

## Advanced Oxidation Processes (AOPs) for Wastewater Treatment and Reuse: A Brief Review

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### ABSTRACT

Although coagulation / flocculation, sedimentation, filtration, and disinfection are promising for waste water treatment, some of the chemical pollutants cannot be eliminated using such methods, hence the need to use advanced methods. Currently, advanced oxidation processes (AOPs) are among the most frequently used approaches to remove pollutants that have low biodegradability or high chemical stability. These methods depend on the generation of hydroxyl free radical (HO\*) as a strong oxidant for the destruction of compounds which cannot be oxidized using conventional oxidants. In this brief-review, we highlighted the AOPs that have shown premises in pollutant removal from wastewater.

### INTRODUCTION

The need to pursue sustainable practices has led to a continuously increasing global concern for the development of alternative water reuse technologies, mainly focused on industry and agriculture [1,2]. Chemical pollution from solvents, dyes, heavy metals, etc., poses a major threat to water quality [3,4]. Traditionally, the focus by environmentalists was on pollutions detection and their negative impacts on ecosystems. With the advancements being experienced in science, the understanding of the chemistry of pollutants has improved and this has led to more cutting edge technologies being implemented for the treatment of erstwhile difficult to treat pollutants [5,6].

Advanced oxidation processes (AOPs) are increasingly being considered as a highly competitive water treatment technology for removing low biodegradability or high chemical stability pollutants [7,8]. While these processes come in handy to treat pollutants with high chemical stability, it is a well-known fact that chemical oxidation for complete mineralization is expensive. In order to reduce the costs incurred, the process is combined with biological treatment [9,10,11,12,13]. While the latter is an interesting approach to waste water treatment, the following discussion is restricted to advanced oxidation processes only.

#### ***1. Wastewater treatment technology selection***

The task of selecting the best treatment option for remedying specific industrial water is usually a complex one. The main factors that one considers in making a decision regarding the wastewater technology to apply include the quality of original water, conventional treatment options, removal of parent contaminants, treatment flexibility, economic studies, the facility decontamination capacity, final waste water treatment system efficiency, potential use of treated water and life cycle assessments for the determination of the compatibility of wastewater treatment technology [9]. In general, the capabilities and possibilities of the conventional treatment methods available are widely known. However, in order to determine the efficiency of new technologies such as AOPs, bench-scale and

pilot-plant studies should be conducted. Such studies may prove decisive in cases where several technologies are to be combined for reuse or decontamination of particular industrial water.

## 2. Physicochemical Process Analysis

The physicochemical method for treating wastewater involves either physical process or chemical process or a combination of both processes. While the basic principles differ, it is usually hard to distinguish the processes as they may occur simultaneously in a single treatment unit [14]. Depending on treatment environment, the physical entrainment of organic micro pollutants in water and wastewater is sometimes associated with biological degradation. Physico-chemical properties such as acidity or lipophilicity determine the behavior of micro pollutants during sorption onto the solids [15]. Determination of affinity of a given substance to effluent organic matter (EfQM) and the sorption effectiveness is done using two types of coefficients, that is,  $K_{oc}$  (organic carbon partition coefficient) and  $K_{ow}$  (Octanol-water partition coefficient). The coefficients take into consideration the two main sorption mechanisms: adsorption (electrostatic interactions that result from the tendency of a substance to be dissociated in aqueous phase or ionized) and absorption (hydrophobic interactions) [16,17].

