

Reduction of COD at Source Using Advanced Oxidation Process in an Active Pharmaceutical Ingredient Effluent

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Abstract

Advanced Oxidation Process (AOP) is the emerging technology used for Wastewater treatment. This study has been carried out on lab scale test and lab scale pilot plant to the effectiveness of the Advanced Oxidation Process (AOP) technology. AOP is basically the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants and COD. The objective of this paper is to evaluate the potential of Advanced Oxidation technology to remove COD in wastewater and also provides an overview of two different oxidants that are mainly used in AOP: Hydrogen peroxide as (Catalyzed Hydrogen peroxide) (i.e. modified Fenton's reagent) and Sodium Persulfate. Each of these oxidants used has their own unique characteristic and the ability to react with contaminants in subsurface; for example, CHP which is a non-selective oxidizing and reducing agent shows degradation results with almost all types of sorbed and non-aqueous contaminants but has lowest stability inside subsurface when injecting for treatment. Persulfate is the latest and least investigated oxidant. It has the potential of both stabilizing and widespread reacting with the contaminants in the subsurface. . Since, these oxidants are reliable enough to treat the contaminants, so, while wastewater treatment with AOP the problem of COD in Wastewater could be sorted out. Although none of these oxidants are ideal to use for Wastewater treatment, but still, have the ability enough to treat the contaminants appropriately than any other AOP technologies being used.

Keywords: Advanced Oxidation Process, Wastewater Treatment, COD Reduction, oxidation, Fenton process.

1. INTRODUCTION

The high standard of living, in highly developed countries in particular, and the increasing availability and affordability of medical treatment in many countries, has led to an increased production and consumption of different classes of pharmaceuticals, both those that require a prescription and those that do not. In recent years, a number of pharmaceuticals have been reported to be potentially toxic substances often found rather widely in the environment. Hundreds of pharmaceutical substances of differing therapeutic class, together with their metabolic by-products, have been detected in different environmental matrices. The major sources of pharmaceuticals in aquatic environments are discharges of WWTP effluents, the pharmaceuticals these contain stemming mainly from their use in households and in hospitals, and from discharges of wastewater from drug producers.

Pharmaceutical compounds are being used for several beneficial purposes in modern society but simultaneously pharmacy industries are releasing very toxic contaminants in the environment directly or after chemical modifications. Moreover, pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, seepage from landfills sites, sewer lines, runoff from animal wastes etc. Even though various physical and biological processes occurring in aquatic ecosystem may cause reduction of many pharmaceutical compounds, trace concentrations of human and veterinary pharmaceutical compounds as well as

their metabolites have been detected in different water bodies like surface water, groundwater and drinking water sources. The pharmaceutical industry in India is the world's third-largest in terms of volume and stands 14th rank in terms of value. It is growing at about 8 to 9 percent annually and is estimated to be worth 4.5 billion dollar. Different industries including pharmaceuticals, chemicals, paints etc. are speedily growing in India which disposes off their effluents into the streams either directly or after partial treatment. It has been found that the pharmaceutical compounds reach the environment and can be considered as environmental pollutants. The environmental exposure routes of pharmaceuticals into the environment are manufacturing units and hospital effluents, land applications (e.g., bio solids and water reuse) etc. However; sewage treatment services are not always successful in removing the active chemicals from waste-water. Consequently, pharmaceuticals find their way into the aquatic environment, where they directly affect aquatic organisms and can be incorporated into food chains. In a recent study, the extraordinarily high levels (mg/L) of several drugs were found in the effluents from local wastewater treatment plant.

2. ADVANCED OXIDATION PROCESS

Advanced oxidation processes (AOPs) have shown to be effective at the removal of various organic contaminants from drinking water and wastewater. AOP typically involve the generation of and use of the hydroxyl free radical (HO^\bullet) as a strong oxidant to destroy compound. Advanced Oxidation Process is the alternative method which involves the chemical transformation of organic pollutants and oxidizes.

Advanced oxidation generally uses strong oxidizing agents like hydrogen peroxide (H_2O_2) or ozone (O_3), catalysts (iron ions, electrodes, metal oxides) and irradiation (UV light, solar light, ultrasounds) separately or in combination under mild conditions (low temperature and pressure).

Advanced oxidation Process (AOP) is the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants. Use of Fenton's reagent, ozone sparging, Persulfate treatment came into widespread use for AOP technologies. To achieve this, various activators and stabilizers may be required to gain proper stability and formation of free radicals.

The formation of radicals involves mainly 3 steps: initiation, propagation and termination. Various initiators transform oxidants into radical species such as, direct activation, alkaline activation, metal salt activation, chelated metal based activation and heat activation. Hereby, we'll experiment with hydrogen peroxide and sodium Persulfate.

3. Hydrogen peroxide



CHP is based on the standard Fenton's reaction, in which dilute hydrogen peroxide is slowly added to a degassed solution of excess iron (II), resulting in the production of hydroxyl radicals (OH^\bullet) in near stoichiometric yields:



The process is based on the catalyzed decomposition of hydrogen peroxide by soluble iron, iron chelates, or iron minerals to generate the strong oxidant hydroxyl radical (OH^\bullet), as well as other reactive oxygen species.

