

Efficient Treatment of Antibiotic Cefalexin Sludge by Wet Oxidation: an Experimental and Theoretical Study

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Abstract. In the present study, wet oxidation of antibiotic cefalexin sludge from pharmaceutical wastewater treatment was investigated. The experiments were carried out in a stainless-steel batch autoclave reactor. The results show that the maximum removal rate of volatile suspended solids (VSS) can reach 91.3% at 260 °C within 60 min with an initial oxygen pressure of 1.0 MPa. Simultaneously, the chemical oxygen demand (COD) removal rate of 64.1% was reached. The antibiotic cefalexin was totally eliminated under wet oxidation conditions. DFT calculation was performed to illustrate the initial reaction pathway. The energy diagram proposed initial thermal hydrolysis pathway of cefalexin. These results indicated that wet oxidation provided a promising treatment method for the antibiotic cefalexin sludge, which can be used for the efficient removal of cefalexin.

Keywords: Wet oxidation; antibiotic; cefalexin; VSS; COD.

1. Introduction

In recent years, antibiotics released in the environment have attracted much attention due to its environmental risk for the humankind. Large amounts of wastewater and excess sludge were produced in pharmaceutical industries, especially in the antibiotic pharmaceutical industries. Significantly, the treatment of antibiotic sludge has become a serious problem because it contains a variety of toxic compounds, including relatively high levels of soluble organics, heavy metals, and recalcitrant antibiotics such as cefalexin, benzylpenicillin, aureomycin, and berberine hydrochloride, which possessed high environmental risk [1,2]. Normally, biotechnology and incineration were chose for the treatment. However, due to the hazardous and toxic characteristics of antibiotics, the biological process is not suitable. On the other hand, incineration may induce secondary pollution. Generally, to treat antibiotics pollution, high treatment and disposal costs are always necessary [3]. Therefore, alternative technology is still a challenging task.

Advanced oxidation processes (AOPs) are potentially for the treatment of hazardous and refractory organic pollutants [4,5]. Wet oxidation (WO) is gained significant attention for some reasons. In WO process, the reaction took place at a temperature of 150–320 °C and a pressure of 20–150 bar [6]. Under these conditions, free radical oxidative agents were produced, which could oxidize organic pollutants into small molecule weight organics, even into CO₂ and H₂O [7]. High VSS and COD removal rates could be achieved [8]. For example, Gasso et al. reported compact jet-mixer wet oxidation reactors as a promising strategy [9]. In fact, wet oxidation allows for high capacities for volume reduction, metal stabilization, sludge mineralization, and resource utilization. Therefore, wet oxidation is assumed to be a sustainable alternative to conventional sludge stabilization and incineration [10–12]. However, to the best of our knowledge, there has been very limited information about the wet oxidation of antibiotics.

Cefalexin was considered as model compound because it is hardly biodegradable by the conventional biological processes, but it is widely used to treat serious infections. However, cefalexin has a biotransformation rate of only 10%, the remaining 90% is excreted unchanged in the urine. It has been found in the coastal waters of Hong Kong, and has also been shown to be present

in municipal wastewater. These phenomena are the evidence of one of the biggest hurdles of dealing with cefalexin. Dodd et al. reported that cefalexin could be eliminated by using ozone and a hydroxyl radical method [13]. Therefore, wet oxidation would be an effective method to oxidize antibiotic cefalexin for the elimination.

In this study, experiments were designed to investigate wet oxidation of antibiotic cefalexin sludge. The effects of reaction parameters were discussed, including reaction temperature, time, and initial oxygen pressure. Because pharmaceutical sludge is a complex and heterogeneous matrix, a great number of compounds are involved in the process. Therefore, certain lumped parameters, such as COD or VSS removal rates, were used for the assessment, as an alternative approach to a detailed microscale description. Under hydrothermal reaction conditions, the in situ technique for experimentally studying the reaction mechanism is very hard. However, the ab initio calculation is very useful for studying the mechanism including reliable structures as well as the energies of the reactants, products, intermediates, and transition states. A theoretical study was conducted by using the DFT calculations, to study the elimination mechanism of cefalexin.

