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Enhanced Wet Oxidation of Excess Sludge from Pharmaceutical Wastewater Treatment by NaOH

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Abstract: In the present study, enhanced wet oxidation of excess sludge from pharmaceutical wastewater by NaOH as an alkaline homogeneous catalyst was investigated. The experiments were carried out in a stainless-steel batch autoclave reactor. The highest volatile suspended solids (VSS) removal rate, 95.2%, was achieved at 260 °C within 60 min with an initial oxygen pressure of 1.0 MPa and NaOH 0.5 $g \cdot L^{-1}$. Simultaneously, the chemical oxygen demand (COD) removal rate of 57.3% was reached. The increase in volatile fatty acids (VFAs) demonstrated that the degradation of sludge was greatly accelerated by NaOH. Interestingly, the production of acetic acid, an intermediate by-product generated from the oxidation of organic compounds, increased significantly. These results illustrated that NaOH is a promising catalyst for the utilization of wet oxidation liquid of excess sludge as a carbon source for the treatment of wastewater.

Keywords: wet oxidation; catalyst; sodium hydroxide; pharmaceutical wastewater

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1. Introduction

In recent years, large amounts of excess sludge have been produced from the wastewater treatment process. Sludge should be treated safely because it contains a lot of organic pollutants. Significantly, the treatment of pharmaceutical sludge has become a serious problem because of its high toxicity [1,2]. Pharmaceutical sludge is a complex and hazardous industrial waste because it contains a variety of toxic compounds, including relatively high levels of soluble organics, heavy metals, and recalcitrant antibiotics such as benzylpenicillin, aureomycin, and berberine hydrochloride, that should be treated as hazardous wastes. In aquatic environments, it has been an increasing phenomenon that antibiotics are detected, even in drinking water. Therefore, pharmaceutical sludge is very dangerous to treat, especially the antibiotic pharmaceutical sludge. Traditionally, biotechnology and incineration have been applied for the treatment of pharmaceutical sludge. However, toxic pollutants always obstruct microbial degradation, which induces low efficiency. Compared with biotechnology, incineration has high efficiency. Unfortunately, the hazardous pollutants were just transferred to a solid or the air, producing dangerous byproducts for further disposal [3,4]. In addition, dewatering treatment before the incineration process increased the treatment cost. Generally, high treatment and disposal costs are always necessary for the treatment of pharmaceuticals [5]. Therefore, alternative technology for the treatment of pharmaceutical sludge is still a challenging task.

Advanced oxidation processes are potentially viable for the disposal of hazardous and refractory organic compounds [6,7]. Among these techniques, wet oxidation (WO) is very effective for the treatment of sludge, which was conducted at a temperature of 150–320 °C and a pressure of 20–150 bar [8]. In the WO process, thermal hydrolysis and subsequent free radical oxidation are two main steps. At first, a large proportion of the sludge is solubilized through the thermal hydrolysis process. Subsequently, these hydrolysis products were oxidized to simple organics by free radical oxidative agents, which were produced under wet oxidation conditions. Finally, these simple organics were further oxidized into CO_2 and H_2O [9]. High VSS and COD removal rates have been reported in lab-scale and industrial-scale studies [10]. For example, Gasso et al. reported compact jet-mixer reactors as a promising strategy [11]. It should be noted that there is almost no secondary pollution. Besides, there is no need for a dewatering step because wet oxidation can directly dispose of liquid and slurry sludge. 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 [12–15]. However, to obtain satisfying treatment efficiency, higher temperature and pressure conditions are necessary, which limits its popularization and application [16].

From this viewpoint, recent studies have focused on the catalyst in the WO process [17–19]. In the presence of the catalysts, the operating temperature could be decreased, and the reaction rate was enhanced. For instance, various solid catalysts have been studied in the wet oxidation of organic compounds [20]. In our previous studies, we also reported some solid catalysts, for example, $CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$, molecular sieve, etc. [21,22]. However, solid catalysts always induce high costs, low efficiency, and secondary pollution. In contrast, the homogeneous catalysts, including Cu^{2+}, Mn^{2+}, and Ni^{2+}, exhibited higher efficiency [23]. However, these catalysts are unsafe because of their heavy metal content. It has been reported that NaOH can be used in the oxidation of alcohols as a homogeneous catalyst [24]. Several studies on the wet oxidation of organic compounds also proved the catalytic effects of NaOH [25–28]. OH^- is considered an initiator or promoter that abstracts a proton from the hydroxyl group. The presence of NaOH would impact not only the reaction efficiency but also the selectivity of the oxidation reactions. In our previous study, the reduction of CuO with guaiacol under hydrothermal conditions was studied. It was found that the yield of Cu was improved with the addition of NaOH. As well, the production of carboxylic acids, such as maleic, fumaric, and acetic acids, was improved. In some chemical reactions, NaOH is always used as a catalyst for the source of OH^-. However, to the best of our knowledge, there has been very limited information about the NaOH catalytic wet oxidation of sludge.

