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## APPLICATION OF ADVANCED OXIDATION PROCESS (H<sub>2</sub>O<sub>2</sub>/UV) FOR REMOVAL OF ORGANIC MATERIALS FROM PHARMACEUTICAL INDUSTRY EFFLUENT

Pharmaceutical wastewater is one of the major complex and toxic industrial effluents containing little or no biodegradable organic matters. In this study, H<sub>2</sub>O<sub>2</sub>/UV based advanced oxidation process (AOP) was used to remove organic materials from pharmaceutical industry effluent. For the chemical oxygen demand (COD) removal radiation of medium pressure mercury vapor UV lamp was used in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>/UV). Results indicated that the efficiency of COD removal depends on the initial concentration of H<sub>2</sub>O<sub>2</sub>, oxidation time and pH. The efficiency of COD removal at low H<sub>2</sub>O<sub>2</sub> concentration was very low even coupled with UV light, which can be attributed to the low generation of hydroxyl radicals (OH<sup>•</sup>). At high concentration of H<sub>2</sub>O<sub>2</sub> (500 mg/dm<sup>3</sup>) and optimum pH (pH = 4), 87.6% removal efficiency could be achieved during 70 min oxidation. For high concentration of H<sub>2</sub>O<sub>2</sub> (500 mg/dm<sup>3</sup>) at pH 3 and 7, the maximum COD removal efficiency was 28.5% and 15.2% respectively, indicating significant roles of pH and H<sub>2</sub>O<sub>2</sub> concentration in the process of COD removal.

### 1. INTRODUCTION

Pharmaceutical wastewater is characterized by high concentrations of organic matter and toxic pollutants [1]. This wastewater contains mainly agents, solvents used in

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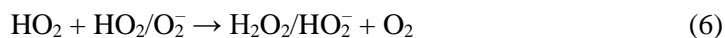
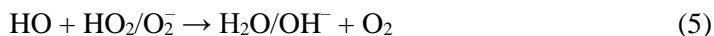
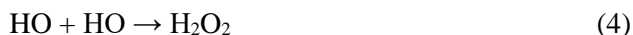
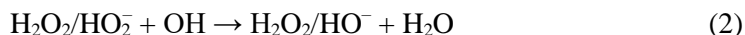
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washing and cleaning processes, and also reactants and catalysts used in manufacturing processes [2]. In many cases, effluents of these industries contain little or no biodegradable organic matters. Therefore, the pollutant loads in terms of biological oxygen demand (BOD) may be negligible and chemical oxygen demand (COD) would be higher than BOD [3]. In fact, many pharmaceutical compounds are only partially removed during biological treatment processes in sewage treatment plants and consequently released into surface waters [4, 5]. For pharmaceutical wastewater treatment, several methods were suggested including anaerobic-aerobic [6] or membrane [7, 8] bioreactors, electrochemical oxidation [9], biochemical combined method [10] and advanced oxidation processes (AOPs) [11–13]. Application of UV process is uncommon for pharmaceutical compounds removal from wastewater. However, many studies on organic pollutant removal from industrial effluents such as pharmaceuticals industry's, focused on UV treatment process in combination with O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>. Such methods are characterized by no byproducts formed and effectiveness for degrading organic matters in aqueous systems [5, 14].

Hydrogen peroxide with ultraviolet photolysis (H<sub>2</sub>O<sub>2</sub>/UV) is one of the most sufficient agents in AOPs for treatment of wastewaters containing toxic organic pollutants [15]. The main reactions of OH<sup>•</sup> generation in H<sub>2</sub>O<sub>2</sub>/UV process are as follows [16, 17]



H<sub>2</sub>O<sub>2</sub>/UV advanced oxidation appears to be the most promising method, in terms of cost-effectiveness and ease of operation [18]. As compared to other AOPs such as chemical oxidation using ozone and ozone/hydrogen peroxide that display problems with off-gas and VOCs, these problems have not been observed in the UV-based AOP [19]. In the present study, applicability of H<sub>2</sub>O<sub>2</sub>/UV oxidation for treating pharmaceutical effluents from drug manufacturing plants producing various antiseptics and disinfectant solutions was tested under laboratory conditions.

