INDUSTRIAL WASTEWATER TREATMENT BY ADVANCED OXIDATION PROCESSES – A REVIEW

ABSTRACT

The selection of an effective water treatment technology is the important issues that relatively dealing with water pollution problems, some pollutants need more than the conventional facilities to be treated and discharged within the national standards. This study highlights some of the advanced treatment methods related to chemical oxidation, which is used in the treatment of some types of pollutants such as heavy metals, pesticides, dyes, etc. and demonstrate their effectiveness in treatment by reviewing what has been concluded in a number of studies in this range.

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Introduction

A major problem facing industrialized nations is contamination of the environment by hazardous chemicals [1] like toxic heavy metals such as Cr, As, Cu, Zn, etc.) [2], dyestuff, salts and high concentration of COD. Advanced Oxidation Processes (AOPs) are more efficient and ecofriendly in the degradation of any kind of toxic pollutants [3]. Advanced Oxidative Degradation Processes (AOPs) comprise of techniques such that, under certain conditions, it could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions [4].

The AOPs can be broadly defined as aqueous phase oxidation methods based on *in situ* generation of highly reactive oxygen species (ROS) such as (primarily but not exclusively) hydroxyl radicals [5]. AOPs mainly consist of heterogeneous and homogeneous. They can be classified in two groups:

- **Non-photo chemical AOP's** (such as Ozonation, ozone/hydrogen peroxide and Fenton-process etc.).
- **Photochemical AOP's** (such as vacuum UV photolysis, UV/hydrogen peroxide, UV/ozone, UV/ozone/hydrogen peroxide, photo-Fenton etc.).

The UV-based ones will form the basis of treatment for developed countries whereas the photo-Fenton process will be presents as a viable solution for the sunny developing countries around the globe [6]. The photo generated electrons and holes are assumed to diffuse to the surface and react with the electrophilic and nucleophile substances absorbed on the photo catalyst surface, respectively, producing activated and unstable products [7]. Photo catalysts are generally utilized in the treatment of water and wastewater using two approaches. The

First approach is the immobilization of catalyst particles on stable and inert substrates and the second is adding catalyst particles to polluted water and using them in a suspended form [7]. In this study, advanced oxidation processes specifically include the application of oxidation technologies using UV/O₃, O₃, O₃/H₂O₂, UV/H₂O₂ and the photo Fenton reaction (UV/H₂O₂/Fe²⁺ or Fe³⁺) [8].

Application of AOPs Technology with wastewater treatment

**Application of UV/H₂O₂**

One way to employ the Homogeneous Photochemical is based on the generation of hydroxyl radical (OH⁻) from hydrogen peroxide. The use of hydrogen peroxide combined with UV radiation generates the hydroxyl radical, which is a chemical agent with great power of oxidation. Radiation below 400 nm is capable of photolysis H₂O₂ causing the split of the molecule into two hydroxyl radicals (Equation 1) [9].

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{OH}^- \]  

A study done by Siedlecka and Stepnowski [10] presented the nonselective degradation of mechanically pretreated oily wastewater by hydrogen peroxide (H₂O₂) in the presence and absence of UV irradiation. The effect of chemical oxidation on wastewater biodegradability was also examined. The exclusive use of H₂O₂ photolyzed by daylight results in quite efficient degradation rates for the low peroxide concentrations used. Higher hydrogen peroxide concentrations inhibit degradation of organic contaminants in the wastewater. The degradation rates of all contaminants are relatively high with an
advanced oxidation system (UV/H$_2$O$_2$), but degradation efficiencies are not distinguishably different when 20 or 45 minutes of UV irradiation is used. The excess of H$_2$O$_2$ used in the process can inhibit phenolic degradation and may lead to the formation of a new phenolic fraction. The biodegradability of port wastewater did not increase significantly following the application of the advanced oxidation process.

