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Waste Water Treatment in Chemical Industries: The Concept and Current Technologies

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Abstract

The world's chemical industries face formidable environmental regulatory challenges in treating their wastewater effluents. The present work aims at highlighting the various industrial wastewater treatment technologies currently available including physico-chemical and biological processes as well as constructed wetland and conventional or advanced oxidation processes. Activated carbon prepared from low cost material, Agricultural by-product materials or modified natural polymers, which is considerably efficient for removal of direct dyes from wastewater, is also discussed. Combinations of anaerobic and aerobic treatment processes are found to be efficient in the removal of soluble biodegradable organic pollutants. The use of membrane in final stage of industrial wastewater treatments is increasing. The chemical oxidation techniques to treat wastewater, classical chemical treatment and advanced oxidation processes, is discussed.

Keywords: Wastewater; Bioreactor; Aerobic; Anaerobic; Oxidations; Adsorption; Coagulation

Introduction

Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an infinitesimal part of the earth's water reserves (approximately 0.03%) constitutes the water resource which is available for human activities. The growth of the world's population and industry has given rise to a constantly growing demand for water in proportion to the supply available, which remains constant. Thus, it is necessary to minimize its consumption and it is also necessary to return it back to the environment with the minimum contamination load because of the limited capacity of self-purification, hence the importance of wastewater treatment process [1].

During the last two decades large scale environmental initiatives have taken place in Europe and the United States, these have resulted in strict environmental regulations on the industrial emissions for the chemical industry. It has been necessary to invest in cleaner technologies and in treatments that are more effective. On the other hand, numerous chemical companies have installed effluent treatment systems to meet the recently elaborated regulations of the country in which they are settled or to meet the regulations of the countries with which they trade.

The chemical industry comprises the companies that produce industrial chemicals. Basic chemicals or "commodity chemicals" are a broad chemical category including pharmaceutical products, polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic/organic chemicals, and fertilizers. The chemical industry is of importance in terms of its impact on the environment.

Chemical industrial wastewaters usually contain organic and inorganic matter in varying concentrations. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply almost non-biodegradable. This means that the production wastewater also contains a wide range of substances that cannot be easily degraded. For instance, surfactant and petroleum hydrocarbons, among others chemical products that are being used in chemical industry reduce performance efficiency of many treatment unit operations [2].

The purpose of this review is to discuss the current wastewater treatment technologies in chemical industry. Because of the specificity of their waste waters, the chemical industry are required either improving the existing waste water treatment processes or developing combinations of various processes. This enables one to emerge with feasible treatment schemes targeting treatment of high strength wastewater.

Technologies to treat chemical industry effluents

In terms of wastewater treatment there are four classifications of treatment. Preliminary treatment involves the removal of large particles as well as solids found in the wastewater. The second classification is primary treatment, which involves the removal of organic and inorganic solids by means of a physical process, and the effluent produced is termed primary effluent. The third treatment is called secondary treatment; this is where suspended and residual organics and compounds are broken down. Secondary treatment involves biological (bacterial) degradation of undesired products. The fourth is tertiary treatment, normally a chemical process and very often including a residual disinfection.

Physico-chemical treatment

Oil –Water Separator–Treatment of oily effluent: Oil and grease (O&G) is a common pollutant in a wide range of chemical industries. Oil refineries, petrochemical plant, chemical plant, textile and food processing industries report high levels of oil and grease in their

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effluents (with an Oil and grease concentration up to 200,000 mg/l) [3,4].

Regulations that govern the allowable discharge of oil and grease into municipal treatment plants and surface waters are becoming increasingly stringent.

New facilities are also subject to more stringent discharge limits than existing sources. For example, existing sources discharging produced water are required in the US to limit O&G levels to less than 48 mg/l as compared to new facilities which have to comply with a limit of 29 mg/l [3,4].

On the other hand, Oil and grease in wastewater can exist in several forms: free, dispersed or emulsified. The differences are based primarily on size. In an oil–water mixture, free oil is characterized with droplet sizes greater than 150 mm in size, dispersed oil has a size range of 20–150 mm and emulsified oil has droplets typically less than 20 mm. Oil and grease concentrations in wastewater as measured by the recommended test procedures of the US Environmental Protection Agency do not determine the presence of specific compounds, but groups of compounds based on their extractability by a particular solvent. Solvents that are commonly used are freon and hexane. Thus, the term "oil and grease" is fairly broad; it could include animal and vegetable source oils, fatty acids, petroleum hydrocarbons, surfactants, phenolic compounds, napthenic acids, etc. [3,4].

Conventional approaches to treating oily wastewaters have included gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation. Gravity separation followed by skimming is effective in removing free oil from wastewater. Oil – water separators such as the API separator and its variations have found widespread acceptance as an effective, low cost, primary treatment step.

The API oil – water separator is designed to separate the oil and suspended solids from their wastewater effluents. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute (Figure 1).

The API separator, however, is not effective in removing smaller oil droplets and emulsions. Oil that adheres to the surface of solid particles can be effectively removed by sedimentation in a primary clarifier. Dissolved air flotation (DAF) uses air to increase the buoyancy of smaller oil droplets and enhance separation. Emulsified oil in the DAF influent is removed by de-emulsification with chemicals, thermal energy or both. DAF units typically employ chemicals to promote coagulation and increase flock size to facilitate separation.

Emulsified oil in wastewater is usually pre-treated chemically to destabilize the emulsion followed by gravity separation. The wastewater is heated to reduce viscosity, accentuate density differences and weaken the interfacial films stabilizing the oil phase.

This is followed by acidification and addition of cationic polymer/alum to neutralize negative charge on oil droplets, followed by raising the pH to the alkaline region to induce flock formation of the inorganic salt. The resulting flock with the adsorbed oil is then separated, followed by sludge thickening and sludge dewatering.