## 2. MATERIALS AND METHODS

### 2.1. CHARACTERISTICS OF RAW WASTEWATER AND SAMPLING

Pharmaceutical wastewater was a real pharmaceutical effluent from a pharmaceutical mill situated in Kermanshah industrial town (West Iran). Samples were collected

from the entrance of treatment plant, prior to any treatment processes. Samples were shipped into 10 dm<sup>3</sup> drums and stored in a refrigerator at 4 °C before the experiments. Some characteristics of the studied wastewater are given in Table 1.

Table 1  
Characteristics of studied wastewater

Parameter	Value
BOD <sub>5</sub> , mg/dm <sup>3</sup>	240
COD, mg/dm <sup>3</sup>	1580
BOD <sub>5</sub> /COD	0.16
TDS, mg/dm <sup>3</sup>	757
TSS, mg/dm <sup>3</sup>	103
pH	7.8
EC, μS/cm	297

## 2.2. OXIDATION REACTOR

Figure 1 shows a schematic of a UV/H<sub>2</sub>O<sub>2</sub> reactor. A custom-made reactor made of Plexiglas with 2 dm<sup>3</sup> capacity equipped with a medium pressure (MP) UV lamp with a 254 nm maximum wavelength and intensity of 50 W (0.315 W/cm<sup>2</sup>) housed inside a quartz box 6 cm in diameter was used for all irradiations.

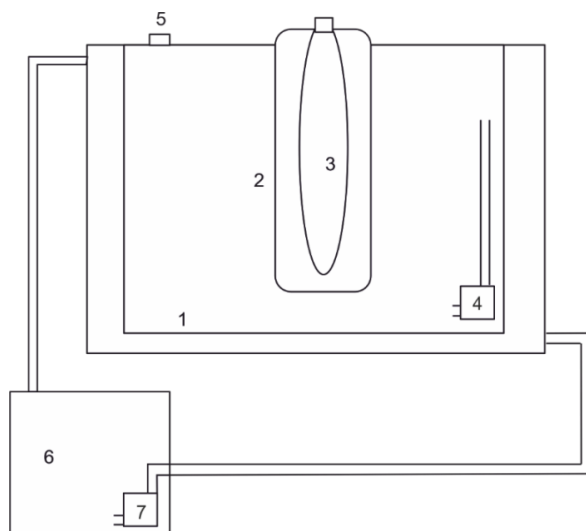


Fig. 1. Scheme of the experimental setup:

- 1 – reactor, 2 – quartz cover, 3 – UV lamp, 4 – circulator pump,  
5 – chemicals injection vessel, 6 – cooling water, 7 – cooling water circulator

To avoid any energy escape, the reactor was covered with aluminum foil sheet. In order to establish equalized conditions throughout the reactor, a circulating pump was used inside the reactor with  $Q_{\max} = 300 \text{ dm}^3/\text{h}$  and  $H_{\max} 0.6 \text{ m}$ . A cooling water flow surrounding the reactor was used to control the temperature inside the reactor.

### 2.3. CHEMICALS AND REACTIONS

The experimental analysis was made according to standard methods [20]. COD tests were performed as recommended by the closed reflux method 5220-C. Merck analytical quality chemicals such as hydrogen peroxide 35% ( $\text{H}_2\text{O}_2$ ), sodium hydroxide ( $\text{NaOH}$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were used in preparation of reagents. The pH was measured by a Jenway 3040 brand pH-meter.

### 2.4. EXPERIMENTAL PROCEDURE

The main objective of this study was to evaluate the performance of advanced oxidation process in oxidizing of refractory organic matter in pharmaceutical industry sewage. Complex organic compounds can be decomposed into simpler compounds by the oxidation process followed by adsorption techniques. Laboratory scale experiments involved treating the pharmaceutical wastewater by  $\text{H}_2\text{O}_2/\text{UV}$  and consequently filtration the oxidized wastewater through granular activated carbon as adsorbent material to remove the COD in a batch system. After turning on the UV lamp, required amount of  $\text{H}_2\text{O}_2$  (50, 200, 500  $\text{mg}/\text{dm}^3$ ) was injected into the reactor at various pH (3, 4, 7) and the sampling was done during 70 min contact time at 10 min intervals.

