

Wet Oxidation Treatment of Waste Activated Sludge of a Pharmaceutical Factory

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Abstract. As the development of pharmaceutical industry, large amounts of sludge was produced, which is a hazardous waste with high environmental risks and high disposal fees. In this study, the wet oxidation treatment of pharmaceutical sludge was investigated. The effects of the reaction parameters on the process performance were discussed, such as reaction time, temperature, initial oxygen supply and catalysts. The results illustrated that the highest removal rate of volatile suspended solids (VSS) and the total chemical oxygen demand (COD) removal rates could reach up to 60.7% and 91.3% separately under 260°C with initial oxygen pressure 1.0 MPa and the reaction time 60 min. Thus, the wet oxidation process provides an economical and feasible alternative for the industrial activated sludge treatment, especially for the pharmaceutical sludge.

1. Introduction

Due to the rapid development and increasing demand of pharmaceutical industry, large amounts of activated sludge were generated in recent years. The sludge from the pharmaceutical industries is especially problematic as it contains recalcitrant antibiotics. Conventional technologies including biological, thermal, and physicochemical treatments are always used for the treatment of these sludges. Generally, biological treatment is the most common and economical treatment method. Solidification/stabilization processes were very popular for the final treatment of the sludge [1]. However, these methods are insufficient to remove all potentially hazardous constituents. This problem has attracted much attention for the environmentally friendly treatment methods.

Recently, advanced oxidation processes (AOPs) have attracted much attention in the area of the treatment of hazardous pollutants [2] and are effective in the decomposition of a wide range of organics [3-4]. Wet oxidation (WO) technology is very promising for the treatment of effluents containing high concentrations of organic or toxic contaminants. In the WO process, the generation of hydroxyl radicals occurs under high temperatures and pressures. Then, the pollutants are degraded to carbon dioxide, water, and small molecule carboxylic acid, etc. Therefore, WO is an interesting alternative for the degradation of activated sludge [5]. Recently, the WO of activated sludge was investigated [6] and the technic-economic and environmental sustainability was assessed [7]. However, in recent years, only a few studies were performed to the examination of real industrial sludge. Therefore, the wet oxidation of real industrial pharmaceutical and hazardous sludge is well worth examining.

In this paper, some experiments were conducted by using a batch reactor. The effects of WO conditions, namely, reaction time, temperature, oxygen supply, and the catalyst, on the process performance were investigated.



2. Material and Methods

2.1. Materials

The chemical activated sludge was collected in a pharmaceutical factory, which is located in the east of China. The characteristics of the raw activated sludge are as follows: the mixed liquor COD is 30 000~40 000 mg/L, VSS is 27.8 ~29.6 g/L and pH 7.5~8.5.

2.2. WO Reaction System

Experiments were conducted in a SUS316 reactor, which was bought from Anhui Kemi Machinery Technology Co. Ltd, China, as shown in Figure 1. The experimental procedure is: pharmaceutical sludge solution with different water ration and catalyst were put into the reactor, and the initial oxygen pressure was 1.0 MPa. Then the reactor was heated. The reactor was removed to cool water to terminate the reaction, after the desired reaction temperature was achieved.



Figure 1. Picture of Experimental Reactor

2.3. Analysis

COD was measured by using Hach Heating System, Hach Corporation, USA, with the potassium dichromate oxidation method. VSS was measured by the Ignition loss method. The COD and VSS removal rates were calculated to assess the treatment efficiency. pH was measured using pH-201, Hanna Corporation, Italy.

3. Results and Discussion

3.1. Effect of Reaction Temperature on the Treatment Efficiency

The effect of reaction temperature on the COD and VSS removal rates was investigated in the range of 180-260 °C with reaction time 60 min and oxygen pressure of 1.0 MPa. As shown in Figure 2, the removal rates of COD and VSS were very high under high reaction temperature, which indicates highly treatment efficiency. COD and VSS removal rate showed a rising trend, and the effect of reaction temperature was also very significant. The results illustrated that the highest removal rates of VSS and COD could reach up to 60.7% and 91.3% separately under 260 °C with reaction time 60 min and the initial oxygen pressure 1.0 MPa. It was reported that the intermediates from wet oxidation of organics were some carboxylic acids with small molecular weights, such as acetic acid and propionic acid, which were resistant to oxidation. Therefore, it could be concluded that the reaction parameters, such as higher temperatures, were favourable for the removal of COD and VSS. On the other hand, higher temperatures could lead to higher operating costs. Therefore, the reaction temperature of 260 °C was used in the later experiments.