Dixit et al. [11] studied the photochemical oxidation of phenol and chlorophenol aqueous solutions in a batch recycle photochemical reactor using ultraviolet irradiation, hydrogen peroxide and TiO$_2$ (as photocatalyst). The study showed that the combined treatment process was the most effective process under acidic conditions and showed a higher rate of degradation of phenol and chlorophenol at a very short radiation time. The reaction was found to follow the first order kinetics and was influenced by the pH, the input concentration of H$_2$O$_2$ and the dosing amount of the TiO$_2$ photocatalyst. The results indicate maximum 74.6% and 79.8% degradation of phenol and chlorophenol respectively within 90 minutes of radiation time. The experimental results showed that the optimum conditions were obtained at a pH value of 4, with H$_2$O$_2$ concentration ranging from 200-550 ml/L, and TiO$_2$ dosing ranging from 1-2 g/L for UV/H$_2$O$_2$/TiO$_2$ combined system. Finally a rough comparison of energy consumption shows that UV/H$_2$O$_2$/TiO$_2$ process reduced the energy consumption by 40-50% compared with the UV/H$_2$O$_2$ and UV/TiO$_2$ processes.

Kalra et al. [12] found that H$_2$O$_2$ alone is quite ineffective in the treatment of textile wastewater at both alkaline and acidic pH, while under UV irradiation, H$_2$O$_2$ are photolysed to form two hydroxyl radicals (2OH$^-$), which react with organic contaminants. Initial dye concentration and H$_2$O$_2$/UV removal efficiency are inversely related. The increase in dye concentration simply increases the number of dye molecules and not the hydroxyl radical concentration. Moreover it induces a rise in internal optical density and the solution becomes more and more impermeable to UV radiation. Consequently the rate of photolysis of hydrogen peroxide, which depends directly on, the incident intensity decreases. So when initial dye concentration in increased, the production of hydroxyl radicals decreases and thus the removal efficiency decreases.

Malhotra et al. [13] concluded that Use of H$_2$O$_2$ as an oxidant has a number of advantages in comparison to other chemicals or photochemical water treatment and the oxidation rate of cyanide is strongly accelerated by the UV/H$_2$O$_2$ process and with increasing wattage of the UV lamp the rate also increases. It was found that cyanide is first oxidized to cyanate and later cyanate is oxidized to carbon dioxide and nitrogen gas. But the rate of cyanate oxidation is slower than that of cyanide. The photo-oxidation of cyanide should be carried out at alkaline pH because at acidic pH, toxic volatile hydrogen cyanide gas will form and it is difficult to oxidize hydrogen cyanide. The power required for complete degradation of 1 kg of cyanide was found to be 167 kWh.

Naumczyk et al. [14] investigated the changes in COD values for different doses of H$_2$O$_2$ (2000–6000 mg/L). Five hours of preliminary sedimentation resulted in 4.6% COD removal. The effect of the process for each sample increased considerably when H$_2$O$_2$ dose was increased to 4500 mg/L. Therefore, this dose can be considered as optimal. The resulted decrease in COD after 60, 120, 240, and 360 min was equal to 32.7,
68.9, 83.6, and 89.2%, respectively. The dose of 5000 mg/L slightly improved the process efficiency 91.0% after 360 min. For doses 5500 and 6000 mg/L the efficiency was approximately the same or slightly lower.

**Application of Ozone O3**

Ozone is a very reactive gas which has a low solubility [15], discovered by Van Marum, the Dutch chemist in 1785 [16]. One of uses of Ozone is for drinking water treatment [17]. The use of O3 as a chemical oxidant has been suggested in the latest literature as a potential technique for COD, AOX and color removal [18]. The formation of Ozone is represented as follow:

\[ O_2 + \text{energy} \rightarrow O^- + O^- \quad (2) \]

\[ O^- + O_2 \rightarrow O_3 \quad (3) \]

According to G. Hey [19], Ozone is considered to be the most efficient chemical oxidant for reducing the concentrations of a large number of different pharmaceuticals, the ozone dose required for this being fairly low (5-10 mg/L), depending upon the characteristics of the effluent. Over 90% of the pharmaceuticals investigated in most of the effluents could be eliminated to 90-100% by use of ozone.

In the pharmaceutical industry ozone is used for disinfection or inactivation of pathogenic organisms [20]. Figure (1) below illustrates the reactions of Ozone.

