ISSN:1991-8178

Australian Journal of Basic and Applied Sciences

Journal home page: www.ajbasweb.com

Review Article: Chemical Oxidation and Membrane Filtration Technologies for Wastewater Treatment

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ARTICLE INFO

Article history:
Received 12 July 2014
Accepted 28 September 2014
Available online 5 October 2014

Keywords:
Wastewater treatment - Chemical Oxidation - Membrane Bioreactors.

ABSTRACT

The following review article describing chemical oxidation technology and membrane filtration technology, including, membrane bioreactors (MBR) which used for wastewater treatment.

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To Cite This Article: Mohamed N. Bayoumi and Raed S. Al-Wasify., Chemical Oxidation and Membrane Filtration Technologies for Wastewater Treatment. ***Aust. J. Basic & Appl. Sci.,*** *9(11): 263-273, 2015*

1. Chemical oxidation technology:

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. Table (1) shows the potentials of the most commonly used oxidizers (Beltrán *et al.*, 1999; Munter, 2001).

Table 1: Oxidation power of selected oxidizing species.

Oxidation species	Oxidation power (V)
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Permanganate	1.67
Hypobromous acid	1.59
Chlorine dioxide	1.50
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chorine	1.36
Bromide	1.09
Iodine	0.54

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. The optimization of the process (Alaton and Gurol, 1992) arises in those conditions in which non-biodegradable material is eliminated, but with a minimum amount of oxidizer. That is to say, leading the oxidation to the formation of biodegradable compounds and not those of CO_2 and H_2O. It can be said that it is an appropriate technique for small loads of pollutants; load meaning the concentration of the pollutant multiplied by the volume of flow of the effluent to be treated. This would otherwise become an expensive technique, because of its large oxidizer consumption, and would have few possibilities in relation to other more appropriate techniques for

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greater loads, as could be the selective absorption of pollutants, when the concentration of the pollutant is high or biological oxidation, for low concentrations. In addition to the polluting load, for the chemical oxidation to be economically profitable, it has to bear in mind the concentration of this in the effluent. This operation is easier to apply in the destruction of compounds like phenol, nitrobenzene, some colorants and its derivatives for concentrations between 100 and 500 mg L^{-1}. In the case of higher concentrations, other operations come into play like selective absorption or incineration, in the case that recuperation is not desired. For lower concentrations, there are techniques like absorption and biological oxidation. In general it can be said that chemical oxidation shows good prospects for use in the elimination of non-biodegradable compounds in the following cases:

(a) For the treatment of high concentrations of the compound to be eliminated, without the interference of other possible compounds. For example, when incineration is not a viable alternative because the volume of flow of the effluent is great. Optimization is obtained because the reactant is consumed in attacking the desired compound. The existence of other compounds, which can oxidize, leads to a high level of consumption of the reactant.

(b) As a pretreatment of currents, to reduce toxicity by avoiding causing problems of inhibition in the biomass when being introduced in a biological treatment (activated sludge). Intermediate levels of oxidation are aimed at, with a reduced consumption of oxidizer, so that the effluent is in conditions to be biologically treated.

(c) As a final treatment for the adjustment of the effluent for the desired discharging conditions.

The chemical oxidation processes can be divided in two classes: Classical Chemical Treatments and Advanced Oxidation Processes (AOPs).

1.1. Classical Chemical Treatments:

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 (Chamarro *et al.*, 2001):

- Chlorine:

This is a good chemical oxidizer for water depuration because it destroys microorganisms. It is a strong and cheap oxidant, very simple to feed into the system and it is well known. Its main disadvantages are its little selectivity that high amounts of chlorine are required and it usually produces carcinogenic organochloride 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 dissolution 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 (Fenton process). Other iron salts can be used as well. Other metals can also be used as catalyst, for example, Al^{3+} and Cu^{2+}. Hydrogen peroxide has some advantages such as: it is one of the cheapest oxidizers that is normally used in residual waters; has high oxidizing power; easy to handle; water-soluble and does not produce toxins or color in byproducts.

- Ozone:

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 (Staehelin and Hoigné, 1982). Therefore, to have the necessary quantity of ozone in the reaction medium a greater quantity has to be used.

1.2. Advanced Oxidation Processes (AOPs):

AOPs were defined by Glaze and *et al*. (1987) 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 kinetics of reaction is generally first order with respect to the concentration of hydroxyl radicals and to the concentration of the species to be oxidized. Rate constants are usually in the range of $10^8 - 10^{11}$

$L.mol^{-1}.s^{-1}$, whereas the concentration of hydroxyl radicals lays between 10^{-10} and 10^{-12} $mol.L^{-1}$, thus a pseudo-first order constant between 1 and 10^{-4} s^{-1} is obtained (Glaze and Kang, 1989). As it can be seen from Table (1), hydroxyl radicals are more powerful oxidants than the chemical agents used in traditional chemical processes. Hydroxyl radicals are also characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it's shown in Table (2). Nevertheless, some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives as chloroform or tetrachloroethane, cannot be attacked by OH radicals. Depending upon the nature of the organic species, two types of initial attacks are possible: the hydroxyl radical can abstract a hydrogen atom to form water, as with alkanes or alcohols, or it can add to the contaminant, as it is the case for olefins or aromatic compounds. The attack by hydroxyl radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization. As a rule of thumb, the rate of destruction of a contaminant is approximately proportional to the rate constants for the contaminant with the hydroxyl radical. From Table (3) it can be seen that chlorinated alkenes treat most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules as mentioned before, have smaller rate constants and therefore are more difficult to oxidize.

