Treatment of Pharmaceutical Wastewater by Advanced Oxidation Process (AOP)

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Abstract

Advanced oxidation process (AOP) is defined as aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical in the mechanism resulting in the destruction of the target pollutant. AOP have been applied to refractory organic pollutants and xenobiotics found in industrial wastewater to improve biodegradability and also increase treatment efficiency. Numerous researchers have evaluated on the treatment of refractory compounds by different AOP processes. However, few studies reported in the literature dealt with pharmaceutical effluents. In this paper, studies of the further polishing of effluent from an aerobic reactor using different types of AOP was presented and discussed. Four types of processes were evaluated, i.e. ozonation (O_3), hydrogen peroxide (H_2O_2), ultraviolet (UV) and Fenton reagent, and a combination of these AOP processes (O_3/UV, H_2O_2/UV, O_3/H_2O_2 and O_3/H_2O_2/UV) for COD removal have also been studied. This additional treatment of the activated sludge reactor effluent contributed substantially to overall COD removal of the pharmaceutical wastewater. Among the AOP processes used in this study, O_3/H_2O_2/UV alternative resulted in the highest COD removal (59%) from the activated sludge effluent. In specific, around 450 mg.L^{-1} of COD had been removed in the O_3/H_2O_2/UV process giving a final COD of 300 mg.L^{-1} in the treated effluent. Other processes (Fenton, O_3, O_3/UV, O_3/H_2O_2 and H2O2/UV) showed nearly constant maximum removal with 38 – 43% COD removal. Further analysis of operating costs to confirm feasibility of AOP should be conducted as the process is expensive to install and operate.

Keywords: advanced oxidation process (AOP); pharmaceutical wastewater; ozonation; hydrogen peroxide, ultraviolet, Fenton reagent

INTRODUCTION

Advanced oxidation processes (AOPs) are defined as aqueous phase oxidation processes which are based primarily on the intermediacy of the hydroxyl radical in the mechanism resulting in the destruction of the target pollutant or xenobiotic compound (Esplugas *et al*., 2002). An extensive review of advanced oxidation processes as primary and secondary treatment methods can be found in Parsons (2004). A brief introduction to different types of AOPs is given below:

i. Ozone (O_3)

Ozone (O_3) is a strong oxidizing agent that can be used to reduce color, eliminate organic waste, reduce odor, and remove COD and TOC in wastewater. There are two possible mechanisms of oxidizing which can be considered: the direct mechanism, because of the reaction between the ozone and the dissolved compounds, and the radical mechanism owing to the reactions between the generated radicals produced in the ozone decomposition (hydroxyl radicals) and the dissolved compounds (Esplugas *et al*., 2002).

ii. Ozone and Hydrogen Peroxide (O_3/H_2O_2)

In this system hydroxyl radicals are generated by a radical-chain mechanism by interaction between the ozone and the hydrogen peroxide. The global reaction is as follows:

$$H_2O_2 + 2O_3 > 2OH? + 3O_2$$
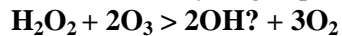
The efficiency of this process can be improved by adding UV radiation.

iii. Ultraviolet (UV)

This method is based on supplying energy to the chemical compounds as radiation, which is absorbed by reactant molecules that can pass to excited states and have sufficient time to promote reactions.
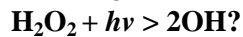
iv. Ozone and Ultraviolet (O_3/UV)

In this process, ozone is fed into a UV photo reactor. In the presence of water, UV-sensitized ozone decomposition yields OH? radicals that oxidize organic compounds. The global reaction being:

$$O_3 + H_2O + hv > 2OH? + O_2$$
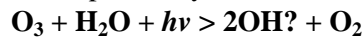
v. Hydrogen Peroxide and Ultraviolet (H_2O_2/UV)

Radiation with a wavelength lower than 400nm is able to photolise H_2O_2 molecule. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two OH? radicals formed per quantum of radiation absorbed according to the following reaction:

$$H_2O_2 + hv > 2OH?$$

vi. Ozone, Hydrogen Peroxide and Ultraviolet (O_3/ H_2O_2/UV)

