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Chemical Degradation of Pharma Effluents by Advanced Oxidation Processes Using Ozone and Hydrogen Peroxide: A Review

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ABSTRACT

Hazardous organic waste in pharma effluents is an emerging issue. APOs are efficient methods to remove organic contamination not degradable by means of biological processes. APOs are a set of processes involving the production of very reactive oxygen species able to destroy a wide range of organic compounds present in pharma effluents. Discussed the effects of AOPs using Ozone and Hydrogen peroxide in COD removal from pharmaceutical waste water.

KEYWORDS Advanced Oxidation Process, Ozone, Hydrogen peroxide, Pharma effluent, Xenobiotics

AOPs refer to set of oxidative treatments which can be applied to effluents at industrial level. AOPs are successful to transform toxic organic compounds (e.g. drugs, antibiotics, pesticides, endocrine disruptors etc.) in to biodegradable substances. AOPs are relatively inexpensive to install, but involve high operation cost owing to the input of chemicals and energy required.

Advanced oxidation generally uses strong oxidizing agents like hydrogen peroxide (H_2O_2) or ozone (O_3), catalysts and irradiation separately or in combination under mild conditions of low temperature and pressure. Different advanced oxidation processes were studied to treat pharmaceutical waste water from aerobic reactor. Among different AOPs we selected ozone and hydrogen peroxide to oxidize pharma effluents so as to remove organic compounds (reduce in COD levels) and discussed possible industrial application in this review.

Essentially the mechanism of Advanced Oxidation Process involves following steps:

1. Oxidative mechanisms are complex involving removal of an electropositive atom, radical or electron or conversely addition of electronegative moiety.
2. Oxidation reactions can be catalyzed by oxygen, heavy metal ions and light, leading to free radicals.
3. This results in the formation of strong oxidative agents such hydroxyl radicals
4. Strong oxidative agents will act on toxic molecules such as xenobiotics present in polluted water and convert them to relatively simpler organic intermediates
5. Simpler organic compounds further cleaved in to water, carbon dioxide, inorganic salts by same oxidative agents i.e. mineralization. Figure shows the mechanism of action by AOPs in treating organic pollutants.

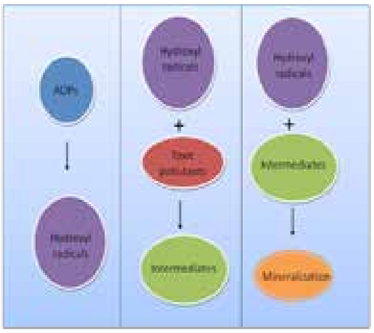

Fig: Mechanism of action by AOPs in treating organic pollutants and resulting mineralization

Pharma effluent consists of substantial amounts of pollutants such as drugs, antibiotics and other xenobiotics which cannot be eliminated or treated in aerobic waste water treatment plants. Such compounds should be subjected to advanced oxidation processes using chemicals such as hydrogen peroxide and ozone. These reagents generate hydroxyl radicals which degrade or cleave the complex xenobiotics in to simpler organic intermediates which eventually degraded in to water, carbon dioxide and inorganic compounds. Such APOs not only degrade refractory organic pollutants but also makes the process more efficient in treating the waste water containing by pharma effluents.

In many cases the APOs are combined for better efficiency. For example, in O_3/ H_2O_2 process, hydroxyl radicals are generated by radical chain mechanism between the ozone and hydrogen peroxide. Numerous reports are available as on today related to effect of APOs on refractory compounds and degradation, however, very little literature is available with respect to APOs effect on pharma effluents containing different xenobiotics compounds.

Earlier reports suggest the unsuccessful attempts at treating such xenobiotic compounds by aerobic and anaerobic processes; however, those resulted only in partial degradation of refractory compounds. Therefore, it becomes important or essential to utilize the APOs which successfully cleave the complex organic pollutants and bring down the COD levels to dischargeable permits. UV radiation, the wavelength range between 200 and 280 nm, can be applied in combination with hydrogen peroxide (H2O2). The major disadvantage of this process is related to the small molar extinction coefficient of H2 O2 . Therefore, relatively small fraction of incident light is exploited especially when organic substrates will act as inner filters. Moreover, the rate of photolysis of aqueous H2O2 is pH dependent: it was found to increase when more alkaline conditions are used [7]. H2O2 occurs also in Fenton based processes: when it reacts with iron in water, under acidic conditions, determines the formation of free radicals. The table shows the technical issues and potential processes with AOP technology.

Technology	Technicalissues	Potentialprocess/combinations
AOP/Chemical AOP	1) Removes organics,especially toxics. 2) Oxidants include UV/H_2O_2/O_3, UV/ H_2O_2,UV/O_3,$KMNO_4$,Hypochlorite,etc 3) Destruction technique 4) Oxygen effective under high temperature and pressure(wet air Oxidation) 5) chlorination /ozonation is used for disinfection of final effluent.	Prior to chemical Oxidation -Biological Process -Membrane Process After chemical oxidation -Biological process.