## 3. RESULTS AND DISCUSSION

The use of  $\text{H}_2\text{O}_2$  in conjunction with UV radiation enhances the degradation of organic compounds due to the contribution of  $\text{OH}^{\bullet}$  radicals generated from the direct photolysis of  $\text{H}_2\text{O}_2$ , i.e. with a quantum yield of two  $\text{OH}^{\bullet}$  radicals formed per quantum of radiation which are absorbed so as to oxidize pharmaceutical compounds. The study of the effect of oxidation conditions such as pH, initial  $\text{H}_2\text{O}_2$  concentration and oxidation time on oxidation performance in COD removal revealed the results described in the following chapters.

### 3.1. EFFECT OF pH

pH is a very effective factor in advanced oxidation processes [21]. Alkaline conditions have been reported unsuitable for such processes [22, 23]. The proper solution for

this process was slightly acidic. Hydroxyl radicals formed in the previous step would subsequently hydrolyse to water molecules under very strong acidic conditions. On the other hand, in slightly acidic and neutral solutions, bonds in  $\text{H}_2\text{O}_2$  molecules cannot be broken to produce hydroxyl radicals. Thus the optimum pH was found experimentally. pH values of 3, 4 and 7 were considered for other parameters being constant.

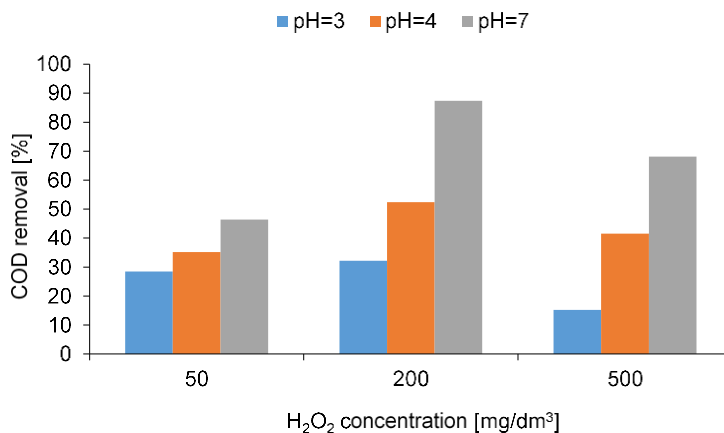


Fig. 2. Effect of pH on  $\text{H}_2\text{O}_2$ /UV oxidation performance

Figure 2 shows the effect of pH on COD removal. In general, it increased at low pH values. However, for  $\text{pH} < 4$ , the efficiency reduced sharply. pH 4 was found the optimum one for  $\text{H}_2\text{O}_2$ /UV process with 87.6% COD removal. From the study, it can be concluded that at pH 7, the formation of  $\text{OH}^\bullet$  radicals is not possible due to lack of  $\text{H}_2\text{O}_2$  dissociation which occurs at lower pH values. On the other hand, organic compounds dissociate rapidly in the presence of  $\text{OH}^\bullet$  radicals at high concentration, and UV radiation.  $\text{H}_2\text{O}_2$  rapidly hydrolyses at  $\text{pH} < 3$ , leading to formation of lower amounts of  $\text{OH}^\bullet$  radicals in comparison with those at pH 4. For this reason, the removal efficiency of organic compounds decreases significantly and reaches 46.4% after 70 min reaction at  $\text{H}_2\text{O}_2$  concentration of  $50 \text{ mg/dm}^3$ .