Coagulation–flocculation: Most wastewater treatment plant includes sedimentation in their process. The sedimentation also called clarification is a treatment process in which the velocity of the water is lowered below the suspension velocity and the suspended particles settle out of the water due to gravity. Settled solids are removed as

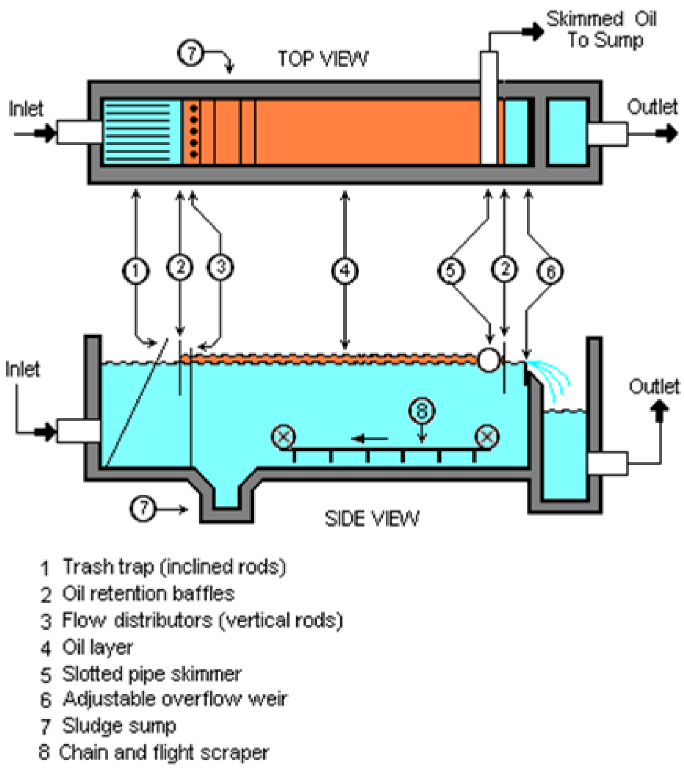

Figure 1: Conceptual Diagram of a gravimetric API separator.

sludge, and floating solids are removed as scum. Wastewater leaves the sedimentation tank over an effluent weir to the next step of treatment. The efficiency or performance of the process is controlled by: retention time, temperature, tank design, and condition of the equipment. However, without coagulation/flocculation, sedimentation can remove only coarse suspended matter which will settle rapidly out of the water without the addition of chemicals. This type of sedimentation typically takes place in a reservoir, sedimentation or clarification tank, at the beginning of the treatment process.

Coagulation-flocculation consists on the addition on the clarification tanks of chemical products that accelerate the sedimentation (coagulants). The coagulants are inorganic or organic compounds such as Aluminium sulphate, Aluminium Hydroxide chloride or high molecular weight cationic polymer. The purpose of the addition of coagulant is to remove almost 90% of the suspended solids from the wastewater at this stage in the treatment process.

Adsorption techniques to treat wastewater: Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid.

Granular activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1,000 square meters.

Granular activated carbon: The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of life. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe), etc. This problem has received considerable amount of attention in recent years. One primarily concern is that marine animals which can readily absorb those heavy metals in wastewater and directly enter the human food chains present a high health risk to consumers. Wastewater from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries, etc. contains one or more of these toxic heavy metals. Industries carries out operations like electroplating, metal/surface finishing and solid-state wafer processing, generate wastewater contaminated with hazardous heavy metals. The concentrations of some of the toxic metals like Cr, Hg, Pb, As, etc. are higher than permissible discharge levels in these effluents. It, therefore, becomes necessary to remove these heavy metals from these wastewaters by an appropriate treatment before releasing them into the environment.

In view of the toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals from wastewaters/effluents before it is released into the environment. Conventional methods for the removal of heavy metals include precipitation, coagulation/flocculation, complexation/sequestration.

Application of above-mentioned methods becomes economically unviable for the removal of heavy metals at lower concentrations. Adsorptive treatment using non-conventional adsorbents, such as agricultural and industrial solids wastes, have been used for the removal of heavy metals [5–7]. A number of other materials have also been used to remove heavy metals from wastewater, such as peat, wool, silk, and water hyacinth. Many papers have appeared on preparation of activated carbon from cheaper and readily available materials [6,7].

Fixed bio film reactor: The fixed bio film reactor is a trickling filter that consists of a bed of highly permeable media on whose surface a mixed population of microorganisms is developed as a slime layer. The word "filter" in this case is not correctly used for there is no straining or filtering action involved. Passage of wastewater through the filter causes the development of a gelatinous coating of bacteria, protozoa and other organisms on the media. With time, the thickness of the slime layer increases preventing oxygen from penetrating the full depth of the slime layer. In the absence of oxygen, anaerobic decomposition becomes active near the surface of the media. The continual increase in the thickness of the slime layer, the production of anaerobic end products next to the media surface, and the maintenance of a hydraulic load to the filter, eventually causes sloughing of the slime layer to start to form. This cycle is continuously repeated throughout the operation of a trickling filter. For economy and to prevent clogging of the distribution nozzles, trickling filters should be preceded by primary sedimentation tanks equipped with scum collecting devices.

Primary treatment ahead of trickling filters makes available the full capacity of the trickling filter for use in the conversion of non-settle able, colloidal and dissolved solids to living microscopic organisms and stable organic matter temporarily attached to the filter medium and to inorganic matter temporarily attached to the filter medium and to inorganic matter carried off with the effluent. The attached material intermittently sloughs off and is carried away in the filter effluent. For this reason, trickling filters should be followed by secondary sedimentation tanks to remove these sloughed solids and to produce a relatively clear effluent.

Due to its simple design, in actual operation the trickling filter is one of the most trouble-free types of secondary treatment processes. It requires much less operating attention and process control than the activated sludge system, but some problems do exist. The following is a summary of some of the more common problems and cures: (a) excessive organic loading without a corresponding higher recirculation rate, (b) use of media which is too small, (c) clogging of under drain system, (d) non-uniform media size or breaking up of media.

Electrosorption: Electrosorption is generally defined as potential polarization induced adsorption on the surface of electrodes, and is a non-Faraday process. After the polarization of the electrodes, the polar molecules or ions can be removed from the electrolyte solution by the imposed electric field and adsorbed onto the surface of the electrode. Because of its low energy consumption and environmentally friendly advantage, electrosorption has attracted a wide interest in the adsorption processes for treatment of wastewater. Although electrosorption has been shown as a promising treatment process, it has been limited by the performance of electrode material. Activated carbon fibre cloth with high specific surface area and high conductivity is one of the commonly used electrode materials. The surface chemistry of activated carbon fibre has been recognized as a key parameter in the control of the adsorption process. To increase the adsorption capacity, a number of modification methods have been employed [8-10].

The adsorption capacity and adsorption kinetics depend on the surface properties of adsorbent. To increase the potentially low adsorption capacity of any adsorbent, a number of modifications including immobilization of a chelating agent on the adsorbent surface have been employed [11]. The adsorption capacities and the feasible removal rates must be substantially boosted by the modification techniques.

Ethylene diamine tetra acetic acid (EDTA) is the most widely used of the amino poly carboxylic acids. EDTA is a chelating agent, forming coordination compounds with most monovalent, divalent, trivalent and tetravalent metal ions. It combines with metal ions in a 1:1 ratio regardless of the charge on the cation. Activated carbon cloth is known for its effectiveness in removing chemicals from water and wastewater. Loading of C-cloth with EDTA provides a more efficient sorbent for the adsorption of metal cations. Modification of C-cloth with EDTA causes a significant increase in the rate and the extent of the adsorption of metal cations. Procedures based on adsorption of some cations at EDTA loaded high-area C-cloth are shown to be effective for removal of them from aqueous solutions. Langmuir model is more successful than Freundlich model in representing experimental isotherm data for the adsorption of the most of the ions on both C-cloths [8,10].

