Study on the Wet Oxidation of a Kind of Pharmaceutical Wastewater with Hydrogen Peroxide

Xiaoming Gan*
Shanghai Academy of Environmental Sciences, 200233, Shanghai, China

*Corresponding author email: ganxmsaes@163.com

Abstract. The wet oxidation of a kind of pharmaceutical wastewater with hydrogen peroxide, i.e. H$_2$O$_2$, was studied in this paper. In this study, H$_2$O$_2$ was utilized as an oxidant. The effects of reaction conditions were investigated, including the initial concentration of the pharmaceutical, the reaction temperature and reaction time, and the additional amount of H$_2$O$_2$. The highest Chemical Oxygen Demand (COD) removal rate among the performed experiments in this study, approximately 89.6%, was obtained at 240 °C for 60 min with the additional amount of H$_2$O$_2$ solution 2 mL. These results illustrated that the wet oxidation process using hydrogen peroxide as an oxidant was effectively for the degradation of this kind of pharmaceutical wastewater.

1. Introduction
In the past recent years, large amounts of some hazardous pharmaceutical wastewaters were generated. However, the treatment of pharmaceutical wastewater is a hard work, which has been paid much attention. Conventional biological methods are not ideal methods, because the special characters of the wastewater. This kind of wastewater is always hazardous, with high concentration of pollutants. Thus, it is hard to be treated with conventional biological method. In this situation, the advanced oxidation process (AOPs), especially the wet oxidation, is probably an ideal choice.

In these AOPs, the wet oxidation is recently paid much attention. Although it is not used widely in China, because it always needs a lot of cost, the development of the wet oxidation is gradually increased. The wet oxidation processes, under the temperature (150~350 °C) and the pressure (2.0~15.0 MPa) conditions, large amounts of hydroxyl radicals (·OH) were produced. Therefore, this process was considered as a kind of especially effective treatment technologies for the treatment of bioresistant organic contaminants [1]. The hydroxyl radicals are very useful, which could lead to the effective degradation of organic pollutants, which would produce large amount of organic acids, such as acetic acid and other small molecule carboxylic acid. Wet oxidation has been proved that it is effective for the treatment of several industrial effluents. In some cases, the reactions could take place using a gaseous oxygen or air. On the other hand, the reaction process is considered as a green and environmental-friendly technology.

Wet Hydrogen Peroxide Oxidation (WHPO) was paid much attention in past decades by using H$_2$O$_2$ as an oxidation agent[2]. WHPO is widely studied for the treatment of some wastewaters and sludge, especially for the treatment of some hazardous organic pollutants. When the hydrogen peroxide was chose and was put in the reaction as an oxidant, the degradation rate is easily to be controlled by the additional amount. Unlike the situation of gaseous air or oxygen conditions, the limitation of the reaction efficiency was determined by the mass transfer of molecular oxygen from the gas to the liquid.
phase. Therefore, WHPO was paid much attention, and widely studied. In some cases, it has been industrially utilized.

In this study, the wet oxidation of an industrial pharmaceutical wastewater was studied. The effects of reaction conditions were investigated, including the initial concentration of the pharmaceutical, the reaction temperature and reaction time, and the additional amount of H$_2$O$_2$.

2. Materials and Methods

2.1. Materials

The pharmaceutical wastewater was tested from a pharmaceutical factory, which was located in the east of China. The COD concentration was 20 000–23 000 mg/L, pH 7.2–8.6. The hydrogen peroxide (solution with the concentration 30%) was used as oxidant.

2.2. WO Reaction System

In this study, the experiments were performed under different conditions in a SUS316 batch reactor. The reaction system was bought from Anhui Kemi Company, China. The typical experimental procedure is the following: desired amounts of the wastewater and H$_2$O$_2$ solution were put into the reactor. Then the reactor was heated to desired reaction temperature, 180–240 °C. After some reaction time was achieved, the reaction was finished. Then, the reactor was moved out and cooled to room temperature. The solution in the reactor was collected to be analyzed.

2.3. Analyze Methods

COD was adopted to assess the reaction efficiency, which was measured by Hach Test System, USA. The pH value was measured by pH-201 meter, Hanna Corporation, Italy.