This is a very powerful method which allows the fast and complete mineralization of pollutants. It is considered to be the most effective treatment for highly polluted effluents.

vii. Fenton's Reagent

Fenton's Reagent is employed as an alternative to AOPs and does not utilize ozone or UV light. Instead ferrous ion complex and hydrogen peroxide is added in to an aqueous system forming a catalytic oxidation process. The mechanism of action of Fenton's Reagent can be represented by the following equation:

$$Fe^{2+} + H_2O_2 > Fe^{3+} + OH? + OH^-$$

Due to the nature of the pharmaceutical wastewater in the present study, a fraction of the wastewater was found to be non-biodegradable during aerobic treatment. Wong *et al*. (1997) stated that complete removal of substrate cannot be expected due to the presence of the refractory material that could not be destroyed aerobically. Consequently, the effluent from the activated sludge reactor was subjected to additional treatment by a range of advanced oxidation processes (AOPs) and the results are presented and discussed. Four types of AOPs were evaluated, i.e. ozonation (O_3), hydrogen peroxide (H_2O_2), ultraviolet (UV) and Fenton reagent, and a combination of these AOPs (O_3/UV, H_2O_2/UV, O_3/H_2O_2 and O_3/H_2O_2/UV) for COD removal were also studied.

MATERIALS AND METHODS

Ozonation (O_3)

The Ozone used in this study was generated by passing compressed oxygen through a Wallace and Tiernan Laboratory Ozonator (Type BA 023, Wallace and Tiernan Ltd, Tonbridge, UK) (Figure 1.1). Initially, the ozonation rate was calibrated by passing oxygen at flow rates of 30, 60, 100 and 150 litres per hour, for periods of 5 - 10 minutes, at an electrical potential of 200 volts, to determine the ideal ozone generation conditions for effluent treatment. The output of ozone gas was determined through two serial KI (Potassium Iodide) traps (trap A and B) for about 10 minutes. Each gas trap was a 250 ml Dreschel bottle containing a known volume (200 ml) of 2% KI. Contents of each trap were poured into a beaker and

10 ml of 2N H_2SO_4 was added. This is then followed by titration with standardized 0.05N $Na_2S_2O_3$ until the yellow iodine color almost disappeared, then 1 – 2 ml starch indicator solution were added before continuing the titration to the disappearance of blue color. Ozone dose efficiency (output) was calculated by the Semi Batch method (18th Edition of Standard Methods). The oxygen flow was set at 1 L.min^{-1} at 200 V and ozone was passed for 5 minutes through two gas washing bottles each of which contains 200 ml of 2% KI. About 128 ml titration was used for trap A and 2 ml for trap B (total 130 ml).

[pic]

Figure 1.1. Schematic diagram of ozonator.

Ultraviolet (UV)

In this study, a recirculated photo reactor was used for the removal of COD from the effluent of aerobic reactor. The photo reactor system consists of reactor chamber, wastewater sample tank and stirrer. The single UV lamp of 6 watts located centrally in the single reactor had a light wavelength of 254 nm primarily. Sample in the feed tank (1.0 L) was pumped through using a peristaltic pump (Watson Marlow 100 series) at circulation speed of 37 ml.min^{-1} (20 rpm) for 180 minutes with active contact volume of 30 ml.

Hydrogen Peroxide (H_2O_2) and Fenton Reagent

Hydrogen peroxide (Aldrich, 30% stabilized) and $FeSO_4 \cdot 7H_2O$ (Baker) were ACS reagent grade and were used as received. The samples were withdrawn at regular time intervals and were filtered with Millipore membrane (2.5 (m) before analysis. Temperature was maintained at 20 ^{o}C in the reactor, which was mixed continuously by a Teflon-coated stirrer at the highest speed (200 rpm) using a Fisher magnetic stirrer for both oxidation methods.

