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Edited by - Olushola S. Ayanda, Ogheneochuko U. Oputu, Olalekan O. Fatoki, Cecilia O. Akintayo, Emmanuel G. Olumayede, and Olusola Solomon Amodu

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Edited by: Dr. Olushola S. Ayanda

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Preface

There exist a large number of publications and technical reports in the field of water purification and remediation where the reader is presented with research reports on a certain water treatment technology without any information describing the mode of operation of the process itself. While individual reviews may exits, there are very few sources that describe water treatment techniques from a textbook approach in order to present a first time reader in this field with an overview of several techniques, especially for comparative purposes. This monograph presents bioremediation, membrane bioreactor and the advanced oxidation processes as other forms of water and wastewater treatment technologies. The basic principles, applications, successes and limitations of these treatment methods were carefully presented and discussed. It also introduces recent relevant research in each field for more advanced readers.

This edition is divided into four parts. It starts with and introduces environmental pollution, concerns about the quality of water, and the different water and wastewater treatment technologies. The description of living organisms and plants used in bioremediation viz mechanism of phytoremediation were detailed in Section 2. Membrane bioreactors as an emerging advanced wastewater treatment technology was briefed in Section 3, while Section 4 extensively appraised the use of the different classification of the advanced oxidation processes for the remediation of environmental pollutants commonly found in water and wastewater.

Finally, recommendations regarding more instructive use of current water treatment techniques still in their budding stages are presented. The most important of these is the extension of the application of these techniques from single modeled pollutants, to group of pollutants found together in real water and wastewater scenarios. Treatment technologies may also be combined in other to bring about commendable pollutant(s) removal.

The authors encourage researchers and instructors to comment on any part of this book; please send comments and suggestions to the authors' or publisher's attention.

Olushola S. Ayanda

Thank you

About Author

Dr. OS Ayanda graduated from the University of Ilorin with a Bachelor of Science B.Sc. (Hons) and Master of Science (M.Sc.) Industrial Chemistry in 2005 and 2009, respectively. He holds a doctorate degree in Chemistry at Cape Peninsula University of Technology, South Africa and proceeded on a Postdoctoral Research Fellowship at the University of the Western Cape, South Africa. He is a member of the Institute of Chartered Chemist of Nigeria, South African Chemical Institute, and editor/reviewer to many international journals. Over the years, he has been involved in the development of nano oxides, adsorbents and composite materials including the synthesis, modification, characterization and application of these materials for the removal of inorganic and organic pollutants from contaminated drinking water and wastewater. He has published over forty-five (45) articles in accredited peer-reviewed journals. The Marquis Who's Who in the World listed Dr OS Ayanda as one of the leading scientific achievers around the world, and was ranked among top researchers in Nigeria by Webometrics.

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I wish to thank Almighty God, for his wonderful work in my life. I thank him for his guidance, protection, care, provision, his love and peace over my life. It has been my pleasure to have studied with many devoted and proficient colleagues, and I acknowledge their influence and motivation. I thank all my present and past students at the Cape Peninsula University of Technology, South Africa and Federal University Oye-Ekiti, Nigeria, it is wonderful working with them. I have also benefited from the supervision and expert advice of my supervisors and teachers, they are: Prof FA Adekola Prof OS Fatoki, and Prof Leslie Petrik. Lastly, my appreciation goes to the reviewers and editorial staffs of OMICS Group, most especially Sara Williams, their comments and valuable advice contributed immensely to the success of this work.

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

Ogheneochuko U. Oputu[1], Olushola S. Ayanda[2*], Olalekan O. Fatoki[1], Cecilia O. Akintayo[2], Emmanuel G. Olumayede[2], and Olusola Solomon Amodu[3]

[1]Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 962, Cape Town, South Africa

[2]Environmental and Nanoscience Research, Department of Industrial Chemistry, Federal University Oye Ekiti, P.M.B 373, Oye Ekiti, Ekiti State, Nigeria

[3]Department of Chemical Engineering, Lagos State Polytechnic, P.M.B 21606, Ikorodu, Lagos, Nigeria

[*]**Corresponding author:** *Olushola S. Ayanda, Environmental and Nanoscience Research, Department of Industrial Chemistry, Federal University Oye Ekiti, P.M.B 373, Oye Ekiti, Ekiti State, Nigeria,Tel.: +2348054642362; E-mail: osayanda@gmail.com

Abstract

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

Keywords: Advanced Oxidation Processes, Bioremediation, catalysis, nanotechnology, phytoremediation, membrane bioreactor, sonolysis

Introduction

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

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

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

Bioremediation

Bioremediation involves the use of living organisms such as microorganisms, fungi, algae, enzymes and plants to degrade/breakdown complex materials (pollutants) into simple end products. It can also be described as the addition of biological materials to contaminated environments to cause an acceleration of the natural biodegradation processes [20], the addition of terminal electron acceptor/donor or control of moisture and temperature conditions to establish microbial consortia [21]. It is a proficient technique of removing contaminants from water and wastewater. It is a simple and inexpensive method of water and wastewater treatment which results to nontoxic by-product.