![Scheme of reactions of ozone added to an aqueous solution](image)

According to E. Lee et al. [22], the COD removal by O_3 performances for 2 h of treatment, based upon corrected COD values is 54 % which is less than other processes like O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV. Ozone can be harmful to humans and it is highly toxic to aquatic organisms at very low levels. Summer felt [23] mentioned that Ozone is capable of oxidizing many biochemical compounds present in living organisms, including amino acids, pyrimidine nucleotides, fatty acids, Flavin, and proteins containing sulfhydryl groups, While Baratharaj [24] mentioned that Ozone is a highly reactive substance that can react with many species. However, most often ozone action is dependent on how it reacts with a pollutant. Though Thermodynamics may favor ozone due to its high Redox potential, it is the kinetic factors that will determine how fast ozone will act against each pollutant. It is because of this fact that Ozone sometimes have not been very useful in certain cases of Waste water Treatment.
**Application of O3/H2O2**

Although ozone is effective in stabilized leachate treatment, its effectiveness will be improved using advance oxidant materials and techniques by employing hydrogen peroxide in advanced oxidation during the ozonation process [25]. The conjugate base of H$_2$O$_2$ at low concentrations increases the rate of decomposition of O$_3$ into hydroxyl radicals [26]. Although O$_3$ is able to produce H$_2$O$_2$ alone by the breakdown of organic matter, it was concluded that the addition of H$_2$O$_2$ artificially to the system greatly accelerated the formation of the hydroxyl radicals necessary for the efficacy of the system and allowed shorter contact times [27].

Šimovičová et al. [28] concluded that the application of O$_3$/H$_2$O$_2$ based processes is a promising procedure for the removal of investigated petrol aromatic hydrocarbons from aquatic environment. An O$_3$/H$_2$O$_2$ system has been used for atrazine removal from the water of the River Seine in Paris at a scale of 5000 m$^3$/h [29] and the results showed better degradation of the pesticide in water treated with it as compared to ozone alone [29]. The O$_3$/H$_2$O$_2$ system was used to remove atrazine from the water of the River Seine in Paris at a scale of 5000 m$^3$/h [29] and the results showed a better degradation of the pesticide in water treated with this system compared to ozone alone [29].

At neutral pH and at low H$_2$O$_2$ concentrations, this combination improved the Ozonation slightly [30]. The adequate pH range of the process is between 7 and 8 [31]. H$_2$O$_2$ induces the decomposition of O$_3$ by electron transfer through a reaction that can be understood as H$_2$O$_2$ activation by O$_3$ (Equation 4) [32].

$$O_3 + H_2O_2 \rightarrow HO^+ + O_2 + HO_2^-$$ (4)

According to Bozena study [33], H$_2$O$_2$ is one of the cheapest oxidants with high oxidative power, soluble in water and thermally stable. The combination of these two oxidizing agents is also beneficial in the treatment of compounds that show little or no reactivity towards the direct attack of the ozone molecule [34].

**Application of UV/ H2O2**

Radiation with wavelength lower than 400 nm is able to photolize the H$_2$O$_2$ molecule [35]. Ultraviolet radiation is used to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical [36]. Efficiency of the UV/H$_2$O$_2$ process for COD removal is dependent on initial wastewater pollution strength or dilution of wastewater, hydrogen peroxide concentration and reaction time [37].

According to Joshi et al. [38], the use of UV:H$_2$O$_2$ for decolourization increase the rate and strength of oxidation, in the same time it is Environment-friendly application but the cost of producing UV irradiation does not compensate for the increase. A. Afzal et al. [39] found that UV:H$_2$O$_2$ was capable of 90% degradation for both pesticides in natural water: bromoxynil and trifluralin, while Muhammad et al. [40] mentioned that the decolourization efficiency may be enhanced by applying UV:H$_2$O$_2$/O$_3$ or increasing the concentration of H$_2$O$_2$ to ensure the availability of hydroxyl radicals. Malhotra et al. [41] resulted that the oxidation rate of cyanide is strongly accelerated by the UV/H$_2$O$_2$ process and with increasing wattage of the UV lamp the rate also increases. Ratpukdi T. [42] concluded that the combined alum coagulation with UV/H$_2$O$_2$ was found to be effective to remove color from Anaerobically Treated Palm Oil Mill (ATPOME) wastewater.