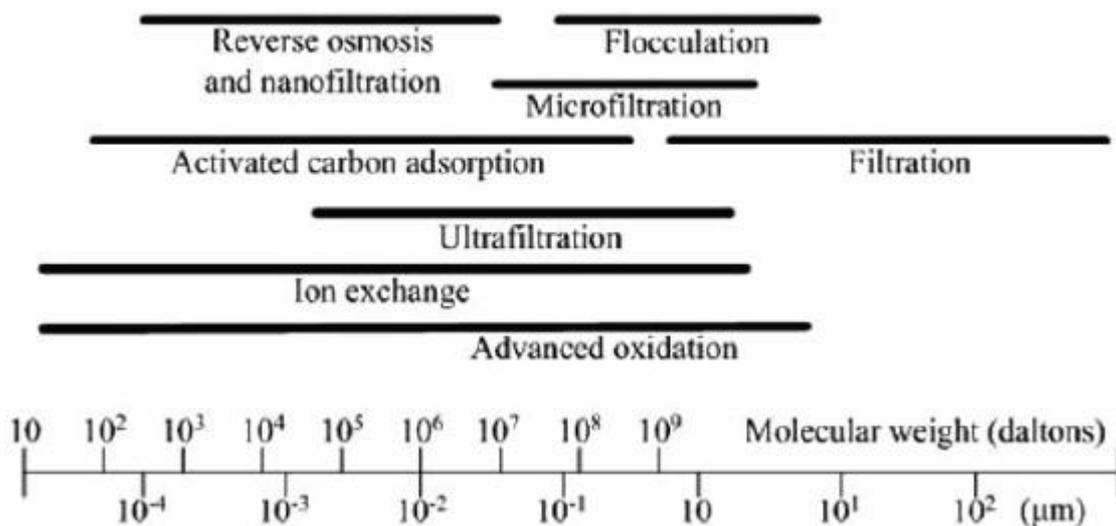


Figure 1: Size ranges of the applied treatments in treating EfQM [18]

## 3. Overview of the Physico-Chemical Processes

One of the key reasons why physicochemical processes are applied in the advanced treatment of sewage effluent that has been biologically treated is the removal of dissolved organic matter ( $DOC < 0.45 \mu m$ ) and removal of particulate organic matter ( $> 0.45 \mu m$ ). Removal of effluent organic matter (EfQM) can be shown in terms of dissolved organic carbon (DOC), molecular weight distribution (MWD), fraction and endocrine disrupting chemicals (EDCs) or personal care products (PPCPs). Removal of PPCPs and EDCs may be used to indicate the smallest MW compounds present in an effluent, fraction indicates the removal of various hydrophobic/philic fractions, while MWD provides one with specific removal of varying organic sizes. The use of DOC is important as it presents a surrogate for general organic contaminant removal through physicochemical processes. How effective

a specific process in the treatment of EfQM is heavily influenced by the structure or size of EfQM. A range of sizes of EfQM that are removed through various treatment methods is as shown in the figure 1. Generally speaking, majority of particulate organic matter are removed by the processes of biofiltration and flocculation.

The removal of dissolved organic carbon is largely dependent on the treatment processes that are being used. Granular activated carbon (GAC) biofiltration and powdered activated carbon (PAC) generally result in levels of DOC removal of EfQM that are higher. This may be viewed as implying that EfQM consists mainly of small molecular weight (MW) organic matter in the biologically treated sewage effluent (BTSE). MWD of EfQM is of utmost importance in understanding the removal of various micro pollutants under different sizes through the use of various treatment methods. The removal of different organic fractions may help in the determination of the efficiency of various sizes of physical-chemical treatments in the removal of transphilic (TP), hydrophobic (HP) and hydrophilic (HL) fractions. The ionic effects of EfQM result to FeCl<sub>3</sub> flocculation being removed at a higher amount of HL fraction.

#### 4. Advanced Oxidation Processes

Commonly referred to as AOPs, Advanced oxidation processes are used to oxidize complex organic contaminants that are found in wastewater and that are difficult to degrade into simpler end products through biological processes [19,20].

