Catalytic wet oxidation of high concentration pharmaceutical wastewater with Fe^{3+} as catalyst

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ABSTRACT

Catalytic wet oxidation of high concentration pharmaceutical wastewater with Fe^{3+} as catalyst was carried out in a batch reactor. Results showed that the degradation of pharmaceutical wastewater was enhanced significantly by Fe^{3+}. The effects of reaction parameters, such as the catalyst dose, reaction temperature, time, and initial oxygen pressure, were discussed. The chemical oxygen demand (COD) removal increased with the increases of catalyst dose, temperature, time and oxygen supply. With the initial COD 34,000–35,000 mg/L, approximately 70% COD removal can be achieved under the conditions of catalyst 1.0 g and oxygen pressure 1.0 MPa at 250 °C after 60 min. The results of kinetic studies showed that two reaction steps existed in this oxidation process, which followed an apparent first-order rate law. This process provides an effective approach for the pretreatment of high concentration pharmaceutical wastewater.

Key words | catalyst, catalytic wet oxidation, Fe, pharmaceutical wastewater

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INTRODUCTION

Large amounts of pharmaceutical wastewater containing hazardous organic pollutants were generated due to the rapid development of the pharmaceutical industry in the past few decades (Zwiener & Frimmel 2000). The treatment of pharmaceutical wastewater has attracted much attention due to its rapid increase of emission amount and high hazardous risk. Because the organic pollutants in pharmaceutical wastewater are always toxic and non-biodegradable, conventional biological methods were not suitable for them. In addition, the heavy metal ions in synthetic pharmaceutical wastewater make this wastewater one of the most toxic industrial wastewaters (Huerta et al. 2011; Jelic & Gros 2011). Thus, a suitable treatment method is highly desirable.

Recently, advanced oxidation processes (AOPs) are considered one of the more effective methods (Yu et al. 2013; Bustillo & Mehrvar 2014). In advanced oxidation processes, the generation of free radicals (·OH) leads to the effective decomposition of organic pollutants (Ghafoori et al. 2013). Notably, wet oxidation (WO) is especially effective and promising for the treatment of pollutants, including benzene, biphenyls, amines, and pyridine (Savage et al. 1995; Veriansyah et al. 2007). This process is performed under high temperature (150–350 °C) and pressure (2.0–15.0 MPa) conditions in gaseous oxygen or air. During this process, the liquid-phase oxidation of toxic or poorly biodegradable compounds occurs and produces intermediates. CO_2 and H_2O are final products of degradation. Water is used as the reaction medium in this process. Therefore, WO is considered a green and environmentally friendly technology.

Catalytic wet oxidation (CWO) has been shown to be an effective and environmentally friendly way to treat many types of organic wastewater (Grosjean et al. 2010). The use of catalysts makes the process more attractive by achieving high conversion at a considerably lower temperature and lower pressure. This process can remove a high proportion of the organic pollutants and consequently improve the B/C ratio (biological oxygen demand to chemical oxygen demand) in the wastewater; thus, biological methods could serve as a complementary process to CWO. Diverse solid catalysts have been used for the CWO treatment of various organic compounds in wastewater (Luck 1996). However, the problems with solid catalysts include low efficiency, volume reduction, high cost, secondary pollution, etc. By contrast, homogeneous catalysts have higher efficiency. $CuSO_4$, $MnSO_4$, and $NiSO_4$ have been reported as homogeneous catalysts that can be used in the CWO process. However, these catalysts involve heavy metal ions, which

are unsafe. Additionally, it has been extensively reported that Cu^{2+} is highly efficient in the CWO of organic pollutants, and this catalyst has been used in industrial applications. Fe has been reported as a regent in the Fenton oxidation process, which is a free radical reaction. Fe can also be used as a catalyst in CWO, which is also a free radical reaction. Therefore, Fe is assumed as an ideal homogeneous catalyst which is suitable for the CWO process.

The aim of this work was to investigate the CWO of high concentration pharmaceutical wastewater with Fe^{3+} as a catalyst. Experiments were conducted by varying the catalyst dosage, reaction temperatures and times, and oxygen supply to investigate the effects of reaction parameters and the kinetics.

