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Determination of Effective Parameters on Removal of Organic Materials from Pharmaceutical Industry Wastewater by Advanced Oxidation Process (H_2O_2/UV)

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Background & Aims of the Study: Pharmaceutical wastewater is one of the major complex and toxic industrial effluents that contain little or no biodegradable organic matters.

Materials & Methods: In this study, H_2O_2/UV base advance oxidation process (AOP) was used to remove organic materials from pharmaceutical industry effluent. Experiments were conducted for the chemical oxygen demand (COD) removal using medium pressure mercury vapor UV lamp coupled with hydrogen peroxide (H_2O_2/UV).

Results: Results indicated that the efficiency of COD removal depends on the concentration of initial H_2O_2, oxidation time and pH as well. The efficiency of COD removal in low H_2O_2 concentration was very low even in coupled with UV light, which can be attributed to the low hydroxyl radicals ($^{\bullet}OH$) generation. In high concentration of H_2O_2 (500 mg/L) and optimum pH (pH=4), 87.496% of removal efficiency could be achieved during 70 minutes of oxidation time.

Conclusions: For high concentration of H_2O_2 (500 mg/l) in pH 3 and 7, the maximum COD removal efficiency was 28.5% and 15.2% respectively, indicating significant roles of pH and H_2O_2 concentration in oxidation efficiency of H_2O_2/UV process in removing the COD.

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Background

Pharmaceutical wastewater is characterized by high concentrations of organic matter and toxic pollutants (1). This wastewater contains the main agents and solvents which were used in washing and cleaning processes; 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 the 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 different alternatives were suggested include anaerobic–aerobic (6) or membrane (7,8) bioreactors, electrochemical oxidation (9), biochemical combined method (10) and advanced oxidation processes (AOPs) (11-13). The application of UV process is uncommon for pharmaceutical compounds removal from wastewater. However, many studies have been conducted about the organic pollutant removal from industrial effluents such as pharmaceutical industries, focused on UV treatment process in combination with O_3 or H_2O_2, because of no byproducts formation and being effective process for degrading organic matters in aqueous systems (5,14).

Hydrogen peroxide in combination with ultraviolet photolysis (H_2O_2/UV) is one of the most effective methods in AOPs for treatment of wastewaters which are contain the toxic organic pollutants (15). The main reactions of •OH generation in H_2O_2/UV process is shown as follows (16,17):

H_2O_2/HO^{2-} +hν → $2HO^{\bullet}$ (1)

H_2O_2/HO^{2-} +OH → H_2O_2/HO^{-} + H_2O (2)

H_2O_2 + HO^{2-}/O_2 → HO + H_2O/OH^{-} + O_2 (3)

HO +HO → H_2O_2 (4)

HO + HO_2/O_2^{-} → H_2O/OH^{-} +O_2 (5)

HO_2 + HO_2/O_2^{-} → H_2O_2/ HO_2^{-} + O_2 (6)

H_2O_2/UV advanced oxidation method 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 by ozone and ozone/hydrogen peroxide with off-gas and VOCs problems; they have not been observed in the UV-based AOP (19).

Aims of the study:

In this study, the applicability of H_2O_2/UV oxidation for treating pharmaceutical effluents from a drug manufacturing plant that produce various antiseptics and disinfectant solutions was tested under laboratory conditions.

Materials & Methods

Characteristics of raw wastewater and Sampling

The pharmaceutical wastewater was a real sample from a pharmaceutical mill situated in Kermanshah industrial town, Iran. Samples were collected from the entrance of treatment plant, prior to any treatment processes. Samples were shipped into 10 L drums and stored in a refrigerator at 4°C before the experiments. Some characteristics of the samples are tabulated in Table 1.

Table1) Characteristics of studied wastewater

Parameter	Value
BOD_5 (mg/L)	240
COD (mg/L)	1580
BOD_5/COD	0.16
TDS(mg/L)	757
TSS (mg/L)	103
pH	7.8
EC (μmoh/cm^2)	297

Oxidation reactor

Figure 1 shows a schematic of UV/H_2O_2 reactor. A custom-made reactor of Plexiglas with 2 liter capacity, included a medium pressure (MP) UV lamp with a 254 nm maximum wavelength and intensity of 50-W (0.315 W/cm^2) housed inside a quartz box with 6 cm in diameter used for all irradiations. To avoid energy wasting, 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 lit/h and, H_{max} 0.6 m. A cooling water flow was used to surround the reactor in order to control the inside temperature of the reactor.

Chemicals and reactions

All the experimental analysis was made according to standard methods (20). COD tests were performed as recommended in the closed reflux method 5220-C. Merck analytical quality chemicals such as hydrogen peroxide %35 (H_2O_2), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4), were used for preparation of reagents. The pH was measured by a Jenway 3040 brand pH-meter.