In this study, experiments were designed to obtain more information about the wet oxidation of sludge by evaluating the effects of NaOH during the wet oxidation process. The effects of reaction parameters were discussed, including the additional amount of NaOH, 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, as an alternative approach to a detailed microscale description, certain lumped parameters, such as COD or VSS removal rates, were used for the assessment. The removal rate of COD or VSS equals the reduced COD or VSS divided by the initial COD or VSS. The production of carboxylic acids from sludge was also discussed.

2. Results and Discussion

2.1. Effect of Additional Amount of NaOH

Experiments were carried out to evaluate the effects of an additional amount of NaOH, varying from 0 to 0.5 $g\cdot L^{-1}$. Compared to the uncatalyzed run, the VSS removal rates increased significantly while increasing the additional NaOH amount (see Figure 1). The maximum value of VSS removal, 95.2%, was obtained in the presence of NaOH 5.0 $g\cdot L^{-1}$ at 260 °C within 60 min with an initial oxygen pressure of 1.0 MPa. In contrast, the COD removal rate reached 57.3% simultaneously. Interestingly, the COD removal rate increased only with a small addition of catalyst. The reason may be that the VSS removal increased notably due to the addition of NaOH, which induced an increase in the soluble COD. The COD removal rate decreased with the further increase in NaOH addition. In our previous study, it was reported that the produced carboxylic acids were inhibited from being oxidized under alkaline conditions. The possible reason is that acetic acid, the main intermediate in the total wet oxidation process, accumulated because it is a refractory compound. Therefore, the COD removal rates decreased when the NaOH was added further. Considering that the carboxylic acids produced in the wet oxidation process could be easily disposed of in biological wastewater treatment, the liquid after the wet oxidation process could be used to increase the BOD/COD ratio of the wastewater. These results illustrated that the additional NaOH effectively enhanced the hydrolysis of the sludge and the wet oxidation process. Compared with other heterogeneous catalysts, the merit of NaOH is that it can be dissolved in the sludge solution easily, which induces a fast catalytic effect. In addition, there is no need to consider the filter process, which is necessary for the heterogeneous catalyst. Compared with other homogeneous catalysts, the cost of NaOH is cheaper and greener. There is no need for a consideration of the influence of heavy metals. Therefore, NaOH is an effective and cheaper catalyst to utilize.