MATERIALS AND METHODS

Materials

The raw pharmaceutical wastewater was from a synthetic pharmaceutical factory. No specific permissions were required for these activities. Because the factory has very complete wastewater treatment system, in contrast, new treatment process aiming to reduce the treatment cost is very welcomed. The field studies did not involve endangered or protected species. The characteristics of the raw wastewater were as follows: chemical oxygen demand (COD) of 34,000–35,000 mg/L and pH of 4.5–5.5. The raw wastewater was used without any treatment. The main pollutants in the wastewater included benzene, phenolic compounds, such as phenol, Chlorinated phenols, etc. $Fe_2(SO_4)_3$, as the source of Fe^{3+}, was used as the catalyst. The analytical chemicals used in the experiments were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The gaseous oxygen used as the oxidant was commercial industrial gas. All chemicals were used as received without further purification.

Experimental procedure

All experiments were conducted in a titanium autoclave with an internal volume of 5.0 L. The autoclave was purchased from Yantai Keli Chemical Equipment Co., Ltd, China. A diagram of the reactor is shown in Figure 1. The typical procedure was as follows. The pharmaceutical wastewater (1 L) was placed into the reactor, which was then sealed and charged with oxygen gas at the desired pressure (0.6–1.2 MPa). The reactor was heated to the desired
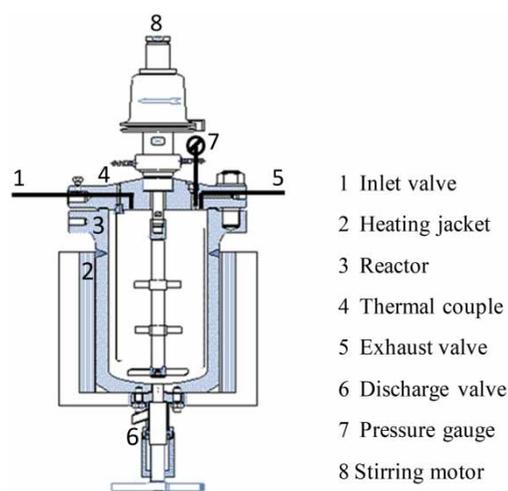

Figure 1 │ Experimental setup of the wet oxidation.

1 Inlet valve
2 Heating jacket
3 Reactor
4 Thermal couple
5 Exhaust valve
6 Discharge valve
7 Pressure gauge
8 Stirring motor

reaction temperature (220–250 °C), and when that temperature was reached, the reaction time started. Once the desired reaction time had elapsed, the reactor was removed from the oven and allowed to cool to room temperature. Generally, approximately 2 h were required to heat the liquid in the reactors to the reaction temperature, and the pressure in the reactor corresponded to the saturated vapour pressure of water at the liquid temperature. Each experiment was conducted at least twice.

Analysis methods

The pH was measured with a pH meter (pH-201, Hanna Corporation, Italy). COD was measured with a COD analyser (HACH-DR1010).

RESULTS AND DISCUSSION

Effect of catalyst dose on COD removal

The catalyst amount was varied from 0 to 2.0 g, while the other parameters remained constant, including a reaction time of 60 min, temperature of 250 °C, and initial oxygen pressure of 1.0 MPa. The results in Figure 2 illustrate that Fe^{3+} has a great effect on COD removal. Even with a catalyst amount of 0.5 g, the COD removal rate increased significantly. As the catalyst amount increased, the COD removal increased gradually. However, as the amount of added catalyst increased from 1.0 to 2.0 g, the COD removal did not change as much. As we know, WO is a free radical reaction. Even with small amounts of catalyst, the effect of
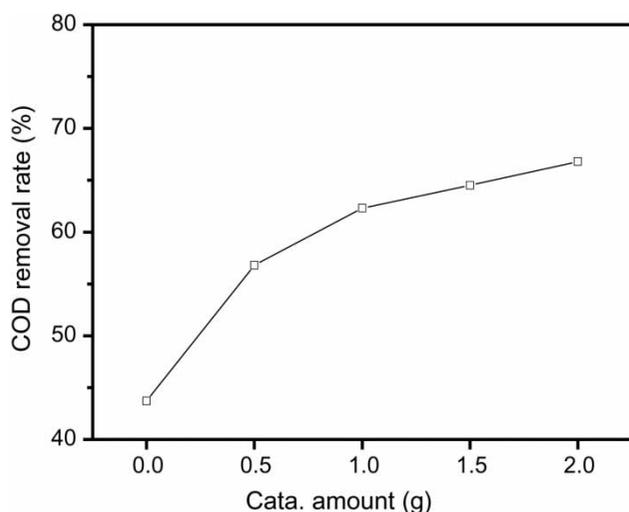
Figure 2 │ Effect of catalyst dose on COD removal (60 min, 250 °C, initial oxygen pressure 1.0 MPa).