Table 2: Oxidizable compounds by hydroxyl radicals.

Compounds	
Acids	Formic, gluconic, lactic, malic, propionic, tartaric.
Alcohols	Benzyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol.
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, trichloroacetaldehyde.
Aromatics	Benzene, chlorobenzen, chlorophenol, dichlorophenol, hydroquinone, phenol, toluene, xylene.
Amines	Aniline, cyclic amines, diethylamine, EDTA, n-propylamine.
Dyes	Anthraquinone, diazo, monoazo.
Ethers	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone.

Table 3: Reaction rate constant (k, $L\ mol^{-1}\ s^{-1}$).

Compounds	$OH^{\bullet}$
Chlorinated alkanes	10^9 to 10^{11}
Phenols	10^9 to 10^{10}
N-containing organics	10^8 to 10^{10}
Aromatics	10^8 to 10^{10}
Ketones	10^9 to 10^{10}
Alcohols	10^8 to 10^{10}
Alkanes	10^6 to 10^9

The versatility of AOPs is also enhanced by the fact that they offer different ways of $HO^{\bullet}$ radicals' production, thus allowing a better compliance with the specific treatment requirements. It has to be taken into account, though, that a suitable application of AOPs to wastewater treatment makes use of expensive reactants as hydrogen peroxide and/or ozone, and therefore they should not replace, whenever possible, the more economic treatments as the biological degradation. As hydroxyl radicals are so reactive and unstable, they must be continuously produced by means of photochemical or chemical reactions. The main processes of producing these radicals are described below. It is very difficult to make a classification of the advanced oxidation processes, for the diverse combinations that are presented among them. For this reason, they are presented in the way that has been considered more appropriate.

1.2.1. UV-based processes:

As it has been commented previously, the slow kinetics achieved by photochemical reactions can be enhanced by the addition of hydrogen peroxide and/or ozone, metallic salts or semiconductors. The UV/oxidizer system involves direct excitation of the substrate due to the radiation with the subsequent oxidation reaction. Even so, there may be synergism between the oxidizer and the ultraviolet radiation, which causes the global effect to be different from the additive effect.

1.2.1.1. UV/O_3 process:

The UV/O_3 system is an effective method for the oxidation and destruction of organic compounds in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 253.7 nm. The extinction coefficient of O_3 at 253.7 nm is 3300 $L.mol^{-1}.cm^{-1}$, much higher than that of H_2O_2 (18.6 $L.mol^{-1}.cm^{-1}$). The decay rate of ozone is about a factor of 1000 higher than that of H_2O_2 (Guittonneau *et al.*, 1991).

The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals, which do not act as they recombine producing hydrogen peroxide (Peyton and Glaze, 1988):

$$H_2O_2 + O_3 \xrightarrow{h\nu} 2\,HO^{\bullet} + O_2$$

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

This system contains three components to produce OH radicals and/or to oxidize the pollutant for subsequent reactions: UV radiation, ozone and hydrogen peroxide. Therefore, the reaction mechanism of O_3/H_2O_2 as well as the combination UV/H_2O_2 is of importance.

1.2.1.2. UV/O_3 /H_2O_2 process:

The addition of H_2O_2 to the UV/O_3 process accelerates decomposition of ozone resulting in increased rate of $HO^{\bullet}$ radicals generation. This is a very powerful method that allows a considerable reduction of the TOC. This process is the combination of the binary systems UV/O_3 and O_3/H_2O_2. Mokrini *et al*. (1997) presented the degradation of phenol by means of this process at different pHs, establishing the optimal H_2O_2 amount. A 40% of TOC reduction was achieved by this method. Trapido *et al*. (2001) reported that the combination of ozone with UV radiation and hydrogen peroxide was found to be more effective for the degradation of nitrophenols than single ozonation or the binary combinations, increasing the reaction rate and decreasing the ozone consumption when using low pH values. Contreras *et al*. (2001) demonstrated that the addition of H_2O_2 to UV/O_3 system slightly improves the rate of TOC removal in solutions of nitrobenzene. With regards to DCDE and textile wastewaters no articles have been found in the literature about the oxidation of these compounds by means of this combined process.