3. Results and Discussion

The experiments was performed under different reaction temperature, 180–240 °C with reaction time 60 min and the additional H$_2$O$_2$ solution 2 mL. The experimental results could be seen in Figure 1. As shown in Figure 1, the removal rate of COD increased significantly with the change of temperature from 180 °C to 240 °C. The highest COD removal rate, 89.6%, was obtained at 240 °C for 60 min with the additional H$_2$O$_2$ solution 2 mL. Commonly, the reaction results could be better under higher reaction temperature, due to the chemical reaction mechanism. However, higher temperature means high money cost, which illustrated that the industrial utilization could be more unsuitable. To obtain higher suitability, the cost of this treatment process should be considered. Therefore, in the following experiments, the reaction temperature 240 °C was used.

The additional H$_2$O$_2$ solution amount was changed from 1.0 to 2.5 mL in the following experiments. The results were shown in Figure 2. In Figure 2 that H$_2$O$_2$ plays an important role. Normally, the increase of oxidant means the reaction efficiency could be better. It should be noted that, the formic
acid and acetic acid were not easily to be oxidized under this conditions, because the reaction needs more energy. However, to obtain sufficient COD removal rate, the additional amount of oxidant should be enough. Therefore, in the following studied experiments, H_2O_2 solution additional amount, 2mL, was used.

**Figure 2.** Effect of additional amount of H_2O_2 (240 °C, 60 min).

The reaction time was changed to acquire the influence of time on the COD removal rate from 15 min to 60 min. Figure 3 shows the studied reaction time effect on the COD removal rate at 240 °C with H_2O_2 solution amount 2 mL. The COD removal rate is very high even in the early reaction time 15 min. It could be concluded that WHPO was easily took place, compared with the reaction conditions with gaseous oxygen and air. Because in the situation, the hydrogen peroxide was used, large amounts of hydroxyl radicals were existed. Therefore, when the reaction started, the organic pollutants were easily to be oxidized and easily to be degraded into small molecule organic pollutants, even CO_2 and H_2O. With the reaction took place, the COD removal rate increased gradually. However, when the COD removal rate was above 90%, it was not easily to be increase any more after 60 min. Because a large amount of formic acid and acetic acid were produced, which were not easily to be degraded. On the other hand, the solution could be used as carbon source solution for the treatment of industrial wastewater with biological method.

**Figure 3.** Effect of the reaction time(240 °C, H_2O_2 amount 2 mL).

Some experiments were done with the wastewater in lower COD concentration 5000~6000 mg/L, to investigate the pharmaceutical concentration effect on the reaction. Because in some situations, the COD was not very high, the hazardous was very remarkable. If these hazardous wastewater was added into the biological wastewater treatment process, the process would be destroyed. Therefore, in this study, the experiments with lower COD concentration were performed. As shown in Figure 4, the
increase trend of temperature is similar with the condition of higher COD concentration. Based on the BOD analysis, we found the increase of B/C value after the reaction. It should be noted that for the treatment of lower COD wastewater, the biological method is probably better, due to the lower hazardous character. The wet oxidation is especially suitable for the treatment of high concentration of pollutant wastewater. Thus, it could be concluded that the wet oxidation was suitable for the treatment of high and low COD concentration.

4. Conclusion
In this study, the wet oxidation of a kind of pharmaceutical wastewater was studied. H$_2$O$_2$ was used as an oxidant. The effects of reaction conditions were investigated, including the initial concentration of the pharmaceutical, the reaction temperature and reaction time, and the additional amount of H$_2$O$_2$. Results showed that highest Chemical Oxygen Demand (COD) removal rate among the performed experiments in this study, approximately 89.6%, was obtained at 240 ºC for 60 min with the additional amount of H$_2$O$_2$ solution 2 mL. These results illustrated that the wet oxidation process using hydrogen peroxide as an oxidant was effectively for the degradation of this kind of pharmaceutical wastewater. In our recent studies, we also found that the wet oxidation with H$_2$O$_2$ as oxidant was suitable for other kinds of pharmaceutical wastewaters. We hope that the wet oxidation would be used widely in the near future.

References
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