2. Material and Methods

2.1 Materials

The raw antibiotic cefalexin sludge was selected for concentrated sludge pond in a synthetic pharmaceutical factory, located in Zhejiang Province, China. The characteristics were as follows. Total COD value of the antibiotic cefalexin sludge solution: from 19,000 to 20,000 $\text{g}\cdot\text{L}^{-1}$. pH was 7.5~8.5. All of the reagents used in this study were of analytical grade and were used as received without further purification. The gaseous oxygen (99.5%) used as the oxidant was commercial industrial gas.

2.2 WO Reaction System

The experimental equipment was composed of a SUS316 autoclave reactor purchased from Anhui Kemi Machinery Technology Co. Ltd., Hefei, China. Figure 8 shows a schematic of the experimental setup. The volume of the reactor was 250 mL. The typical experimental process is as follows: [14]. Initially, the reactor was charged with certain amounts of sludge solution (100 mL) and catalyst. Then the reactor was purged using O_2 to remove air and pressurized to 0.2~1.0 MPa. The reaction temperature for individual reaction processes was set from 180 to 260 $^{\circ}\text{C}$ and the time from 15 to 60 min. The stirrer speed was adjusted to 300 rpm. The pressure in the reactor was due to self-pressurization with saturated vapor pressure. Once the desired temperature was reached, this moment was taken as the zero time of the reaction. After the desired reaction time, the reactor was removed from the oven and allowed to cool to room temperature. Then the wet oxidation liquid was collected and analyzed.

2.3 Analysis of Reaction Samples

The analyses performed to characterize the sludge included VSS and COD. The detailed analysis information could be found elsewhere [15]. Identification and quantitative analysis for liquid samples were conducted using high-performance liquid chromatography (HPLC). Perchloric acid (1 mmol/L) was used as the mobile phase, and bromothymol blue solution was used as a coloring reagent, mixed in the immediate aftermath of the column.

2.4 Computational Details

DFT calculations, including a consideration of van der Waals (VDW) interactions, were adopted by using Gaussian 16. The B3LYP density functional method with the D3 (GJ) dispersion correction was employed to carry out all of the computations. An SDD basis set was used for Fe atoms and a 6-31G+G (d,p) basis set was used for remaining atoms. Polarizable continuum model

(PCM) calculations of water as the solvent were used in this work. Vibrational frequency analyses were conducted at the same level of theory to characterize stationary points as local minima. Intrinsic reaction coordinate (IRC) computations were carried out to confirm the transition states.

3. Results and Discussion

3.1 Effect of Reaction Temperature

The reaction temperature is important in the wet oxidation, according to Arrhenius' law. Higher reaction temperatures will increase the reaction efficiency. One more important thing is that oxygen solubility increases with temperature. On the other hand, the wet oxidation is an exothermic phenomenon. Therefore, the reaction efficiency could be very high once the exothermal process provides enough heat. To discuss the effect of reaction temperature, a series of experiments were conducted at a constant reaction time of 60 min, an initial oxygen pressure of 1.0 MPa, varying the reaction temperature from 180 to 260 °C. As shown in Figure 1, the COD removal rates accelerated significantly with increasing temperatures. However, at lower reaction temperatures, the COD removal rate is rather low, which means that the reaction needs considerable energy. In contrast, the VSS removal rates was very high even at 180 °C, because VSS removal mainly comes from the thermal hydrolysis process. However, higher temperatures will induce more severe corrosion problems, which will increase the cost of building the reaction system. Therefore, for cost saving and energy conservation reasons, the temperature of 260 °C was selected in the later reactions.