1.2.1.3. Fe^{3+} / UV-vis process:

Among the AOPs, the iron photo-assisted system Fe^{3+} /UV-vis, without addition of other electron acceptor than O_2 from air, has received special attention as a potential wastewater treatment process. The interesting point in such a system, compared to the photo-Fenton process is that no addition of hydrogen peroxide is needed. The excitation of $[Fe(OH)(H_2O)_5]^{2+}$, the dominant monomeric species of aqueous ferric ion in acidic solution, is known to yield $HO^{\bullet}$ (eq. 1.7 similar to 1.17) with a quantum yield of 0.075 at 360 nm (Benkelberg and Warneck, 1995).

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet}$$

Where $Fe(OH)^{2+}$ refers to $[Fe(OH)(H_2O)_5]^{2+}$.

This electron transfer process has been efficiently used to study the degradation of several organic pollutants in aqueous solution.

1.2.1.4. UV/TiO_2 (Heterogeneous photocatalysis):

Over the last few years the tendency has been to carry out chemical oxidation in the presence of a catalyst that serves as a generator of hydroxyl radicals, and, therefore, the addition of an oxidizer in the medium is not necessary. Heterogeneous photocatalytic process consists on utilizing the near UV radiation to photoexcite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radical or free holes, are generated. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum (wavelength shorter than 380 nm) what transforms it into a good option to be used at big scale (Malato *et al.*, 2002). Many catalysts have been tested, although TiO_2 in the anatase form seems to possess the most interesting features, such as high stability, good performance and low cost (Andreozzi *et al.*, 1999). It presents the disadvantage of the catalyst separation from solution, as well as the fouling of the catalyst by the organic matter. Minero *et al*. (1994) studied the photocatalytic degradation of NB on TiO_2 and ZnO, reporting that complete mineralization with TiO2 was achieved. Phenolic compounds have been successfully degraded by photocatalytic process (Minero *et al*., 1994). Regarding DCDE, no references about the use of photocatalysis heterogeneous has been found. Few studies have been found in the literature regarding the photocalytic oxidation of textile wastewaters (Balcioglu and Arslan, 2001).

1.2.2. H_2O_2 -based processes:

The most important advanced oxidation treatments based in the use of H_2O_2 are:

1.2.2.1. H_2O_2 /UV process:

The H_2O_2/UV system involves the formation of $HO^{\bullet}$ radicals by hydrogen peroxide photolysis and subsequent propagation reactions. The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals:

$$H_2O_2 \xrightarrow{h\nu} 2\,HO^{\bullet} \qquad \lambda \leq 400\ nm$$

It presents the advantage compared when working with ozone that it provides a cheap and sure source of radicals, eliminating this way the problem of the handling of ozone. The major drawback of this process is that if the solution presents a strong absorbance this can compete with hydrogen peroxide for the radiation, thus cloudy waters or containing compounds absorbing UV radiation can present problems at being treated by this method. The effectiveness of the UV/H_2O_2 system in the treatment of aromatic compounds such phenol and NB has been widely studied. However, in the case of DCDE, no reference was found. Alaton and Balcioglu (2002) show the effectiveness of H_2O_2/UV system as pretreatment or in combination with other advanced oxidation process in the treatment of textile wastewater.

1.2.2.2. H_2O_2 /O_3 process:

Addition of hydrogen peroxide to ozone offers another way to accelerate the decomposition of ozone, leading to the formation of OH radicals. Hydrogen peroxide in aqueous solution is partially dissociated in the hydroperoxide anion (HO^{2-}), which reacts with ozone, decomposing this and giving rise to a series of chain reactions with the participation of hydroxyl radicals. In the global reaction two ozone molecules produce two hydroxyl radicals (Glaze and Kang, 1989).

$$H_2O_2 + 2\,O_3 \rightarrow 2\,HO^{\bullet} + 3\,O_2$$

As this system does not depend on the UV radiation transmission to activate the ozone or hydrogen peroxide molecules, its greatest advantage is to be able to work with turbid waters without problems. Balcioglu and Arslan (2001) studied the efficiency of ozonation and O_3/H_2O_2 of reactive dyes and textile dye-bath wastewater. They found a considerable improvement in COD and color removal rates at pH=11, which is normally the pH of textile wastewaters.

1.2.2.3. Fenton and photo-Fenton reaction:

The Fenton reaction was discovered by H.J.Fenton in 1894. Forty years later the Haber-Weiss (1934) mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. Since then, some groups have tried to explain the whole mechanism that will be treated in details in the next two chapters. The Fenton reaction can be outlined as follows:

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

Where M is a transition metal as Fe or Cu.

In the absence of light and complexion ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyperoxyl ($HO_2^{\bullet}/O^{2-}$) and hydroxyl radicals HO• (Gallard and De Laat, 2000). The $HO^{\bullet}$ radical mentioned before, 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.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet}$$

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

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^-$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2$$

$$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{+3} + HO_2^-$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light (Ruppert *et al.*, 1993; Sun and Pignatello, 1993). During the reaction, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. Photochemical regeneration of ferrous ions (Fe^{2+}) by photoreduction of ferric ions (Fe^{3+}) is the proposed mechanism. The new generated ferrous ions reacts with H_2O_2 generating a second $HO^{\bullet}$ radical and ferric ion, and the cycle continues.