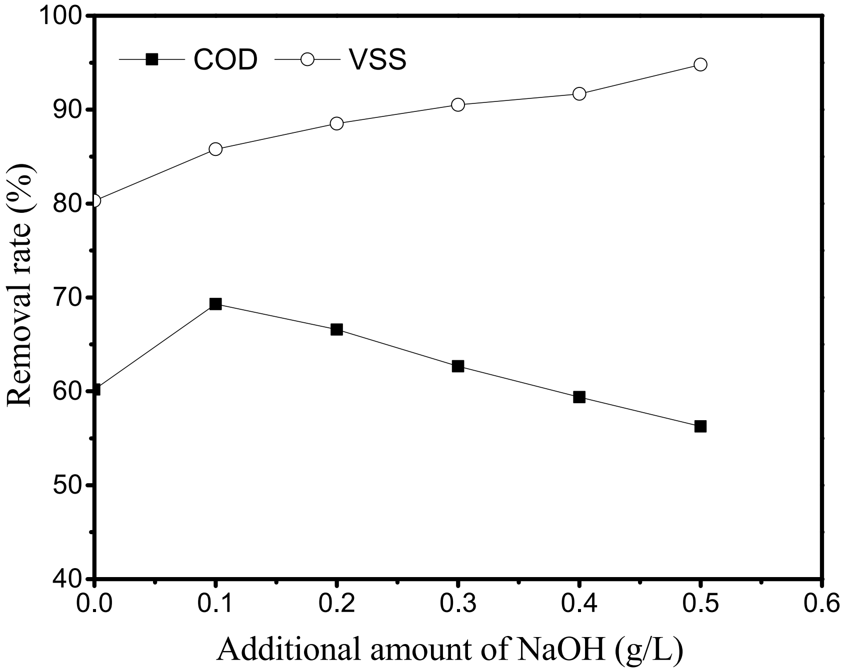


Figure 1. Effect of additional amount of NaOH (260 °C, 60 min, initial oxygen supply 1.0 MPa).

2.2. *Effect of Reaction Temperature*

The reaction temperature is always considered an important parameter in the wet oxidation process. Higher reaction temperatures normally induce higher reaction efficiency, according to Arrhenius' law. It should be noted that oxygen solubility increases with temperature when the reaction temperature is above 100 °C. Because the wet oxidation of sludge is an exothermic phenomenon, a slight change in reaction temperature would have an impact on the reaction results. For organic materials with lower activation energy, the reaction efficiency could be very high once the exothermal process provides the required heat. Then, 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, and a NaOH concentration of 0.5 $g \cdot L^{-1}$. The COD removal rates accelerated significantly with increasing temperatures from 180 to 260 °C (see Figure 2). According to Arrhenius' law, once the reaction temperature is high enough, the reaction efficiency could be very high [19]. 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 did not increase much. Because VSS removal mainly comes from the thermal hydrolysis process, which takes place easily even at 180 °C. Theoretically, the VSS and COD removal rates will increase with higher reaction temperatures. 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.

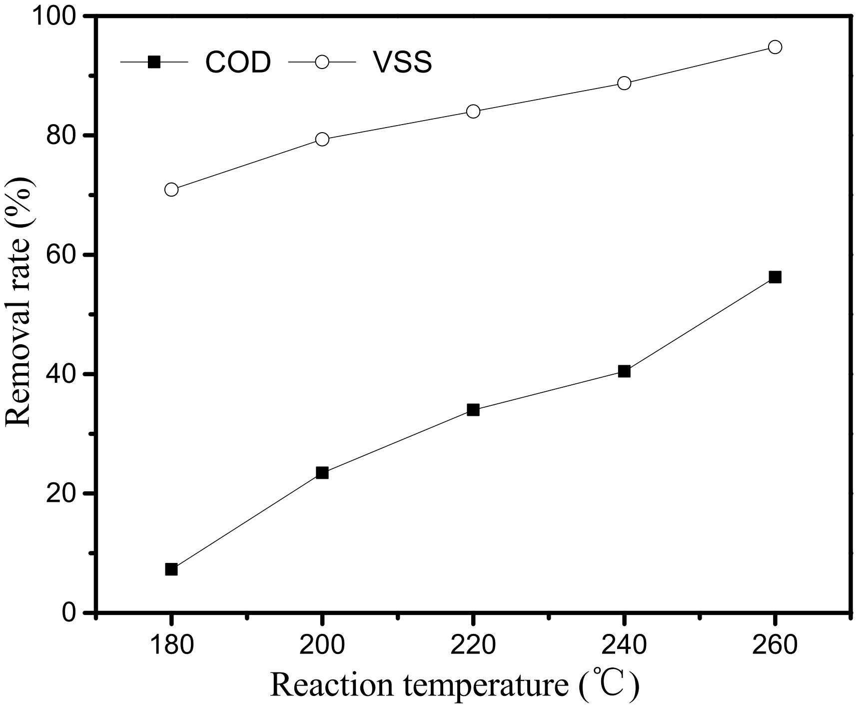


Figure 2. Effect of reaction temperature (60 min, NaOH 0.5 g·L^{-1}, initial oxygen supply 1.0 MPa).