Graphitizable carbons with a large surface area, a high pore volume and a porosity made up of mesospores can be synthesised by means of the template technique by using mesostructured silica materials as templates. Thus, the silica porosity is filled with a carbon precursor, which is converted into graphitizable carbon after the carbonisation step. The pore structure of the graphitizable carbons can be tailored as a function of the silica that is used as template. Thus, a carbon with a well-ordered porosity is prepared from silica, whereas a carbon with a wormhole pore structure is obtained if silica is used as template. Heat treatment of the graphitizable carbon at high temperature (2300°C) gives rise to a porous carbon with a well-developed graphitic order. This treatment leads to a significant reduction in the BET surface area and pore volume with respect to the graphitizable sample.

The anodic oxidation of activated carbon fibres (ACFs) leads to an increase in the surface functional groups without significantly changing the surface area. As a result, the amount of adsorption and the adsorption rate of toxic heavy metal such as Cr(VI) from an aqueous solution increase due to a larger content of the surface functional groups on ACFs.

All those techniques are mainly used by chemical industries that produce wastewater with elevated concentration of heavy metals. One should keep in mind that in these industries precipitation techniques can be used as primary treatment to lower the heavy metals content of their wastewater followed by adsorption techniques to remove the remaining heavy metals.

Membrane technology: Membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are increasingly being applied for treating oily wastewater. Of the three broad categories of oily wastes – free-floating oil, unstable oil/water emulsions, and highly stable oil/water emulsions – membranes are most useful with stable emulsions, particularly water-soluble oily wastes. Free oil, on the other hand, can be readily removed by mechanical separation devices which use gravitational force as the driving force. Unstable oil/water emulsions can be mechanically or chemically broken and then gravity separated. Pre-treatment to remove large particles and free oil is needed, especially if thin-channel membrane equipment is used.

The membrane unit is usually operated in a semi-batch recycle. The wastewater feed is added to the process tank at the same rate as clean permeate is withdrawn, thus keeping a constant level in the tank. The retentive retention containing the oil and grease is recycled to the process tank. When the oils and grease and other suspended matter reach a certain predetermined concentration in the tank, the feed is stopped and the retentive allowed to concentrate. Usually, this result in a final concentrate volume that is only 3-5% of the initial volume of oily wastewater fed to the process tank. The system is then usually cleaned.

Membranes have several advantages, among them: (1) The technology is more widely applicable across a wide range of industries; (2) The membrane is a positive barrier to rejected components. Thus, the quality of the treated water (the permeate) is more uniform regardless of influent variations. These variations may decrease flux, but generally does not affect quality of its output, (3) No extraneous chemicals are needed, making subsequent oil recovery easier, (4) Membranes can be used in-process to allow recycling of selected waste streams within a plant, (5) Energy costs are lower compared to thermal treatments, and (6) The plant can be highly automated and does not require highly skilled operators.

The chemical nature of the membrane can have a major effect on the flux. For example, free oils can coat hydrophobic membranes resulting in poor flux (emulsified oil is usually not as much of a problem, unless it is concentrated to such a high level that the emulsion breaks, releasing free oils). Hydrophilic membranes preferentially attract water rather than the oil, resulting in much higher flux. Hydrophobic membrane can be used, but usually in a tubular configuration that allows a high degree of turbulence (cross – flow velocity) to be maintained to minimize oil wetting of the membrane.

Membrane processes have some limitations: (i) Scale-up is almost linear above a certain size. Thus capital costs for very large effluent volumes can be high, and (ii) Polymeric membranes suffer from fouling and degradation during use. Thus they may have to be replaced frequently, which can increase operating costs significantly.

In spite of the above disadvantages, membrane processing of oily wastewaters, sometimes in conjunction with other methods for treating the residuals, is a commercial success with more than 3000 polymeric UF/MF installations and over 75 inorganic/ceramic units worldwide. Even polymeric membranes are reported to last 3 – 7 years, depending on the severity of the application, due in part to the low frequency of cleaning. Membranes are gaining wider acceptance for two reasons: it consistently produces effluents of acceptable discharge quality and it is perceived to be a simple process from an operational viewpoint.

Membrane technology is widely used for the treatment of wastewater from a broad band of chemical industry that produces inorganic substances.

Biological treatment of chemical industry wastewater

Aerobic treatment: In the wastewater treatment sector, biological processes deal primary with organic impurities. Microbial-based technologies have been used over the last century for the treatment of liquid waste domestic stream. The development of these technologies has provided excellent process for the destruction of waste constituents that are readily biodegradable under aerobic conditions. Therefore, processes similar to those used for conventional domestic wastewater treatment have applied successfully to the treatment of many industrial wastewaters.

Aerobic degradation in the presence of oxygen is considered to be a relatively simple, inexpensive and environmentally sound way to degrade wastes. Factors that are critical in the optimal degradation of the selected substrate include the temperature, moisture, pH, nutrients and aeration rate that the bacterial culture is exposed to, with temperature and aeration being two of the most critical parameters that determine the degradation rates by the microorganism.

Soluble organic sources of biochemical oxygen demand (BOD) can be removed by any viable microbial process, aerobic, anaerobic or anoxic. However, aerobic processes are typically used as the principal means of BOD reduction of domestic wastewater because the aerobic microbial reactions are fast, typically 10 times faster than anaerobic microbial reactions. Therefore, aerobic reactors can be built relatively small and open to the atmosphere, yielding the most economical means of BOD reduction.

On the other hand, the major disadvantage of aerobic bioprocesses for waste treatment, relative to anaerobic processes, is the large amount of sludge produce. A relatively high accumulation of biomass occurs in the aerobic bioreactor because the biomass yield (mass of cell produced per unit mass of biodegradable organic matter) for aerobic micro-organisms is relatively high, almost 4 times greater than the yield for anaerobic organisms. The sludge present in the reactor effluent can contain residual BOD that may need to be reduced in an additional process, and must ultimately be disposed of as a solid waste.

There are many mechanisms that are utilised by the microorganisms during the aerobic degradation process. Some of these include the attack on the xenobiotics by organic acids produced by the microorganisms, the production of noxious compounds like hydrogen sulphide and the production of chelating agents which are able to increase the solubility of any insoluble xenobiotics, making them more available to the microorganisms and mechanical degradation.

The wastewater from chemical industries may exert a toxic effect on the microorganisms present in conventional activated sludge reactor. Chemical compounds found in these wastewater streams cannot be utilised as a sole carbon source by microorganisms and will vary in toxicity. Inhibition of growth of the microorganisms by these components therefore plays a crucial role in the degradation process, as this can cause the treatment system to fail [12-14].

