity were also studied (sulfonimides).

The presence of a myriad of pharmaceuticals such as antibiotics in the aquatic environment continues to be a matter of concern since these compounds may favor the selection of antibiotic-resistant bacteria and in some cases cause toxic and endocrine-disrupting effects to humans and other living organisms [3,4]. Conventional biological and physicochemical treatments processes show limited success for the destruction of antibiotics. On the contrary, AOPs usually show higher rates of removal for these emerging pollutants from water matrices; among AOPs, ultrasonic (US) degradation is growing quickly in interest. In this case powerful oxidizing species such as hydroxyl radicals ($^{\bullet}OH$) are generated by pyrolysis of water molecules during cavitation [5]. Nevertheless, the use of high-frequency US for the treatment of water contaminated by sulfonamides still deserves further investigation.

Electron beam irradiation as an alternative to reduce whole toxicity in effluents

In Brazil ecotoxicity of pharmaceuticals have been determined on different living organisms. Fluoxetine hydrochloride, Prozac's active substance, is taken as an example of a high toxic substance that was decomposed by Electron Beam Irradiation, as an alternative treatment (EBI). When talking about high contaminated samples it is common to use ecotoxicity for measuring acute effects on living organisms, before discharging wastewater to the environment [6]. Water fleas are commonly applied for effluents assessments and risk analysis. *Daphnia magna* is commonly used in Europe, due to the high hardness of water, while *Daphnia similis* are growing in a hardness range between 20 to 50 ppm ($CaCo_3$). For common toxicity assay the immobility is the end point for daphnia water flea and the EC_{50} value means the average concentration of chemical (or effluent) which immobilized 50% of daphnids after exposition (usually 48 hours), Figures 1 and 2.

Another application of toxicity assays have been the confirmation if the new techniques for treating wastewater are effective for removing toxicity. It is a way to confirm that the degradation process is not generating more toxic byproducts.

The use of electron beam accelerator for the decomposition of organics is related to the absorbed dose of radiation for a given amount/volume of material. This transferred energy is defined as the absorbed dose. Absorbed dose is reported as Gray, (Gy), according to SI unit (absorbed dose is joule per kilogram (J/kg)). The yield of chemical products produced by ionizing radiation is expressed as the quantity of product obtained divided by the dose, or G value [7].
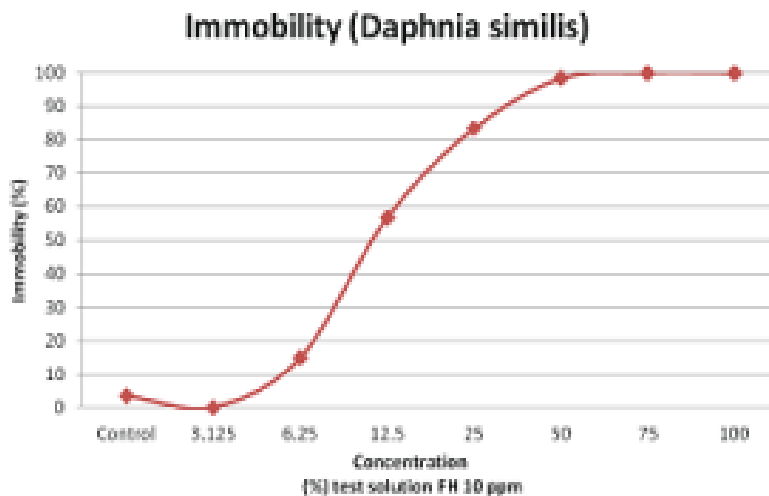
Figure 1: Immobility of *Daphnia similis* exposed to several concentration of fluoxetine hydrocholoride (48 hours) – average effective concentration = 1.37 ± 0.31 ppm. A typical dose response curve obtained during toxicity measurements.
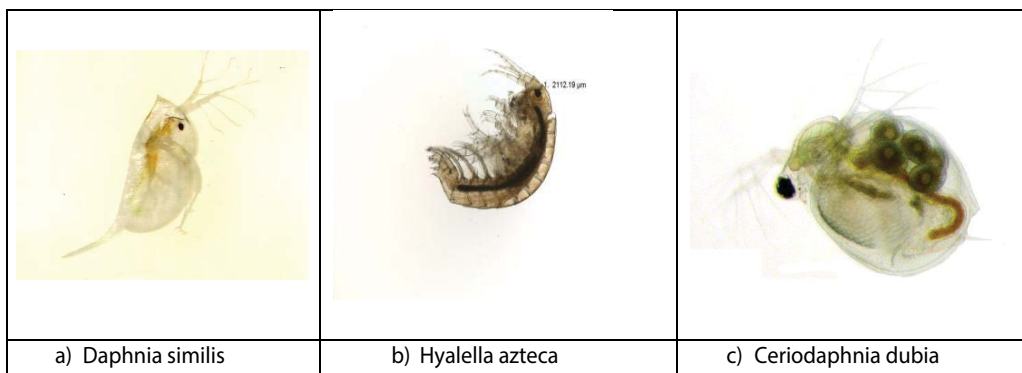

| a) Daphnia similis | b) Hyalella azteca | c) Ceriodaphnia dubia |

Figure 2: Example of living-organisms commonly used for toxicity assessments in Brazil.

The water radiolysis is an important mechanism to introduce the oxidative species into the water or wastewater while EB irradiation is applied. In the book Environmental Applications of Ionizing Radiation a lot of information was organized on the basic of radiation chemistry and possible uses of radiation for environment applications.

Accelerators are machines designed for industrial technology and material processing, as well as for radiotherapy. Several needs have grown the interest in dedicated and small machines for environmental benefits [8]. Other studies evidenced the potency of radiation for microbial reduction at 1 kGy (coliforms in secondary treated sewage) but the degradation of organic compounds in wastewater is the relevant interest concerning industrial wastewaters and pharmaceuticals into waters [9,10].