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet}$$

1.2.3. AOPs combined with biological treatments:

Biological treatment of wastewater, groundwater, and aqueous hazardous wastes is often the most economical alternative when compared with other treatment options. The ability of a compound to undergo biological degradation is dependent on a variety of factors, such as concentration, chemical structure and substituents of the target compound. The pH or the presence of inhibitory compounds can also affect the biological degradation. Although many organic molecules are readily degraded, many other synthetic and naturally occurring organic molecules are biorecalcitrant (Adams *et al.*, 1997). Several chemical processes, which use oxidizing agents such as ozone, hydrogen peroxide, etc. have been carried out to mineralize many synthetic organic chemicals. However, costs associated with chemical oxidation alone can often be prohibitive for wastewater treatment. A potentially viable solution is the integration of chemical and biological treatment processes as an economical means for treating biorecalcitrant organic chemicals in wastewater. The chemical process would be used as a pre-treatment in order to increase the biodegradability of the wastewater (Sarria *et al.*, 2001). The oxidation of organic compounds in water with AOPs usually produces oxygenated organic products and low molecular weight acids that are more biodegradable (Ledakowicz *et al.*, 2001). With the AOPs, toxic compounds would be removed until no inhibition due to its toxicity was there and/or non-biodegradable compounds turned into more biodegradable. This feature is economically interesting, as investment and operating costs are much lower for a biological process than a chemical one: investments costs for biological processes range from 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide, while treatment costs range from 3 to 10 times less. In these combined processes, if we want to determine the variation of biodegradability as a function of the chemical reaction conditions (time of pre-treatment, concentration of the oxidizing agent, temperature, etc), a biodegradation test is required. Methods for measuring biodegradability in these systems have been proposed by a number of authors. BOD and BOD/COD or BOD/TOC are commonly used (Chamarro *et al.*, 2001). Other biodegradability measures including substrate destruction, total organic carbon (TOC) evolution, oxygen uptake, EC50 toxicity measurements, cell growth counts and

intracellular ATP levels also have been used (Pulgarin *et al.*, 1999). Alaton and Balcioglu (2002) reported that ozonation and H_2O_2/UV as pretreatment of a textile wastewater were found to enhance the effectiveness of a subsequent biological treatment. Besides this, Pala and Tokat (2002) outlined that due to the low biodegradability of the textile wastewaters and due to the not very efficient performed of the biological treatment in the color removal, it should be carried out in combination with activated carbon.

2. Membrane filtration technology:

A membrane is defined as a material that forms a thin wall capable of selectively resisting the transfer of different constituents of a fluid and thus effecting a separation, of the constituents. Biological treatment technologies have been utilized in wastewater reclamation for over a century. Out of the many different processes employed, the activated sludge system has proven to be the most popular (Tchobanoglous *et al.*, 2003). The implementation of membranes within the treatment sequence of a water pollution control facility was initially limited to tertiary treatment and polishing. Ultra-filtration, micro-filtration, or reverse osmosis units were utilized in areas where discharge requirement were very stringent or direct reuse of the effluent was desired (Tchobanoglous *et al.*, 2003). High capital and operational costs as well as inadequate knowledge on membrane application in waste treatment were predominant factors in limiting the domain of this technology. However, with the emergence of less expensive and more effective membrane modules and the implementation of ever-tightening water discharge standards, membrane systems regained interest. Membrane modules have evolved from being utilized solely in tertiary wastewater treatment to being integrated into secondary wastewater treatment. These systems are now most commonly referred to as membrane bioreactors (MBRs). Figure (1) summarizes the evolution of membrane use in wastewater treatment and demonstrates the basic differences in the treatment trails.

2.1. Membrane Bioreactor Systems:

Bioreactors are reactors that convert or produce materials using functions naturally endowed to living creatures. Reactors using immobilized enzymes, microorganisms, animal, or plant cells and those applying new methodologies such as genetic manipulation or cell fusion are typical bioreactors. Bioreactors differ from conventional reactors as living organisms present in the reactors operate under milder conditions of temperature and pressure. The ranges of operating conditions within bioreactors are usually determined by the biocatalyst (organism) and are usually small. Membrane Bioreactor (MBR) systems essentially consists of combination of membrane and biological reactor systems. These systems are the emerging technologies, currently developed for a variety of advanced wastewater treatment processes. In general, MBR applications for wastewater treatment can be classified into four groups, namely:

1. Extractive Membrane Reactors.
2. Bubble-less Aeration Membrane Bioreactors.
3. Recycle Membrane Reactors.
4. Membrane Separation Reactors.