### 3.2. EFFECT OF $\text{H}_2\text{O}_2$ CONCENTRATION AND CONTACT TIME

With UV/ $\text{H}_2\text{O}_2$  advanced oxidation, organic matters will be degraded by UV direct photolysis and the  $\text{OH}^\bullet$  radical oxidation pathway [24]. To determine the effect of  $\text{H}_2\text{O}_2$  concentration, its range ( $50, 200$  and  $500 \text{ mg/dm}^3$ ) was considered as variable and other parameters as constant. Experiments were performed for various contact times (10, 20, 30, 40, 50, 60 and 70 min). Figure 3 presents the effect of  $\text{H}_2\text{O}_2$  concentration on the COD removal. A significant improvement of degradation efficiency was achieved when

the  $\text{H}_2\text{O}_2$  concentration was increased from 50 to 500  $\text{mg}/\text{dm}^3$  due to increased availability of  $\text{OH}^\bullet$  radicals in the oxidative environment. As  $\text{H}_2\text{O}_2$  concentration and the amount of generated  $\text{OH}^\bullet$  radicals decreased gradually, the dissociation rate of pollutants also decreased.

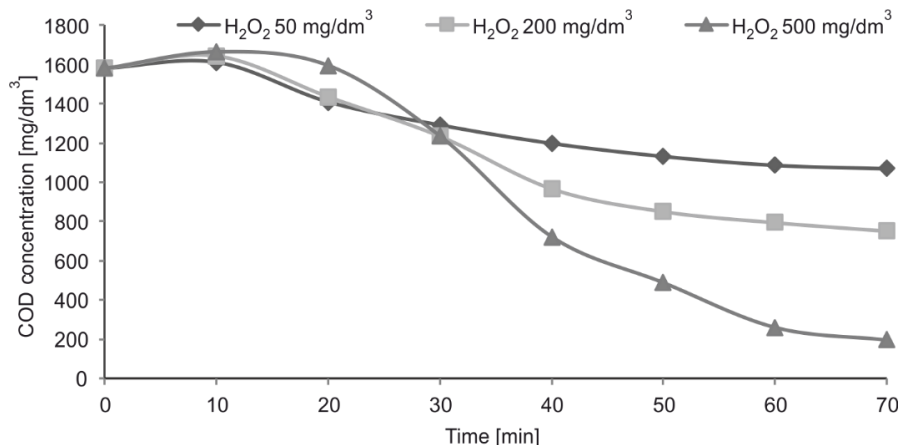


Fig. 3. Effect of  $\text{H}_2\text{O}_2$  concentration and contact time on the COD removal efficiency at pH 4

A relative increase in the COD up to 20 min of onset of oxidation in all trials was recorded. This may be due to residual concentration of  $\text{H}_2\text{O}_2$  that has oxidized dichromate resulting in the increase of COD value. With increasing the amount of  $\text{H}_2\text{O}_2$ , the COD removal increased. Maximum removal of COD was achieved in 500  $\text{mg}/\text{dm}^3$  of  $\text{H}_2\text{O}_2$ . According to Jung et al. study on amoxicillin removal by UV and UV/ $\text{H}_2\text{O}_2$  processes [18] only 10% removal was achieved after 80 min of UV irradiation with the addition of 0.5 mM  $\text{H}_2\text{O}_2$ . But when  $\text{H}_2\text{O}_2$  concentration increased to 10 mM, TOC removal increased over 50% after 80 min irradiation [18].

### 3.3. KINETIC STUDY

To determine the effect of hydrogen peroxide concentration on the rate constant ( $k$ ) of COD removal, experiments were conducted at various  $\text{H}_2\text{O}_2$  concentration (50, 200 and 500  $\text{mg}/\text{dm}^3$ ),  $\text{COD}_0 = 1580 \text{ mg}/\text{dm}^3$ ,  $\text{pH} = 4.0$  and  $T = 25 \pm 1 \text{ }^\circ\text{C}$ . The results are shown in Fig. 4. The value of the rate constant  $k$  ( $\text{min}^{-1}$ ) was determined by fitting the experimental data to the following equation [15, 25]:

$$\ln \frac{C_0}{C_t} = kt \quad (7)$$

where  $C_0$  – initial COD concentration at  $t = 0$  ( $\text{mg}/\text{dm}^3$ ),  $C_t$  = COD concentration at the moment  $t$  ( $\text{mg}/\text{dm}^3$ ),  $k$  – pseudo-first order rate constant ( $\text{min}^{-1}$ ),  $t$  – time of reaction (min).