2.3. Effect of Reaction Time

The reaction efficiency of the wet oxidation process showed a strong dependence on the reaction time, as shown in Figure 3. With the extension of reaction time, the VSS and COD removal rates increased. It should be noted that the COD removal mainly came from the oxidizing reaction of organic compounds with the soluble oxidant, i.e., gaseous oxygen, which would be influenced easily by the gas-liquid mass transfer. Compared with the COD removal rates, the VSS removal rates did not change much. The reason may be that the VSS removal was mainly due to the thermal hydrolysis of sludge, which took place rapidly within a short time. Therefore, when the reaction time was increased, the increase in VSS removal was insignificant. In Pintar's study, byproducts and free radical species were identified [27]. The hydroxyl radical was proven to be most active in oxidizing the organic compounds to small carboxylic acids, even CO_2 and H_2O. With the extension of reaction time, that refractory compound (i.e., acetic acid) accumulated in the wet oxidation process. Therefore, the total COD removal rate was not very high. However, the VSS had already been largely removed. OH- has been widely considered the most active species in wet oxidation systems. In Ricq's study, the reaction mechanism of sewage sludge degradation by wet air oxidation was studied [29]. Cellulose was selected as a model compound for activated sludge, and the results induced the identification of by-products and free radical species participating in the reaction. With the extension of time, the degradable organics in the liquid accumulated. Organic matter with higher activation energy began to oxidize, so that the overall reaction rate was greatly improved. 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 transferred into the liquid phase within a short time, which leads to a high VSS removal rate. However, the COD removal rate was not high. The reason may be that carboxylic acids with small molecule weights, such as formic acid or acetic acid, were formed in the wet oxidation process and were not easily oxidized. Thus, the produced acetic acid and other carboxylic acids accumulated, which induced an increase in the COD removal rate. From the above results, we can conclude that the COD removal rate would be stable once the organic materials, which are easily oxidized, had been oxidized. Thus, considering the oxidation efficiency and economic factors, we chose 60 min as the reaction time for the subsequent study of wet oxidation.

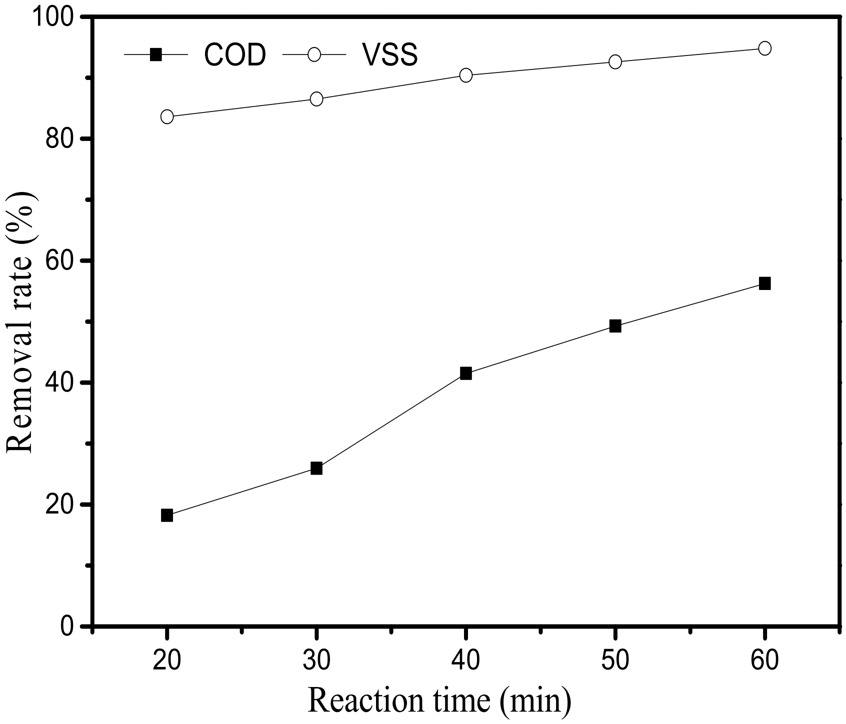


Figure 3. Effect of reaction time (260 °C, NaOH 0.5 g·L^{-1}, initial oxygen supply 1.0 MPa).