2.1.1. Extractive Membrane Bioreactors:

Extractive membrane bioreactors (EMBR) enhance the performance capabilities of biological treatment of wastewater by exploiting the membrane's ability to achieve a high degree of separation while allowing transport of components from one phase to another. This separation aids in maintaining optimal conditions within the bioreactor for the biological degradation of wastewater pollutants. For example, degradable toxic organic pollutants from a wastewater could be transferred through a nonporous membrane, to a growth bio-medium for subsequent degradation. In this case the mass transfer of toxic compounds across the membrane takes place due to the presences of a concentration gradient, while the bio-medium functions as a sink.

The extractive membrane bioreactor can be operated in two modes as illustrated in Figure (2):

• Mode 1, where the membrane is immersed in the bio-medium tank. Here the toxic wastewater is circulated through the membranes, and due to the concentration gradient, the toxic compounds are selectively transported to the surrounding bio-medium. Specialized microbial cultures could be cultivated in the reactor, which could be easily optimized for the degradation of the pollutants.

• Mode 2, where the membrane forms an external circuit with the bio-medium tank. The wastewater containing toxic organic pollutants is circulated on the shell-side of the membrane modules. While the bio-medium liquid is pumped through the membrane lumens. Due to the presence of a concentration gradient, the toxic pollutant is transferred to the bio-medium. Within the bio-medium the toxic pollutant is continuously degraded by specialized microorganisms operated in optimum conditions in pH, temperatures, dissolved oxygen, nutrient concentration etc. Whereas the organic pollutant extracted wastewater is removed on the other end of the membrane shell.

In both systems, since the bioreactor is unaffected by the toxic wastewater within the membranes, the conditions within the bioreactor can be optimized to ensure efficient degradation of the toxic compounds. This technology has been successfully demonstrated for treatment of priority pollutants such as chloroethanes, chlorobenzenes, chloroanilines, toluene etc.

2.1.2. Bubble-less Aeration Membrane Bioreactors:

In a conventional aerobic wastewater treatment unit such as an activated sludge process, the process efficiency is controlled by the availability of air. Due to inefficient mode of air supply, 80-90% of the oxygen diffused as air in an activated sludge process is vented to the atmosphere. Oxygenation with pure oxygen as opposed to air as an aeration medium would lead to an increase in the overall mass transfer and biodegradation rate. However, since conventional aeration devices have high power requirements due to the high rate of mixing, these devices cannot be used with biofilm processes. Biofilm processes are advantageous as they enable retention of high concentrations of active bacteria. The membrane aeration bioreactor (MABR) process use gas permeable membranes to directly supply high purity oxygen without bubble formation to a biofilm. Here the bubble free aeration is achieved by placing a synthetic polymer membrane between a gas phase and a liquid phase. This membrane is used to transfer large quantity of air/oxygen into the wastewater. As the gas is practically diffuse through the membrane, very high air transfer rate is attained. The membranes are generally configured in either a plate-and-frame or hollow fiber module. However, current research has focused on the hollow fiber arrangement with gas on the lumen-side and wastewater on the shell-side. The hollow fiber modules are preferred since the membrane provides a high surface area for oxygen transfer while occupying a small volume within the reactor. Here the membrane also acts as a support medium for the biofilm formation, which reduces the potential for bubble formation and air transfer rate.