Figure 3 │ Effect of reaction temperature on COD removal (60 min, initial oxygen pressure 1.0 MPa, catalyst 1.0 g).

Fe^{3+} was very clear. The reason for the slow improvement in COD removal using large amounts of catalyst may be that the electron capture and loss processes were influenced when extra Fe^{3+} was added, which then influenced the production of free radicals. To avoid the consumption of the catalyst, 1.0 g of catalyst was used in the subsequent experiments. In Fenton oxidation process, ferrous iron was used as a catalyst for the production of free radical reaction. Ferrous iron is oxidized to ferric iron: $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^-OH + \cdot OH$; ferric iron is reduced by $O_2^{\cdot-}$ and is then changed to ferrous iron: $O_2^{\cdot-} + Fe^{3+} \rightarrow Fe^{2+} + O_2$. The reaction mechanism for this process is probably due to the catalytic free radical reaction with the addition of Fe^{3+}, which is similar with the Fenton oxidation.

Effect of the reaction temperature on COD removal

The effect of the reaction temperature (in the range of 220–250 °C) on the WO of pharmaceutical wastewater was investigated with a reaction time of 60 min and a catalyst amount of 1.0 g. As shown in Figure 3, when the temperature increased, the oxidation reaction in terms of COD removal accelerated, as expected with consideration of the Arrhenius law in the kinetic regime. The COD removal was relatively low when the temperature was below 220 °C, indicating that this reaction requires a high temperature for the oxidation of pollutants in wastewater. Theoretically, COD removal can be very efficient at high reaction temperatures with a sufficient amount of oxidation agent. However, even at 250 °C for 60 min, the COD removal was still
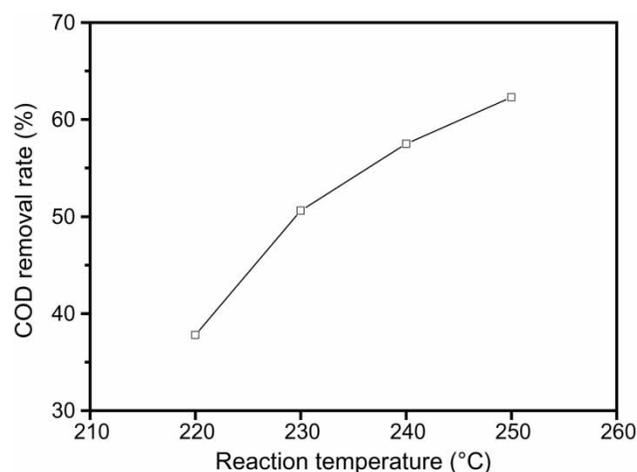
incomplete, and the COD removal efficiency was 60–70%. It has been reported that carboxylic acids with small molecular weights, such as formic acid or acetic acid, are not easily oxidized under hydrothermal conditions (Jin et al. 2012). In addition, some of the byproducts formed during the degradation of organic compounds cannot be oxidized and remain in the final solution. As a pre-treatment method for pharmaceutical wastewater with high concentrations of pollutants, a reaction temperature of 250 °C can be considered satisfactory for COD removal for energy and efficiency reasons. Therefore, 250 °C was adopted as the temperature in the subsequent experiments when other operating parameters were considered.

Effect of the reaction time on COD removal

Figure 4 shows the effect of the reaction time on COD removal at 250 °C with an initial oxygen pressure of 1.0 MPa and 1.0 g of catalyst. The results showed that COD removal efficiency is very high, even with a reaction time of 30 min, which suggests that the CWO processes are highly efficient. This behaviour was expected, as extensive studies have reported that the WO process is a free radical reaction. The COD removal increased gradually as the reaction time increased from 60 min to 120 min. Based on the energy costs and efficiency, a reaction time of 60 min is sufficient.