2.4. *Effect of Initial Oxygen Pressure*

The effect of the initial oxygen pressure was studied by varying it from 0.2 to 1.0 MPa. The VSS and COD removal rates increased remarkably (see Figure 4). Because oxygen plays an oxidation agent role, the oxygen amount is very important. Once the oxygen gas was not sufficient, the wet oxidation of sludge would not be sufficiently reacted. In addition, the amount of dissolved oxygen increased with increasing oxygen pressure, which induced an increase in free radicals, i.e., the strong oxidation species; therefore, the oxidation efficiency increased. However, when the initial oxygen pressure changed from 0.8 to 1.0 MPa, the VSS and COD removal ratings increased little. The reason may be that the oxidizing agent is not enough under this condition. As the pressure continued to increase, the removal rate of COD increased, but the rate of increase slowed. The catalyst changed the oxygen utilization rate. COD removal was also obviously increased at a low initial oxygen pressure. Under higher oxygen pressures, the dissolved oxygen concentration increased and favored the formation of strong oxidative species, which resulted in enhanced oxidation. Therefore, the high pressure could efficiently accelerate the oxidation reaction rate and eliminate organic compounds, resulting in high COD and VSS removal.

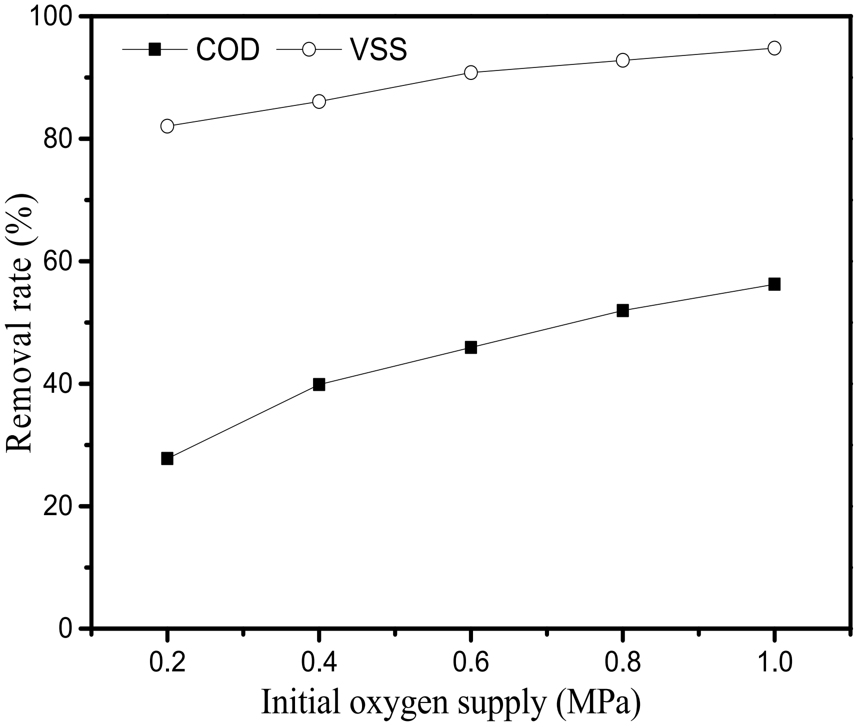


Figure 4. Effect of initial oxygen supply (260 °C, 60 min, NaOH 0.5 g·L^{-1}).

2.5. Discussion

To date, it is very rare to see relevant research on the oxidation mechanism of sludge under hydrothermal conditions. Actually, the reaction mechanism is very complicated because large amounts of intermediates were produced in the wet oxidation process. Normally, wet oxidation is assumed to be a free radical oxidation process, as shown in Equations (1)–(5) [30,31]. In the first step, the organic compounds reacted with oxygen molecules and produced many free radical agents, mainly ·OH. Then, the intermediates reacted with ·OH and degraded into small molecule carboxylic acids, such as acetic acid. Eventually, the organic acids were oxidized into CO_2 and H_2O.

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R\cdot} + \mathrm{HOO\cdot} \tag{1}$$