##### 4.1 Theory of Advanced Oxidation

The basic principle of advanced oxidation processes entails the generation of hydroxyl free radical (HO<sup>\*</sup>), non-selective chemical oxidant (Table one), as a strong oxidant for destroying organic compounds which cannot be oxidized by conventional oxidants such as ozone, oxygen and chlorine [21]. Hydroxyl radicals are effective in the destruction of organic chemicals due to the fact they are reactive electrophiles which not only react rapidly, but also non-selectively with almost all organic compounds that are electron-rich [22]. Their oxidation potential is quantified as 2.80V and this makes them to exhibit faster rates of oxidation reactions compared to conventional oxidations [23]. Once the hydroxyl radicals are generated, they are able to attack organic chemicals through electron transfer, hydrogen abstraction and radical combination [24]. The reactions that take place are as follows:



Table 1: Oxidation potential of various oxidants [25,26]

Oxidant	Oxidation Potential (v)	EOP Relative to Chlorine
Fluorine	3.03	2.25
Hydroxyl radical (OH <sup>*</sup> )	2.80	2.05
Oxygen (Atomic)	2.42	1.78

Ozone	2.08	1.52
Hydrogen Peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine Dioxide	1.27	0.93
Molecular oxygen	1.23	0.90

It is not always necessary to carry out complete oxidization of a given compound or a group of compounds. In most of the cases encountered, and bearing in mind the desired end product quality, partial oxidation is usually sufficient to reduce the toxicity of specific compounds or render them more amenable to subsequent biological treatment. The extent of degradation that can be implemented is usually classified into four groups. These include primary degradation, acceptable degradation or defusing, ultimate degradation or mineralization and unacceptable degradation or fusing. In primary degradation, a structural change in the parent compound takes place. For acceptable degradation, the structural change taking place in the parent compound is such that the level of toxicity is reduced. During mineralization, organic carbon compounds are converted into inorganic carbon dioxide. Unacceptable degradation refers to the structural change in the parent compound that results to increased toxicity and is therefore undesirable [20,27,28,29].