The key to successful bioremediation technology of some chemical industries wastewater is to modify or optimise the cell/substrate contact time, so that biodegradation can proceed in a reasonable time and potential toxicity of the wastewater of the wastewater to the microflora is reduced.

According to the literature, the best option for bioremediation of this type of wastewater is a membrane bioreactor (MBR) that has been inoculated with activated sludge, which has been shown to effectively treat high-strength organic wastes. On the other hand, the two-phase partitioning reactor has also been effective with toxic substrates [15]. The following section details two activated aerobic sludge systems that have been shown to facilitate degradation of xenobiotics in the presence of toxic compounds.

Membrane bioreactors: Membrane bioreactors use a combination of the activated sludge process with an additional membrane separation process. A simplified MBR diagram is shown in Figure 2. The two most common configurations are submerged membranes and external membranes.

The advantages offered by MBRs over traditional activated sludge systems include reduced footprints, a decrease in sludge production, improved effluent quality and efficient treatment of wastewaters

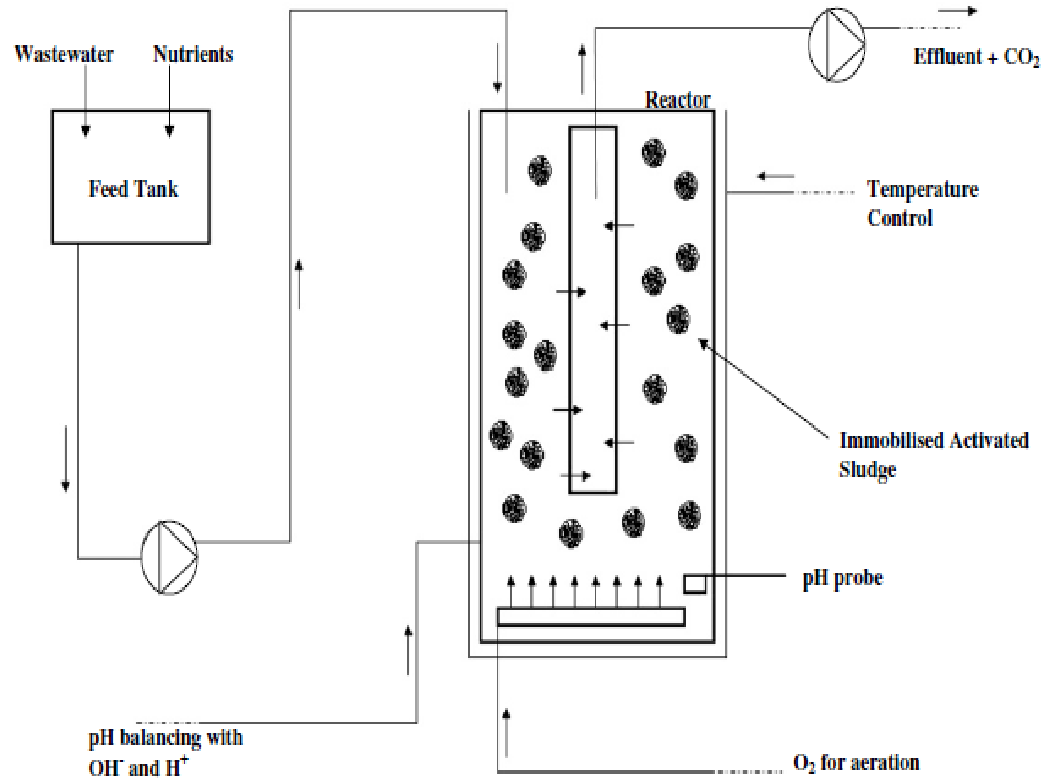

Figure 2: Diagram showing the basic configuration of a membrane bioreactor.

with varying contamination peaks. Some disadvantages of this system include frequent membrane monitoring and maintenance requirements, relatively high running costs and there is a limitation as to the pressures, temperatures and pH to which the system can be exposed.

These reactors have been used in the treatment of a vast range of different wastewaters from municipal or industrial such as pharmaceutical industry [16-18].

Livingston [16] looked at the degradation of 3-chloronitrobenzene from an industrial wastewater stream. It was noted in the study that the degradation of the 3-chloronitrobenzene created chloride ions in stoichiometric quantities, and that transfer tests indicated limited transfer across membranes of the microorganisms and so the levels were not considered to be harmful to the microorganisms. With a flow rate of 64 ml/h, Livingston was able to show > 99% removal of both 3-chloronitrobenzene and nitrobenzene from the wastewater stream with the majority of the carbon entering the system being evolved in the form of CO_2. This is an interesting observation and would need to be considered in the design of a reactor with regard to the release of gas.

Details of process design considerations vary greatly depending on the wastewater being treated as well as the type of membrane reactor used. Operational design of the reactor is crucial as the membrane reactors are prone to membrane fouling. This disadvantage has been given as the major reason for MBRs not being as widely utilised in large scale wastewater treatments in comparison to traditional activated sludge plants [19,20].

Numerous papers have been published investigating innovative ways in which membrane fouling can be controlled. The critical flux is a widely accepted parameter used to characterise membrane fouling and can be defined as the flux below which no fouling of the membrane occurs.

Heavy metals found in wastewater streams with low pH values pose significant environmental problems and so many precipitation methods have been introduced but some of these, such as lime precipitation, create carbonates and hydroxides with the latter product being unstable. Membrane Bioreactors containing sulphate-reducing bacteria have been seen as an alternative to the precipitation process with lime.

This technique is used for the treatment of industrial wastewater such those from textile, pharmaceutical and petroleum industry.

Two phase partitioning bioreactor: Two-phase partitioning bioreactors use a nonbiodegradable, biocompatible and non-volatile organic solvent placed on top of an aqueous phase, which is aerated. A simplified diagram of the two-phase bioreactor is shown in Figure 3. These were developed for the high yield production of inhibitory products [21,22]. Potential was later shown for the bioremediation of toxic compounds due to the systems' ability to supply sub-inhibitory amount of the toxic compound to the aqueous phase due to equilibrium considerations [21].