An alternative radiation source is the cobalt-60, if accelerators are not available for such a type of research [11]. Electron beam machines may be classified according to the energy of machine, what is a relevant parameter for the penetration of electrons into material. The studies presented here were based on a Dynamitron type accelerator with a 1.5 MeV and current up to 25 mA. During this irradiation a 4 mm thick of sample was used and controlled by the volume of samples displayed in the vessels, (Figure 3).
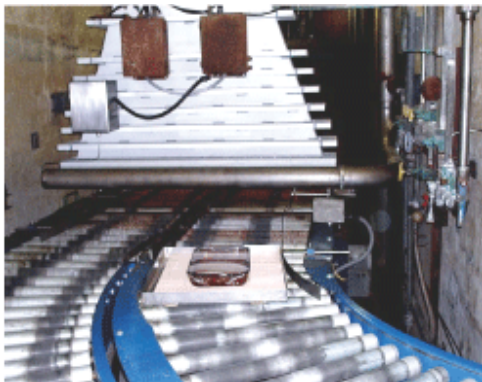
Figure 3: Electron beam scanning system, used during irradiation of liquid samples for pollutant abatement. RD Inc accelerator, fixed energy at 1.4MeV; variable electric current according to required dose (IPEN/CTR).

The mains reactive species obtained through the interaction of radiation into the water are very important for organic compound degradation and even for killing the microorganisms, which means that radiation technology may reduce both organics and microorganisms at the same time. H_2O_2, H_2, e^-_{aq}, $^\bullet OH$ and H ions are first reactive species introduced into water system by irradiation. The yields of them are presented at Table 1.

pH	e^-_{aq}	H	OH	H_2	H_2O_2
Liquid Water					
3-11	2.63	0.55	2.72	0.45	0.68
0.46	0	3.65	2.90	0.40	0.78

Table 1: Water radiolysis: radical and molecular product yields formed by the irradiation of water after100eV transferred energy, according to pH range.

Hidrochloride fluoxetine decomposition by EB irradiation: from different radiation doses applied for fluoxetine degradation 2.5 kGy was enough for an important decomposition. On the other hand, using fluoxetine in water solution > 80% acute effects were reduced by 0.5 kGy, *D. similis* exposed for 48 hours, see (Figure 4).
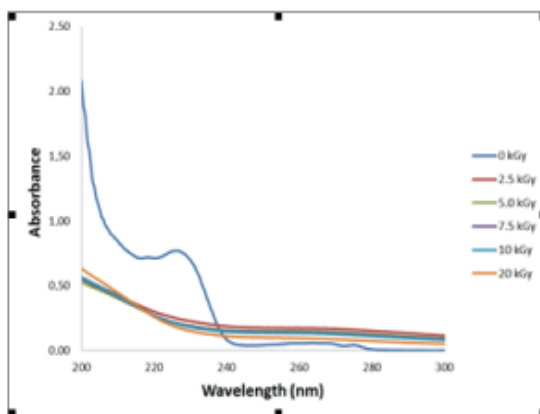

Figure 4: UV-Vis absorption spectrum of fluoxetine versus radiation (226 nm) [9].

When the same experiment was carried out in the presence of raw sewage (50% in volume) 5 kGy was required to get the same efficacy. Lower efficacy was obtained for *V.*

fischeri, from 17% up to 21% at 5 kGy. As recommended by Rand (1995), it was noticed the importance of different classes of living organisms be applied for effluents and treatment processes evaluations [2]. Organic acids were detected after irradiation of pharmaceuticals, reducing slightly the samples pH [10].

Pesticides and pharmaceutical as emerging pollutants and photolysis as an AOP

Pesticides have been detected in surface waters and ground water all around the world. They have been included amongst Persistent Organic Pollutants (POPs) due to their resistance to natural degradation processes and to the risks they have to human health as well as for the environment. Pesticides can reach surface waters through discharge of industrial synthesis processes and agro-industry wastewaters, from spray equipment and pesticide containers, spills due to improper handling and disposal, agricultural runoff, etc. [12-15].

Silva *et al.,* (2014) studied the removal of atrazine (ATZ) from water by photolysis [16]. ATZ is one of the most commonly used herbicides in the world, a possible human carcinogen and endocrine disruptor [16,17]. The authors discussed the effects of the photon emission rate and ATZ initial concentration on the herbicide photolytic degradation rate, under 254 nm-UV radiation.