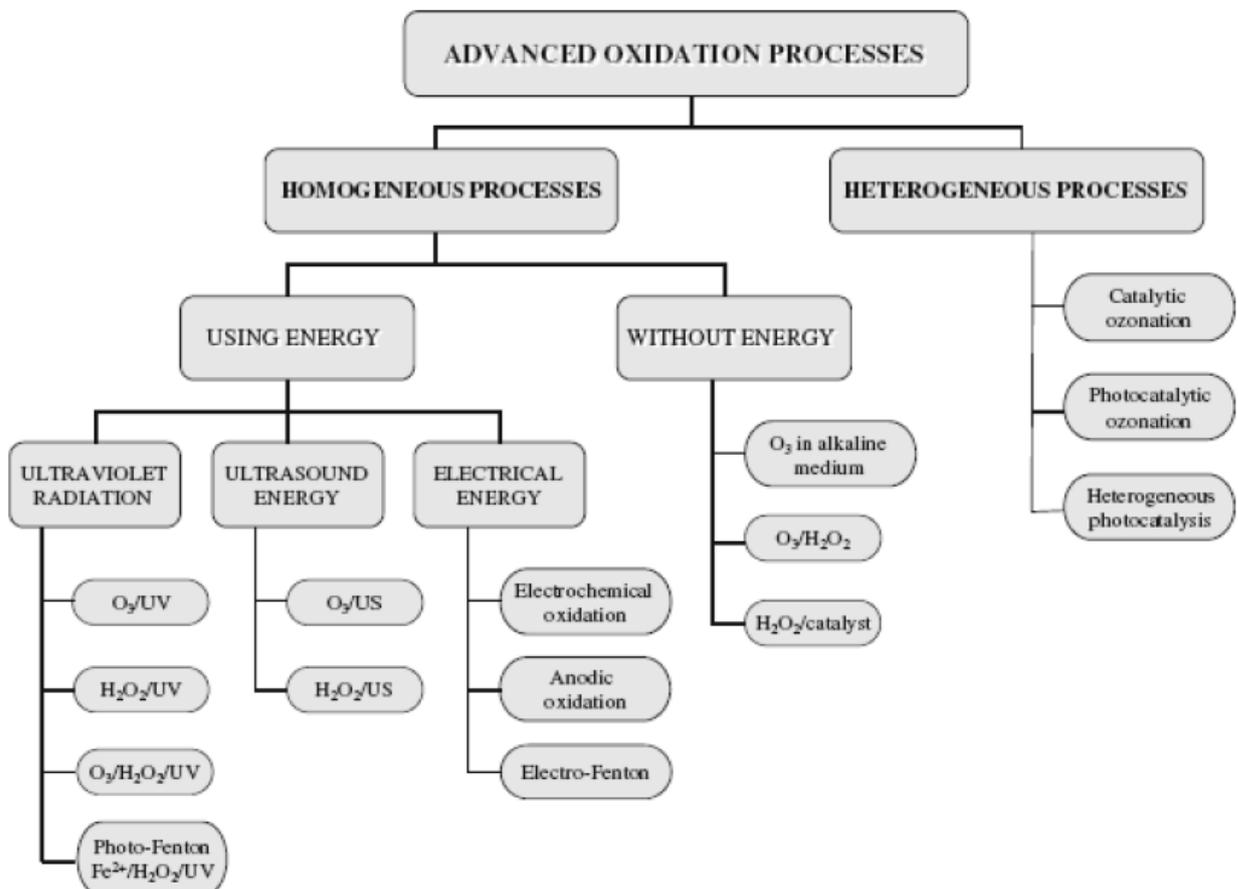


Figure 2: Classification of Advanced Oxidation Processes

## 4.2 Classification of AOPs

There are several methods that are classified under the broad definition of advanced oxidation processes. Most of these methods combine a strong oxidizing agent such as H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> with a catalyst such as transition metal ions and irradiation such UV. Evidence from literature shows titanium dioxide/UV light process, Fenton's reactions and hydrogen peroxide/UV light as the most popular AOP producing hydroxyl radicals [9]. Various AOPs are classified as being either heterogeneous or homogeneous. The latter are usually further subdivided on the basis of the energy used.

### 4.2.1 Homogenous Advanced Oxidation Processes

Homogenous AOPs that use UV radiation are normally used for degrading compounds which absorb UV radiation within the corresponding range of the spectrum. The compounds absorbing UV light at lower wavelengths render themselves suitable for such kind of photodegradation process.

#### 4.2.1.1 Photolytic Ozonation (O<sub>3</sub>/UV)

O<sub>3</sub>/UV is an advance water treatment method which is effectively used to oxidize and destroy the toxic organic compounds in waste water. Typically, aqueous systems saturated with ozone are irradiated with UV light of 254 nm. It was found that the O<sub>3</sub>/UV is so effective for the destruction of chlorophenols (CPs) than UV photolysis and ozonation [30,31,32,33]. However, Leitus and his coworkers [34] have found that photolytic ozonation is only more effective than ozonation alone in some cases.

#### 4.2.1.2 Hydrogen Peroxide and Ultraviolet Radiation (H<sub>2</sub>O<sub>2</sub>/UV)

In this advanced oxidation process, hydroxyl radicals are formed and generated by photolysis of H<sub>2</sub>O<sub>2</sub> and a number of propagation reactions that are corresponding to the process. The process of photolysis of hydrogen peroxide occurs once UV radiation is applied and is shown in the following equation:



This method requires a much longer UV exposure and/ or a relatively high dose of H<sub>2</sub>O<sub>2</sub>. Various studies showed that the rate of photolysis of hydrogen peroxide is largely pH dependent and tends to increase with increase in alkaline conditions [35]. UV lamps with output that is at lower wavelengths may be used for increasing the molar absorptivity of hydrogen peroxide which is low at 253.7nm. One of the drawbacks of this method is that in situations where the water to be treated has a higher absorbance, there is a tendency for it to compete with the hydrogen peroxide for radiation [36]. The H<sub>2</sub>O<sub>2</sub>/UV system has the ability to completely mineralize any organic compound, with the products being water and CO<sub>2</sub>. However, this process is usually not necessary as the toxicity of oxidation products is not a problem due to the fact that their degradation is quite easy. Addition of hydrogen peroxide may be either as multiple points in the system or as a single slug dose. Determination of the optimum dose