The system is considered to be self-regulatory as the xenobiotic is delivered to the aqueous phase at a rate determined by the consumption rate of the microorganisms. There are distinct advantages to this system compared to traditional activated sludge systems and other aerobic systems, including the limited exposure of the microorganisms to organic components in the wastewater, thus reducing any toxic effects as well as offering distinct and clear increased initial loading

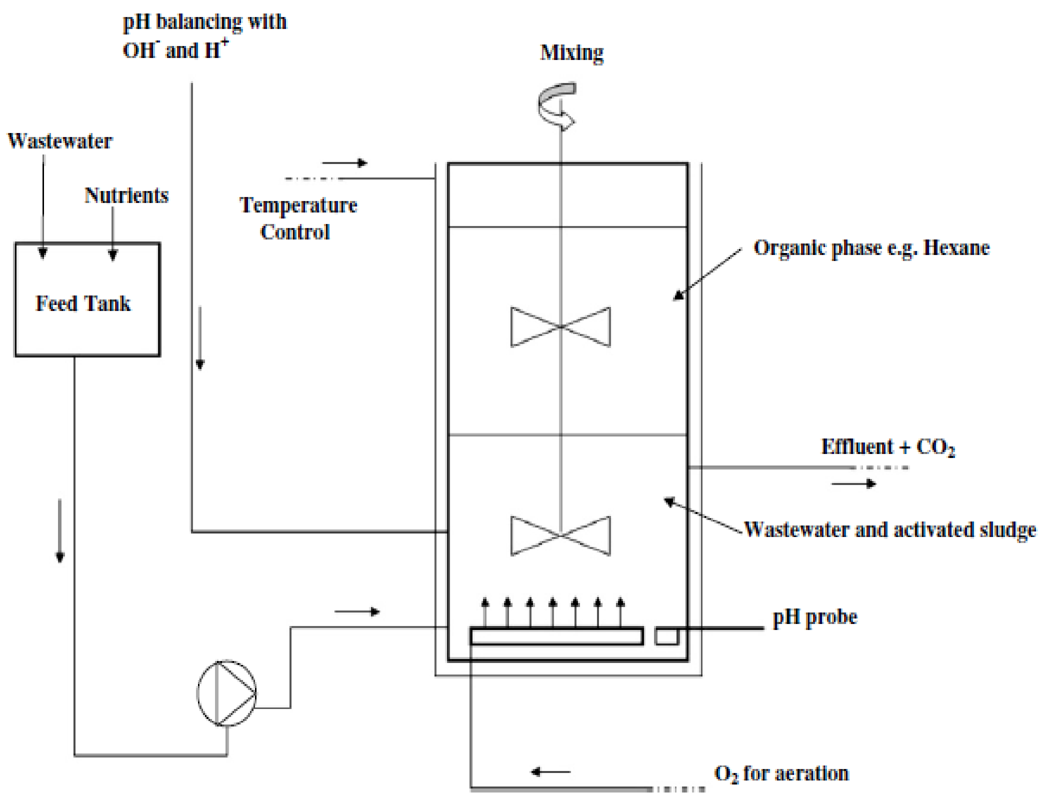

Figure 3: Diagram of simple two – phase reactor configuration.

rates of xenobiotics. Potential disadvantages include the contact of the biodegrading microflora with the metal ions, resulting in an additional step of biomass removal before effluent discharge.

Several studies have focused on degradation of xenobiotics using this type of aerobic degradation reactor configuration. The scope of research on xenobiotic degradation covers the degradation of single xenobiotics and complex mixtures of xenobiotics in two-phase reactor systems. In one such study looking at the degradation of benzene in a two-phase reactor using Alcaligenes xylosoxidans Y234 it was shown that 63.8% of the benzene added into the system was degraded during a 24 h period while 36.2% was stripped by aeration [21]. Benzene was identified as an important xenobiotic, as it is known to be toxic to numerous microorganisms and is hard to degrade when found at high concentrations. The stripping effect was then adjusted in order to encourage more biological degradation of the benzene and results from the adjusted parameters showed a 99.7% degradation of the initial loaded 7000 mg [21]. These results demonstrate the effectiveness of the two-phase reactor in dealing with potentially toxic xenobiotics. Therefore, all wastewater from chemical industry that may contain toxic xenobiotics compounds can be treated with two-phase partitioning bioreactor.

Sequencing batch reactor: A sequencing batch reactor (SBR) is a reactor in which an activated sludge process is carried out in a time-oriented, sequential manner using a single vessel for all the phases of the process. The same steps involved in a conventional, continuous activated sludge process (such as aeration, pollutant oxidation, sludge settling, and recycling) are now conducted in batch one after the other.

In an SBR process, each cycle starts with the reactor nearly empty except for a layer of acclimated sludge on the bottom. The reactor is then filled up with the wastewater and the aeration and agitation are started. The biological degradation process begins during the filling step and proceeds, once the reactor has been filled up, until a satisfactory level of degradation of the pollutant is achieved. Then the aeration and agitation are stopped, and the sludge begins to settle. Depending on the time allowed for the sedimentation, anaerobic reaction can occur, which may reduce the organic content of the sludge. Once the sludge has settled, the clear top layer of treated wastewater is discharged and a new cycle can begin. Anaerobic sludge digestion may also be included as one of the steps in the cycle.

The main advantage of SBRs is that they can accommodate large fluctuations in the incoming wastewater flow and composition without failing. The same may not be true in conventional activated-sludge processes, in which an increase in the incoming flow rate results in a lower residence time of the wastewater in the aeration tank and of the sludge in the clarifier, with potential failure of one of them or both. In addition, toxic shocks or significant changes in organic loading may produce alteration in the makeup of microbial populations of conventional activated-sludge processes, with consequent bulking or process failure. Instead, the wastewater residence time in SBRs can be extended until the microbial population has recovered and completed the degradation process. Similarly, the settling time can be varied to allow complete settling before discharging. In other terms, SBR processes, like all batch processes, are more flexible. On the other hand, the use of SBRs to treat a continuous wastewater flow requires the simultaneous use of multiple reactors and/or the presence of holding facilities to store the wastewater until an SBR becomes available. SBRs have been used also in denitrifying application [23,24].

Sequencing batch reactor technology (SBR), a periodic discontinuous process can be considered for various types of wastewater treatment (domestic wastewater, medium and low strength landfill leachates, specific organic pollutants, various types of industrial wastewaters and contaminated soils) using diverse types of reactor configurations.

Anaerobic treatment: Anaerobic reactor differs from the aerobic reactors primarily because the former must be closed in order to exclude oxygen from the system, since this could interfere with anaerobic metabolism. An anaerobic reactor must be providing with an appropriate vent or a collection system to remove the gazes (mainly methane and carbon dioxide) produced during anaerobiosis.

Anaerobic microbial processes are known to have several important advantages over aerobic microbial processes: (1) lower production rate of sludge, (2) operable at higher influent BOD and toxics levels, (3) no cost associated with delivering oxygen to the reactor, and (4) production of a useful by-product, methane (biogas). However, anaerobic processes have higher capital and operating expenses than aerobic processes because the anaerobic systems must be closed and heated. Thus, anaerobic bioprocesses for treatment of hazardous wastewater streams are typically limited to treatment of low-flow-rate streams such as industrial effluent.