The stability of ATZ in aqueous solution in the absence of light, regardless of pH, was confirmed through hydrolysis experiments. Photolysis experiments were performed in a tubular photochemical reactor equipped with a concentric low-pressure mercury vapor lamp, using four different photon emission rates on a per unit reactor volume basis ($E_{P,0}$), namely 3.6×10^{18}, 1.9×10^{18}, 1.1×10^{18}, and 8.7×10^{17} photons L^{-1} s^{-1} (Figure 5). ATZ removal by photolysis was shown to follow apparent first-order decays during the first 10 minutes (Figures 5c and 5d) and high percent ATZ removals were achieved after 30 min of irradiation, with more than 80% and 65% removals for $[ATZ]_0$ = 5 mg L^{-1} and 20 mg L^{-1}, respectively.
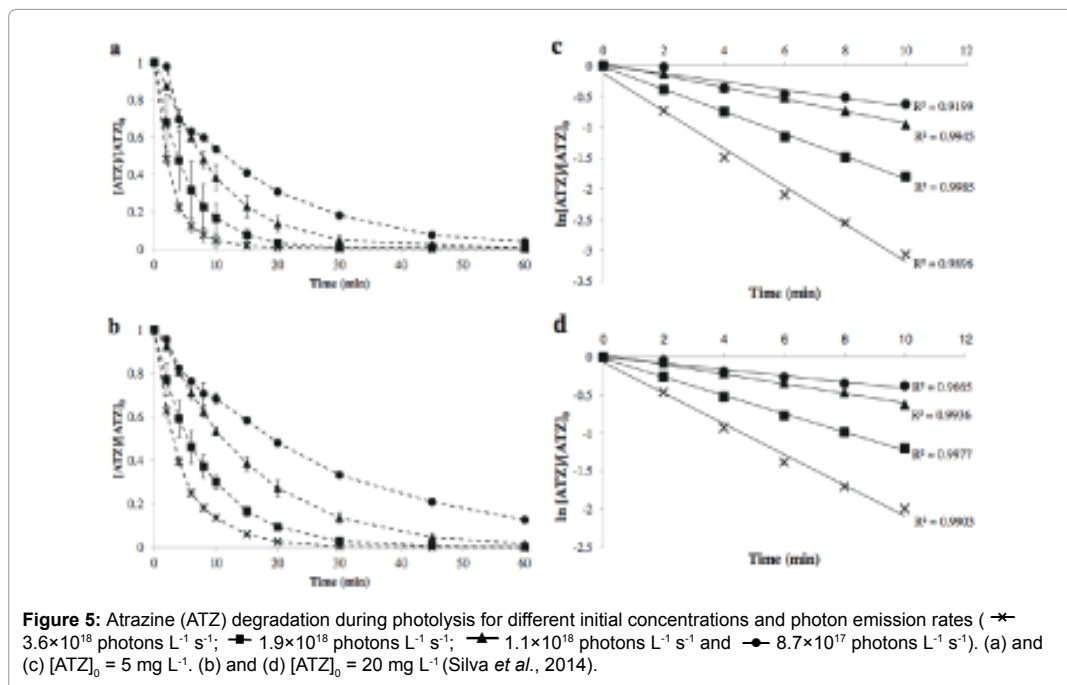

Figure 5: Atrazine (ATZ) degradation during photolysis for different initial concentrations and photon emission rates (✳ 3.6×10^{18} photons L^{-1} s^{-1}; ▪ 1.9×10^{18} photons L^{-1} s^{-1}; ▲ 1.1×10^{18} photons L^{-1} s^{-1} and ● 8.7×10^{17} photons L^{-1} s^{-1}). (a) and (c) $[ATZ]_0$ = 5 mg L^{-1}. (b) and (d) $[ATZ]_0$ = 20 mg L^{-1} (Silva *et al.*, 2014).

It was noted that the higher the initial ATZ concentration, the lower the values of the

apparent first-order photolysis rate constants k, the higher the pesticide half-lives and the lower the percent removals after 30 minutes of irradiation. Silva *et al.*, (2014) assigned the dependence of the amount of substrate destroyed and apparent rate first-order rate constants with $[ATZ]_0$ by the fact that the higher the ATZ initial concentration, the higher the amount of degradation products formed, therefore competition by incident photons increase.

A direct relationship between ATZ degradation and the photon emission rate was observed, with proportionality constants of 0.085 and 0.056 for 5 mg L^{-1} and 20 mg L^{-1} respectively. Dechlorination was the dominant mechanism during the initial steps of ATZ photolysis, as shown in Figure 6 by the comparison between the release of chloride ions in solution and ATZ photolytic degradation. The difference between the amount of Cl released and the amount of ATZ degraded suggest the persistence of very small amounts of chlorinated degradation products. Moreover, no appreciable carbon removal was observed after 60 minutes of ATZ photolysis owing to the presence of persistent degradation products [16].
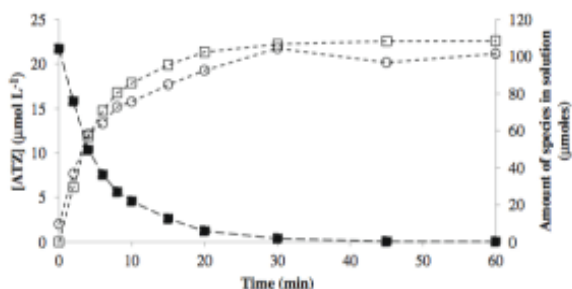

Figure 6: Comparison between the release of chloride ions in solution and ATZ photolytic degradation. $[ATZ]_0$ = 5 mg L-1 and $E_{P,0}$ = 3.6×10^{18} photons L^{-1} s^{-1}. -■- [ATZ]; -⊖- amount of Cl$^-$ released; -□- amount of ATZ degraded (Silva *et al.*, 2014).

Based on the experiment with the best performance for ATZ removal during photolysis, despite the presence of persistent degradation products, acute toxicity to *Daphnia similis* was efficiently removed after 60 minutes of exposure to UV radiation. Finally, by means of additional experiments in the presence of a suppressor of singlet oxygen, using a radical scavenger and by varying the amount of dissolved oxygen in reaction medium, the authors pointed out reactive oxygen species (hydroxyl radicals and singlet oxygen) as important actors during the photolytic degradation of atrazine.

Regarding treatment technologies possibilities, Lastre-Acosta *et al.*, (2015) investigated the degradation of sulfadiazine (SDZ) (25 mg L^{-1}) in aqueous solution by high frequency ultrasonic treatment (580, 862, and 1142 kHz) [17]. In this study, the effects of a radical scavenger and the incorporation of Fenton reagent (sono-Fenton) were analyzed. With this aim, an ultrasound multifrequency generator (MeinhardtUltraschalltechnik), operating in continuous mode at high frequency greater than 100 kHz and variable electric power output, was connected to a stainless steel transducer (E 805/T/M) placed directly inside solution and used in sonication experiments. The authors observed higher SDZ percent removals and removal rates for the lowest operating frequency (580 kHz), higher dissipated power and lower pH. The addition of *n*-butanol (22-fold molar concentration of *n*-butanol to sulfadiazine) considerably reduced SDZ degradation, with only 16% SDZ removal after 120 minutes and a pseudo-first order rate constant of $1.7×10^{-3}$ min^{-1}, therefore confirming that the attack of •OH radicals to SDZ at the interface of collapsing bubbles is an important mechanism involved in antibiotic degradation. The corresponding values in the absence of *n*-butanol were 71.5% and $10.1×10^{-3}$ min^{-1}, respectively [17].