of  $H_2O_2$  required is usually on the basis of pilot-scale and bench testing. Key advantages of the technique are that  $H_2O_2$  is highly soluble and may therefore be added to the source water at high concentration and the fact that  $H_2O_2/UV$  processes are able to generate larger amounts of hydroxyl radicals compared to  $O_3/UV$  for equal amounts of energy used. Major disadvantages of the method are that it is expensive due to the additional costs of necessary devices and energy requirements and the fact that the presence of residual hydrogen peroxide in the treated effluent tends to promote biological re-growth within the distribution system [37].

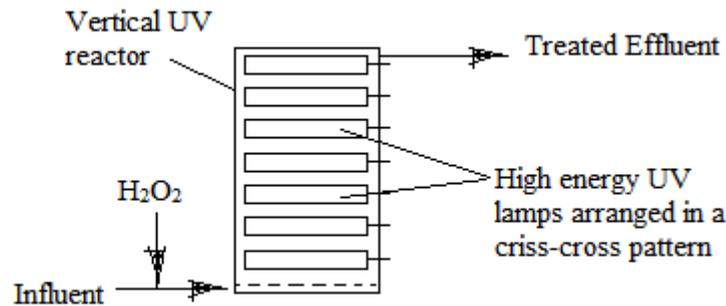


Figure 3: Schematic flow diagram of Hydrogen peroxide and UV radiation advanced oxidation process

#### 1.2.1.2 UV – Photolysis

The process of direct photolysis involves the interaction of light with molecules (in addition to water), to enable the molecules to be dissociated into fragments through the mechanistic pathway shown below:



The process is less effective compared to other processes in which radiation is combined with ozone or hydrogen peroxide, or where homogeneous, heterogeneous photocatalysis or catalysis are employed. The most common sources of UV light employed include continuous wave medium pressure mercury vapor lamps, low-pressure mercury vapor lamps and pulsed xenon arc lamps [38]. The former two produce a series of line outputs, while the latter produces a continuous output spectra.

#### 4.2.1.3 Fenton and Photo Fenton's Oxidation

Discovered by Henry J.H. Fenton, the Fenton reagent is a mixture of iron (II) salt and hydrogen peroxide. Fenton described the oxidation power of hydrogen peroxide on various organic molecules in which  $OH^-$  radicals are produced from  $H_2O_2$  through addition of  $Fe(II)$  as the catalyst [39]. The system developed by Fenton is viewed as the most promising treatment among AOPs for remediation of waters that are highly contaminated. Due to its simplicity, the Fenton reaction is the process most often applied in situations where it becomes necessary to remove recalcitrant compounds. The major drawback of the process is that it leads to the production of iron sludge waste. To eliminate this drawback, the photo-Fenton process was developed and it uses solar light or UV for reducing

Fe(III) oxalate back to Fe(II) oxalate and this results in drastic reduction in sludge waste. The extent of mineralization achieved by the Fenton process is around 60-70% [40].

In order to enhance the degradation velocity of organic pollutants, UV-visible light at wavelengths that are greater than 300nm is used in the reaction. The process differs from the Fenton process in that photolysis of iron (III) complexes enables regeneration of iron (II), and this can further react with more hydrogen peroxide [41]. The process is advantageous compared to the Fenton process in that it reduces the formation of sludge waste that occurs in the Fenton process. However, one has to ensure that they exhaustively control the PH of the medium, with the range used being between 2.6 and 3 for optimum performance of the system.