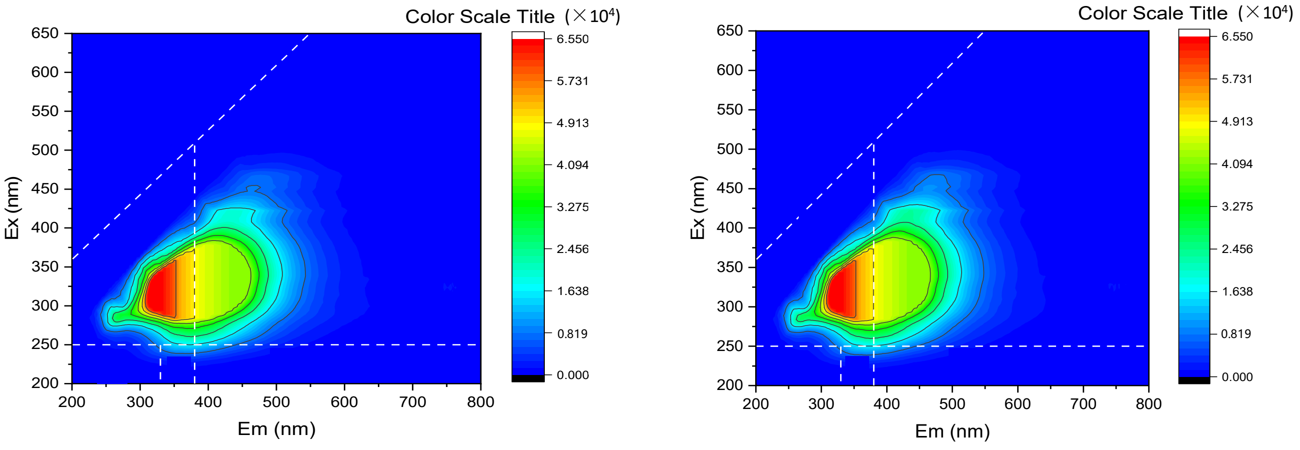
$$\mathrm{R\cdot} + \mathrm{O_2} \rightarrow \mathrm{ROO\cdot} \tag{2}$$

$$\mathrm{RH} + \mathrm{\cdot OH} \rightarrow \mathrm{R\cdot} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{ROO\cdot} + \mathrm{RH} \rightarrow \mathrm{Acids} + \mathrm{R\cdot} \tag{4}$$

$$\mathrm{Acids} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{5}$$

Three-dimensional excitation–emission matrix fluorescence spectroscopy (3DEEM) was applied to characterize the change of different molecular weight organic matter in wet oxidation liquid. As shown in Figure 5, the UV fulvic-like fluorophore, the protein-like fluorophore, the visible fulvic-like fluorophore, and the humic-like fluorophore were detected. It can be seen clearly that the humic-like fluorophore was enhanced significantly with the addition of NaOH, which increased the formation of carboxylic acids. Wang studied the thermal hydrolysis of sludge [31]. In Wang's study, four fluorescence peaks were identified in 3DEEM of the raw sewage sludge and thermally hydrolyzed sewage sludge: Peak A, Peak B, Peak C, and Peak D, which could be attributed to the UV fulvic-like fluorophore, the protein-like fluorophore, the visible fulvic-like fluorophore, and the humic-like fluorophore, respectively. Results of the peak intensity in different molecular weight organic matter in thermally hydrolyzed sewage sludge showed that in the thermal hydrolysis process, the main reaction of the fulvic-like organic matter and the humic-like organic matter was the dissolving process, while the main reaction of the protein-like organic matter was the hydrolyzing process. Compared with Wang's study, the result of wet oxidation is different from that of thermal hydrolysis, mainly liquification. Wet oxidation includes the oxidation of the products from the thermal hydrolysis of sludge. Therefore, the molecular weight of the matter in the wet oxidation liquid is smaller than that of the thermal hydrolysis products. To sum up, NaOH plays an important catalytic role in the wet oxidation of sludge, which enhances the decomposition of the sludge and the degradation of intermediates produced in the wet oxidation process.



(**a**) (**b**)

Figure 5. 3D Excitation-emission matrix spectra of wet oxidation liquid (**a**): without NaOH; (**b**): with NaOH.

In Figure 6, the concentration of carboxylic acids in wet oxidation liquid was analyzed, including acetic acid, formic acid, and oxalic acid. As shown in Figure 6, the concentration of acetic acid increased by about 2000 $mg \cdot L^{-1}$ when comparing the results with and without the addition of NaOH. The reason may be that the oxidation of acetic acid was inhibited by the addition of NaOH. It is evident that the addition of NaOH also increased the production of formic acid and oxalic acid. It is very interesting that the concentration of acetic acid increased with the increase in reaction temperature. However, the concentrations of formic acid and oxalic acid decreased with the increase in reaction temperature. The possible reason may be that higher temperatures are favorable for the production of acetic acid. However, formic acid and oxalic acid were easier to oxidize than acetic acid. Then the concentrations of formic acid and oxalic acid decreased. These results showed that acetic acid would be the main product of sludge oxidation. Because sodium acetate is always used as a carbon source for wastewater treatment, the produced wet oxidation solution was suitable for the utilization of carbon sources in wastewater treatment. The wet oxidation liquid is promising for its utilization as a carbon source, which is economical compared with the consumption of sodium acetate or methanol.