There are two main approaches to bioremediation:

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

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

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

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

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

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

Phytoremediation

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

Mechanism of phytoremediation

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

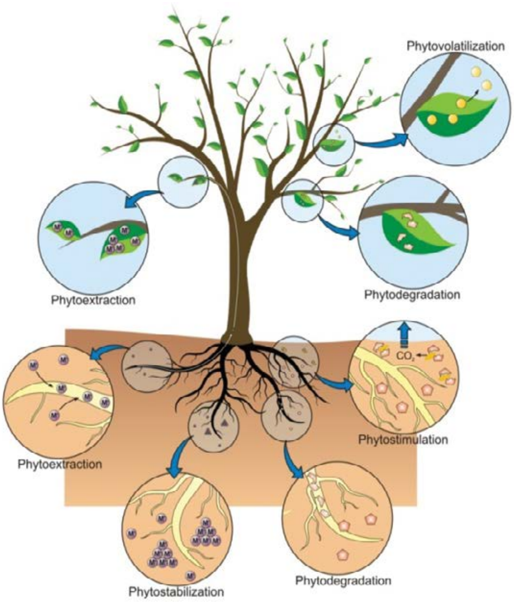

Figure 1: Mechanism of phytoremediation [30].

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

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

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

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

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

Rhizofiltration: This is the filtration of water through a mass of roots to remove toxic substances or excess nutrients. The pollutants remain absorbed in or adsorbed to the roots. Examples of plants known to remove pollutants through rhizofiltration are duckweed, water spinach, calamus etc.

Ndimele *et al.* [31] reported the ability of water hyacinth (*Eichhornia crassipes* (*Mart.*) *Solms.*) to absorb and translocate Fe and Cu. Their investigation revealed that Cu had better translocation capacity than Fe, while the accumulation potential of Fe by water hyacinth is higher than Cu. They concluded that *Eichhornia crassipes* can be effectively utilized for the phytoremediation and adequate for biomonitoring programmes for contaminated water. Syuhaida *et al.* [32] carried out the comparison of the phytoremediation abilities of water mimosa (*Neptunia oleracea*) and *Eichhornia crassipes*. Their results indicated that *Neptunia oleracea* has lower heavy metals uptake and bioconcentration factor value compared to *Eichhornia crassipes*. However, it was reported that both plants accumulate high heavy metals in the roots compared to stems and leaves and that both plants use rhizofiltration process to remove heavy metals. Pedro *et al.* [33] evaluated the capacity of *Salicornia ramosissima* (*S. ramosissima*) on Cd phytoremediation under different salinities and Cd concentrations in a greenhouse experiment. They reported that the highest Cd accumulation was detected in the roots, and decreased with increase salinity and Cd concentration. They suggested *S. ramosissima* as a potential candidate for Cd phytoremediation at salinities close to 0 and that the ability of *S. ramosissima* in Cd phytoaccumulation and phytostabilization was found to be remarkable. The phytoremediation of water polluted by thallium, cadmium, zinc, and lead with the use of *Callitriche cophocarpa* (*C. cophocarpa*) was reported by Augustynowicz *et al.* [34]. After a 10-day incubation period, shoots of *C. cophocarpa* were found to effectively biofiltrated the water so that it met (for Cd, Zn, and Pb) appropriate quality standards. They reported that the *C. cophocarpa* significantly eradicated polluted water toxicity according to the Microtox bioassay and that *C. cophocarpa* exposed to metallic pollution did not exhibit significant changes in its physiological status compared with the control. Marrugo-Negrete *et al.* [35] investigated the the phytoremediation of mercury-contaminated soils by *Jatropha curcas (J. curcas).* The authors assessed the growth behavior, mercury accumulation, translocation and bioconcentration factors of *J. curcas* and reported that the different tissues in *J. curcas* was in order of decreasing accumulation Hg as: roots > leaves > stems, and that *J. curcas* species showed high bioconcentration factor and low translocation factor, and their use could be a promising approach to remediating mercury-contaminated soils. The uptake and biotransformation of Trichloroethylene (TCE) by hybrid poplars in artificial aquifer was reported by Newman *et al.* [36]. They reported that nearly one to two percent of the applied TCE was completely mineralized to carbon dioxide by the poplar cell cultures and that unaltered TCE and TCE metabolites (trichloroethanol, trichloroacetic acid, dichloroacetic acid and reductive dechlorination products) were detected in the aboveground portion of the hybrid poplars.