RESULTS AND DISCUSSIONS

Preliminary Investigations

Effluent from the activated sludge reactor which had a typical COD value of 825 mg.L^{-1} was treated using various advanced oxidation processes (AOPs). During this preliminary phase, the pH of the effluent from the activated sludge process was not adjusted and therefore, experiments with AOPs were conducted at the effluent pH of 7.8. COD removal efficiency (maximum COD removal) of individual treatments (O_3, H_2O_2, UV and Fenton) was around 9 - 15% and for the combination AOP processes (O_3/UV, H_2O_2/O_3, H_2O_2/UV, Fenton/UV and H_2O_2/O_3/UV) was in the range of 11 - 40%. It was concluded that treatment of the activated sludge reactor effluent at pH 7.8 was not satisfactory, and further investigation should be carried out to improve the COD removal efficiency. Balcio?lu and Ötker (2003) reported that pH adjustment is essential for the treatment of pharmaceutical wastewater containing antibiotics by AOPs for efficient removal of COD. Consequently, the effect of pH was incorporated into subsequent studies.

Fenton Process

Initial investigations into the effect of pH on the COD removal by the Fenton's process were carried out. The experiment investigated pH between 2 and 7. $FeSO_4$ provided Fe^{2+} ion needed for Fenton's reagent. Optimum pH that resulted in the highest COD removal was determined by initially running the reactor under varying pH but constant H_2O_2 and $FeSO_4$, and showed that pH of 5 was optimal (data not presented). After pH optimization, the reactors were first run with constant $FeSO_4$ but variable H_2O_2 at pH of 5. Subsequently, the same operations were repeated for constant H_2O_2 but variable $FeSO_4$ at pH of 5. The results are shown in Figure 1.2 and Figure 1.3, respectively. Consequently, optimum conditions were determined as follows; pH = 5, H_2O_2 = 500 mg.L^{-1} and $FeSO_4$ = 600 mg.L^{-1} for the effluent from the

activated sludge reactor, and these additions resulted in 40% COD removal efficiency for the Fenton process.

Ozonation

Since ozone itself is a strong oxidizing agent and effective at high pH values (Shu and Huang, 1995), further experiments were carried out to study the COD removal efficiency at elevated pH values. Ozonation experiments were performed for 120 minutes at four different initial pH values, i.e. at pH 2.5, 7, 10 and pH 12. During all experiments, the pH decreased considerably as a consequence of acid product formation. Figure 1.4 depicts the effect of various pH values on the effect of COD removal by ozonation. COD removal efficiency varied from 5% up to 41% during ozonation. Alkaline conditions showed better removal efficiency and the highest COD removal was observed at pH of 12 for an ozone dose rate of 1.87 $g.L^{-1}$ h. Moreover, the COD removal increased with increasing pH due to accelerated ozone decomposition to free radicals which is particularly pronounced at pH ?11.0 (Staehelin and Hoigne, 1982). In general, ozone reacts with organic compounds in wastewater by two different mechanisms; the direct mechanism, because of the reaction between the ozone and the dissolved compounds, and the radical mechanism owing to the reactions between the generated radicals produced in the ozone decomposition and the dissolved compounds (Esplugas *et al*., 2002). Moreover, molecular ozone is the major oxidant at acidic pH, whereas less selective and faster free-radical oxidation becomes dominant at pH > 7, as a result of OH^- accelerated ozone decomposition (Langlais *et al*., 1991). Consequently, in this study the degradation of the organic compounds in the sample mainly proceeded by radical mechanism, when direct oxidation by ozone was the dominant reaction mechanism (e.g. at acidic pH - 2.5), only 5% COD removal was found (Figure 1.4) compared to pH 12, where an average of 41% COD removal was observed when radical mechanism predominates. It can be concluded that the COD removal method of ozonation seemed to change and was more efficient at elevated pH values, especially when the pH was above 10. There was no significant increase in process efficiency after 120 minutes of reaction time, which resulted in a 41% COD removal.