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 broke down into simpler one by the oxidation process using adsorption techniques to remove. Laboratory scale experiments involved treating the pharmaceutical wastewater by H_2O_2/UV process and consequently filtration the oxidized wastewater by granular activated carbon as adsorbent material to remove the COD in a batch system. After turning on the UV lamp, required amount of H_2O_2 injected into the reactor and at intervals of 10 minutes, the sampling was done.

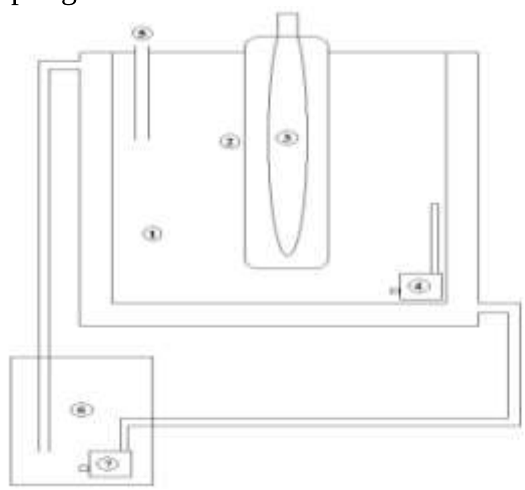

Figure 1) 1- Reactor, 2- Quartz cover, 3- UV lamp, 4- circulator pump, 5- chemicals injection vessel, 6- cooling water, 7- cooling water circulator

Results

The use of H_2O_2 in conjunction with UV, enhances the degradation of organic compounds due to the contribution of OH• radicals generated from the direct photolysis of H_2O_2, i.e. with a quantum yield of two OH• 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 H_2O_2 concentration and oxidation time on oxidation performance in COD removal revealed the following results:

pH

pH is a very effective factor in advanced oxidation processes (21). Alkaline conditions have been reported as an unsuitable things for advanced oxidation processes (22,23).In order to study the effect of pH on the process, pH range (3,4,7) was considered as variable and other parameters as constant. Figure 2 shows the effect of pH variations on COD removal. In general, the COD removal increased in acidic condition (low pH values). However, in pH<4, the efficiency reduced sharply. pH 4 was found the optimum pH for H_2O_2/UV process with 87.6% COD removal.

COD removal by H_2O_2 concentration with time

With UV/H_2O_2 advanced oxidation, organic matters will be degraded by UV direct photolysis and the OH radical oxidation pathway (24). To determine the effect of H_2O_2 concentration, its range (50, 200 and 500 mg/L) was considered as variable and other parameters as constant. Some experiments were performed at different contact times (10, 20, 30, 40, 50, 60 and 70 minutes). Figure 3 presents the effect of H_2O_2 concentration on the COD removal. In general the COD removal increased with time. It was also observed that through increasing H_2O_2 concentration from 50 to 500 ml/L, COD removal increased.

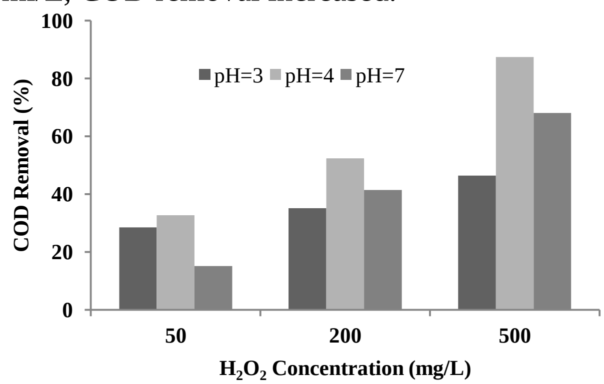

Figure.2) Effect of pH on H_2O_2/UV Oxidation performance

Kinetic study

To determine the effect of hydrogen peroxide concentration on the kinetic constants (k_{ap}) of COD removal, some experiments were designed at different H_2O_2 concentration (50, 200 and 500 mg/L) and condition of COD_0 = 1580 mg/L and pH=4.0 and T=25±1 °C. The results are shown in Figure 5. The value of the parameter k (min^{-1}) was determined by fitting the experimental data to Eq. 1 and 2 (25):

$$ln\frac{C_t}{C_0} = -kt \qquad (1$$

$$k = \frac{1}{t}ln\frac{C_0}{C_t} \qquad (2$$

Where:
C_0 = Initial COD concentration at instant t=0 (mg/L)
C_t = COD concentration at instant t (mg/L)
k = First order rate constant (min^{-1})
t = Time of reaction (min)
This is known as a kinetic equation for a first-order reaction. The pseudo-first-order kinetic model seems to be well applicable to the COD removal under the given test conditions (Figure 4). The estimated values of k are given in Figure 5.