Membrane Bioreactors

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

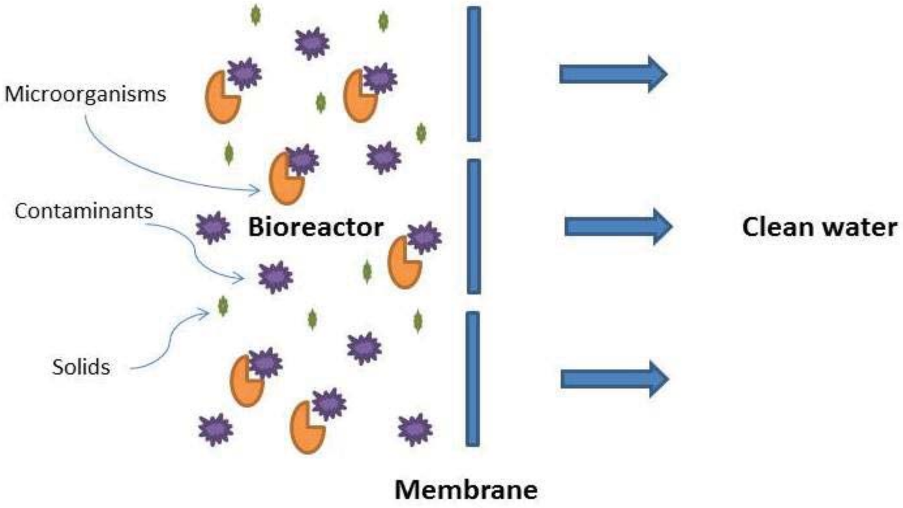

Figure 2: A simple schematic description of Membrane Bioreactor.

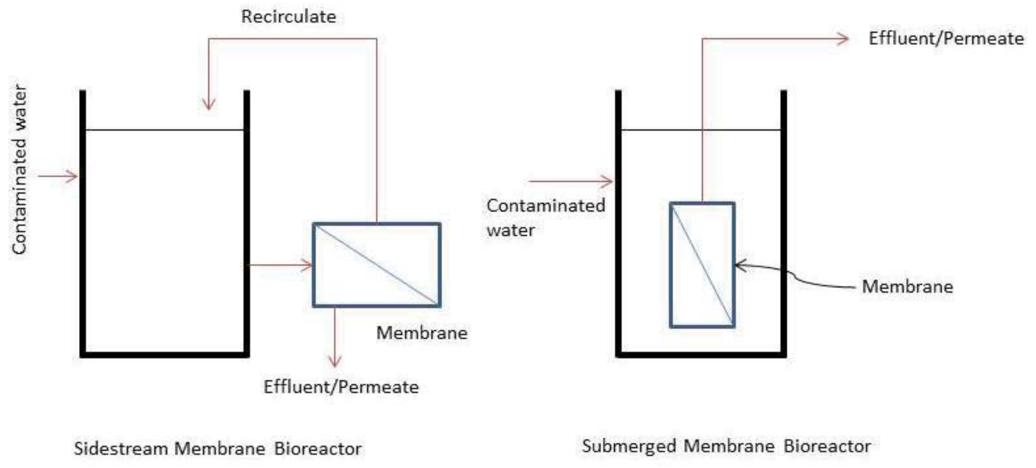

Figure 3: Membrane bioreactor configuration.

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

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

Advanced oxidation processes

AOPs were defined in 1987 by Glaze [38] as “near ambient temperature and pressure treatment processes which involve the generation of hydroxyl radicals in sufficient quantities to effect water purification”. Hydroxyl radical is traditionally thought to be the active species responsible for the destruction of pollutants. In the light of recent evidence, this definition may require a revision as several publications have reported the use of other radicals such as the sulfate radical [39-41] and azide radical [39] generated in-situ for the degradation of organic pollutants in wastewater. The use of the AOPs also referred to as the Advanced Oxidation Technologies (AOTs) have been reported to bring about complete mineralization of toxic xenobiotic organics frequently detected in water and wastewater. AOPs have also been successfully applied to the removal of disease causing pathogens in water [42]. Several workers have reported the use of AOPs for removal of pharmaceuticals [43, 44], endocrine disruptors [45], pesticides [46-48], surfactants [49] and a wide range of other industrial toxicants such as phenols [50, 51], humic acids and benzene derivatives [52, 53] commonly detected in surface, ground and wastewaters. These techniques are superior to the conventional chlorination of water as they can be optimized to also oxidize disinfection by-products such as the halomethanes and haloacetic acids associated with chlorination of water [54]. Since the end products of complete mineralization are carbon dioxide and water, the AOPs offer another significant advantage in avoiding the production of a secondary pollutant encountered when using other conventional techniques. Furthermore, the AOPs have been applied to several real waste scenarios such as dye effluents from dye industry [55], pulp mill effluents high in phenolics [56, 57], land fill leachates [58] and drinking water [59, 60]. These have shown better treatment efficiency when compared with conventional processes. In combined mode with other techniques, they have also been used as pre-treatment or post-treatment unit operations as part of the multiple barrier approach for water purification [55, 61, 62]. The possible application of AOPs in hybrid water treatment processes based on adsorption and catalytic wet air oxidation has recently been proposed [63].