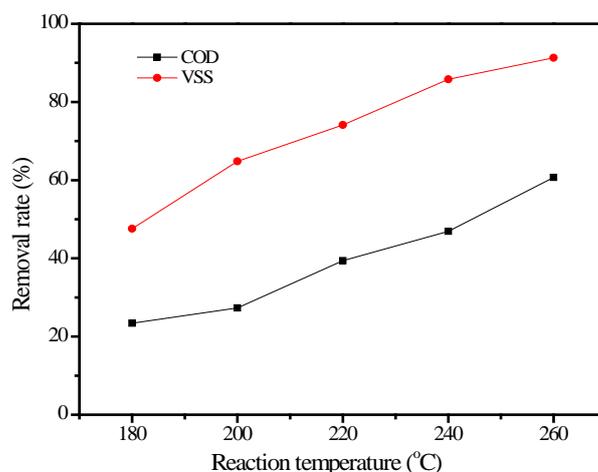


Figure 2. Effect of Reaction Temperature (60 min, O₂ initial pressure 1.0 MPa)

3.2. Effect of Reaction Time on the Treatment Efficiency

Figure 3 shows the effect of reaction time on the treatment efficiency at 260 °C with an initial oxygen pressure 1.0 MPa. In these experiments, the reaction time was changed in the range of 15 to 60 min. The results indicate that reaction time has a significant effect, as shown in Figure 3. The removal rates of COD and VSS gradually increased with the increase of reaction time. At the same time, the degradable organics in liquid accumulated. Therefore, with the increase of the reaction time, the removal rates of COD and VSS increased, because of the degradation of the organic compounds.

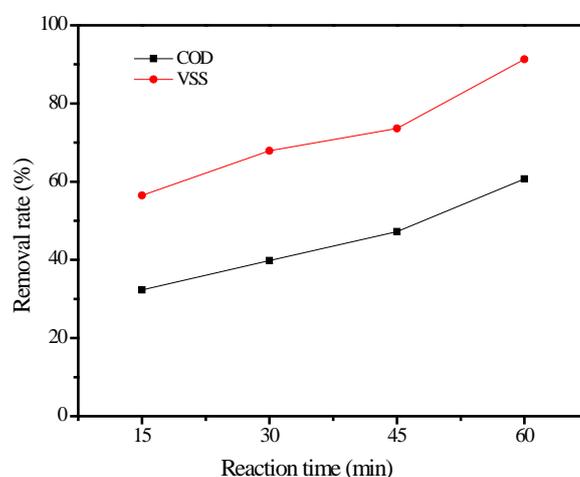


Figure 3. Effect of Reaction Time (260 °C, O₂ initial pressure 1.0 MPa)

3.3. Effect of Oxygen Pressure on the Treatment Efficiency

Experiments were performed by changing the initial oxygen pressures in the range of 0.6 to 1.0 MPa to investigate the effect of oxygen pressure on the treatment efficiency. The results could be seen in the Figure 4. As shown in the Figure 4, the initial oxygen pressure has a great impact on the removal rates of COD and VSS. The probably reason is that the reaction took place under the hydrothermal conditions is an oxidation process, which means that the oxygen was used as an oxidation agent. Therefore, the increase of oxygen pressure means the increase of the reaction materials. On the other hand, the increase of the oxygen pressure also increased the concentration of the dissolved oxygen in the solution. It would be helpful for the oxidation of the oxidation species of the organic pollutants.

Therefore, with the increase of oxygen pressure, the removal rates of COD and VSS increased. On the other hand, once the oxygen was surplus, the increase of the removal rates stopped.

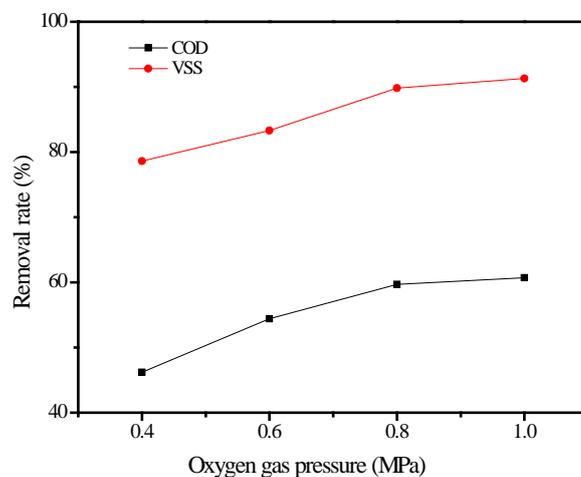


Figure 4. Effect of Initial Oxygen Pressure (60 min, 260 °C)