In the past decade has been an increased research activity in the application of anaerobic reactor technology for treatment of various types of industrial wastewaters, such as those from food processing, textile industry, paper and pulp industry. Anaerobic digestion consists of several interdependent, complex sequential and parallel biological reactions, during which the products from one group of microorganisms serve as the substrates for the next, resulting in transformation of organic matter mainly into a mixture of methane and carbon dioxide. Anaerobic digestion takes place in four phases: hydrolysis/liquefaction, acidogenesis, acetogenesis and methanogenesis. To ensure a balanced digestion process, it is important that the various biological conversion processes remain sufficiently coupled during the process so as to avoid the accumulation of any intermediates in the system. There are different anaerobic reactors such as the Up flow Anaerobic Sludge Blanket (UASB) and the Anaerobic Sequencing Batch Reactor (ASBR), which have been used mainly for industrial wastewater treatment.

USAB reactor: Anaerobic treatment is now becoming a popular treatment method for industrial wastewater, because of its effectiveness in treating high strength wastewater and because of its economic advantages.

Developed in the Netherlands in the late seventies (1976-1980) by Prof. Gatze Lettinga, Wageningen University, UASB reactor was originally used for treating wastewater from sugar refining, breweries and beverage industry, distilleries and fermentation industry, food industry, pulp and paper industry. In recent times the applications for this technology are expanding to include treatment of chemical and petrochemical industry effluents, textile industry wastewater, landfill leachates, as well as applications directed at conversions in the sulfur cycle and removal of metals.

The Essential Components of an UASB reactor is depicted in Figure 4. The UASB reactor has four major components: 1) Sludge bed, 2) Sludge blanket, 3) Gas – sludge – liquid separator (GSL) and 4) Settlement compartment.

The specific of an UASB are existence of granules sludge and internal three-phase GSL device (gas/sludge/liquid separator system). In an UASB reactor, anaerobic sludge has or acquires good

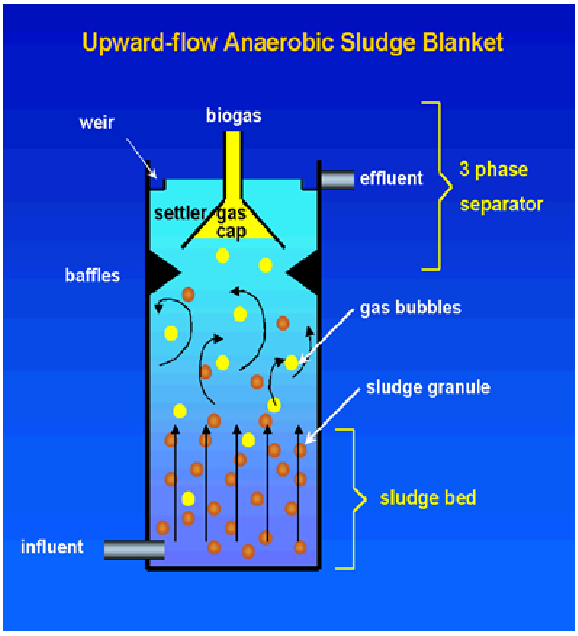

Figure 4: The upward-flow anaerobic sludge bed (UASB) reactor concept.

sedimentation properties, and is mechanically mixed by the up-flow forces of the incoming wastewater and the gas bubbles being generated in the reactor. For that reason mechanical mixing can be omitted from an UASB reactor thus reducing capital and maintenance costs. This mixing process also encourages the formation of sludge granules.

ASBR reactor: Anaerobic sequencing batch reactor (ASBR) is a high rate anaerobic process developed by Dague and co-workers at Iowa State University. The promising feature of the ASBR process is that granular biomass can be achieved, and in this way higher biomass can be maintained in the reactor with efficient biomass setting and a long solids retention time (SRT). There are five stages to treatment: (1) Fill, (2) React, (3) Settle, (4) Decant, and (5) Idle.

Anaerobic sequencing batch reactors allow typical biological anaerobic metabolism from substrate consumption to methane and carbon dioxide production and operate according to the following cyclic steps: feed, reaction, settling and discharge [25]. The main advantages of this type of operation are its operational simplicity, efficient quality control of the effluent, possibility of eliminating the settling step for both the affluent and effluent wastewater and flexibility of use in the wide variety of wastewaters to be treated. These characteristics indicate its potential application in situations requiring compliance with strict environmental control standards as well as when sewage is produced intermittently and has variable characteristics as a result of the type of downstream process.

The technological potentials of this reactor have already been assessed for some types of effluents such as food processing wastewater and low-strength synthetic wastewater [25]. However, Zaiat et al. [26] demonstrated that many engineering process features still have to be studied in order to achieve better insight into the operational aspects of this reactor, thereby enabling application in real situations with an optimized procedure.

In many municipal and industrial wastewater treatment plants, the sludge effluent from primary and secondary treatment is fed to an anaerobic bioreactor (often termed anaerobic digester or stabilizer) to reduce the residual BOD of the sludge. The anaerobic conditions promote methanogenic microbial degradation of the BOD, thus rendering the sludge fit for landfill disposal. If toxic organic compounds are sorbed to the sludge, the methanogenic conditions of the digester can stimulate degradation of many of these toxic organics. Thus, if the primary fate of toxic organics entering conventional treatment is sorption to sludge, the ultimate fate of the compounds may be biodegradation in the anaerobic digester. Typical operating parameters for the anaerobic digester are 10- to 20- day liquid and solids residence time and a temperature of 35°C. The methane produced from the methanogenic microbial activity is often burned to help heat the bioreactor.

This technique can be used for the treatment of sulphate bearing chemical wastewater, automobile industry wastewater, hypersaline composite chemical wastewater among others.

Integrated treatment process: An integrated or hybrid system is designed to take advantage of unique features of two or more processes. In order words, integrated systems are defined here as those waste treatment processes that utilize both aerobic and anaerobic organisms to achieve the desired objective of producing an environmentally accepted and stable final waste product. As more knowledge becomes available on the microbiology of each the two classes of microorganisms, they are likely to be selectively used to solve more difficult wastewater treatment problems by exploiting the specific degradation potentials of each group. In turn, this will require the design of appropriate reactor configuration capable of maintaining the desired conditions for the microbial activity to take place. Some of those systems are now examined.

It is cost effective to treat high-strength wastewater effluents with a combination of anaerobic-aerobic processes. This was recently shown by Eckenfelder et al. [27], whose economic analysis pointed out that if the wastewater has a BOD in excess of 1000 mg/L a combined anaerobic-aerobic process can be advantageous. This approach has been used in different applications, including a recent one involving the combined use of powered activated carbon and both anaerobic (first) and aerobic (second) stages [28,29]. These applications were developed primarily to treat high-strength wastewater. In all these case the reactors used for each stage were of the type described above for each class of organisms.