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

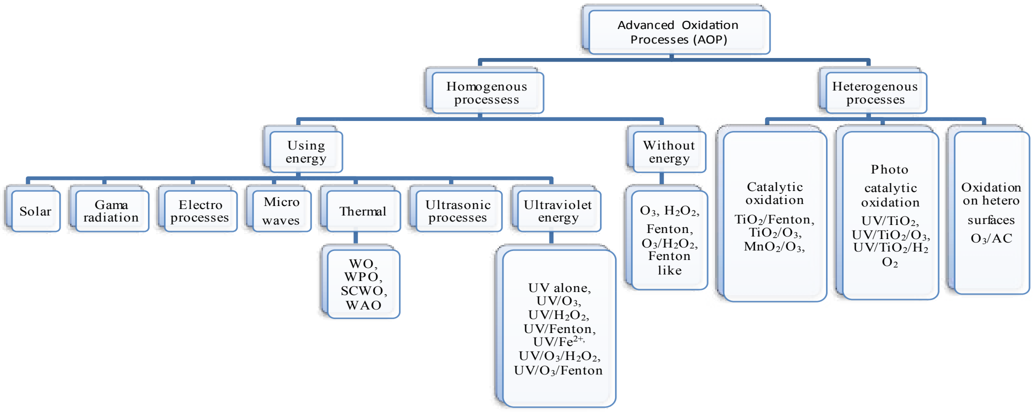

Figure 4: A schematic classification of the advanced oxidation processes.

Abbreviations: O_3 ozonation; H_2O_2 peroxide; AC activated carbon; UV ultraviolet; TiO_2 Titanium Oxide; WO wet oxidation; WPO Wet Peroxide Oxidation; SCWO supercritical wet oxidation .

These AOPs summarized in Figure 4 may be classified as homogeneous or heterogeneous [66]. The major distinguishing factor between these two broad classes is the absence of a solid phase catalyst or promoter in the homogeneous process. In homogeneous processes, reagents such as H_2O_2, soluble O_3 and/or aqueous metals are used to generate OH radicals in aqueous phase for oxidizing dissolved organics. Energy sources such as solar, microwave, thermal and others presented in figure 4 are not considered as a separate phase from the aqueous medium. On the other hand, heterogeneous processes utilize a solid catalyst phase or surface upon which radicals are generated. The generation of radicals by UV generated holes on TiO_2 solids dispersed in an aqueous medium is a typical example. Others such as O_3 break down on solid metal oxides may be specifically regarded as catalytic processes and are broadly classified under heterogeneous processes.

Homogeneous processes can be further subdivided into processes that are driven by external energy and processes that do not operate on external energy sources. These energy sources include UV light, solar energy, electrochemical, ultrasonic (sonolysis), microwave, thermal and gamma radiation.

Homogeneous AOPs without energy

Ozonation In Alkaline Medium

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

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

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

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

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

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

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

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2 \tag{7}$$

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2 \tag{8}$$

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

Oxidation using H_2O_2

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

undergoes solar photolysis, providing radicals in a way similar to UV photolysis of H_2O_2 and as such the participation of the $OH^\bullet$ during H_2O_2 oxidation cannot be ruled out. The process of H_2O_2 breakdown without a catalyst is slow and has been largely regarded as ineffective for the treatment of organics in wastewater. In a study by Coca *et al.* [76], peroxide alone added to brown coloured molasses obtained from a fermentation factory in Spain, did not bring about any change in colour of the wastewater even after 18 hr of contact. Continued stepwise addition of peroxide (0.02 M) up until 23 hr also did not lead to a significant change in the brown colour of the syrupy wastewater. The use of UV combined separately with chlorine and H_2O_2 as a novel AOP for the treatment of trichloroethylene in drinking water was evaluated by Wang *et al.* [77]. In their study, the rate of trichloroethylene decay by UV, UV/chlorine and UV/H_2O_2 at different pH values were studied and compared. They reported that the UV/chlorine process was more efficient than the UV/H_2O_2 process at pH 5, but in the neutral and alkaline pH range, the UV/H_2O_2 process became more efficient. An earlier article published by Prado and Esplugas [78] had shown that the formation of hydroxyl radical by hydrogen peroxide in the absence of UV light was only favorable at high pH. They reported the effect of varying pH on the oxidation of atrazine (a pesticide) by At pH 4.8 and 6.8, atrazine removal of 4% and 9% (respectively) was observed over a 24 hr period. However, at higher basic pH (11.4), a 100% removal of the pesticide was achieved within 180 min. The mechanism of generation of the radicals suspected to be involved in the oxidation process at high pH has however not been investigated.

In another study, Yasar and co-workers in Pakistan [42] studied the use of H_2O_2 (a well-known disinfectant) for the immobilization of pathogens in industrial effluents. Results obtained under optimized oxidant dose of 170 mg/L showed that the oxidant was capable of removing 99% of the pathogens present in the wastewater. As a drawback to its use the authors highlighted that pathogens immobilized by H_2O_2 were reactivated after an incubation period, which varied depending on the reaction condition. This problem was overcome when H_2O_2 was used in combination with other processes such as UV and O_3.

Base on the findings of the referenced literature, we may infer that the use of H_2O_2 for water treatment is significantly affected by pH and only effective at alkaline pH. Also, when applied as a disinfectant for living cells (pathogens), colony regrowth is only suppressed when H_2O_2 is used in conjunction with other processes. Another disadvantage of this process is the presence of residual peroxide, which may require further attention after the water treatment itself. Some other researchers have reported the use of peroxide as an oxidant for organics [53, 79].