In the range of operating conditions studied, the addition of hydrogen peroxide showed detrimental effects on SDZ degradation rate in comparison with the performance of the ultrasound-driven process alone. On the contrary, the Fenton chemistry combined with US treatment remarkably improved sulfadiazine removal rate. Therefore the sono-Fenton process seems to be more efficient for the removal of the antibiotic than sonolysis alone, as shown in (Figure 7). In fact, the extent of SDZ degradation was higher for the $US/Fe(II)/H_2O_2$ process as compared to H_2O_2 alone, $Fe(II)/H_2O_2$, US/H_2O_2, US and $US/Fe(II)$. In this case, the synergistic effect is clearly demonstrated.
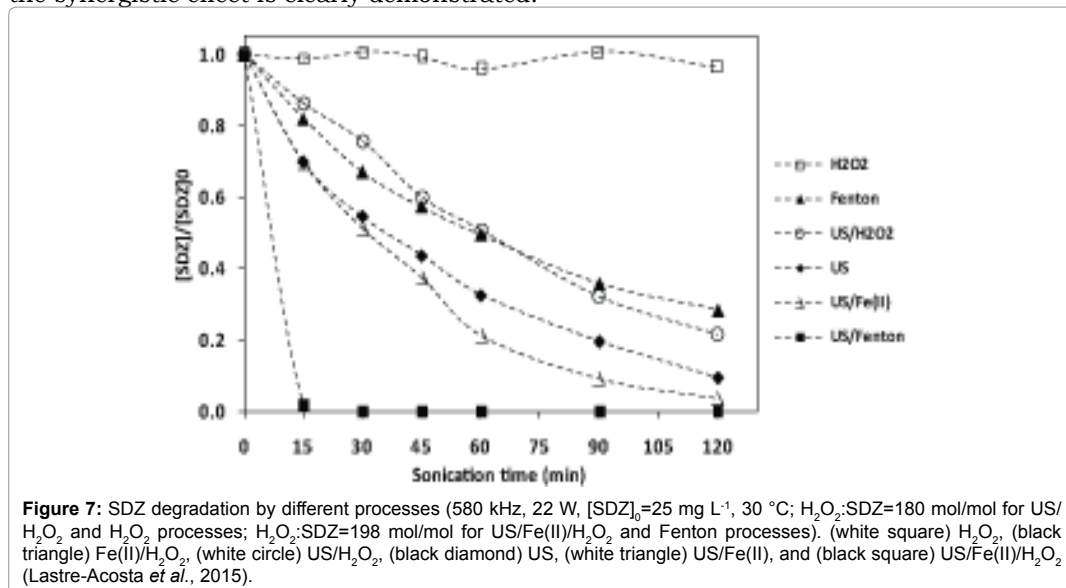

Figure 7: SDZ degradation by different processes (580 kHz, 22 W, $[SDZ]_0=25$ mg L^{-1}, 30 °C; H_2O_2:SDZ=180 mol/mol for US/ H_2O_2 and H_2O_2 processes; H_2O_2:SDZ=198 mol/mol for $US/Fe(II)/H_2O_2$ and Fenton processes). (white square) H_2O_2, (black triangle) $Fe(II)/H_2O_2$, (white circle) US/H_2O_2, (black diamond) US, (white triangle) $US/Fe(II)$, and (black square) $US/Fe(II)/H_2O_2$ (Lastre-Acosta *et al.*, 2015).

Electrophilic addition of hydroxyl radicals (HO•) offers the possibility to degrade sulfonamides in aqueous solutions due to the existence of π electrons in their molecules. Among the different processes available for generating HO• radicals [18]. UV-based technologies are considered efficient in aqueous treatment containing recalcitrant sulfonamides [19-22]. These technologies include the photo-excitation of Fe(III)-complexes, the photo-Fenton processes, photo-induced processes, and photo-initiated oxidation processes.

Photo-Excitation of Fe (III)-Complexes

Photo-excitation of Fe(III)-complexes induces reduction of ferric (Fe^{3+}) to ferrous (Fe^{2+}) ions and formation of HO• radicals. Reactions involving Fe(III)-complexes are important in surface water and can promote the degradation of contaminants in aqueous solutions. The presence of diverse organic ligands in Fe(III)-complexes leads to sulfonamides degradation at different reaction rates [23]. Hydrogen peroxide (H_2O_2) can be generated from the photolysis of Fe(III)-oxalate which react with Fe^{2+} to produce HO•. Furthermore, the oxidation of organic ligands in Fe(III)-complexes generates organic radicals that may reduce dissolved oxygen (O_2) to yield radical species such as the superoxide radical anion, $O_2^{•-}$[24]. During photolysis of Fe(III)-oxalate (Figure 8a), the oxidation of the oxalate ligand generates carboxylate radical anions ($CO_2^{•-}$) which, in the absence of O_2, react with Fe(III)-oxalate to form Fe^{2+} ions. In aerated systems, $CO_2^{•-}$ reduces O_2 giving $O_2^{•-}$. Similarly, the photolysis of Fe(III)-citrate produces Fe^{2+} ions and also the 3-hydroxyglutarate anion radical (3-GHA$^{•2-}$), which generates both the 3-oxoglutarate (3-OGA^{2-}) ion and $O_2^{•-}$ after reaction with O_2, with fast generation of unstable acetone and carbon dioxide as byproducts (Figure 8b).
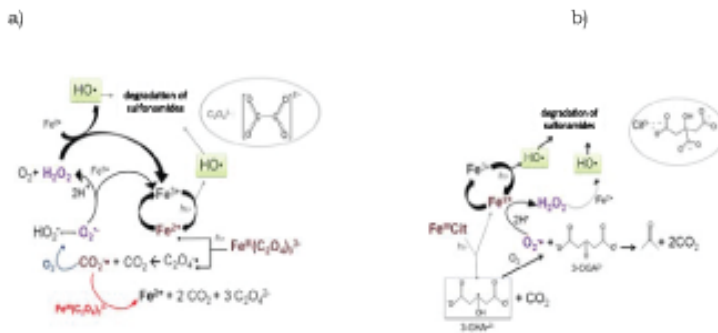
Figure 8: Scheme of photolysis of Fe(III)-complexes: (a) Fe(III)-oxalate and (b) Fe(III)-citrate.