The pseudo-first order kinetic model seems to be well applicable to the COD removal under given conditions (Fig. 4). The estimated values of  $k$  are given in Table 2.

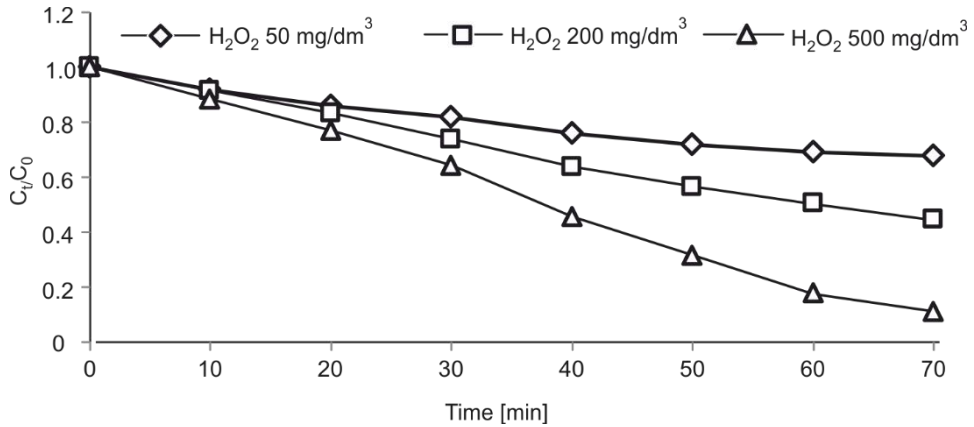


Fig. 4. First-order representation of COD removal ( $C_t/C_0$ ) versus time for various  $H_2O_2$  concentrations (pH = 4)

Table 2

Values of  $k$  for COD removal for various initial  $H_2O_2$  concentrations ( $t = 70$  min, pH = 4)

COD [mg/dm <sup>3</sup> ]		$H_2O_2$ [mg/dm <sup>3</sup> ]	$\ln \frac{C_0}{C_t}$	$k$ [min <sup>-1</sup> ]
Initial	Final			
1580	1071	50	0.38883	0.00555
1580	725	200	0.74244	0.01060
1580	196	500	2.08706	0.02981

The value of  $k$  increases upon increasing initial  $H_2O_2$  concentrations. In other word, the rate constant of COD removal increased with the increase of  $H_2O_2$  concentration similar to the results obtained by Cristtenden et al. [17]. Also according to Jung et al. [18] study on removal of amoxicillin by UV and UV/ $H_2O_2$  processes, the degradation rate of amoxicillin fitted pseudo first order kinetics, and the rates increased up to six fold with increasing  $H_2O_2$  addition at 10 mM  $H_2O_2$  compared to direct photolysis (UV only). The values of  $k$  for various initial  $H_2O_2$  concentrations (50, 200 and 500 mg/dm<sup>3</sup>) are given in Table 2, which shows that when  $OH^\bullet$  radicals efficiently are available, a maximum rate can be observed. Similar results reported Mohey El-Dein et al. [26] in the study of kinetic model for the azo dye Reactive Black 5 and Beikmohammadi et al. [27] in the decolorization of Yellow-28 Azo dye by UV/ $H_2O_2$  process.

#### 4. CONCLUSIONS

Applicability of H<sub>2</sub>O<sub>2</sub>/UV advanced oxidation process for COD removal from a pharmaceutical industry effluent was investigated and suitable pH and H<sub>2</sub>O<sub>2</sub> concentration for operation have been determined. pH 4 and H<sub>2</sub>O<sub>2</sub> concentration 500 mg/dm<sup>3</sup> were found as optimum ones resulting in 87.6% COD removal. A detail kinetic modeling was developed to understand the mechanisms and kinetics of the COD removal by the technique used. The results showed that the initial H<sub>2</sub>O<sub>2</sub> concentration was the main factor strongly influencing the kinetic rate constant. H<sub>2</sub>O<sub>2</sub>/UV advanced oxidation process operated in suitable condition is suggested as an effective method for the treatment of pharmaceutical effluent.

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