**Application of Fenton**

A century ago, the catalytic oxidation of tartaric acid in the presence of ferrous salts
and hydrogen peroxide was reported by Fenton [43] which can be represented by the following equation:

$$\text{Fe}^{2+} \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (5)$$

Introduction of UV source into the Fenton process called Photo-Fenton [44]. The main advantage of Fenton’s reagent over other OH· systems are its simplicity [45]. Ali and Ameta [46] concluded that the rate of degradation of dye in presence of photo-Fenton reagent is higher as compared to Fenton reagent, while S.A. Abo-Farha [47] concluded that, the decolourization degree of the two azo dyes (Acid Orange 8 and Acid Red 17) is strongly dependent on Fe$^{2+}$ and Fe$^{3+}$ ion concentrations, the H$_2$O$_2$ concentration, the initial dye concentration and the solution pH. Mohammad Ali Zazouli et al. [48] mentioned that the Fenton processes are applicable for the treatment of highly toxic leachate and noticeably exhibit faster kinetics as compared with the biological treatment processes. UV-C light enhanced the photo-Fenton oxidation of paracetamol and the process is more efficient over Fenton oxidation [49]. N. Martinez [50] concluded that in the first 10 min of the Fenton’s reaction, more than 90% of COD removal can be achieved. This finding is of special interest in the industrial application of Fenton’s reagent, because it permits a significant COD reduction in a very short period of time. According to T. Dantas et al. [51], no significant differences were observed after Fenton and photo-Fenton processes for the treatment of tannery wastewater, in relation to kinetics, toxicity or ammoniac nitrogen removal. Fenton processes were able to achieve acceptable high COD reduction results (> 60%) without adjusting the initial pH value of the solution, which is close to neutral [52]. A study done by A. Vilar et al. [53] confirmed that the Fenton process can be useful to improve the biodegradability of the leachate pretreated biologically up to a level compatible with the biological treatment. M. Shanthi et al. [54] founded that both the combined ferrous and ferrioxalate processes are viable and efficient methods for organic pollutant (benzyl alcohol) wastewater treatment within a short time.

**Application of photo Fenton**

The combination of H$_2$O$_2$/UV and iron salt produces more hydroxyl radicals compared with a conventional Fenton process or photolysis, thus the technique enhances the degradation of treated pollutants. The use of photo-Fenton for the treatment of non-biodegradable or toxic compounds can be an alternative to the conventional processes [55]. The photo-Fenton reaction was at first investigated by atmospheric researchers to clarify natural mechanisms of hydrogen peroxide production and oxidation of several pollutants in atmospheric water droplets [56].

According to D. Kumar [57], the rate of the oxidation depends on various parameters like substrate, H$_2$O$_2$, FeSO$_4$, pH, polarity of solvent and the catalyst variation. A. Fajardo [58] mentioned that UV-Fenton offered a slightly better efficiency than solar-Fenton with respect to mineralization rates; however the intrinsic low-cost associated with solar energy turned out to be efficient in treating phenol as compared to UV light. According to M. Rodríguez [59], Photo-Fenton process was found to be the most effective method in the treatment of phenol in aqueous solution and the use of solar radiation in the photo-Fenton process is a good alternative in the treatment of phenol-polluted waters. Y. Huang et al. [60] found that the application of UV light can improve the degradation efficiency of the Fenton process and overcome the inhibition of hypophosphite binary components. Nora M.
Hilal [61] concluded that the degree of degradation in presence of photo-Fenton process are more effective and faster than other advanced oxidation processes in decolonization of Reactive Dyeing Wastewater. Md. Ahsan Habib [62] concluded that photo-Fenton process is more efficient than Fenton for degradation of brilliant golden yellow dye. The efficiency of the photo-Fenton process can be further enhanced by using organic Carboxylic acids to complex Fe (III) [63].

Conclusion
The application of advanced oxidation processes showed effective results in water treatment although that there are some differences in their effectiveness according to the kind and concentration of pollutants. There is a persistent need to applicate these processes especially with industrial wastewater. Design requirements, economical considerations and technological means are important things to consider when choosing the right technique for treatment.

References