3.4. Effect of Catalysts on the Treatment Efficiency

It was reported that homogeneous catalysts can enhance the wet oxidation efficiency significantly. Therefore, in this section, some homogeneous catalysts were collected to study the effects of homogeneous catalysts, including FeSO_4 , MnSO_4 , $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$. As shown in Figure 5, the COD degradation was accelerated significantly when the homogeneous catalyst was added. The effect of $\text{Cu}(\text{NO}_3)_2$ was the highest. After the reaction, small molecule carboxylic acids, such as formic acid or acetic acid, were produced. These small molecule carboxylic acids are not easily to be oxidized. The VSS removal rates showed that there was almost no difference. In addition, it should be noted that the obtained data indicate that some of them are non-oxidizable under the wet oxidation conditions.

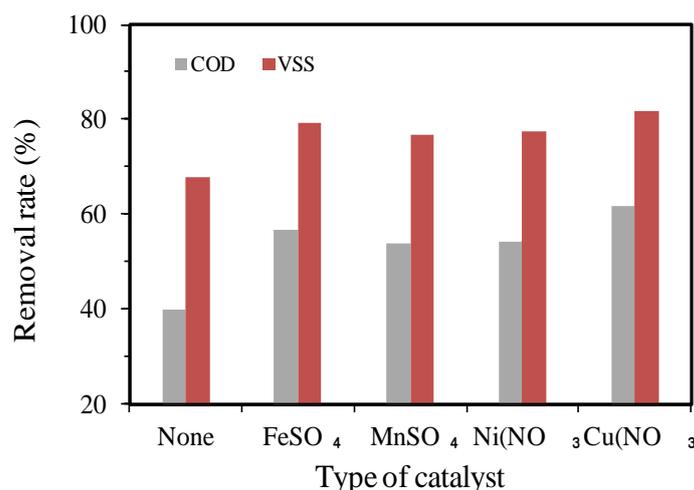


Figure 5. Effect of Catalysts (240 °C, 60 min, initial oxygen pressure 1.0 MPa, catalyst 0.1 g).

4. Conclusions

In this study, the wet oxidation of industrial pharmaceutical sludge was investigated by using a batch reactor. The effects of reaction parameters on the process performance were discussed, such as

reaction time, temperature, initial oxygen pressure and catalyst. The results illustrated that the highest removal rates of VSS and COD could reach up to 60.7% and 91.3% separately under 260 °C with initial oxygen pressure 1.0 MPa and the reaction time 60 min. Thus, the wet oxidation process provides a favourable and feasible alternative for the industrial activated sludge treatment, especially for the pharmaceutical sludge.

5. Acknowledgments

This work was financially supported by the National Key R&D Program of China, Key Technologies and Engineering Demonstration for the Treatment and Resource Utilization of Pharmaceutical Sludge by Hydrolysis-Wet Oxidation Process (2018YFC1902103).

6. References

- [1] Cioffi R., Lavorgna M., Santoro L. Environmental and technological effectiveness of a process for the stabilization of a galvanic sludge. *J Hazard Mater*, 2002, 89, 165–175.
- [2] Malato, S., Blanco, J., Vidal A., Richter, C. Photocatalysis with solar energy at a pilot-plant scale: an overview. *Appl. Catal. B*, 2002, 37, 1-15.
- [3] Arana, J., Rendón, E. T., Rodríguez, J. D., Melián, J. H., Diaz O. G., Pena, J. P. Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR. *Chemosphere*, 2001, 44, 1017-1023.
- [4] Luck, F. Wet air oxidation: Past, present and future. *Catal. Today*, 1999, 53, 81-91.
- [5] Tu, Y. T., Xiong Y., Tian S. H. Catalytic wet air oxidation of 2-chlorophenol over sewage sludge-derived carbon-based catalysts. *J. Hazard. Mater*, 2014, 276, 88-96.
- [6] Bertanza, G., Canato, M., Heimersson, S., Laera, G., Salvetti, R., Slavik, E., Svanström, M. Techno-economic and environmental assessment of sewage sludge wet oxidation. *Environ. Sci. Pollut. Res.*, 2015, 22, 7327-7338.
- [7] Bertanza, G., Galessi, R., Menoni, L., Zanaboni, S. Wet oxidation of sewage sludge from municipal and industrial WWTPs. *Desalin. Water Treat*, 2015, 57, 2422-2427.