Effect of oxygen supply on COD removal

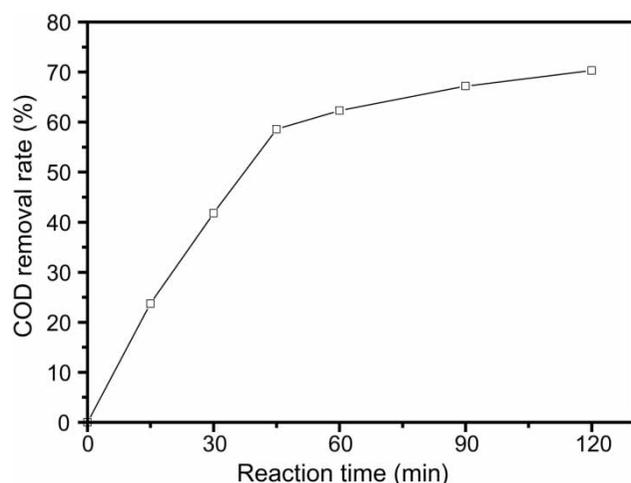Four different initial oxygen pressures, 0.6, 0.8, 1.0, and 1.2 MPa, were tested in the reactions at 250 °C for 60 min

Figure 4 | Effect of reaction time on COD removal (250 °C, initial oxygen pressure 1.0 MPa, catalyst 1.0 g).

with 1.0 g of catalyst to study the effect of the oxygen supply on COD removal. The theoretical stoichiometric amount is defined as the amount of oxygen required to chemically mineralize all the pollutants in the wastewater, and it is related to the COD value. An oxygen pressure of 0.6 MPa was almost 100% of the theoretical requirement for oxygen. As shown in Figure 5, the COD removal, not surprisingly, increased as the oxygen supply increased because the concentration of dissolved oxygen in the liquid phase is proportional to the corresponding oxygen pressure.

However, even when the oxygen supply was greater than the theoretical demand for complete chemical mineralization of all pollutants, the COD removal was still approximately 70%. This finding is likely because the
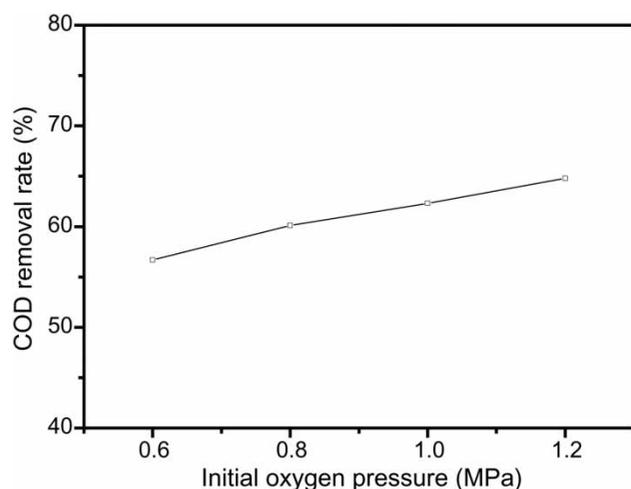

Figure 5 | Effect of oxygen supply on COD removal (60 min, 250 °C, catalyst 1.0 g).

removal of COD is the overall result of the oxidation reaction and thermolysis (Li et al. 1991). Additionally, some of the byproducts, e.g. carboxylic acids with small molecular weights, such as formic acid or acetic acid, are not easily oxidized under hydrothermal conditions. However, as a pretreatment method, a COD removal of approximately 70% is sufficient.

Kinetics discussion

For the WO treatment process, two kinetic models have been proposed (Li et al. 1991). The first one represents the WO treatment process of many phenolic wastewaters with two first-order reactions; the second one represents the oxidation of organic compounds, which can be directly oxidized to the end products, with the generalized model. The generalized kinetic model is represented by the following reaction pathway:

