Study on the Wet Oxidation of an Industrial High Concentration Caprolactam Organic Wastewater

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Abstract. In this study, wet oxidation of an industrial high concentration caprolactam organic wastewater using oxygen gas as an oxidant was investigated. Different experiments were conducted to discuss the effects of the reaction temperature, time, the initial oxygen pressure and dilution ratio of raw wastewater, using a batch reactor with COD removal rate as a standard for assessing. Results show that the highest removal rate of COD, 76.6%, was obtained at 250 ºC for 30 min with the oxygen pressure 1.7 MPa and dilution ratio 10. The biodegradability of the wastewater improved greatly after the wet oxidation process. These results illustrated that wet oxidation with oxygen gas as an oxidant displayed effectively for the pretreatment of high concentration caprolactam organic wastewater.

1. Introduction

The chemical wastewater treatment has attracted much attention due to its large amount and high hazardous risk. Normally, biological methods were not suitable for the treatment of these wastewaters. These wastewaters always include pollutants which are resistant to biological degradation. Especially some organic pollutants make chemical wastewater as one of the most toxic industrial wastewaters[1]. Therefore, the effective treatment of chemical wastewaters has become a challenging problem. Caprolactam, as an important organic chemical raw material, has a large amount of demand in China. However, in the process involved in the production of caprolactam, a large amount of high concentration caprolactam organic wastewater was produced, including ammonium sulfate, toluene and benzoic acid. It is one of the big challenges in the wastewater treatment industry. The treatment of such wastewater has become an important work.

Chemical treatment processes were studied extensively for the treatment of industrious wastewater. Advanced oxidation processes (AOPs) has gained much attention, because of high efficiency for the decomposition of bioresistant organic contaminants [2,3]. Among these AOPs, wet oxidation has shown its special effectiveness and promising property for the difficult treatment wastewaters[4,5]. Wet oxidation method uses gaseous source of oxygen or air to decompose the pollutants as an oxidant under high temperature (150~350 ºC) and pressure (2.0~15.0 MPa) [6]. In this process, reactive species, such as hydroxyl radicals (∙OH), were generated to oxidize the organic pollutants [7], performing the liquid-phase oxidation of toxic or poorly biodegradable compounds. When sufficient temperatures is used,
oxidation occurs. In most cases, higher-molecularweight pollutants are easily to be oxidized to lowmolecular-weight carboxylic acids, which is not easily to be oxidized further. However, these lowmolecular-weight carboxylic acids are easily to be utilized by biological treatment process, which means that the wet oxidation could be used as pretreatment method.

The aim of this research was to investigate the possibility of wet oxidation as a pretreatment method. In this study, wet oxidation of an industrial high concentration caprolactam organic wastewater using oxygen gas as an oxidant was investigated. Different experiments were conducted to discuss the effects of the reaction temperature, time, the initial oxygen pressure and dilution ration of raw wastewater, using a batch reactor with COD removal rate as a standard for assessing.

2. Materials and methods

2.1. Materials
The real caprolactam organic wastewater was collected in a chemical factory, located in the east of China. The characters of the raw wastewater is as shown in Table 1. The materials used in this experiments were purchased from Sinopharm Chemical Reagent (Shanghai, China). All the chemicals were used as received without further purification.

| pH  | COD (mg/L) | NH₃-N (mg/L) | Color         |
|-----|------------|--------------|---------------|
| 12.5~13.5 | 430000~440000 | 120~130     | Reddish brown |

2.2. Experimental procedure
All experiments were conducted in a SUS316 reactor with an internal volume of 250 mL which was purchased from Anhui Kemi Machinery Technology Co. Ltd, China. The typical procedure is the following: desired amounts of synthetic pharmaceutical wastewater and hydrogen peroxide were put into the reactor, which was then increased the temperature to 180~250 °C. After the desired reaction temperature was achieved, the reaction time was started. Once desired reaction time elapsed, the reactor was removed from the oven and allowed to cool to room temperature. Then, the liquid was sampled and analyzed.

2.3. Analysis method
pH was measured by pH meter (pH-201, Hanna Corporation, Italy). COD removal rate was used to assess the treatment efficiency, which was measured by the potassium dichromate oxidation method (Hach Heating System, Hach Corporation, USA).