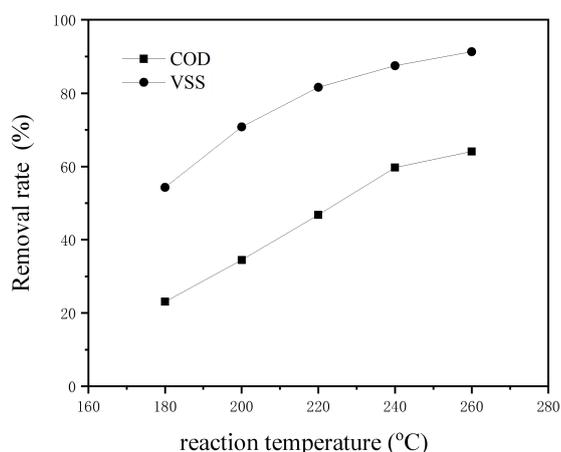


Fig. 1 Effects of reaction temperature

3.2 Effect of Reaction Time

The reaction efficiency showed a strong dependence on the reaction time. As shown in Figure 3, the VSS and COD removal rates increased with the extension of reaction time. Compared with the COD removal rates, the increase of VSS removal rates was not very high. The reason may be that the VSS removal was mainly came from the thermal hydrolysis of sludge, which could happen easily within a short time. However, the COD removal mainly came from the oxidation of organic compounds, which was easily influenced by the gas-liquid mass transfer. The COD and VSS removal rates increased gradually with the increase in reaction time, and the change trends were similar. These phenomena indicate that the solid-phase organic matter was dissolved into the liquid, which leads to a high VSS removal rate. The carboxylic acids with small molecule weights, such as formic acid or acetic acid, were produced. It can conclude that the COD removal rate would be stable once the organic intermediates were oxidized. Therefore, we chose 60 min as the reaction time, considering the oxidation efficiency and economic reason.

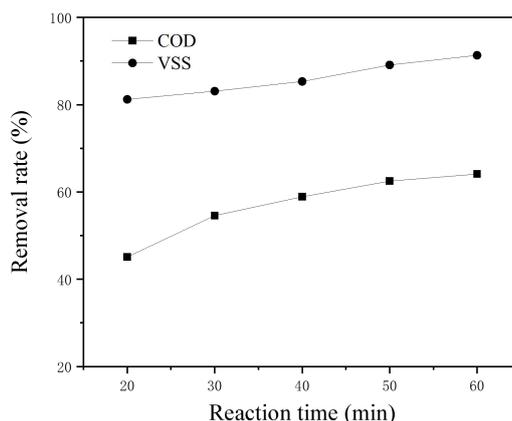


Fig. 2 Effects of reaction time

3.3 Effect of Initial Oxygen Pressure

The oxygen amount is very important, because oxygen plays an oxidation agent role. Once the oxygen gas was not sufficient, the wet oxidation would not be sufficiently happened. The effect of the initial oxygen pressure was studied by varying it from 0.2 to 1.0 MPa. As shown in Figure 3, the COD removal rates increased remarkably. The amount of free radicals increased with the dissolved oxygen gas increased. However, when the initial oxygen pressure changed from 0.8 to 1.0 MPa, the VSS and COD removal ratings changed little. Under higher oxygen pressures, the dissolved oxygen concentration increased, which resulted in the improvement of the oxidation. Therefore, the high oxygen pressure could efficiently accelerate the oxidation reaction rate and eliminate organic compounds, resulting in high COD and VSS removal.