Fenton and Fenton-like processes

More than a century ago, H. J. Fenton described the oxidation power of H_2O_2 on certain organic molecules in which OH radicals are produced from H_2O_2 in the presence of Fe(II) as catalyst. Later on, a reaction mechanism was proposed by Walling [80] and is illustrated by Equations 9-11.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{9}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \tag{10}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{11}$$

The renewed interest of researchers for this classic old reactive system is today underscored by a significant number of investigations devoted to its application in wastewater treatment. Due to its simplicity (requiring neither special apparatus nor reactants), the Fenton process is one of the most widely applied and researched processes for treatment of recalcitrant compounds. Mandal *et al.* [62] investigated the use of Fenton reagent for the degradation of wastewater collected from industrial effluent plants in India. They investigated the effect of operating variables such as pH, temperature, peroxide and Fe(II) dose for the reduction of Chemical Oxygen Demand (COD) in the wastewater sample. The Fenton process requires strict pH control and several published data places optimum pH for the process in the range: 2.5-3.5. The authors observed that at optimized conditions of pH 3, Fe(II) 6 mg/L, and peroxide dose of 220 mg/L, the COD removal after 30 min was 90%. Extending the time to 24 hr only increased the COD removal by an additional 5%. It was therefore suggested that the process be used in combination with biological treatments for total removal of organics in the wastewater, as it was ineffective for low concentrations of the organic in their study. Chen *et al.* [81] also utilized the Fenton process for the degradation of model pollutant (salicyclic acid) in aqueous solution. Salicyclic acid removal efficiency under optimized conditions was 96% after 150 min, and COD reduction was 80%. As shown by the results, the Fenton process was effective for the degradation of salicyclic acid. The complete mineralization was however not as efficient as the degradation of the pollutant. Several other reports concerned with the application of Fenton process for the amelioration of organics in wastewater abound in the literature [15, 82-85]. All processes which involve the use of Fe^{3+} ions (either as hydroxyl complexes or as oxalate complexes) or oxidizing metals such as manganese (as permanganate) are referred to as Fenton-like processes. Especially important amongst them is the ferrioxalate complex which has a strong absorption at wavelengths above 400 nm and therefore undergoes reactions that can be photo-catalyzed by visible light. The photo degradation of hydroxyl and oxalate complexes of Fe(III) generate Fe^{2+} ions which catalyses the decomposition of H_2O_2 to OH radicals. Equations 12-16 shows the participation of Fe as oxalate in the production of hydroxyl radical.

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH^{\bullet} \tag{12}$$

$$Fe(C_2O_4) + H_2O_2 \rightarrow Fe(C_2O_4)^{+} + OH^{\bullet} + OH^{-} \tag{13}$$

$$Fe(C_2O_4)_3^{3-} + hv \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \tag{14}$$

$$Fe(C_2O_4)_3^{3-} + C_2O_4^{-\bullet} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \tag{15}$$

$$C_2O_4^{-\bullet} \rightarrow CO_2 + CO_2^{-\bullet} \tag{16}$$

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

Ozone/H_2O_2 (peroxone) process

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

$$H_2O_2 + 2O_3 \rightarrow 2OH^{\bullet} + 3O_2 \tag{17}$$

$$HO_2^{-} + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet} \tag{18}$$

The hydro-peroxide ion produced by the decomposition of H_2O_2 reversibly recombines with hydrogen ions in solution to give H_2O_2 (Equation 19)

$$HO_2^{-} + H^{+} \rightleftharpoons H_2O_2 \tag{19}$$

Indeed the decomposition of ozone at high pH also produces the hydro-peroxide ion which reversibly produces peroxide as shown by Equation 2. The external addition of H_2O_2 to aqueous solution of ozone would therefore enhance the decomposition of ozone to give OH radicals according to the Le' Chatelier principle. The influence of pH is also evident since in the ozone decomposition mechanism the active species is the conjugate base OH_2^- whose concentration is strictly dependent on pH. An increase in pH and addition of H_2O_2 to an aqueous solution of ozone would thus result in higher hydroxyl radical production and the attainment of a higher steady state concentration of OH in the radical chain decomposition process. It is worthy to note that the adoption of this AOP does not bring about a significant change in the apparatus or industrial reactor since it is only necessary to add an H_2O_2 dosing system. Cortez and co-workers applied the peroxone system for the treatment of landfill leachates in Portugal with the aim of increasing the biodegradability of the treated leachate in a combined chemical/biological process [58]. While both ozonation and peroxone process significantly improved the Biochemical and Chemical Oxygen Demand Ratios (BOD/COD), implying improved biodegradability, the peroxone process presented higher ratios and hence higher biodegradability of the treated leachates. The application of one process over the other would therefore depend on the running cost of chemicals weighed against the desired quality of effluent required for subsequent biological treatment. The use of ozone in combination with H_2O_2 has been widely accepted to increase the generation of the non-selective $OH^\bullet$ during ozonation, leading to improved elimination of refractory organic compounds [60, 76, 86,87].

Homogeneous AOPs using UV

Homogeneous AOPs using UV radiation are generally applied for the degradation of compounds that adsorb UV radiation. These are usually dyes and aromatic hydrocarbons capable of absorbing UV energy. As previously mentioned, the UV is not considered a separate phase from the aqueous medium to which it is applied [88].