The conditions in which the Fenton and Photo Fenton processes are carried out as well as the constituents of the water have an effect on the reaction rates and the stoichiometry as a result of the effects in the solution chemistry. One of the major factors affecting the processes is PH. The performance of the reactive system formed is a function of the prevailing PH levels and it has a profound influence on the decomposition of organic compounds [42]. A review of available literature [43,44,45] on the process shows that it is most efficient at an optimum PH of 3. At higher PH values, there is a tendency for the decomposition rates to decrease as a result of precipitation of Fe(OH). For pH values below the optimal, there is a decrease in the rate as a result of lower light absorption coefficient that is associated with the complexes that are formed.

The second factor that has an influence on the Fenton and Photo Fenton processes is hydrogen peroxide concentration [46]. The concentration affects the extent and rate of degradation of organic compounds. There is a tendency for the reaction rate to increase with increasing concentration of hydrogen peroxide [47]. The series of intermediates taking place in the process implies that sufficient hydrogen peroxide must be added in order to push the reaction beyond the point. This is usually experienced when performing a pretreatment of a complex organic waste water for reduction in toxicity. As the dose of hydrogen peroxide is increased a steady reduction in COD may take place with little or no change in toxicity until the attainment of a threshold. Addition of excess hydrogen peroxide beyond the optimum limit has no influence on the degradation efficiency and this is attributable to the auto decomposition of hydrogen peroxide into water and oxygen and also the recombination of OH<sup>-</sup> radicals [46].

The catalytic ferrous ion concentration [Fe<sup>+2</sup>] has an effect on both the Fenton and Photo Fenton processes. The feature of having an optimum dose range for iron catalyst is usually characteristic of the Fenton's reagent, although there is a tendency for the range to have a variation between contaminated waters [48]. Common ranges for application are 1 part iron per 5-25 parts of hydrogen peroxide. Adding iron salt above the specified optimum dose has no effect on the degradation even with the doubling of concentration. The reason for this is that at a Fe(II) concentration that is higher than the optimum hydroxyl radicals tend to be consumed by side reactions before their utilization for removal of pollutants [38].

Key advantages of the Fenton and Photo Fenton processes include lower energy requirements compared to other technologies utilizing ozone or UV radiation, lack of vapor emissions and hence no air permits required, lack of mass transfer limitations due to the fact that reactions take place in the homogeneous phase and the fact that the process is carried out at room pressure and temperature. Major disadvantages of the processes are that iron extraction system is required for the removal of residual iron, a very low pH (less than 4) is needed to keep iron in the solution and the use of artificial light for the photo-Fenton process requires additional energy consumption for running the lamps.

#### ***4.2.1.4 Electro Fenton***

An alternative advanced oxidation process is the electro Fenton method also referred to as the EF technology. The technology is based on the continuous electro generation of  $H_2O_2$  at a suitable cathode that is fed with  $O_2$  or air, with the addition of an iron catalyst to the treated solution for the production of  $OH^*$  at the bulk through a Fenton reaction [49]. The advantages of the method include on-site production of  $H_2O_2$  and higher degradation rate of organic pollutants as a result of the continuous regeneration of  $Fe^{2+}$  at the cathode, which also results to the minimization of sludge production [48].

#### ***4.2.1.5 Anodic Oxidation***

Another advanced oxidation process that one may use for the treatment of waste water is the anodic oxidation [50]. By definition, anodic oxidation refers to an accelerated electrochemical process that is intensified by the natural oxide skin of the aluminium. With time, the transparent oxide layer becomes considerably thicker compared to the natural oxide layer. A significant advantage of using the process is the long term protection and the strong resistance to corrosion [49].

### ***Heterogeneous Advanced Oxidation Processes***

In the heterogeneous AOPs, catalysts are used for carrying out compounds' degradation. In this context, the term "heterogeneous" refers to the fact that there is presence of contaminants in the aqueous phase while the catalyst is usually in the solid phase. The latter results in the acceleration of chemical processes due to the presence of electron-hole pairs. The photogenerated electrons and holes result in oxidation and reduction processes respectively. For aqueous solutions, oxidization of water molecules absorbed to the catalyst results in  $OH^-$  radicals. The process is normally implemented in aerobic conditions with the species to be reduced being oxygen, a process which generates a superoxide radical.