In addition to the advantages mentioned above, anaerobes can have an additional feature that makes them attractive in wastewater. Anaerobic organisms have recently been shown to be responsible for a number of reductive reaction processes that could have a significant impact on the treatment of certain classes of hazardous compounds. In particular, anaerobic organism have been shown to be capable of reductively dehalogenating a number of toxic compounds, such as chlorinated aromatics, that are very recalcitrant to aerobic degradation [30]. Therefore, a possible alternative for the treatment of such compounds is their sequential exposure to specialized anaerobic and aerobic cultures. If the process is operated continuously, it requires the sequential use of two reactors maintained under anaerobic and aerobic conditions, respectively.

Several laboratory-scale investigations have illustrated the potential of sequential anaerobic/aerobic bio treatment steps for textile wastewater [31]. Anaerobic pre-treatment offers several potential advantages such as better removal of colour, absorbable organic halogens (AOX), and Heavy metals. Improved heavy metal removal may follow sulphide production [32], while the improvement of the colour and AOX removal from the rapid reduction and cleavage under anaerobic conditions of the azo groups in arylazo pollutants and of electron-withdrawing chloro or nitro substituent's [33].

The combined activity of anaerobic/aerobic bacteria can also be obtained in a single step if the bacteria are immobilized in bio films since O_2 penetration seldom exceeds several hundred micrometers [33]. In addition to providing anaerobic/aerobic zones, fixed film reactors offer the advantages of higher sludge retention time (SRT) necessary to prevent washout of adapted microorganisms, protection against toxicants such as azo dye acid Orange 7, and low sludge production [34].

The combined anaerobic/aerobic process was successfully used to treat saline wastewater for nutrient (COD, N, P) removal. In addition to the removal of these pollutions, the combination of anaerobic/aerobic processes made it possible to address biological nitrogen and phosphorous removal from saline wastewater.

Chemical oxidation

Oxidation, by definition, is a process by which electrons are transferred from one substance to another. This leads to a potential expressed in volts referred to a normalized hydrogen electrode. From this, oxidation potentials of the different compounds are obtained.

Chemical oxidation appears to be one of the solutions to be able to comply with the legislation with respect to discharge in a determined receptor medium. It can also be considered as an economically viable previous stage to a secondary treatment of biological oxidation for the destruction of non-biodegradable compounds, which inhibit the process.

A reference parameter in case of using chemical oxidation as treatment process is the chemical oxygen demand (COD). Only waters with relatively small COD contents (≤ 5 g.L^{-1}) can be suitably treated by means of these processes since higher COD contents would require the consumption of too large amounts of expensive reactants. In those cases, it would be more convenient to use wet oxidation or incineration: waste water with COD higher than 20 g.L^{-1} may undergo autothermic wet oxidation [35].

The chemical oxidation processes can be divided in two classes:

- Classical Chemical Treatments

- Advanced Oxidation Processes (AOPs)

Classical chemical treatment: Classical chemical treatments consist generally on the addition of an oxidant agent to the water containing the contaminant to oxidize it. Among the most widely used it is possible to emphasize [35] the following classical oxidants.

- Chlorine: it is a good chemical oxidizer for water evaporation because it destroys microorganisms. It is a strong and cheap oxidant, very simple to feed into the system and it is well known [35]. Its main disadvantages are its little selectivity that high amounts of chlorine are required and it usually produces carcinogenic organo chloride by-products.

- Potassium permanganate: It has been an oxidizer extensively used in the treatment of water for decades. It can be introduced into the system as a solid or as a solution prepared on site. It is a strong but expensive oxidant, which works properly in a wide pH range. One of the disadvantages of the use of potassium permanganate as an oxidizer is the formation of magnesium dioxide throughout oxidation, which precipitate and has to be eliminated afterward by clarifying or filtration, both of which mean an extra cost.

- Oxygen: The reaction of organic compounds with oxygen does not take place in normal temperature and pressure conditions. Needed values of temperature and pressure are high to increase the oxidizing character of the oxygen in the reaction medium and to assure the liquid state of the effluent. It is a mild oxidant that requires large investments in installations. However, its low operating costs make the process attractive.

- Hydrogen peroxide: It is a multipurpose oxidant for many systems. It can be applied directly or with a catalyst. The catalyst normally used is ferrous sulphate (the so-called Fenton process, which will be presented below). Other iron salts can be used as well. Other metals can also be used as catalyst, for example, Al^{3+}, Cu^{2+}. Its basic advantages are: (i) it is one of the cheapest oxidizers that is normally used in residual, (ii) waters, (iii) it has high oxidizing power, (iv) it is easy to handle, (v) it is water-soluble, (vi) it does not produce toxins or color in by products. It can also been used in presence of ultraviolet radiation and the oxidation is based on the generation of hydroxyl radicals that will be considered an advanced oxidation process.

An option to the ending of hydrogen peroxide to the reaction medium is its production on site. One production possibility is by electro reduction of the oxygen dissolved in the reaction medium [35]. This option is not used very much, because it is expensive and increases the complexity of the system.

- Ozonation: It is a strong oxidant that presents the advantage of, as hydrogen peroxide and oxygen, not introducing "strange ions" in the medium. Ozone is effective in many applications, like the elimination of color, disinfection, elimination of smell and taste, elimination of magnesium and organic compounds.

In standard conditions of temperature and pressure it has a low solubility in water and is unstable. It has an average life of a few minutes [35]. Therefore, to have the necessary quantity of ozone in the reaction medium a greater quantity has to be used.

Among the most common oxidizing agents, it is only surpassed in oxidant power by fluorine and hydroxyl radicals. Although included among the classical chemical treatments, the ozonation of dissolved compounds in water can constitute as well an AOP by itself, as hydroxyl radicals are generated from the decomposition of ozone, which is catalyzed by the hydroxyl ion or initiated by the presence of traces of other substances, like transition metal cations [35]. As the pH increases, so does the rate of decomposition of ozone in water.

The major disadvantage of this oxidizer is that it has to be produced on site and needs installation in an ozone production system in the place of use. Therefore, the cost of this oxidizer is extremely high, and it must bear this in mind when deciding the most appropriate oxidizer for a given system. In addition, as it is a gas, a recuperation system has to be foreseen and that will make the obtaining system even more expensive. Ozonation is used in many drinking water plants as a tertiary treatment and also for the oxidation of organic pollutants of industrial (paper mill industry) or agriculture (water polluted by pesticides) effluents.

Advanced Oxidation Processes (AOPs): AOPs were defined by Glaze and Chapin [36] as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules.