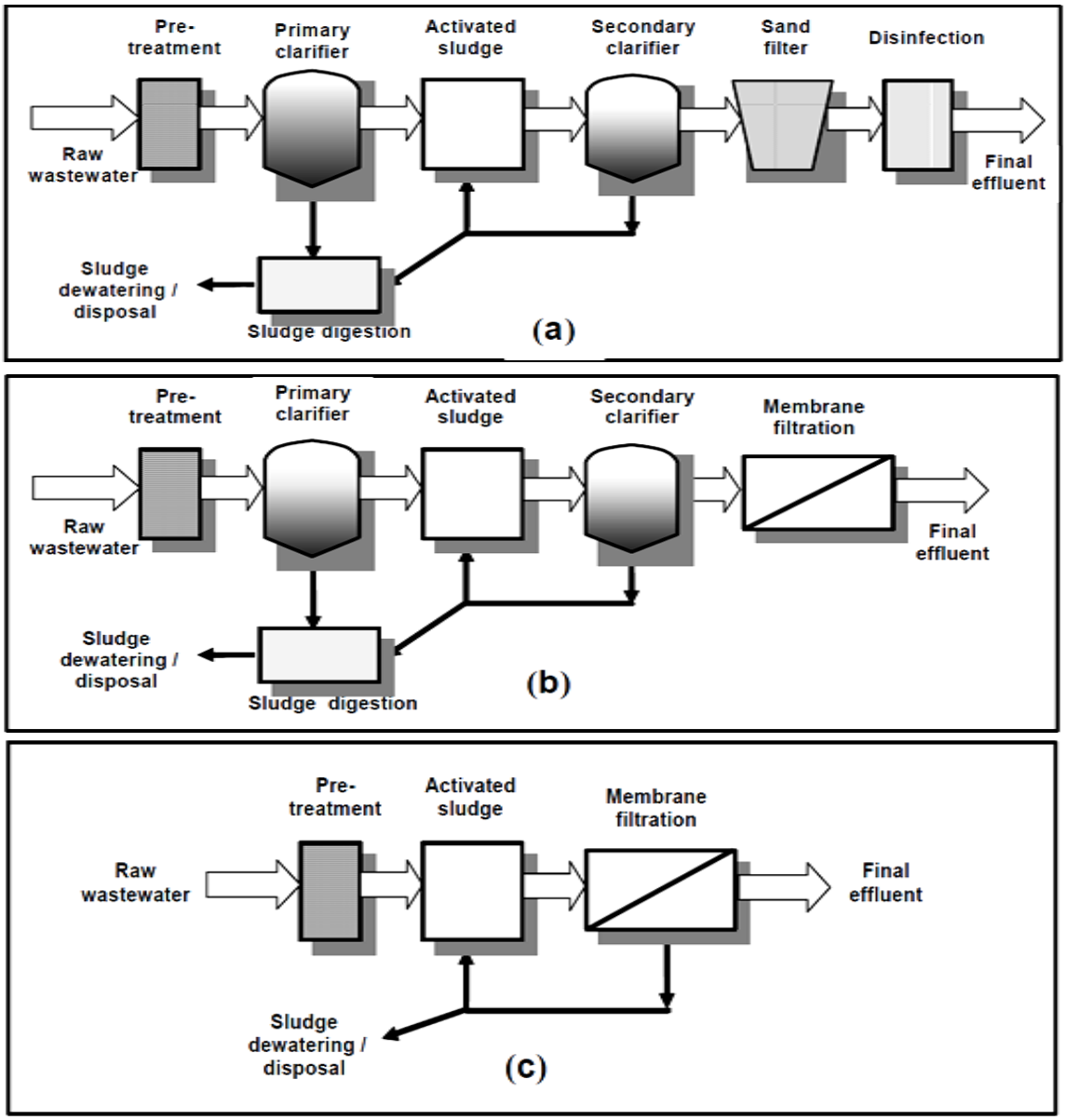

Fig. 1: Flowcharts for (a) conventional wastewater treatment; (b) conventional treatment including tertiary membrane filtration; and (c) membrane bioreactors.

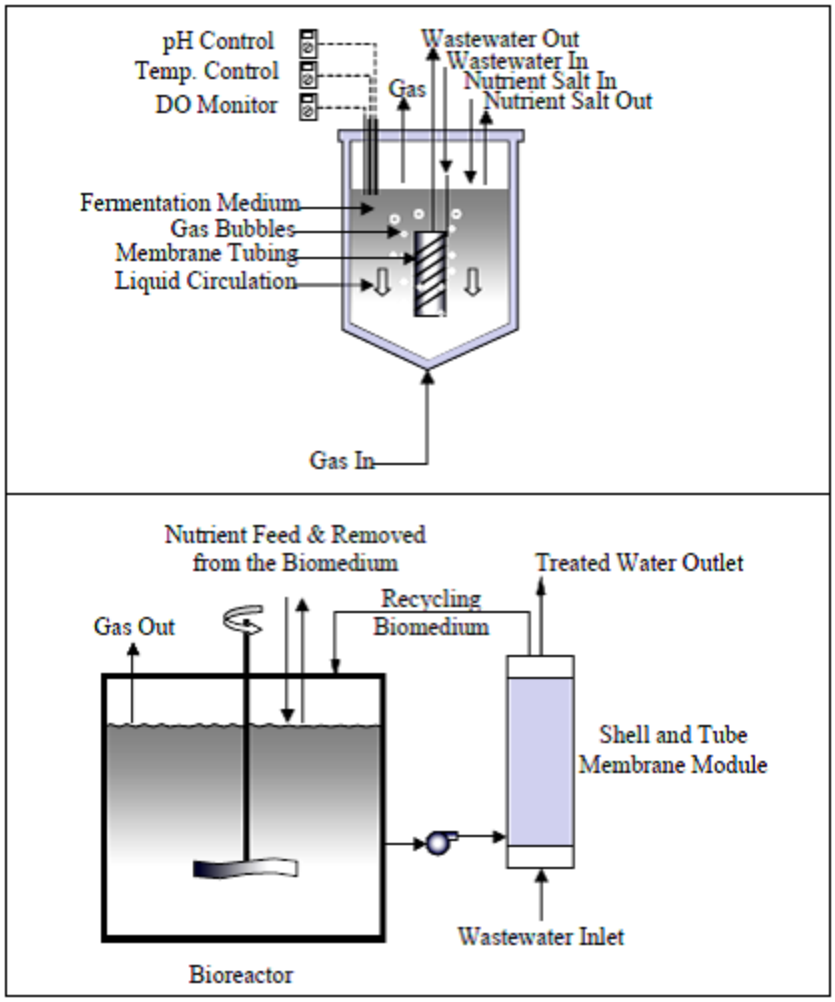

Fig. 2: Two different operational modes of Extractive Membrane Bioreactors Systems.