UV/Ozone

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

$$H_2O + O_3 + UV \rightarrow 2OH^{\cdot} + O_2 \qquad 20$$

$$2OH^{\cdot} \rightarrow H_2O_2 \qquad 21$$

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

UV/ H_2O_2

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

$$H_2O_2 + UV \rightarrow 2OH \qquad 22$$

UV/H_2O_2 system can totally mineralize any organic compound reducing it to CO_2 and water. However, in real-life scenarios, such a drastic process is not necessary. The toxicity of oxidation products is not a problem since they are easily biodegraded [91]. The major drawback of this process is the smaller extinction coefficient of H_2O_2 which is 18.6 $M^{-1}cm^{-1}$ at 257 nm, thus only a relatively small fraction of the incident UV light is exploited for AOP. Nevertheless, several studies have been carried out to optimize this process for purification of water. This is justified by the relative ease of handling H_2O_2 and the cost of chemicals. The use of UV/H_2O_2 for the detoxification of raw textile wastewater prior to biological treatment with dehydrogenase has been reported [92]. The decrease in inhibitory effect from 30% when UV was used alone to 26% for UV/ H_2O_2 was attributed to the synergistic effect of the combined treatment. The raw wastewater inhibited the enzyme activity by 47%. They concluded that the AOP was an effective method for detoxification of textile wastewater. The positive impact has been demonstrated by a significant decrease of inhibitory action of microbial growth on activated sludge during subsequent biodegradation. Kestioglu and co-workers have applied the UV/ H_2O_2 process for the treatment of raw effluent from an olive mill treatment plant in Turkey [93]. The effluent was characterized by a very low pH (<2), high COD (10, 240 mg/L) and total phenol (975 mg/L). Treatment periods of 400 and 1440 min reduced the COD to 3060 and 3650 mg/L, respectively. The total phenol for optimized peroxide dose was also reduced to 22 and 10 mg/L, respectively, accounting for 99% of COD and phenol removal. The use of this method as an AOP for treating contaminant in wastewater has also been reported in other studies [94-97].

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

The rate of degradation of an organic pollutant with Fenton-Fenton like reagents is strongly accelerated by irradiation with UV-vis light [94, 98-99]. This is an extension of the Fenton process which takes advantage of energy derived from photons in UV-vis irradiation at wavelength values higher than 300 nm. In these conditions, the photolysis of iron (III) hydroxide complex, that is, the product of Fenton process (Equation 11) allows for the regeneration of Fe^{2+} as given by Equation 23.

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + OH^{\bullet} \qquad 23$$

In this scheme using UV radiation, Fe^{2+} acts as a real catalyst as it is regenerated and recycled during the production of radicals after reaction with H_2O_2. Another advantage of this process is the reduction in the formation of Fe^{3+} sludge which is associated with the conventional Fenton process. Despite the great deal of work devoted by researchers to these processes, scanty indications have been found about their industrial application. This is not surprising since the application of the Fenton processes requires strict pH control. Generally, pH range between 2.5 and 3.0 are regarded as the best for this system. Huang *et al.* [100] studied the oxidation of dye-reactive black-B using the UV/Fenton process and compared the results with experiments run for the Fenton and an electro-Fenton process. UV light source was from a UV-A lamp, wavelength 365 nm, with dye concentration 10,000 mg/L. Optimum pH for the process was established as 2.5 and mineralization was found to be 98%. The synergistic effect of the UV light was apparent when compared to the Fenton process which brought about a 78% mineralization. They also identified two degradation intermediates i.e. oxalic acid and formic acid. While the process readily mineralized the formic acid, the oxalic acid intermediate was more persistent to the chemical treatment. The degradation mechanism of carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methylcarbamate), a frequently used carbamate derivative pesticide considered to be a priority pollutant, using the UV/Fenton process, was reported by Javier Benitez and co-workers [84]. The carbamate concentration was 4.52 x 10^{-4} M, temperature 20°C and pH 3. At H_2O_2 and Fe^{2+} concentrations 50 x 10^{4} and 5 x 10^{-4}M, respectively, the process brought about a complete mineralization of carbofuran in 5 min, with a rate constant 30 times higher than a similar experiment conducted in the absence of UV radiation. The authors concluded that the synergic effect observed in the photo-Fenton system was due to the generation of OH radicals in several reactions and to the catalytic character of the Fenton's reaction in the presence of UV radiation. Other relevant discussions on the use of this process are well presented in the literature [56, 100-104].