In the light of the research articles on radical reviews it is noticed that high reactivity of many pharmaceuticals to O3 and OH and the successful application of ozonation in pilot-scale,it is observed that ozonation is promising tool for the control of pharmaceuticals in water treatment.With reference to the nature of organic species two types of initial attacks are possible.In the first type hydroxyl radicals adsorb hydrogen atom from water with alkenes and or alcohols,or it also added to the pollutant in this case of olefins or aromatic compounds. In one of such studies, pharma effluent was obtained from activated sludge reactor and subjected to four kinds of APOs including Ozone and Hydrogen peroxide individually and in combination to remove the COD levels.

.The photocatalytic reduction of Cr(VI) ions in aqueous solutions by using UV/TiO2 process was investigated by C. M. Ma et al. The influence of various experimental parameters on the photocatalytic reduction was studied.

In "Photocatalytic treatment of shower water using a pilot scale reactor," a pilot scale study of photocatalytic degradation of impurities in real shower water was performed using titanium dioxide as the photocatalyst in a continuous slurry recirculation mode. More than half of the total organic carbon (TOC) elimination was obtained after 6 hours of treatment. Importantly, photocatalysis was successfully transposed from bench scale to pilot scale.

R. M. Mohamed and M. A. Barakat synthesized the Pt-doped ZnO/SiO2 photocatalysts and their photocatalytic activity was tested by using phenol as a model pollutant. The synthesized photocatalysts were characterized by using advanced analytical techniques.

V. Naddeo et al. studied the degradation of diclofenac by using various advanced oxidation processes such as ozonation (O3) and sonolysis (US) and their combined application (US+O3). The above researchers cover six types of advanced oxidation processes, including radiation, photolysis and photocatalysis, sonolysis, electrochemical oxidation technologies, Fenton-based reactions, and ozone-based processes. Controversial issues in pollutants degradation mechanism were being discussed. They review the application of these processes for removal of different kinds of toxic pollutants from wastewater, including aromatic compounds, dyes, pharmaceutical compounds, and pesticides, with emphasis on the parameters evaluated, removal effectiveness, and the various degradation mechanisms of pollutants. Other examples of AOP include H2O2/UV, Fenton (Fe2+/H2O2), photo- and electro-Fenton, chelating agent assisted Fenton/photo-Fenton, heterogeneous photooxidation using titanium dioxide (TiO2), γ-radiolysis, and sonolysis. The •OH radicals are extraordinarily

Hyper-reactive species with the rate constants of reactions with the majority of organic molecules in the order of 106 -109 M -1 s -1 . Also, their lack of selectivity is a big advantage when dealing with highly contaminated waters. The major advantage of the photolytic oxidation based processes can be operated at room temperature and the possibility to use sunlight or near UV for irradiation, which could result in considerable economic savings especially for large-scale plant operations.

The pH value decreased rapidly due to the formation of organic acids during the ozonation, which inhibited further % COD removal. It was also noted that the COD removal by ozonation was improved from 49% to 86% using phosphate buffer at pH 11.5.

Photo-Fenton and photo-Fenton-like processes [2 mM Fe2+ or Fe3+, 20 mM H2O2, a 21-W low pressure Hg lamp, l= 253.7 nm (1.73 · 101)] are equally effective in COD and TOC removals: 56 and 66% COD removal and 51 and 42% TOC removal, respectively. Complete conversion of 400 mg/L amoxicillin was also confirmed using ozonation at pH 11.5 and photo-Fenton process (Arslan-Alaton and Dogruel, 2004). Biodegradability of the penicillin formulation (amoxicillin + clavulanic acid) wastewater was improved

The results indicate substantial reduction in COD levels where the combination of Ozone and Hydrogen peroxide decreased the COD level by ~40% as compared to individual treatments.

The following conclusions can be draw with respect to oxidation of pharma effluents by ozone and hydrogen peroxide.

- Ozonation can be employed as an additional step after the aerobic treatment in waste water treatment plant to remove the xenobiotic compounds which otherwise is remained in the effluent.
- The amount of ozone is required for the removal of pharmaceuticals is related to the Aromaticity of organic compounds present in it.
- Ozone mediated decomposition can be enhanced by addition of Hydrogen peroxide which leads to reduction in reaction time and reaction volumes which are advantageous when things are planned at industrial level.
- APOs mediated processes are relatively costly and require engineering guidance in establishment and operations.
- However, they are very efficient to treat almost all organic pollutants and remove some toxic metals and works also for water disinfection.

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