$$A+O_2 \xrightarrow{k_1} CO_2 + H_2O$$
$$A+O_2 \xrightarrow{k_2} B+O_2 \xrightarrow{k_3} CO_2 + H_2O$$
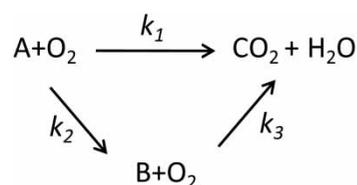
where A is the initial and other relatively unstable intermediate organic compounds, B the refractory intermediate product (acetic acid) (Lin et al. 1996), and k_i the associated rate coefficient. It was reported extensively that acetic acid was produced in the WO process, which is not easily to be oxidized to CO_2 and H_2O (Mishra et al. 1995). The first-order kinetics could be given by $\ln(C_0/C_t) = kt$; in which C_t and C_0 are, respectively, the initial COD concentration and that at time t and k is the rate coefficient. The rate coefficient is related to the reaction temperature according to the Arrhenius equation: $k = A \cdot \exp(-\Delta E/RT)$; where A is the frequency factor, ΔE the activation energy, R the gas constant, and T the temperature.

The data obtained for the CWO of pharmaceutical wastewater (in Figure 4) were utilized to carry out kinetic studies. Figure 6 shows the first-order kinetic model fit of the COD removal data. The two-step first order reaction kinetic model was employed to simulate the experimental processes. As shown in Figure 6, the kinetic rate coefficient for each step was obtained. In the first step, the k value is −0.0194, and the R^2 value is 0.9965. In the second step, the k value is −0.0044, and the R^2 value is 0.9855. Results show that the two reaction step fit an apparent first-order reaction. Many studies reported similar kinetic model, for
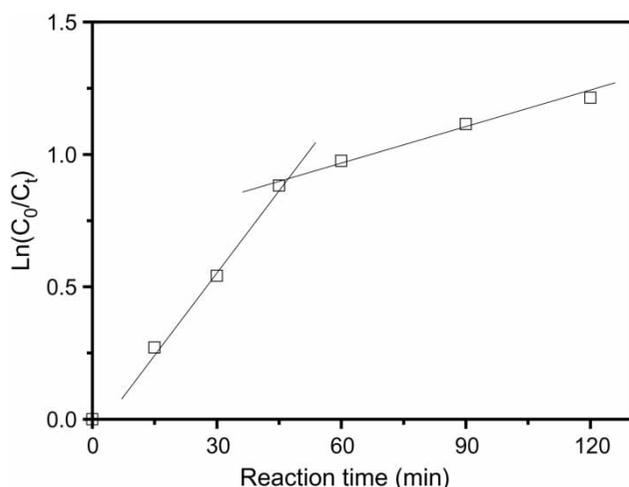
Figure 6 │ First-order kinetic model fit of COD removal data (250 °C, initial oxygen pressure 1.0 MPa, catalyst 1.0 g).

instance, for the oxidation of reactive orange dye and 2,4-dichlorophenol (Yoo 2002; Momani *et al.* 2004). Other researchers also reported that the oxidation of selected azo dyes followed second-order reaction kinetics whether using homogeneous or heterogeneous reactions (Sun *et al.* 2009; Zhang *et al.* 2011). However, for our kinetic study, the reaction could not fit the second-order reaction model well. With the kinetic data in Figure 6, it was found that both of the two reaction steps in this study follow an apparent first-order rate law. As discussed above, it has been reported that carboxylic acids, such as formic acid or acetic acid, are not easily oxidized under hydrothermal conditions (Jin *et al.* 2012). The kinetic reaction model confirmed that the oxidation speed decreased.

CONCLUSIONS

In this study, the CWO of high concentration pharmaceutical wastewater with Fe^{3+} was carried out in a batch reactor. Results showed that the degradation of pharmaceutical wastewater was enhanced significantly by Fe^{3+}. The effects of reaction parameters, such as the catalyst dose, reaction temperature, time, and initial oxygen pressure, were discussed. The COD removal increased with the increases of catalyst dose, temperature, time and oxygen supply. With the initial COD 34,000–35,000 mg/L, approximately 70% COD removal can be achieved under the conditions of catalyst 1.0 g and oxygen pressure 1.0 MPa at 250 °C after 60 min. The results of kinetic studies showed that two reaction steps existed in this oxidation process, which followed an apparent first-order rate law. The kinetic model fitting confirmed the presence of a significant amount of refractory compound (acetic acid) during the WAO treatment process. This process could provide an effective approach for the treatment of high concentration pharmaceutical wastewater.

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