Hydroxyl Radical Reaction

The oxidant of interest in CHP has traditionally been hydroxyl radical, one of the strongest oxidants found in nature. The most common reactions of hydroxyl radical are electrophilic substitution to aromatic compounds and addition to alkenes. Another class of hydroxyl radical reactions is hydrogen abstraction from saturated compounds such as

alkenes, a pathway that proceeds at a slower rate relative to electrophilic substitution and addition. The rate of reaction of hydroxyl radical with an organic compound (C) is described by the second-order rate expression:

$$-\frac{dC}{dt} = k [C] [\text{OH}^{\cdot}] \quad (2)$$

Rate constants $>10^9 \text{ M}^{-1} \text{ s}^{-1}$ are considered high enough to be effective for treatments, while rate constants $<10^8 \text{ M}^{-1} \text{ s}^{-1}$ are considered too low to be effective. Table 3.1 shows that almost all aromatic compounds, even those with a high degree of halogenations, react rapidly with hydroxyl radical. In particular, chlorinated and fluorinated alkenes such as carbon tetrachloride, chloroform, hexachloroethane, and freons (e.g., 1,1,2-trichloro-2,2,1 trifluoroethane), are effectively nonreactive.

Non-Hydroxyl Radical Species

With the high concentrations of hydrogen peroxide used for AOP (i.e., 2–20% (0.6–3.6 M)), hydroxyl radical generated in the Fenton's initiation reaction (Eq. 1) reacts with hydrogen peroxide to promote a series of propagation reactions:



The rates of generation of perhydroxyl radical (HO_2^{\cdot}), superoxide radical anion ($\text{O}_2^{\cdot-}$), and hydroperoxide anion (HO_2^-) become significantly greater at higher hydrogen peroxide concentrations and provide a mixture of oxidants, reductants, and nucleophiles that can degrade almost all organic contaminants.

4. SODIUM PERSULFATE

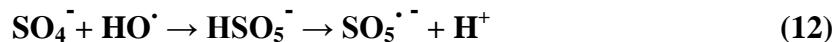
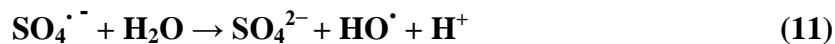
Persulfate (peroxydisulfate) is the newest chemical oxidant to be used for AOP, having received attention over just the past few years. The formation of Persulfate radicals ($\text{SO}_4^{\cdot-}$) involves mainly 3 steps: initiation, propagation and termination. Various initiators transform Persulfate into radical species such as, direct activation, alkaline activation, metal salt activation, chelated metal based activation, heat activation. Initiation reactions result in the formation of sulfate radicals:



In addition, hydroxyl radicals (OH^{\cdot}) are generated during Persulfate propagation reactions:



The following reactions takes place during the activation of Persulfate:



Among these radicals, $\text{SO}_4^{\cdot-}$ is the strongest oxidant followed by $\text{SO}_5^{\cdot-}$ and $\text{SO}_3^{\cdot-}$. Sulfate radicals and hydroxyl radicals are strong oxidants that can potentially oxidize many common contaminants. Second order rate constant for Persulfate is shown below in Table 3.2

The use of Persulfate as an agent for AOP appears to have advantages like it can percolate down the surface up to hundreds meters, unlike peroxide, from the point of injection with greater stability of about 12- 14 days.

4. TREATABILITY STUDIES

Treatability studies are almost always required prior to designing and implementing pilot- and full-scale AOP. These studies should be short to cut down the expenses, yet in detail giving answers to all doubts and questions. The result must show (1) the correct oxidant to use to treat all the contaminants, (2) the amount of dosage to be used, (3) the activation method, if to be applicable along with its dosage and type of activator to be used, (4) the conditions under which the oxidant should be used like pH range, temperature range etc.

The number of samples on which to conduct the treatability study is based on the type of wastewater and its heterogeneity; the size of the treatability study. An important parameter in the evaluation of the effectiveness of AOP treatment is the lifetime of the oxidant source.

5. SUMMARY AND CONCLUSION

AOP is gaining increased popularity for wastewater treatment. Mainly, two oxidants are in use for AOP, and each has their own characteristics and contaminant reactivity. Hydrogen peroxide based CHP has near-universal reactivity with all sorbed and soluble organic contaminants; however, it is unstable in the subsurface. Persulfate is the latest and least investigated oxidant. It has the potential of both stabilizing and widespread reacting with the contaminants in the subsurface. COD that is being imparted to Wastewater is due to the organic matter present as contaminant in it. Since, these oxidants are reliable enough to treat the contaminants, so, while Wastewater treatment with AOP the problem of COD in Wastewater could be sorted out. As more and more research will be carried on this, the more reliable data will be collected which will help in future for more rapid site remediation.

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