O_3/UV and H_2O_2/UV

The effects of varying pH between 2.5 and 12 were assessed in the first place for the UV experiments. The same sample that had been used in the ozonation experiment above was utilized into O_3/UV experiment. Figure 1.5 shows the effect of pH on the COD removal during O_3/UV process and the highest COD removal efficiency was 43% at pH = 12. For the H_2O_2/UV process, the effect of pH was determined by maintaining the H_2O_2 concentration at 200 $mg.L^{-1}$ and Figure 1.6 shows the highest COD removal was 38% at pH = 2.5. Following the determination of the best pH in terms of best COD removal, the UV experiments with hydrogen peroxide were repeated under the best pH with varying H_2O_2 peroxide concentrations in order to determine the best hydrogen peroxide concentration. Figure 1.7 shows that the best hydrogen peroxide concentration was 300 $mg.L^{-1}$ and at this concentration, 42% of COD was removed after 90 minutes.
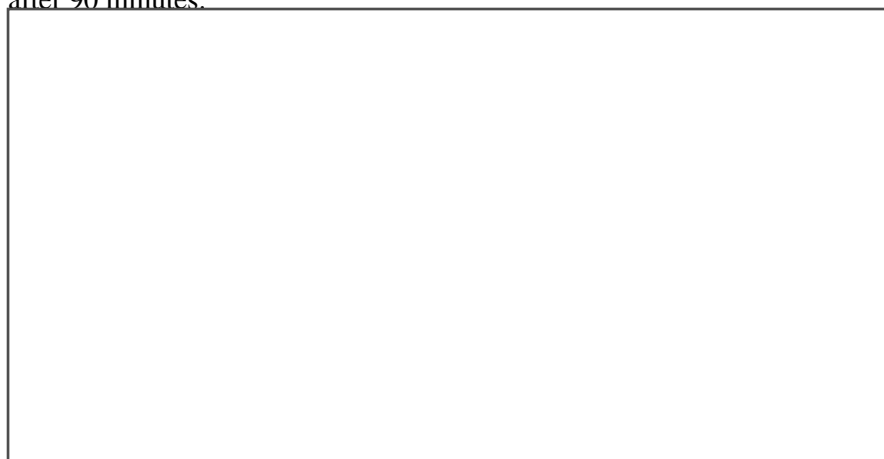
Figure 1.2. Effect of H_2O_2 dosages at pH=5 and $FeSO_4$= 300 mg.L^{-1} on the COD removal from the activated sludge reactor effluent by Fenton's process. Initial soluble COD = 815 mg.L^{-1}, T = 20°C.

Figure 1.3. Effect of varying $FeSO_4$ dosages at pH=5 and H_2O_2=500 mg.L^{-1} on the COD removal from the activated sludge reactor effluent by Fenton's process. Initial soluble COD = 815 mg.L^{-1}, T = 20°C.

Figure 1.4. Effect of pH on the COD removal from the activated sludge reactor effluent during ozonation. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, applied ozone dose = 1.87 g.L^{-1} h, T = 20°C.
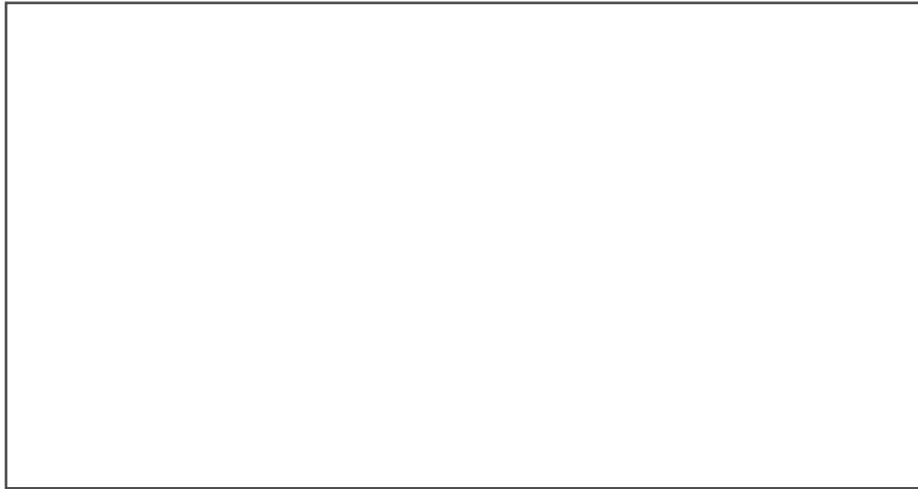
Figure 1.5. Effect of pH on the COD removal from the activated sludge reactor effluent during O_3/UV process. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, applied ozone dose = 1.87 g.L^{-1} h, T = 20°C.