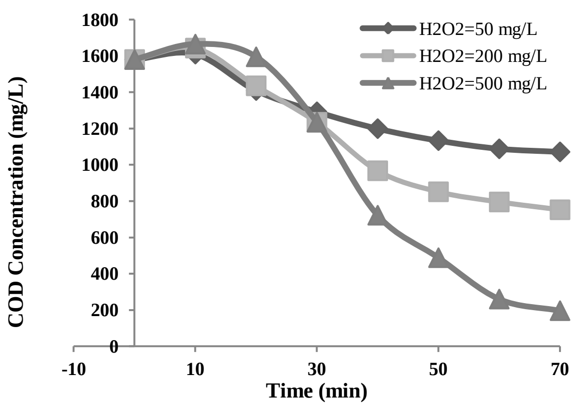

Figure 3) Effect of H_2O_2 concentrationand contact time on the COD removal efficiency in pH 4

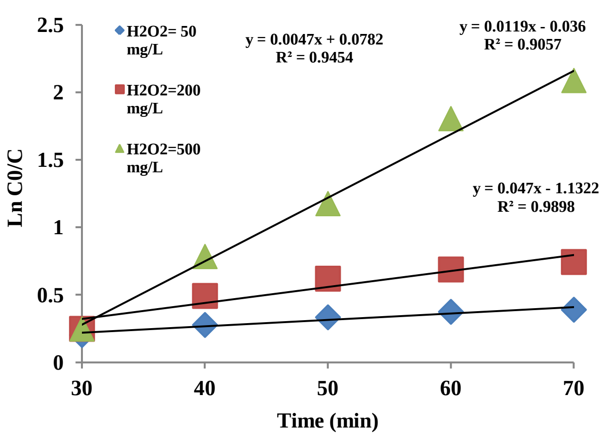

Figure 4) First-order kinetics of various H_2O_2 concentrations (pH=4)

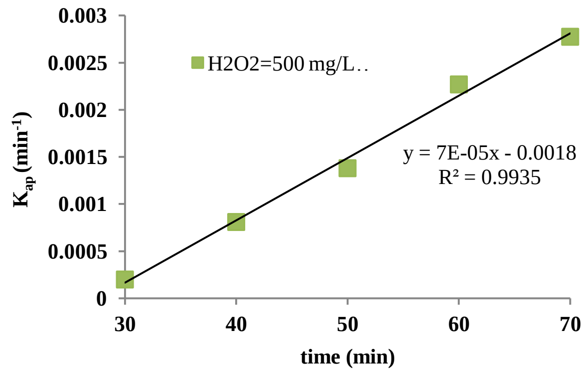

Figure 5) Plot of K for COD removal in initial H_2O_2 = 500 mg/L and pH=4

Discussion

Applicability of H_2O_2/UV advanced oxidation process for COD removal from a pharmaceutical industry effluent was investigated, suitable pH and H_2O_2 concentration for operation were determined. pH 4 and 500 mg/L H_2O_2 concentration was found an optimum 87.6% COD removal result. A relative increase in the COD up to 20 minutes of onset of oxidation in all trials was recorded. This may be due to the residual concentration of H_2O_2 that has oxidized dichromate result in the increase of COD value. Increasing the amount of H_2O_2 resulted in the COD removal increase. Maximum removal of COD was achieved in 500 mg/L of H_2O_2. According to Jung et al. study on amoxicillin removal by UV and UV/H_2O_2 processes only 10% removal was achieved after 80min of UV irradiation with the addition of 0.5 mM H_2O_2. But when H_2O_2 concentration increased to 10 mM, TOC removal increased to higher than 50% after 80 min irradiation time (18). 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_2O_2 concentration was the main factor that affect the kinetic constant K. It can be observed that the value of k increases linearly with oxidation time (figure 5). The k 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). A plot of K as a function of UV intensity Io for (H_2O_2)=500 mg/L (Figure 5) gives a straight line, which shows that when OH radicals efficiently are available, a maximum rate can be observed and K value increases with time. Similar results was showed in Mohey El-Dein et al. study for kinetic model of the azodye Reactive Black 5 by UV/H_2O_2 process (26). The success key of the study was high efficiently removal of the COD. So H_2O_2/UV advanced oxidation process operated in suitable condition mentioned is suggested as an effective method for the treatment of pharmaceutical effluent of Bakhtarbioshimi industry in Kermanshah, Iran.

Conclusion

Briefly, we conclude that advanced Oxidation Process (H_2O_2/UV) has high efficiency in the removal of organic matter from organic Materials from Pharmaceutical Industry Wastewater. For high concentration of H_2O_2 (500 mg/L) in pH 3 and 7, the maximum COD removal efficiency was 28.5% and 15.2% respectively, indicating significant roles of pH and H_2O_2 concentration in oxidation efficiency of H_2O_2/UV process in removing COD.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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