Fe(III)-oxalate was shown to be more effective to sulfonamides degradation than Fe(III)-citrate using UV irradiation. The remaining carbon from Fe(III)-citrate photolysis was shown to be disadvantageous toward sulfonamides degradation. A significant increase in sulfonamides degradation rate was reported using sunlight irradiation in the presence of Fe(III)-oxalate [19].

Photo-Fenton Processes

Among UV-based technologies, photo-Fenton processes may be a suitable technology for the degradation of sulfonamides in aqueous solution. Based on the electron transfer from ferric/ferrous ions system, the decomposition of H_2O_2 is catalyzed by Fe^{2+}, making UV absorption by hydrogen peroxide (H_2O_2) not essential for the generation of HO• radicals. However, the highly acidic solution needed to avoid the formation of hydroxylated iron species, the complexation of iron ions by sulfonamide molecules (or their byproducts) which hinder Fe^{3+} photoreduction, and the regulation regarding the maximum concentration of iron.

Studies of sulfonamides degradation performed at low initial concentration (≤ 0.1 mmol $L^{-1}/25$ mg L^{-1}) resulted in such good efficacy that Solid Phase Extraction (SPE) techniques were required for increasing the sensitivity of the analytical method [15].

SPE technique was conducted at low pH using the Strata-X Phenomenex cartridge since neutral or protonated sulfonamide molecules have good extraction recoveries for hydrophilic sorbent.

Photo-induced and photo-initiated oxidation processes

The use of UV-driven technologies has enhanced the efficiency of oxidation processes including photo-induced and photo-initiated oxidation in circumneutral solution. Photo-induced oxidation of organic compounds has been investigated and shown to be an important process for the removal of sulfonamides from natural waters [25,26]. The formation of sulfonamides in the triplet excited state is an important phenomenon during the photo-induced oxidation processes and is related to the generation of reactive species [20,27]. The phenomena induced by the interactions between UV radiation and sulfonamide molecules can promote degradation from reaction with singlet oxygen and radical species during photosensitized processes occurring simultaneously with direct photolysis. The singlet excited state of the sulfamethazine molecule ($^1C_{12}H_{14}N_4O_2S^*$) may undergo intersystem crossing to a triplet excited state ($^3C_{12}H_{14}N_4O_2S^*$) to produce reactive oxygen species (ROS) via electron/energy transfer to dissolved molecular oxygen ($^3O_2$). The ROS were able to oxidize SMT molecules at relatively higher initial concentration (≥ 0.1 mmol L^{-1}) compared to that found in natural waters.

Photo-initiated oxidation processes involve absorption of photons by auxiliary oxidants, such as hydrogen peroxide, to generate HO• radicals. For example, sulfamethazine degradation was evaluated by photo-induced and photo-initiated oxidation under 254 nm-UV radiation. Slow degradation rates were reported for the photo-induced oxidation of sulfamethazine under low-pressure UV radiation. Besides, relevant improvement of sulfamethazine degradation was observed in the presence of auxiliary oxidants. The pH of sulfamethazine solutions decreased during oxidation, suggesting the presence of acidic transformation products formed from the oxidative cleavage of hydroxylated aromatic rings [21].

Integrated Fixed-film Activated Sludge (IFAS) As a Co-treatment of Landifill Leachate in the Presence of Sewage Using an Integrated Biological System

The solid waste management is one of the important issues in megacities. Considerable costs are involved for the correct disposal of solid wastes. One of the technologies is the landfills, from which water percolates through waste. It promotes and assists the process of decomposition by microorganisms. Nonetheless the biological decomposition is the most significant path for waters cleaning and even when talking about solids residues at landfills. These processes in turn release chemical by-products and rapidly use up any available oxygen, creating an anoxic environment. As a result of an increasing temperature and actively decomposing waste, the changes in pH rises, interfering in the solubilization of metals, many metal ions that are relatively insoluble at neutral may become dissolved in the developing leachate [28,29].

The physical appearance of leachate when it emerges from a typical landfill site is a strongly odoured black-, yellow- or orange-coloured cloudy liquid. The smell is acidic and offensive and may be very pervasive because of hydrogen-, nitrogen- and sulfur-rich organic species such as mercaptans [30,31]. The decomposition processes themselves release more water, which adds to the volume of leachate. The residues released in the leachate may also form a large component of the landfill gas.

On the other hand, how to treat the tons of liters of landfill leachate? The limitation for carbon biological degradation and general pollutants is that many designed biological systems were not suitable for decomposition leachate (from landfill), same for the pesticides, pharmaceuticals and biocides.

Once the biological treatment is based on microorganisms decomposition, such type of residues (from leachate) may often act as source of toxins, damaging the sludge activity. In Brazil many biological systems for municipal Wastewater Plant (WWTP) receive the landfill leachate for treatment into the biological system. How may a hard mixture of chemicals affect the activated sludge? Considering the possible mixture of sewage and landfill leachate the ratio for the combination is quite important. Toxicity data was obtained to assess those values as well as to evaluate the application of an auxiliary midia for the improvement of the biological decomposition of organic matter.

In a landfill that receives a mixture of municipal, commercial, and mixed industrial waste, landfill leachate may be characterized as a water-based solution of four groups of contaminants: dissolved organic matter (alcohols, acids, aldehydes, short chain sugars etc.), inorganic macro components (common cations and anions including sulfate, chloride, iron, aluminium, zinc and ammonia), heavy metals (Pb, Ni, Cu, Hg), and xenobiotic organic compounds such as halogenated organics, polychlorinated biphenyl, PCBs and also pharmaceutical residues [29,31,32].