3. Results and discussion
Effect of reaction temperature on the COD removal rate. Experiments were conducted by varying the reaction temperature from 180 to 250 °C to assess the effect of reaction temperature at residence time of 30 min with initial oxygen pressure 1.7 MPa, and dilution ration 10. The results can be seen in Fig. 1. As shown in Fig. 1, as expected, the oxidation reaction in terms of COD degradation accelerates when increasing the temperature, considering the Arrhenius law in the kinetic regime. After the oxidation of organic pollutants, some carboxylic acids with small molecule amount, such as formic acid or acetic acid, were produced. In addition, the obtained data illustrated that a plateau is observed with the reaction temperature from 240 °C to 250 °C, which indicated that some of the products are non-oxidizable and remain in the final solution under the employed conditions. From the point view of energy cost, the temperature, 250 °C, can satisfy the need of pretreatment of pharmaceutical wastewater. Because when pollutant with large molecular amount was oxidized and converted to small molecule amount material, the products are always easy to be degraded by biological method.
Figure 1. Effect of temperature on the COD removal rate (Time 30 min, Oxygen pressure 1.7 MPa, Dilution Ratio 10).

Effect of reaction time on the COD removal rate. Experiments were conducted to investigate the effect of reaction time. As shown in the Fig. 2, the COD removal rate increased gradually with the reaction time changed from 15 min to 60 min. The results showed that the COD removal rate is very high even with the reaction time 15min, which means that the wet hydrogen peroxide oxidation process took place quickly. This behavior was expected because the free radical reaction was very fast. From the point view of energy cost and the reactor investment, in this process the cost can be saved significantly. Therefore, shorter reaction time is desired, i.e. the reaction time 30 min is suitable.

Figure 2. Effect of time the COD removal rate (Temperature 250, Oxygen pressure 1.7 MPa, Dilution Ratio 10).

Effect of dilution ratio on the COD removal rate. Due to the high concentration of the pollutants, experiments were conducted with different dilution ration. The results are shown in Figure 3. It can be seen that dilution ration plays an obvious role in COD removal. It is found that COD removal increases with increasing dilution ration. This behaviour was expected because the increase of the pollutant...
concentration usually leads to a decrease in the oxidation rate. These results indicate that high concentration organic wastewater should be diluted to gain high COD removal.

![Figure 3](image1.png)

**Figure 3.** Effect of dilution ration on the COD removal rate (Temperature 250, Time 30 min, Oxygen pressure 1.7 MPa).

![Figure 4](image2.png)

**Figure 4.** Effect of oxygen pressure on the COD removal rate (Temperature 250, Time 30 min, Dilution Ratio 10).

**Effect of oxygen supply on the COD removal rate.** Experiments were conducted under initial oxygen pressures varying from 0 to 1.7 MPa. The results are shown in Figure 4. It can be seen that oxygen pressure plays an important role in COD removal. It is found that COD removal increases with increasing oxygen pressure. This behaviour was expected because the increase of the oxidant concentration usually leads to an increase in the oxidation rate. These results indicate that high oxygen pressures effectively eliminate refractory organic compound in the process. Under high oxygen pressures, the amount of dissolved oxygen increases in the solution, which can be helpful for the formation of strong oxidation species. With the initial oxygen pressure 1.7 MPa, the COD removal rate was the highest.
4. Conclusion
In this study, wet oxidation of an industrial high concentration caprolactam organic wastewater using oxygen gas as an oxidant was investigated. Different experiments were conducted to discuss the effects of the reaction temperature, time, the initial oxygen pressure and dilution ratio of raw wastewater, using a batch reactor with COD removal rate as a standard for assessing. Results show that the highest removal rate of COD, 76.6%, was obtained at 250 ºC for 30 min with the oxygen pressure 1.7 MPa and dilution ratio 10. The biodegradability of the wastewater improved greatly after the wet oxidation process. Therefore, wet oxidation with oxygen gas as an oxidant displayed effectively for the pretreatment of high concentration caprolactam organic wastewater.

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