The advanced oxidation processes (AOPs) are: UV/O_3 process, UV/H2O2, O3/H2O2, Fe^{3+}/ UV-vis process, UV/TiO_2 (Heterogeneous photocatalysis), H2O2 / Fe^{2+} (known as Fenton's reagent).

Among various AOPs, the Fenton reagent ($H2O2_2$/ Fe^{2+}) is one of the most effective methods of organic pollutant oxidation. The Fenton reagent has been found to be effective in treating various industrial wastewater components including aromatic amines, a wide variety of dyes as well as many other substances, e.g. pesticides and surfactants [35]. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide [35,37]. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. However, disadvantages in using the Fenton reagent include the production of a substantial amount of $Fe(OH)_3$ precipitate and additional water pollution caused by the homogeneous catalyst that added as an iron salt, cannot be retained in the process [35]. To solve these problems, the application of alternative iron sources as catalysts in oxidizing organic contaminants has been studied extensively. A number of researchers have investigated the application of iron oxides such as hematite, ferrihydrite, semicrystalline iron oxide and crystalline goethite [35]. They generally have observed a greatly accelerated decomposition of hydrogen peroxide but variable amounts of contaminant were lost.

The Fenton reaction was discovered by Fenton in 1894 [38]. Forty years later the Haber-Weiss [39] mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical.

The Fenton reaction can be outlined as follows:

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + HO^{-} + HO^{\bullet} \quad (1)$$

where M is a transition metal as Fe or Cu

The $HO^{\bullet}$ radical mentioned above, once in solution attacks almost every organic compound. The metal regeneration can follow different paths. For Fe^{2+}, the most accepted scheme is described in the following equations [40].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + HO + HO\bullet \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (3)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{\bullet-} \quad (4)$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

$$Fe^{3+} + HO^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (6)$$

$$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2 \quad (7)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{\bullet-} \quad (8)$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light [41].

The AOPs techniques are mainly used as a pre-treatment stage for industrial wastewater remediation. These techniques improve the destruction of persistent contaminants.

Wetland to treat industrial wastewater

Constructed wetlands (CWs) are engineered systems that have been designed and constructed to utilize natural processes involving wetland vegetation, soils and the associated microbial assemblages to assist in treating wastewaters. They are designed to take advantage of many of the processes that occur in natural wetlands but do so within a more controlled environment. Constructed wetlands were initially utilized for nutrient removal in residential and municipal sewage, storm water and agricultural runoff displaying a wide range of removal efficiencies. Since 1990s, the constructed wetlands have been used for all kinds of wastewater including landfill leachate, runoff (e.g. urban, highway, airport and agricultural), food processing (e.g. winery, cheese and milk production), industrial (e.g. chemicals, paper mill and oil refineries), agriculture farms, mine drainage or sludge dewatering [42]. The accelerating industrialization in developing countries with an enormous consumption of metals constitutes an environmental contamination hazard. The application of wetlands for industrial wastewater treatment is a promising alternative. In addition, wetlands have significant merits of low capital and operating costs compare with conventional system as activated sludge, aerated lagoon system and so on.

The basic classification is based on the type of macrophytic growth (emergent, submerged, free floating and rooted with floating leaves), further classification is usually based on the water flow regime (surface flow, sub-surface vertical or horizontal flow). Recently, the combinations of various types of CWs (so-called hybrid systems) have been used to enhance the treatment effect, especially for nitrogen. The capability of water hyacinth to purify wastewater is well documented [43,44]. The extensive root system of the weed provides a large surface area for attached microorganisms thus increasing the potential for decomposition of organic matter. Plant uptake is the major process for nutrient removal from wastewater systems containing water hyacinth plants, and it is related to nutrient loading to the system [43,44]. Nitrogen is removed through plant uptake (with harvesting), ammonia is removed through volatilization and nitrification : denitrification, and phosphorus is removed through plant uptake. Treatment systems with water hyacinth are sufficiently developed to be successfully applied in the tropics and sub-tropics where climatic conditions favour luxuriant and continuous growth of the macrophyte for the whole year.

It has been found that the proper vegetation management not only improves treatment effect but also improves substantially wildlife value of the constructed wetland.

Davies et al. [45] studied the enzymatic processes responsible for removal and degradation of azo-dyes using constructed wetlands planted with Phragmites sp.

It has been found that the proper vegetation management not only improves treatment effect but also improves substantially wildlife value of the constructed wetland. The function of macrophytes within constructed wetlands has been reviewed extensively by researchers including Kouki et al. [46], Türker et al. [47] and Verlicchi and Zambello [48].

Conclusion

The world's chemical industries face formidable environmental regulatory challenges in treating their wastewater effluents. Therefore, this review shouldered the task of passing in revue the different technologies issued to treat industrial wastewaters. Several physicochemical options and biological wastewater treatment processes are widely utilised in the successful treatment of industrial wastewaters. These options are being shown to be technologically and economically feasible. API – oil separator is an excellent technique for oil removal from industrial wastewaters. Both aerobic and anaerobic treatment systems are feasible to treat wastewater from all types of industrial effluents. However, a combination using an anaerobic process followed by an aerobic treatment system is a better option, as it can make use of the advantages of both the treatment processes. Those hybrid systems produce a high removal of toxic pollutants. Membranes merely serve to separate or fractionate wastewater components, hopefully into more useful and/or less polluting streams, and cannot break down or chemically alter the pollutants. Fouling, not surprisingly, is frequently cited as the most important factor limiting the utilization of membranes in wastewater treatment. Constructed wetlands (CWs) have been implemented as wastewater treatment facilities in many parts of the world, but to date, the technology has been largely ignored in developing countries where effective, low cost wastewater treatment strategies are critically needed. CWs may be an economical option for secondary treatment of stabilization pond effluent, the most common treatment system in use in economically poor countries. Given the tropical location of many developing nations, CWs may be successfully established with plant species acclimated to the tropical environment. The type of plant and the stage position (first or second unit in the series) seemed to have a major effect on the dynamics of bacterial communities. Advanced oxidation processes face strict limitations, both technical and economical, in their application to the whole site wastewater flow, whereas they are quite effective in converting rather recalcitrant compounds into intermediates amenable to biological oxidation (via recirculation to the inlet of the biological unit) or even better completely mineralizing these compounds when applied in the outlet of a biological treatment facility as a final polishing step. The activated carbons can be used for the removal of metals, chloride, fluoride and COD from industrial effluents. Activated carbon prepared from low cost material, Agricultural by-product materials or modified natural polymers, is considerably efficient for removal of direct dyes from wastewater. Alleviating demand for clean water by replacing it with treated wastewater wherever possible in industry can ameliorate water stress in arid/semi arid mining regions of Africa and Australia.

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