#### ***Photocatalysts***

For a photocatalyst to be perceived as good, it should be biologically and chemically inert, photoactive, able to utilize visible or near UV light inexpensive, photostable and non-toxic. Examples of catalysts include Si, ZnO,  $WO_3$ ,  $TiO_2$ , CdS,  $SrTiO_3$ , ZnS,  $SnO_2$ ,  $Fe_2O_3$   $WSe_2$  [51]. The most commonly used of the catalysts is Titanium

dioxide ( $\text{TiO}_2$ ) and it has been demonstrated to be an excellent catalyst for the photo-oxidation of a variety of inorganic and organic compounds [52].

### ***Titanium Oxide***

One of the most abundant elements on the earth's crust (ninth), titanium is found in three possible crystalline forms in its most stable form as an oxide. The forms include rutile, anatase, and brookite. From a photocatalytic view, only anatase and rutile are relevant, with the latter having the highest catalytic activity [53]. Fundamentally, the process takes place through  $\text{TiO}_2$  producing pairs of electrons and holes through absorption of UV radiation, light source or sunlight. The electrons become excited once illuminated with the excess energy being used to promote the electron to the conduction band of titanium dioxide, thus, leading to the creation of positive hole and negative electron. Key operating parameters for the process include amount of the catalyst, initial concentration of the reactant and effect of pH [53].

The amount of catalyst concentration to be used should be up to the optimum value. Use of excess catalyst leads to the reduction in the amount of photo-energy that is being transferred in the medium as a result of the opacity that is offered by the catalyst particles. The optimum value of the catalyst to be used is dependent on the concentration and type of pollutant, in addition to the rate at which free radicals are generated. For effluents that are highly concentrated, no destruction is observed and dilution is usually essential. The manner in which pH affects rates of photocatalytic oxidation is complicated, with the observed effect being generally dependent on the zero-point charge of the semiconductor use and the type of pollutant. Generally speaking, the adsorption of the pollutant, and therefore the rates of degradation will be maximum near the zero-point charge [52,53].

### ***5. Applications of AOPs***

Studies have shown AOPs to be more effective than any of the individual agents (for example, hydrogen peroxide, UV or Ozone). AOPs are normally applied to wastewaters with low COD due to the low cost of  $\text{H}_2\text{O}_2$  and/ or ozone required for the generation of hydroxyl radicals. Materials that were previously resistant to degradation are now able to be transformed into compounds requiring further biological treatment. Key application of AOPs is disinfection of treated wastewater and treatment of refractory organic compounds [54].

The reasoning behind using AOPs for disinfection is that free radicals that are generated from ozone are more powerful oxidants than ozone alone and this makes them effective for oxidization of microorganisms and refractory organic materials in wastewater. However, the fact that the half-life of the hydroxyl free radicals is short and as a result it is impossible to achieve high concentrations. Extremely low concentrations imply that the required detention times for disinfection of microorganisms are much higher and are determined on the basis of CT concept. For this reason, hydroxyl radicals are rarely used for disinfection and instead are more commonly applied for the oxidation of trace elements of refractory organic compounds present in effluents that are highly treated. Once

generated, the hydroxyl radicals can attack the organic molecules through hydrogen abstraction, radical addition, radical combination and electron transfer [55].

## 6. CONCLUSIONS

Advanced oxidation processes have emerged as an important approach to treat waste water. Majority of the processes for waste water treatment are physicochemical in nature, physical or chemical processes or combine both. As one of the advanced methods, AOPs are based on a basic principle that entails the generation and use of a hydroxyl free radical ( $\text{HO}^*$ ) as a strong oxidant for the destruction of compounds which cannot be oxidized using conventional oxidants. AOPs have shown premises in various water treatment sectors due to its superior efficiency in pollutant elimination.

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