Treatment of pharmaceutical sludge by wet oxidation under mild reaction conditions

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Abstract. In this study, the wet oxidation treatment of pharmaceutical sludge was investigated. The effects of the reaction parameters on the removal rate of volatile suspended solids (VSS) and the total chemical oxygen demand (COD) were discussed. The results illustrated that the highest could reach up to 68.9% and 93.7% separately under 260 °C with initial oxygen pressure 1.5 MPa and the reaction time 60 min. The addition of Cu²⁺ could increased the COD removal rate significantly. The results demonstrated that wet oxidation showed promising as an economical and feasible alternative for the pharmaceutical sludge treatment.

1. Introduction
Due to the rapid development of pharmaceutical industry, huge amounts of activated sludge containing hazardous and refractory organic pollutants were generated from the treatment of pharmaceutical wastewater. The pollutants in the pharmaceutical wastewater are always nonbiodegradable and persistent to the biological systems, which make pharmaceutical wastewater as one of the most toxic industrial wastewaters [1-3]. Therefore, the treatment of pharmaceutical sludge is a big problem which has been paid much attention. Physicochemical treatment methods always need high costs. Incineration is the most efficient and useful method. However, incineration could release noxious compounds into the atmosphere. Thus, the treatment of pharmaceutical sludge needs more efficient and environmentally-friendly system.

Recently, extensive researches have studied new approaches for the treatment of pharmaceutical sludge. Advanced oxidation processes (AOPs) are considered as one of the most effective treatment technologies for the decomposition of organic contaminants [4, 5]. In these AOPs treatment methods, the generation of sufficient reactive species such as hydroxyl radicals (·OH) leads to the effective decomposition of organic pollutants [6, 7]. Especially, wet oxidation (WO) is very promising for the treatment of effluents containing high content of organic matter or toxic contaminants [8]. In WO process, the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures [9]. Then the pollutants are oxidized to carbon dioxide, water, and other products. WO is an interesting alternative for the solubilization and mineralization of activated sludge [10]. The study on the WO of sludge showed high COD and VSS removal rate [11]. Gasso et al. studied the wet oxidation of toxic effluents which showed good results for the COD removal [12]. From the environmental points of view, the wet oxidation technology is a clean and environmentally benign process. Because the low molecular weight oxygenated compounds, for example, acetic acid and propionic acid, are biodegradable. Furthermore, the WO process requires no additional heat and can be
self-sustaining or even useful for producing heat from wastes [13-14]. Therefore, the WO technology was studies extensively for their industrial utilization.

In this study, the wet oxidation treatment of pharmaceutical sludge was investigated. The effects of the reaction parameters on the removal rates of VSS and COD were discussed.

2. Another section of your paper

2.1. Materials
The pharmaceutical sludge was collected in a chemical synthesis pharmaceutical factory, which is located in the east of China. The characters of the raw activated sludge is as follows: the mixed liquor chemical oxygen demand (COD) 16 000–18 000 mg/L, and pH 7.6–8.2. The sludge was adopted for the experiments without any treatment. The materials used in these experiments, such as NaOH, Fe(NO3)2, Cu(NO3)2, were purchased from Sinopharm Chemical Reagent, China. All the chemicals were used as received without further purification.

2.2. WO reaction system
The wet oxidation experiments were took place in a SUS316 batch reactor with an internal volume of 200 mL which was purchased from Jiangsu Xingjian Chemical Equipment Co. Ltd, China. The typical procedure is the following: a desired amount of sludge mixed liquor was put into the reactor. Then, the reactor was sealed and oxygen gas was input with the initial pressure. The temperature was increased. After the desired reaction temperature was achieved, the reaction time was started. Once desired reaction time elapsed, the heater was stopped, the reactor was cooled below 100 °C to be sampled and analyzed. The speed of stirrer was 120 r/min.

2.3. Analyze methods
COD and VSS removal rates of the mixed liquor were used to assess the treatment efficiency. COD was measured by the potassium dichromate oxidation method (Hach Heating System, Hach Corporation, USA). VSS was measured by Ignition loss method. pH was measured by pH meter (pH-201, Hanna Corporation, Italy).

