Application of Advanced Oxidation Process for Water and Wastewater Treatment : A Review

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***Abstract*— Advanced oxidation process is a highly efficient and modern method, first proposed in 1980s used for treatment of water purification and recovery. In this treatment, hydroxyl (OH^-) radicals and sulfate (SO_4^{-2})radicals are used. AOPs are excellent method for remediation of contaminated waste waters containing recalcitrant organic pollutants. hydroxyl radicals generated are highly efficient in removing the non easily removable organic compounds from waste water. This paper presents a review of various advanced oxidation process and describe various materials used in the process. AOPs utilize the potential of ozone (O_3), UV, Hydrogen Peroxide (H_2O_2) and hence provide a powerful treatment of water and waste water.**

Keywords—Advanced oxidation, Hydroxyl Radical, organic, waste water.

I. INTRODUCTION

Industrial and municipal waste water contains a wide range of non easily degradable compounds. As these compounds are resistant to biodegradation and various other biological treatment systems, hence pose several problems in biological treatment systems. So to eradicate or overcome this problem, the use of alternative treatment technologies like AOPs is required for transformation of refractory molecules into other easily degradable simple molecules. AOPs have been used for treatment of waste water containing recalcitrant organic compounds such as pesticides, surfactants, coloring dyes and other disrupting chemicals. They have been successfully used as pretreatment methods for the reduction of concentration of toxicants from water.

In AOPs main mechanism is the generation of hydroxyl radicals. These radicals react with toxic pollutants and help them in their degradation. These radicals are quite effective in destroying organic chemicals as they are rapid and non selective in nature and combines with nearly all electron rich compounds. The oxidation potential of hydroxyl radicals is around is around 2.33 V and hence their oxidation rate is faster than any other conventional method.

In the following reaction 'R' is organic compound:-

$$R + OH \cdot \rightarrow ROH \quad (1)$$

$$R + OH \cdot \rightarrow R \cdot + H20 \quad (2)$$

$$Rn + OH \cdot \rightarrow Rn - 1 + OH - \quad (3)$$

The generated radical attack organic chemicals by addition reaction (equation 1), abstraction of hydrogen (equation 2) and transfer of electrons (equation 3).

In AOPs there are various methods as the definition is quite broad. Among all methods, the most popular technologies are titanium dioxide/ UV light process, hydrogen peroxide / UV light process and Fenton's reaction. In the present study, a mini review of all the AOPs technologies has been performed. The main reactions and the parameters that affect these processes are discussed.

II. ADVANCED OXIDATION PROCESSES AOPs

In the 1980s, concept of AOPs was first proposed, Advanced Oxidation Processes are defined as the processes in which the hydroxyl radicals are generated by the oxidation reactions. the generated hydroxyl radicals are in sufficient quantity and hence effect the water purification to great extent. Initially only hydroxyl radicals are used for AOPs but later on the introduction of sulfate radicals has extended the AOP concept. Instead of using ozone and chlorinated compounds which posseses the ability of both decontamination and disinfection , nowadays the use of these radicals through AOPs is becoming popular. although these radicals cannot be employed for disinfection because of their short half life (on order of microseconds) so their small concentrations cannot provide sufficient detention time and residuals for future disinfection. When AOPs are used for water and waste water treatment, these radicals being powerful oxidizing agent breaks the recalcitrant compound and convert them into simple and easily biodegradable compounds, hence provides an ultimate solution for treatment of water and waste water.

(a) Hydroxyl Radical-Based AOPs

The most reactive oxidizing agent for water treatment is hydroxyl radical. The oxidation potential of hydroxyl radical has been given as 2.8 V and 1.95 V.Hydroxyl radical produce carbon centred radicals(R· or R·⁻OH). when they react with organic pollutants. Their reaction mechanism is based on four pathways which are radical addition, abstraction of hydrogen, transfer of electrons and then combining of radicals. These radicals with carbon as their centre get converted into peroxy radicals. These radicals further form highly reactive species which degrade and transform the complex organic compounds.