An Integrated fixed-film activated sludge was studied as one of the technologies for treatment of such leachates and the system was designed for treating a mixture of landfill

leachate and raw sewage, applying a new media as support of microorganisms, called as Integrated Fixed-Film Activated Sludge (IFAS).

Parameters	1ª step (5%)	2ª step (10%)	3ª step (20%)
COD total ($mgO_2.L^{-1}$)	510	500	610
$BOD_{5,20}$ total ($mgO_2.L^{-1}$)	220	220	290
TOC ($mgC.L^{-1}$)	59	71	84
TKN ($mgN.L^{-1}$)	110	160	230
NH_4^+-N (mgN-$NH_4^+ .L^{-1}$)	60	110	120
Alcalinity ($mgCaCO_3.L^{+1}$)	200	400	600

Table 2: Chemical characterization according to the percentage of landfill leachate into the sewage influent mixture (steps 1, 2 and 3).

A biological reactor was used during the treatement process for the domestic sewage and landfill leachate mixture. Hibrid system was constructeded on a pilot scale at Sao Paulo Univesity, Centro Tecnológico de Hidráulica (CTH/EPUSP), Departamento de Engenharia Hidráulica e Ambiental. The biomidia applied during the conjugated process was presented as (Figure 9).

Figure 9: The small and clean biomidia applied for the biofilm improvement and the dirty used biomidias (Anox Kaldnes®), obviously related to the exposure of the biomidia to the effluent, during the treatment proposed studied.

The reactor material was acrylic, designed in two parts: 270 liters for the first anoxic chamber for pre-denitrification. The second part for 800 liters, in an oxigenated chamber and 4 difusors, installed at the bottom of the system. The compressor/difusors introduced air into the system in order to achieve from 3.0 up to 4.0 mg.L^{-1} of dissolved oxygen. The second part of the system was a circular secondary decantador, receiving 2 m³.d^{-1} of the mixture. Sludge recirculation was 0,5. The biomidia Anox Kaldnes® was applied for both systems. The filling volume was 70% of total volume to aeration tank and 50% for the anoxic chamber (Figure 10).
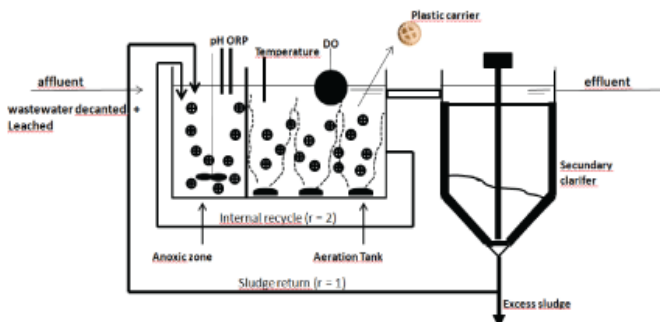

Figure 10: The designed system included biomidia Anox Kaldnes® , aeration tank, secondary clarifier and measurements apparatus.

The toxicity was an important parameter for the evaluation of the efficacy of proposed treatment as well as to evaluate the toxic charge (EC_{50} X volume of influent) of the influent of IFAS system. *Vibrio fischeri* bacteria and *Daphnia similis* crustacean were the biological indicators used for toxicity assessment and the samples applied during the IFAS in a ratio of 5%, 10% and 20% of landfill leachate in raw sewage, reported as influent. One of the most important questions was the amount of leachate is feasible into an activated biological treatment system? Peristaltic pump injected leachate into the system, followed by characterization and organic matter. The toxicity assessment was carried out for the mixture content for different percentage of landfill leachate (5, 10 and 20% of the total volume).

Taking operational conditions into account and the characteristics of influent (Table 2) the application of organic charge and nitrogen charge (in volume) varied from 0.4 up to 0.9 $kgBOD.m^3.d^{-1}$ and 0.32 up to 0.7 $kgN.m^3.d^{-1}$. It was possible to note the contribution of leachate addition in different parameters, such as Total Nitrogen (TN), amoniacal nitrogen (NH_4^+-N) and alcalinity, higher after 10% and 20% of landfil leachate. The volatile solids content into the reactor varried according to the literature database (2000 a 5000 $mg.L^{-1}$), (Figure 11).
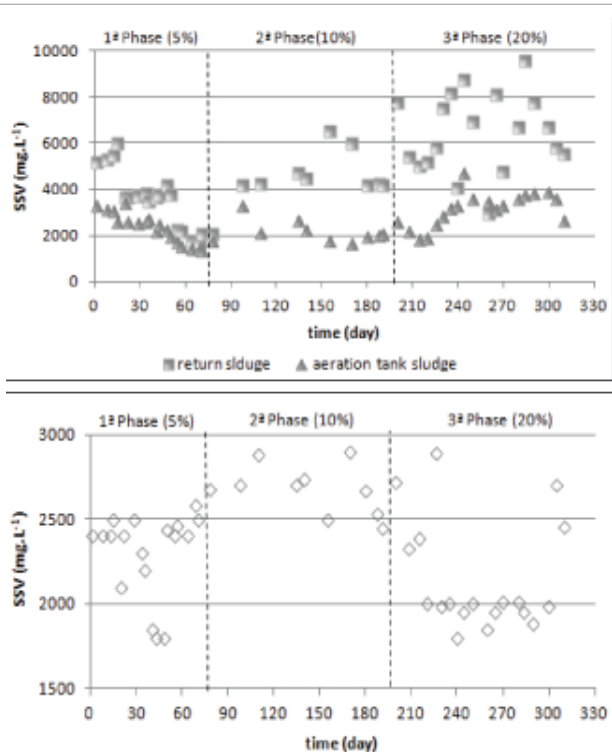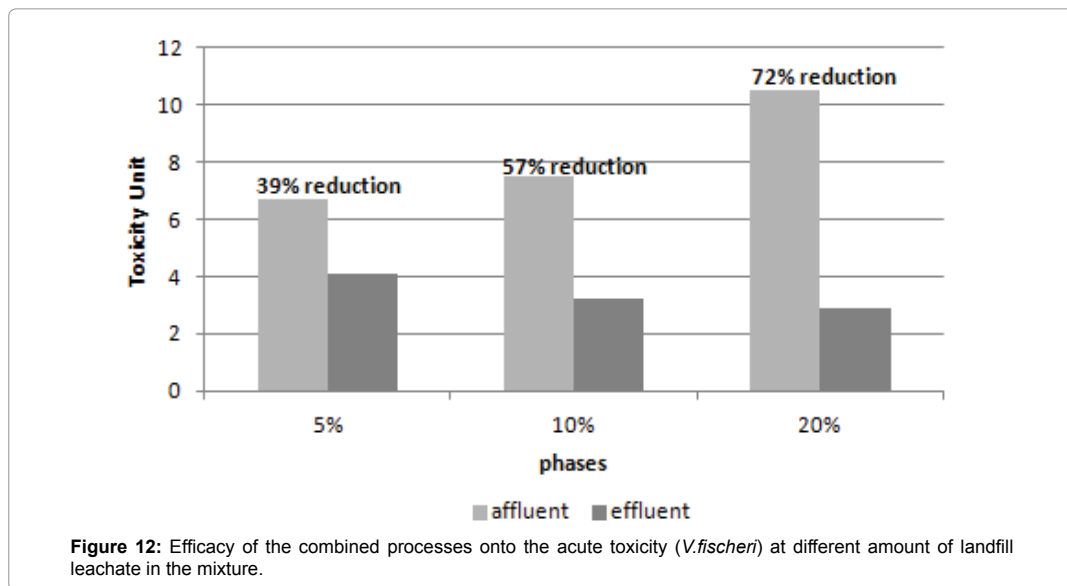