3. Organization of the Text
The effect of reaction temperature (in the range of 180-260 °C) on the COD and VSS removal rate of pharmaceutical sludge is investigated at residence time of 60 min with oxygen pressure 1.5 MPa. As shown in Figure 1, the COD and VSS removal rate were very high under high reaction temperature, which means highly efficient degradation of the sludge. COD and VSS removal rate showed a rising trend, the effect of reaction temperature is also very significant. It has been reported that the intermediates of wet oxidation of organics were mainly carboxylic acids with small molecule weights, such as acetic acid and formic acid, which were resistant to be oxidized. From the above results, we concluded that higher temperatures were favorable for the degradation of pharmaceutical sludge. The results illustrated that the highest could reach up to 68.9% and 93.7% separately under 260 °C with initial oxygen pressure 1.5 MPa and the reaction time 60 min. However, from the practical point of view, higher temperatures lead to higher operating costs and more severe corrosion problems. Therefore, the reaction temperature of 245 °C was adopted in the following runs when other operating parameters were discussed.
Figure 1. Effect of reaction temperature on the COD and VSS removal rate (Time: 60 min, Initial oxygen pressure: 1.5 MPa).

Figure 2 shows the effect of reaction time on the COD and VSS removal rate at 260 °C with initial oxygen pressure at 1.5 MPa. The reaction time was changed from 0 min to 80 min. As shown in Figure 2, the results show that that reaction time has certain effect on sludge treatment. With the extension of time the removal rate gradually increased. These phenomena indicate that the solid phase organic matter transferred into the liquid phase within a short time, which means the high VSS removal rate. With the extension of time, the degradable organic in liquid accumulated. The organic matter of higher activation energy began to oxidize, so that the overall reaction rate has been greatly improved. After the reaction time 60 min, the COD and VSS removal rate increased a little, which illustrated that the reaction time 60 min is sufficient for the oxidation process. Considering the oxidation efficiency and the economic factors, we choose 60 min as the reaction time for the subsequent study of wet oxidation.

Figure 2. Effect of reaction time on the COD and VSS removal rate (Temp.: 260 °C, Initial oxygen pressure: 1.5 MPa).

To gain better insight into the effect of oxygen pressure on COD and VSS removal rates, experiments were conducted under initial oxygen pressures varying from 0 to 1.5 MPa. The results are shown in Figure 3. It can be seen that the treatment of pharmaceutical sludge, the initial oxygen pressure has a
great impact to the COD removal rate. With the increase of oxygen pressure, VSS removal rate is gradually increased. The reason is probably that the COD removal was mainly come from the oxidation of the organic compounds in the solution, and the VSS removal was due to the decomposition of the solid partition of the sludge. Considering the treatment of the liquids after the reaction, the oxygen supply should be sufficient. However, large amounts of organic carboxylic acids were produced after the reaction, such as formic acid and acetic acid, which are not easily to be oxidized. Therefore, the additional oxygen amount should be kept in suitable balance.

Figure 3. Effect of initial oxygen pressure on the COD and VSS removal rate (Temp.: 260 °C, Time: 60 min).

To investigate the effect of catalyst, experiments were performed with the addition of NaOH, Fe(NO₃)₂, Cu(NO₃)₂. The amount of the additional catalyst was 0.1% in the quality rate. Results can be seen in Figure 4. As shown in Figure 4, comparing with the experimental result without the addition of catalyst, the addition of catalyst could increase the COD and VSS removal rate. Especially, the COD removal rates increased significantly, which means that the addition of catalyst could increase the decomposition of organic compounds in the solution. Under the hydrothermal reaction conditions, the VSS removal rate was mainly come from the decomposition of organic partition of the total SS. Therefore, the VSS removal rated increased slightly. To be noted that, the addition of Cu²⁺ increased the COD removal rate notably, this is similar with the literature’s results.

Figure 4. Effect of catalyst on the COD and VSS removal rate (Temp.: 240 °C, Time: 60 min, Initial oxygen pressure: 1.5 MPa).
4. Conclusion
In this study, the wet oxidation of real industrial pharmaceutical sludge was performed. The experiments were conducted in a batch reactor. The effects of reaction conditions on process performance were discussed, such as temperature, reaction time, oxygen supply, and the addition of catalyst. The results illustrated that the highest could reach up to 68.9% and 93.7% separately under 260°C with initial oxygen pressure 1.5 MPa and the reaction time 60 min. The effects of catalyst should be studied subsequently later. The wet oxidation showed promising as an economical and feasible alternative for the pharmaceutical sludge treatment.

Acknowledgments
This work was financially supported by the National Key R&D Program of China (No. 2018YFC1902101).

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