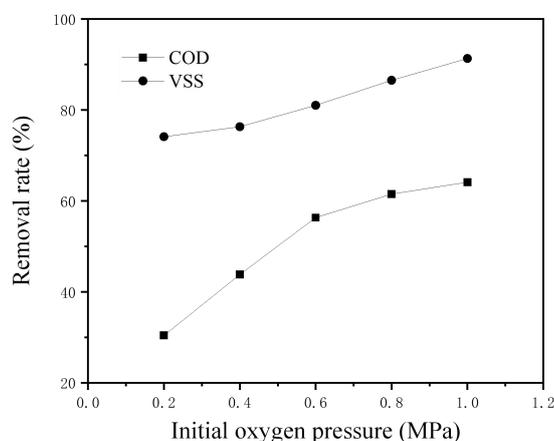


Fig. 3 Effects of initial oxygen pressure

3.4 Theoretical Study

The ab initio DFT calculation was performed to illustrate the initial reaction pathway of cefalexin. The energy diagram illustrated initial thermal hydrolysis pathway of cefalexin, which provided information for the efficient removal mechanism. As shown in Figure 4 and 4, the activation energy of the TS from the initial state was 83.52 kJ/mol. Once the energy barrier was overcome, the reaction took place for the decomposition of cefalexin. The O(43)H(45) attacked C(7), then the bond of C(7)-N(8) broken. Then cefalexin was hydrolysis into two parts, which is important for the removal of cefalexin and wet oxidation reaction subsequently. The C(7)-O(43) bond distance in the transition state was approximately 1.776 Å, and the Mulliken charge of O(43) in the transition state species was -0.555. These species were afterwards transformed into short-chain carboxylic acids including acetic, formic, and oxalic acids, which were finally degraded into inorganic products like CO₂. Zhang reported the mineralization, kinetics and oxidation products

in Fenton reaction system, which is also free radicals reaction [16]. These results are useful for a deeper understanding of degradation mechanisms of cefalexin in wet oxidation. To be noted, the present calculation is for the first step of cefalexin removal. The detailed reaction mechanism is quite complicated, which still needs more research.

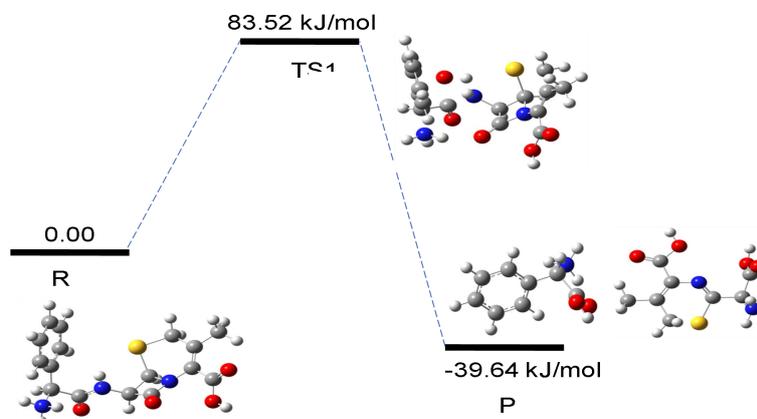


Fig. 4 Calculated energy of the thermal hydrolysis of cefalexin

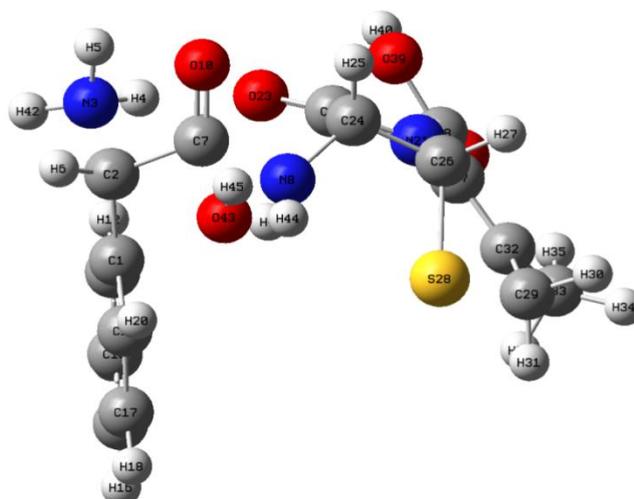


Fig. 5 Calculated transition state

4. Conclusions

In this study, wet oxidation of antibiotic cefalexin sludge from pharmaceutical wastewater treatment was investigated. The experiments were carried out in a stainless-steel batch autoclave reactor. The highest VSS removal rate, 91.3%, was achieved at 260 °C within 60 min with an initial oxygen pressure of 1.0 MPa. Simultaneously, the COD removal rate of 64.1% was reached. The antibiotic cefalexin was totally eliminated under wet oxidation conditions. The ab initio DFT calculation was performed to illustrate the initial reaction pathway of cefalexin. The energy diagram illustrated initial thermal hydrolysis pathway of cefalexin, which provided information for the efficient removal mechanism. These results indicated that wet oxidation provided a promising treatment method for the antibiotic cefalexin sludge, which can be used for the efficient removal of cefalexin.

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