2.1.3. Recycle Membrane Bioreactors:

The membrane recycle bioreactor consists of a reaction vessel operated as a stirred tank reactor and an externally attached membrane module. The substrate (feed wastewater) and biocatalyst are added to the reaction vessel in pre-determined concentrations. Thereafter, the mixture is continuously pumped through the external membrane circuit. The smaller molecular compounds, the end products of the biodegradation reaction, are permeated through the membrane. While the large molecular size biocatalyst are rejected and recycled back into the reaction tank. Traditionally batch processes are used in biotechnology applications. Due to this, the efficiency is lower than continuous processes with a batch-to-batch variation in product. In these processes, the microbial population would have to be separated out at the end of the run since the microbial species are attached to the membrane via adsorption, entrapment, micro encapsulation etc. However, membrane recycle reactors are continuous processes that are being adopted for biotechnology applications. The advantages of adopting a continuous process are lower operating cost since the enzymes are more effectively utilized and the product is more uniform and consistent. Inhibitory end products are continuously removed from the system thus there is a reduced likelihood of biocatalyst poisoning. The disadvantages of membrane recycle process are the loss of activity of between 10 to 90 % due to enzyme substrate orientation and diffusional resistances. However, research efforts of late have been directed toward the effective adsorption of biocatalysts onto the membrane surface thereby maximizing the degradation potential of the recycle membrane reactor.

In industrial applications, the recycle membrane bioreactors are utilized essentially in two basic configurations, namely: tubular and beaker type. In the beaker type system, the feed wastewater together with the biocatalyst is placed in a beaker, which serves as the reaction vessel. U shaped bundle of fibers immersed into the beaker and product is continuously filtered through the membranes. Tubular configurations are preferred in large-scale

industrial applications where the biocatalysts can be loaded or trapped either in the shell-side (annular space between the membrane fibers and the housing) or the tube side of a tubular membrane module. If the biocatalyst is trapped inside the membrane tube, the feed substrate is pumped through the shell side. The pumping rate has to be controlled to maintain a residence time within the membrane tubes for total biodegradation. This type of bioreactor has been tested on industrial scale for bioremediation activities, for the removal of aromatic pollutants and pesticides.

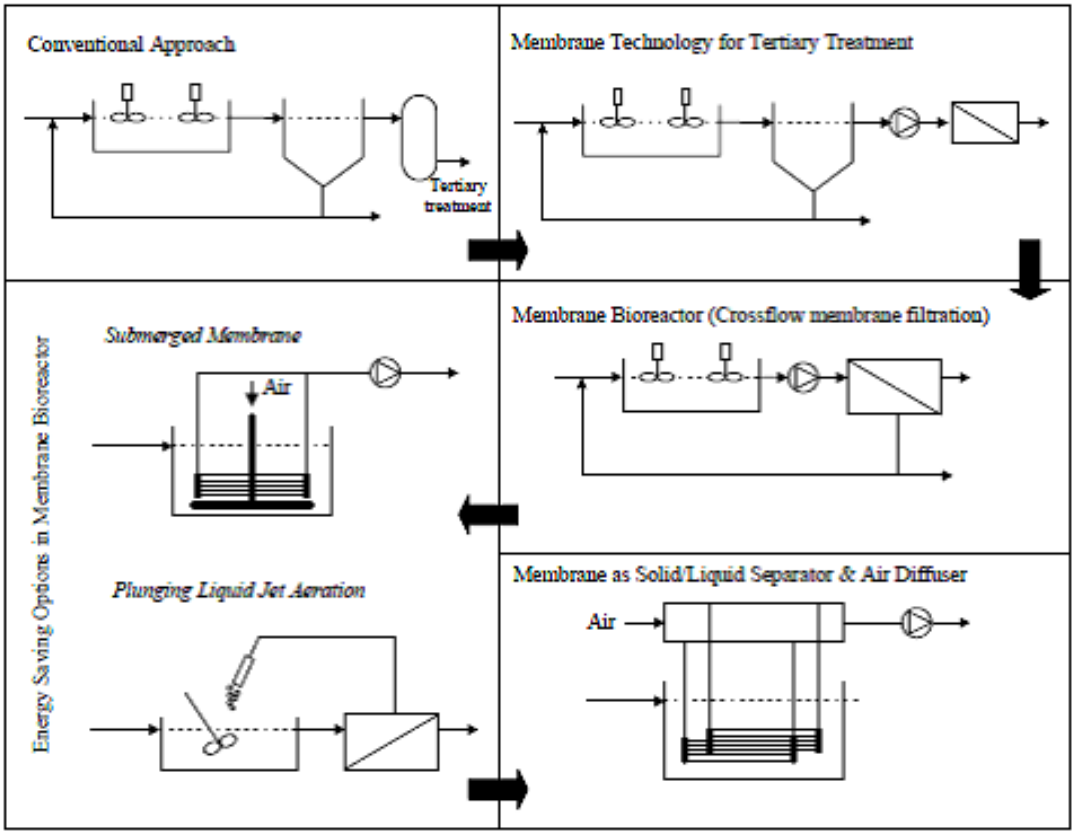

Fig. 3: Developments in membrane separation bioreactors.