Homogeneous AOP using ultrasound (Sonolysis)

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

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

$$H_2O?(??()))))H^o + OH^{(o)} \qquad 24$$

$$O_3 \overset{)))}{\rightarrow} O_2 + O \qquad 25$$

$$O + H_2O \rightarrow 2OH^{\bullet} \qquad 26$$

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \qquad 27$$

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \qquad 28$$

$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + OH^{\bullet} \qquad 29$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2 \qquad 30$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \qquad 31$$

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

$$H_2O_2 \overset{)))}{\rightarrow} OH^{\bullet} + OH^{\bullet} \qquad 32$$

$$H_2O_2 + O_2 \overset{)))}{\rightarrow} 2HO_2^{\bullet} \qquad 33$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad 34$$

Homogeneous process using solar energy

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

Wet oxidation process using thermal energy

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

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

Oxidation using microwave energy

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

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

In another experiment utilizing the microwave technique, Wang and co-workers [113] applied the microwave–H_2O_2 AOP for the pretreatment of sewage sludge obtained from Gaobeidian municipal sludge process plant in Beijing, China. The effect of catalase on the efficiency of the process was investigated. Catalase present as a biological component of the sludge is a terminal respiratory enzyme which attacks H_2O_2, breaking it to molecular O_2 and 2 electrons [114-115]. By monitoring the reduction of residual H_2O_2 with increasing temperatures, the workers were able to establish that the activity of the catalyst was significantly reduced above 45°C. Compared to control experiments, a considerable increase in sludge solubilization with increasing temperatures was also observed. The degree of sludge solubilization was strongly affected by H_2O_2 ratios with increasing amounts of soluble COD and TOC been released into the supernatant as H_2O_2 dosing ration increased. Although the AOP (microwave/H_2O_2) was effective for sludge pretreatment in the study, there were still high concentrations of residual H_2O_2 in the sludge, ranging 436-18773 mg H_2O_2/L. The higher the H_2O_2/TCOD dosing ratio was, the lesser the amount of consumed H_2O_2 that was consumed by the process. The proper evaluation of residual H_2O_2 would therefore prove crucial in the practical application of this AOP.

Heterogeneous catalytic oxidation

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

Heterogeneous catalysis at ambient conditions

Materials applied as catalyst at ambient conditions include Activated Carbon (GAC), metals supported on metal oxide surfaces (TiO_2, Al_2O_3, ZrO_3, CeO_2, FeOOH, MnO_2, Cu-Al_2O_3, and Cu-TiO_2) or supported on activated carbon. The catalyst support serves to increase the surface area of the catalyst, decrease sintering and improve hydrophobicity as well as the thermal and chemical stability of the material [117]. Heterogeneous catalytic ozonation is an AOP in which the oxidative property of ozone is improved by adding solid catalytic materials. The process is potentially a low cost AOP which has been operated successfully at ambient conditions by several workers and may be relatively easier to apply in a water treatment plant [118]. It has been demonstrated that GAC can enhance ozone transformation into OH radicals [87, 118-120]. Electrons in the graphenic layers and basic surface groups on GAC are the main factors responsible for the decomposition of O_3 into $OH^\bullet$ [119, 121-122]. These generated hydroxyl radicals are responsible for the oxidation of organics using O_3/GAC process. Besides the catalytic role, GAC also serves as an important adsorbent for the organics been treated and would be effective for the removal of hydrophobic micro-pollutants that cannot be oxidized by ozone. Sanchez-Polo *et al.* [87] applied the O_3/GAC AOP for the treatment of Para-Chlorobenzoate (pCBA) and compared the efficiency of this process with the conventional homogeneous ozonation in alkaline medium (pH 7 and 9) and peroxone processes (O_3/H_2O_2). pCBA was selected for the study because of its low reactivity with O_3 (K_{O3}= 0.15 $M^{-1}s^{-1}$) and slow adsorption kinetics on GAC. Their report showed that the O_3/GAC system was inferior to the homogeneous processes. Radical generation in the heterogeneous system involved the adsorption of ozone onto the activated carbon and its subsequent breakdown to radicals. Since this process requires more than one phase, it is therefore more slower compared to the system where O_3 and the species (OH, H_2O_2 or soluble metals) initiating its breakdown are in the same phase. Despite this disadvantage, the use of heterogeneous catalyst for ozone breakdown is gathering interest. This is because the possibility of catalyst regeneration and reuse out ways the inefficiency of the heterogeneous process. More so, the use of metals in homogeneous process poses another problem as these metals whether toxic or not would require removal after the treatment process.

In a recent work, Oputu and co-workers [150] applied FeOOH as potential catalyst for removal of 4-chlorophenol from aqueous medium. While the catalyst showed potential, reducing reaction time by one-third, the possibility of metal leaching was of concern. Further work by the group was centered on supporting the catalyst on support NiO to eliminate the catalyst breakdown and increase possibility of reuse. The uses of catalyst supports have become the trend of heterogeneous catalysis.