Figure 11: a) Volatile Suspended Solids, (VSS), versus time, at aeration tank and at sludge return - operation period; b) The influence of treatment into SSV as a function of biofilm adhered to the biomidia and time (Campos, F., 2014).

The fixed biomass decreased in the 3o. Step of the process - Kaldnes® (K1), 300 $m^2.m^3$, reaching 8 $gSSV.m^{-2}$ as adhered biofilm. The SSV biofilm is about 15 $gSSV.m^{-2}$ [33,34].

The main objective of any WWTP is to remove organic mater and nitrogen. Another important issue is the solids which contain relevant chemical and biological contaminants such as parasite eggs, coliforms, virus etc. In this developed system, under stable operational conditions the efficacy of the three steps (including 5/10 and 20% of leachate) the accounted

for 85% of $BOD_{5,20}$ and 90% as COD removal. Regarding nitrogen, 90% was the TNK and NH_4^+ for the two firs steps and 80% for the last one. As the WWTP receive leachate to be treated with the sewage more studies are necessary for achieving a safe treatment condition such as controlable toxic charge, sludge quality and treated sewage controling and quality [35].

The proposed IFAS was quite effective for BOD and amonia removal, resulting also in less toxic effluents, specially for the step 3, where 20% of landifill leachate was added to the sewage. 72% of whole toxicity was achieved for *Vibrio fischeri* bacteria for 15 minutes exposure (Figure 12).

Figure 12: Efficacy of the combined processes onto the acute toxicity (*V.fischeri*) at different amount of landfill leachate in the mixture.

Regarding to acute ecotoxicity data, the highest percentual of leachate received from the landifill was 20% in the sewage mixture, keeping the same efficiency for organic matter and nitrogen. Nonetheless the residual toxicity was detected for *Vibrio fischery* (measured by Microtox®). The *D.similis* crustacean was less sensitive than the vibrio bacteria. These data reinforce the needs for toxicity assessment involving more than one biological class of living organisms for the evaluation of wastewater and their treatments, chronic effects assays are also recommended, before discharge of treated wastewater into the rivers.

Concluding remarks: Why treatment technologies are important? These examples were chosen due to the relevance of chemical classes of contaminants and developing technologies. And how Ecotoxicology can contribute to this proposed subject and to reduce contamination? These ecotoxicity assays are also used for fixing standard limits and for assuring safety discharges to the environment, our further actions for preservation. From this chapter it was possible to confirm the efforts that have been carried out to reduce the presence of pharmaceuticals and other chemicals in waters. There is no other way to protect environment if not education, collaboration, safety and technologies.

References

1. Lyons G (2014) Pharmaceuticals in the environment: a growing threat to our tap water and wildlife. A Chem. Trust report.

2. Rand GM (1995) Fundamentals of Aquatic Toxicology: effects, environmental fate and risk assessment, (2nd ed), Taylor & Francis, Washington.

3. Chatzitakis A, Berberidou C, Paspaltsis I, Kyriakou G, Sklaviadis T, et al. (2008) Photocatalytic degradation and drug activity reduction of chloramphenicol. Water Research, 42, 386.

4. Mendez-Arriaga F, Torres-Palma RA, Petrier C, Esplugas S, Gimenez J, et al. (2008). Ultrasonic treatment of water contaminated with ibuprofen. Water Research, 42, 4243.

5. Bagal MV, Gogate PR (2014) Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review. Ultrasonic Sonochemistry, 21, 1.

6. Borrely SI, Gonçalves AA, Oikawa H, Duarte CL, Rocha FR, et al. (2004) Electron beam accelerator for detoxification of effluents. When radiation processing can enhance the acute toxicity? Radiat. Phys. and Chem., 71, 453-456.

7. Cooper, Randy & O'shea (1998) Advanced Oxidation Processes for Water and Wastewater. John Wiley & Sons, Inc., New York.