Figure 1.6. Effect of pH on the COD removal from the activated sludge reactor effluent during H_2O_2/UV process. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, H_2O_2=200 mg.L^{-1}, T = 20°C.

Figure 1.7. Effect of H_2O_2 on COD removal from the activated sludge reactor effluent during H_2O_2/UV process. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, pH=2.5, T = 20°C.

O_3/H_2O_2

Combining ozone with hydrogen peroxide to enhance oxidizing ability has been extensively researched recently and is considered to be a promising alternative for refractory organics removal from aqueous solutions (Zhou and Smith, 2002). It was shown that the conjugate base of H_2O_2 at low concentrations could initiate the decomposition of ozone much more rapidly into hydroxyl radicals than with the hydroxide ion (Staehelin and Hoigne, 1982). Therefore, ozonation of the aerobic effluent was performed in the presence of H_2O_2 up to 600 mg.L^{-1}. The COD removal percentages obtained is presented in Figure 1.8 as a function of H_2O_2 concentration. Final COD removal values were obtained as 25%, 24%, 31%, 35%, 42% and 39% for initial concentrations of 100, 200, 300, 400, 500 and 600 mg.L^{-1} H_2O_2, respectively. However, at H_2O_2 concentrations of 600 mg.L^{-1}, COD removal rates began to decrease revealing that inhibition of COD removal may have occurred when H_2O_2 was applied in excess. This optimum or critical value (600 mg.L^{-1}) has also been found by other researchers working on treatment of Penicillin formulation
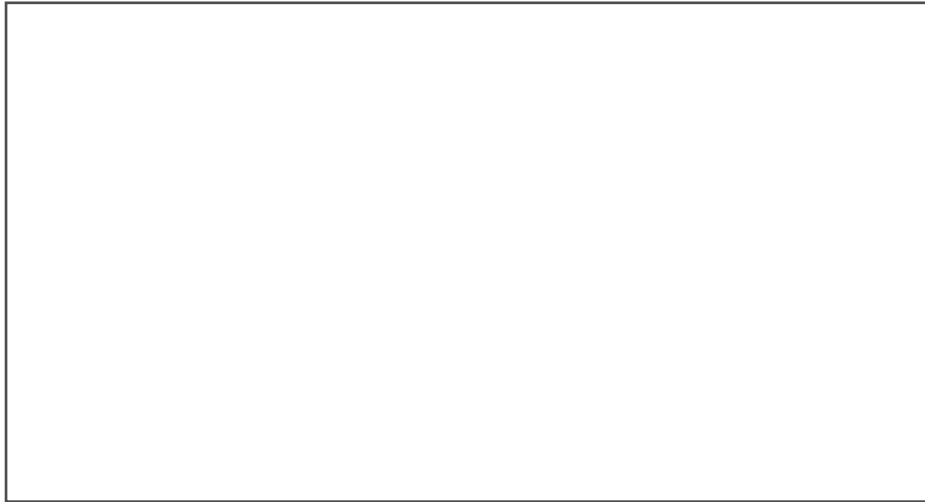
effluent (Arslan-Alaton *et al*., 2004).

Figure 1.8. COD removal rates from the activated sludge reactor effluent at varying initial H_2O_2 concentrations. Experimental conditions: ozonation time = 120 minutes; initial soluble COD 795 mg.L^{-1}; O_3 feed rate = 1.87 g.L^{-1} h; pH sample = 12.0

$O_3/H_2O_2/UV$

Initially the effects of varying pH between 2.5 and 12 were assessed for the UV experiments similar to those conducted for the O_3/UV and H_2O_2/UV processes above to determine the best pH. After identifying the best pH, the UV experiment was carried out with various hydrogen peroxide concentrations in order to determine the best hydrogen peroxide concentrations. Figure 1.9 shows the effect of pH on the COD removal efficiency and it seems that $O_3/H_2O_2/UV$ processes require acidic conditions (pH= 2.5) for optimum COD removal (57%). Figure 1.10 shows the effect of H_2O_2 on COD removal during $O_3/H_2O_2/UV$ process and indicates that a H_2O_2 concentration of 400 mg.L^{-1} achieved the highest COD reduction of 59%.