(b) Ozone-Based AOPs

Ozone is a very effective and strong oxidizing agent. Ozone hardly reacts with the compounds in neutral form rather it reacts with the compounds which are present in ionized and dissociated form. The mechanism of generation of hydroxyl radical from ozone and overall reaction mechanism has been described below

$$3O_3 + H_2O \rightarrow 2OH\cdot + 4O_2 \quad (4)$$

the OH· yield can thereby be improved to a great extent by using various radiation and other reaction enhancers. For example, in the so called peroxone (O_3/H_2O_2) system, the O_3 decomposition. and OH production are enhanced by hydroperoxide (HO_2^-) produced from H_2O_2

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad (5)$$
$$HO_2^- + O_3 \rightarrow OH\cdot + O_2^- + O_2 \quad (6)$$

In the O3/ultraviolet (UV) irradiation, H_2O_2 is generated as an additional oxidant primarily through O3 photolysis (Eq. 7)

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \quad (7)$$

photolysis of H_2O_2 is the last step , as shown in Eq. 8

$$H_2O_2 + hv \rightarrow 2OH\cdot \quad (8)$$

(c) UV-Based AOPs
The initiation of hydroxyl radicals can also be done by use of catalysts and oxidizing agents.
titanium dioxide (TiO_2) is used significantly for the purpose.. TiO_2 particles are excited to produce positive holes in the valence band (hv^+_{vb}) with an oxidative capacity, and negative electrons at the conduction band (e^-_{cb}) with a reductive capacity, as follows:

$$TiO_2 + hv \rightarrow e-_{cb} + hv+_{vb} \quad (9)$$

With the reactions of OH^-, H_2O, and $O_2^{\cdot-}$ at the surface of TiO_2, these holes and electrons can further form hydroxyl radicals.

$$.hv^+_{vb} + OH^-_{(surface)} \rightarrow OH\cdot \quad (10)$$

$$hv^+_{vb} + H_2O_{(absorbed)} \rightarrow OH\cdot + H^+ \quad (11)$$

$$e-_{cb} + O_{2\,(absorbed)} \rightarrow O_2^{\cdot-} \quad (12)$$

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \quad (13)$$

In addition, at a wavelength less than 242 nm, OH· can also be produced possibly through photolysis of H_2O.

$$H_2O + hv \rightarrow OH\cdot + H\cdot \quad (14)$$

(d)Fenton-Related AOPs
Iron is most commonly used material for the generation of hydroxyl radicals in the treatment process of waste water. The process is called as fenton process. In this process ,H_2O_2 reacts with Fe^{2+} to generate strong reactive species. The reactive species produced are traditionally recognized as hydroxyl radicals, though other substances such as ferry ions are proposed. The classical
Fenton radical mechanisms primarily involve the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH- \quad (15)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\cdot_2 + H^+ \quad (16)$$

$$OH\cdot + H_2O_2 \rightarrow HO\cdot_2 + H_2O \quad (17)$$

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH\cdot \quad (18)$$

$$Fe^{3+} + HO._2 \rightarrow Fe^{2+} + O_2H^+ \quad (19)$$

$$Fe^{2+} + HO\cdot_2 + H+ \rightarrow Fe^{3+} + H_2O_2 \quad (20)$$

$$2HO\cdot_2 \rightarrow H_2O_2 + O_2 \quad (21)$$

Through electron transfer, the hydroxyl radical is produced as shown in equation 15. This OH· produced is then exhausted by various fenton reagents as shown in equation 16 and 17. To minimize the wastage of hrdroxyl radical produced, there is a need to determine the optimal molar ratio of iron ion with respect to hydrogen peroxide. the produced
Fe^{3+} from Eq. 15 can be reduced to Fe^{2+} as indicated by equation 16. The rate constant in the equation 15 is several order of magnitude greater than that in equation 16. That is the reason for which iron can not act as a catalyst in the fenton system. Thus iron sludge is formed in the treatment of waste water. Thus this sludge should be disposed off separately thus increasing the complexity of this process and also the cost. It has been noted that the generation of hydroxyl radical through the fenton based processes is efficient for acidic range of ph. Thus the use of this method is limited in practice.

III. CONCLUSIONS

The AOPs proves to be a efficient strategy on technical and economical grounds as it helps in the treatment of toxic wastes and reduces their harmful impacts when they enter the environment. This technique is found to be effective for small volumes of wastes but for treating enormous amount of wastes, it is required to modify and develop the existing technologies. the water is basic necessity of life and it has been deteriorating at a very fast rate so it is the need of the hour to develop an efficient protection of ground and surface waters.
By using the approach of AOPs, an effective, economical, environment friendly and to a large extent easy to handle, cost effective water treatment technologies are required. In this review it has been described that these AOPs are highly effective in the purification of waste water containing heavily organic pollutants. In the last few decades, many researchers have proved by their work on AOPs that these methods are of great interest from ecological and environmental point of view. Thus it can be concluded that water treatment by AOPs are generally simple, clean and more efficient than classical treatment methods.

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