8. Han B, Kim JK, Kim Y, Choi JS, Jeong KY, et al. (2012) Operation of industrial-scale electron beam wastewater treatment plant. Radiat. Phys. and Chem., 81: 1475-1478.

9. Ogihara-Silva VH (2014) Avaliação da toxicidade e da degradação do farmaco cloridrato de fluoxetina, em solução aquosa e em mistura com esgoto doméstico, empregando irradiação com feixe de eletrons. Master thesis. IPEN/USP. Brasil.

10. Homlok R, Takács, E, Wojnárovits L (2011) Elimination of diclofenac from water using irradiation technology, Chemosphere, 85: 603–608.

11. Guo Z, Zhou F, Zhao Y, Zhang C, Liu F, et al. (2012) Gamma irradiation-induced sulfadiazine degradation and its removal mechanisms. Chemical Engineering Journal, 191, 256.

12. Curini R, Gentili A, Marchese S, Marino A, Perret , et al. (2000) Solid phase extraction followed by high-performance liquid chromatography-ion spray interface-mass spectrometry for monitoring of herbicides in environmental water. Journal of Chromatography A, 874.

13. Carabias-Martinez R, Rodriguez-Gonzalo E, Revilla-Ruiz P (2006) Determination of endocrine-disrupting compounds in cereals by pressurized liquid extraction and liquid chromatography–mass spectrometry. Study of background contamination. Journal of Chromatography A, 1137.

14. McMurray, TA Dunlop, PSM, Byrne, JA (2006) The photocatalytic degradation of atrazine on nanoparticulate TiO_2 films. Journal of Photochemistry and Photobiology A: Chemistry, 182, 43.

15. Silva MP, Batista APS, Borrely SI Silva, VO Teixeira ACSC (2014) Photolysis of atrazine in aqueous solution: role of process variables and reactive oxygen species. Environmental Science and Pollution Research, 21, 12135.

16. Hleli S, Martelet C, Abdelghani A, Burais N, Jaffrezic-Renault N, et al. (2006) Atrazine analysis using an impedimetric immunosensor based on mixed biotinylated self-assembled monolayer. Sensors and Actuators B, 113, 711.

17. Lastre-Acosta AM, Cruz-González G, Nuevas-Paz L, Jáuregui-Haza UJ, Teixeira, ACSC, et al. (2015) Ultrasonic degradation of sulfadiazine in aqueous solutions. Environmental Science and Pollution Research, 22, 918.

18. Legrini O, Oliveros E, Braun AM (1992) Photochemical processes for water treatment. Chemical Reviews, 93, 671.

19. Batista APS, Cottrell BA, Nogueira RFP (2014)Photochemical transformation of antibiotics by excitation of Fe(III)-complexes in aqueous medium. J. of Photochemistry and Photobiology A: Chemistry, 274, 50.

20. Batista APS, Nogueira RFP (2012) Parameters affecting sulfonamide photo-Fenton degradation-iron complexation and substituent group. Journal of Photochemistry and Photobiology A: Chemistry, 232, 8.

21. Batista APS, Pires FCC, Teixeira ACSC (2014) Photochemical degradation of sulfadiazine, sulfamerazine and sulfamethazine: Relevance of concentration and heterocyclic aromatic groups to degradation kinetics. Journal of Photochemistry and Photobiology A: Chemistry, 286, 40.

22. Silva MP, Batista APS, Borrely SI Silva, VO Teixeira, A.C.S.C. (2014) Photolysis of atrazine in aqueous solution: role of process variables and reactive oxygen species. Environmental Science and Pollution Research, 21, 12135.

23. Faust BC, Zepp, RG (1993) Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. Environmental Science and Technology, 27, 2517.

24. Jeong J, Yoon J (2005) pH effect on $^\bullet$OH radical production in photo/ferrioxalate system. Water Research, 39, 2893.

25. Lam, M W, Mabury S A (2005) Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters. Aquatic Sciences, 67:177.

26. Boreen AL, Arnold WA, McNeill K (2004) Photochemical fate of sulfa drugs in the aquatic environment: Sulfa drugs containing five-membered heterocyclic groups. Environmental Science and Technology, 38, 3933.

27. Moore DE (1998) Mechanisms of photosensitization by phototoxic drugs. Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, 422, 165.

28. Aucott M (2006) The fate of heavy metals in landfills: A Review, Pollution Prevention and the NY-NJ Harbor Project of the New York Academy Sciences.

29. VanLoon, GW and Duffy SJ (2005) Environmental chemistry a global perspective. 433-458, New York.

30. Christensen TH, Kjeldsen P, Bjerg PL, Jensen DL, Christensen JB, et al. (2013) Biogeochemistry of landfill leachate plumes. HBRC Journal, 9(2) 187-192.

31. Campos F (2014) Influência do recebimento de lixiviado de aterro sanitário sobre o tratamento de esgoto em processo de lodo ativado e reator integrado de lodo ativado com biofilme em leito móvel. PhDThesis – Faculdade de Saúde Publica, Universidade de São Paulo.

32. Çecen F , Çakirolum D (2001) Impact of Landifill Leachate on the Co-Treatment of Domestic Wastewater, Biotechnology Letters, 23, 821.

33. ABNT – NBR 12209 (2011) Elaboração de projetos hidráulicos-sanitarios de estações de tratamento de esgotos sanitários.

34. Gaul T, Marker S, Kunst S (2005) Start-Up of Moving Bed Biofilm Reactors for Deammonification: The Role of Hydraulic Retention Time, Alkalinity and Oxygen Supply. Water Science & Technology, 2, 7: 127–133.

35. Wiszniowsk J, Surmacz-Gorska J, Robert D, Weber JV (2007) The Effect of Landfill Leachate Composition on Organics and Nitrogen Removal in a Activated Sludge System With Bentonit Additive. Jornal of Environmental Management, 59-68.

36. Woods R (1998) Radiation chemistry and its application to environmental pollution. In Environmental applications of ionizing radiation, 1-31. New York.