From the above results, it can be concluded that the combination of $O_3/H_2O_2/UV$ process gives highest COD removal. A comparison of various AOPs has been presented in Table 1.1.

Figure 1.9. Effect of pH on the COD removal from the activated sludge reactor effluent during $O_3/H_2O_2/UV$

process. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, applied ozone dose = 1.87 g.L^{-1} h, H$_2$O$_2$ = 200 mg.L^{-1}, T = 20°C.
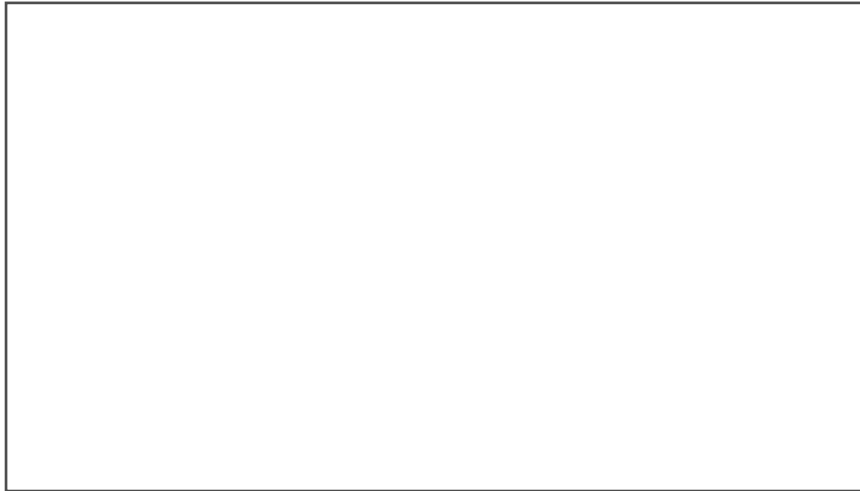
Figure 1.10. Effect of H$_2$O$_2$ dosages on the COD removal from the activated sludge reactor effluent during O$_3$/H$_2$O$_2$/UV process. Experimental conditions; initial soluble COD = 815 mg.L^{-1}, applied ozone dose = 1.87 g.L^{-1} h, pH = 2.5, T = 20°C.

Table 1.1. Results of studied alternatives in terms of COD removal.

Process	COD Removal (%)	H$_2$O$_2$ (mg.L^{-1})	FeSO$_4$ (mg.L^{-1})	O$_3$ (g.L^{-1} h)	pH
Fenton	40	500	600	-	5
O$_3$	41	-	-	1.87	12
O$_3$/UV	43	-	-	1.87	12
O$_3$/H$_2$O$_2$	42	500	-	1.87	12
H$_2$O$_2$/UV	38	300	-	-	2.5
O$_3$/H$_2$O$_2$/UV	59	400	-	1.87	2.5

CONCLUSIONS

Additional treatment of the activated sludge reactor effluent by different AOPs also contributed substantially to overall COD removal of the pharmaceutical wastewater. Among the AOP processes used in this study, the combination process (O$_3$/H$_2$O$_2$/UV) resulted in the highest COD removal (59%) from the activated sludge effluent. Specifically, around 400 mg.L^{-1} of COD was removed in the O$_3$/H$_2$O$_2$/UV process giving a final COD of 300 mg.L^{-1} in the treated effluent. Other AOPs (Fenton, O$_3$, O$_3$/UV, O$_3$/H$_2$O$_2$ and H$_2$O$_2$/UV) showed nearly constant maximum removal with 38 – 43% COD removal. A full cost evaluation should be conducted in future as AOP processes are expensive to install and operate, and confirmation of economic feasibility is therefore required.

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Ozonator

Oxygen Supply

Sample

   A   **B**
  (KI Absorbers 2%)

Vent

Power Supply