Heterogeneous wet oxidation

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

Catalytic Wet Air Oxidation

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

An overview of the catalytic pattern of homogeneous (Cu^{2+}, Fe^{3+}, Mn^{2+}) and ceria-supported ($CuCeO_x$, $MnCeO_x$) transition metals in the CWAO of phenol has been reported [124]. Catalyst test were carried out at 150°C and 1.4 MPa using a PTF-lined autoclave containing 0.25 mL, 1000 mg/L phenol and operated in a semi-batch mode. The catalytic homogeneous wet air oxidations were observed to proceed via an unselective autocatalytic free-radical path leading to refractory C1-C2 acids, while the CWAO on heterogeneous ceria gave superior efficiency and was accounted for by the Langmuir-Hinshekwood (L-H) mechanism. In a recent study, Yu and co-workers applied Ru supported on γ-Al_2O_3 and Ce/γ-Al_2O_3 for CWAO of isopropyl alcohol, phenol, acetic acid and N,N- dimethylformamide [128]. The efficiency of the catalyst was observed to increase with increasing temperature. The Ru-Ce/γ-Al_2O_3 catalyst produced superior removal efficiency compared to the Ru-γ-Al_2O_3 for all the substrates studied and ascribed to the better dispersion of the Ru particles on the Ce/γ-Al_2O_3 surface as well as increase in number of effectively active sites on the cluster-derived catalyst surface. The efficiency of platinum (Pt) supported on activated carbon and on multi-walled Carbon Nano-Tubes (CNT), as heterogeneous catalyst in CWAO of selected pharmaceuticals was investigated by Benitez and coworkers [125]. Supported platinum catalyst has been reported to be highly effective in the oxidation of organic compounds [135-136]. Operating variables such as catalyst type, dose, temperature (120-140°C), and oxygen pressure (20-40 bar) were considered. There was significant enhancement in the removal of the pharmaceuticals using CWAO relative to WAO. Pt supported on activated carbon gave greater removal efficiency compared to Pt supported on CNT under the same conditions, reflecting the contribution of adsorption effects in addition to oxidation pathways for the removal of the pharmaceuticals under study.

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

Catalytic Wet Peroxide Oxidation

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

Heterogeneous photocatalysis

The most common nanoparticle applied as a heterogeneous photo-catalyst in AOP is TiO_2. To this end, a vast number of articles have been devoted to studies of the application of this oxide to various pollutants, and in combination with other processes such as the ozonation and ultrasound-assisted-photolytic processes [96, 108, 143-152]. Others heterogeneous catalyst applied in AOP include: ZnO, SnO_2, Al_2O_3, In_2O_3, ZnS, Fe_2O_3, CeO_2, ZrO_2, SiO_2, CuO, MnO_2 and CdS [50, 123, 146-148]. While the physical, chemical and catalytic properties of these catalysts vary markedly, the principle of operation as photo-catalysts remains the same. The adsorption of electromagnetic energy (in the UV or visible region) by electrons on the surface of a photo-catalyst brings about an excitation of these surface electrons. When the energy absorbed is greater than the band-gap energy (ΔE), the excited electrons move from the valence-band to the conduction-band. This mechanism generates active species which promotes redox reactions. The absorption of photons with energy lower than ΔE or longer wavelengths usually causes energy dissipation in the forms of heat. A good schematic diagram illustrating the principle of TiO_2 photo-catalysis leading to the formation of a positive hole (h^+) in the valence band and an electron (e^-) in the conduction band has been described by Ahmed and co-authors [146-147].

Photo-Catalytic Oxidation

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

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

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

Photo-Catalytic Ozonation

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

$$TiO_2 \xrightarrow{hv} h^+ + e^- \qquad 35$$

$$O_3 + e^- \rightarrow O_3^- \qquad 36$$

$$O_3^- \rightarrow O_2 + O^- \qquad 37$$

$$H_2O + O^- \rightarrow OH^- + OH^{\bullet} \qquad 38$$

Even though the actual mechanism may be more complicated [159], the principle has been widely applied for the treatment of environmental pollutants in water [160-166]. The UV/TiO_2/O_3 process was reported to be superior to O_3, UV/O_3, and UV/TiO_2/O_2 process for the degradation of neonicotinoid insecticide in water [162]. The synergistic effect of O_3 on TiO_2 was evident at neutral and acidic pH. At basic pH, decomposition of O_3 by reaction with OH^- was the prevailing mechanism for OH radical production [162, 164]. A similar synergistic effect was also reported for the photo-catalytic ozonation of dimethyl phthalate using laboratory prepared TiO_2 [163]. The rate constants for the UV/TiO_2/O_3 process was 2.5(5.2) times more than that in UV/TiO_2/O_2 (UV/O_3) process. The TOC removal of the photo-catalytic ozonation process increased with increasing ozone dosage and was describe by the Langmuir-Hinshelwood model.

Conclusion

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

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

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

The AOP treatments in some cases have been reported to bring about complete mineralization of xenobiotic organic pollutants in water. AOPs have emerged as versatile technologies for the treatment of contaminated water and wastewater; however, many articles have only reported the efficiency of AOPs without necessarily identifying the reaction intermediates or characterizing the final end products left in solution. It is important to note that the complete removal of a pollutant from matrix may not bring about a cleaner water stream as the end product water may contain more toxic organics which are resistant to the applied AOP. It is therefore recommended that analytical techniques for determinations be combined with other methods to monitor the complete mineralization of pollutants and their intermediates. More work is also needed to be done in the area of catalyst development in photolytic systems with interest being on visible light application, and in developing catalysts capable of operating at near ambient conditions in wet oxidation processes. Also the application of AOP to composite mixture of pollutants requires further study as rates and mechanisms for single and mixed systems would vary markedly. Furthermore, the development and application of catalysts to ozonation processes which would improve efficiency of the process or limit restrictions from operating variables such as pH would also be of interest.

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

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