2.1.4. Membrane Separation Bioreactors:

The activated sludge process is the most widely used aerobic wastewater treatment system to treat both municipal and industrial wastewater. Its operational reliability is one of the major reasons for the success for this technology. However, the quality of the final effluent from this treatment system is highly dependent on the hydrodynamic conditions in the sedimentation tank and the settling characteristics of the sludge. Consequently, large volume sedimentation tanks offering several hours of residence time are required to obtain adequate solid/liquid separation. At the same time, close control of the biological treatment unit is necessary to avoid conditions, which could lead to poor settleability and/or bulking of sludge. Application of membrane separation (micro or ultra-filtration) techniques for biosolid separation in a conventional activated sludge process can overcome the disadvantages of the sedimentation and biological treatment steps. The membrane offers a complete barrier to suspended solids and yields higher quality effluent. Although the concept of an activated sludge process coupled with ultrafiltration was commercialized in the late 1960's by Dorr-Oliver, the application has only recently started to attract serious attention with considerable development and application of membrane processes in combination with biological treatment over the last ten years. This emerging technology of biomass separation bioreactor is a combination of suspended growth reactor for biodegradation of wastes and membrane filtration. In this system, the solid-liquid membrane separation bioreactor employs filtration modules as effective barriers. The membrane unit can be configured either external to or immersed in the bioreactor. Figure (3) schematically represents the various stages of development of this MBR system, for biological wastewater treatment. The conventional approach to attain a reusable quality water from an activated sludge process is by applying tertiary treatment techniques such as multimedia filtration, carbon adsorption, etc., on biologically treated secondary effluents. As a first step, these tertiary treatment methods were replaced with membrane (ultra/micro) filtration, which ensures almost bacterial and viral free effluent in addition to colloids and solid removal without

modifying existing treatment facilities. This type of coupling of membrane technology provides good quality effluent. Later, in view of utilizing membrane technology more effectively, the secondary sedimentation tanks were replaced with cross-flow membrane filtration. Here membranes are placed in an external circuit, where the biomass is circulated at a higher velocity on the membrane surface. The higher energy cost to maintain the cross flow velocity led to the development of submerging externally skinned membranes in the reactor itself and withdrawing the treated water through the membranes. As a further attempt at energy saving in membrane coupled bioreactors, the possibility of using jet aeration in the bioreactor was introduced. The main feature of this bioreactor is that the membrane module is incorporated into the liquid circulation line for the formation of the liquid jet, thereby accomplishing both operations of aeration and membrane separation using only one pump. The jet aeration works on the principle that, a liquid jet after passing through a gas layer plunges into a liquid bath entraining considerable amounts of air. Recently, the invention of the air back-washing technique for membrane de-clogging led to the novel approach of using the membrane itself as a clarifier as well as an air diffuser.

The major advantages of the membrane separation bioreactors are:

• Since suspended solid are totally eliminated through membrane separation, the settleability of the sludge, which is a problem in conventional activated sludge, has absolutely no effect on the quality of the treated effluent. Consequently, the system is easy to operate and maintain.

• Sludge retention time (SRT) is independent of hydraulic retention time (HRT). Therefore a very long SRT can be maintained resulting in complete retention of slowly growing microorganisms, such as nitrifying bacteria, in the system.

• The overall activity level can be raised since it is possible to maintain high concentrations in bioreactors while keeping the microorganisms dispersed as long as desired and as a result, reactor volume will be reduced. In addition, the system requires neither sedimentation nor any post-treatment equipment to achieve reusable quality water, so the space saving is enormous.

• Treatment efficiency is also improved by preventing leakage of undecomposed polymer substances. If these polymer substances are biodegradable, there will be no endless accumulation of substances within the treatment process. On the other hand, dissolved organic substance with low molecular weights which cannot be eliminated by membrane separation alone can be taken up, broken down and gasified by microorganisms or converted into polymers as constituents of bacterial cells, thereby raising the quality of treated water.

• Removal of bacteria and viruses can be expected, so the disinfection process is ecologically sound.

• Compared to conventional activated sludge processes, maintaining low F/M (food/microorganisms) ratio will produce less excess sludge to be handled and treated.

• The fluctuations on volumetric loading have no effect on the system hence a high sludge capacity can be maintained.

• Since all the process equipment can be tightly closed no odor dispersion can occur.

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