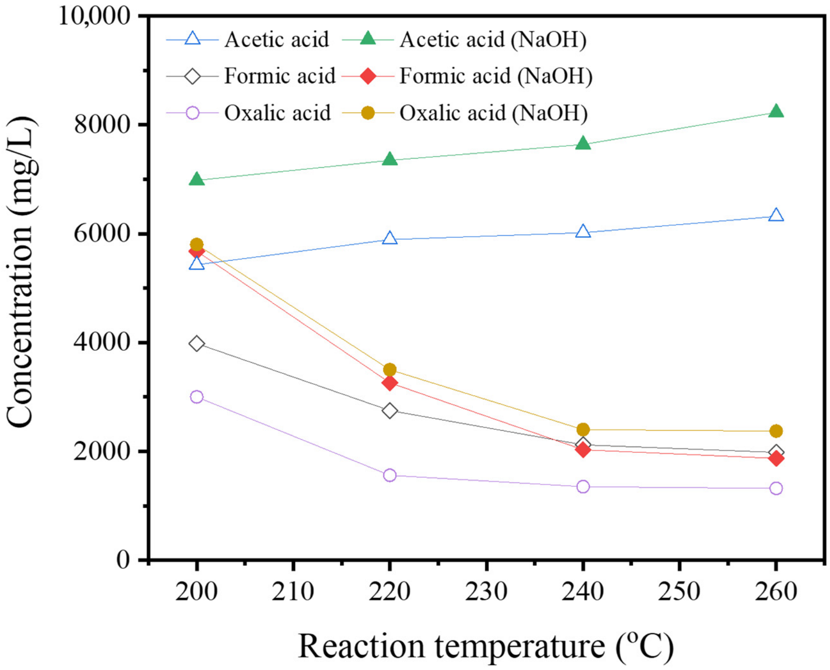


Figure 6. Concentration of carboxylic acids in wet oxidation liquid.

The reaction pathway of sludge oxidation was discussed, as shown in Figure 7. From the experimental results and discussion above, we suppose that, in the first step, the existence of NaOH accelerated the thermal hydrolysis of sludge, which produced a mixed liquid with soluble organic compounds and inorganic solids. As a result, the VSS removal rate was very high, even for such a short time. In the second step, the soluble organic compounds reacted with free radical species and produced carboxylic acids, such as acetic acid. Urrea reported the wet oxidation mechanisms of sludge [32]. In the first step, the reaction is mainly thermal hydrolysis, with the outer fractions of microbial hydrolysis occurring before the inner fractions. A large partition of proteins, lipids, and other insoluble organic matter is transferred into liquid. This releases intracellular content, and the complex molecular compounds and cellular content are broken down. Once the thermal hydrolysis process was finished, large amounts of organic compounds were diluted into the liquid, which was easily oxidized by free radicals. These phenomena were similar to the results of this study. On the other hand, the existence of NaOH accelerated the thermal hydrolysis, which induced high VSS removal in this process. The final pH was 9.5~10.2 with the addition of NaOH. The BOD/COD ratio was about 0.58~0.65 after the reaction. In addition, the existence of OH could accelerate the reaction efficiency of free radical agents. Therefore, NaOH is assumed to be a bifunctional catalyst, including the catalytic effect for thermal hydrolysis in the first step and for wet oxidation in the second step. The low-molecular-weight carboxylic acids produced, including acetic acid, showed potential for further commercial development and could be utilized as carbon sources in the wastewater treatment process. The solids after the reaction are mainly inorganic substances, which could be used for the manufacture of building materials. One of the advantages of wet oxidation is that little pollutant gas is produced, which can be treated easily. From the point of view of energy consumption, exothermic reactions can maintain the reaction owing to the oxidation of pollutants. Therefore, wet oxidation can be regarded as an ideal method for the volume reduction and resource utilization of pharmaceutical sludge. These results illustrated that the wet oxidation of sludge provided a promising method for industrial utilization. Furthermore, these results indicated that NaOH is a promising alkaline catalyst in wet oxidation processes for the high-efficiency degradation of pharmaceutical sludge.

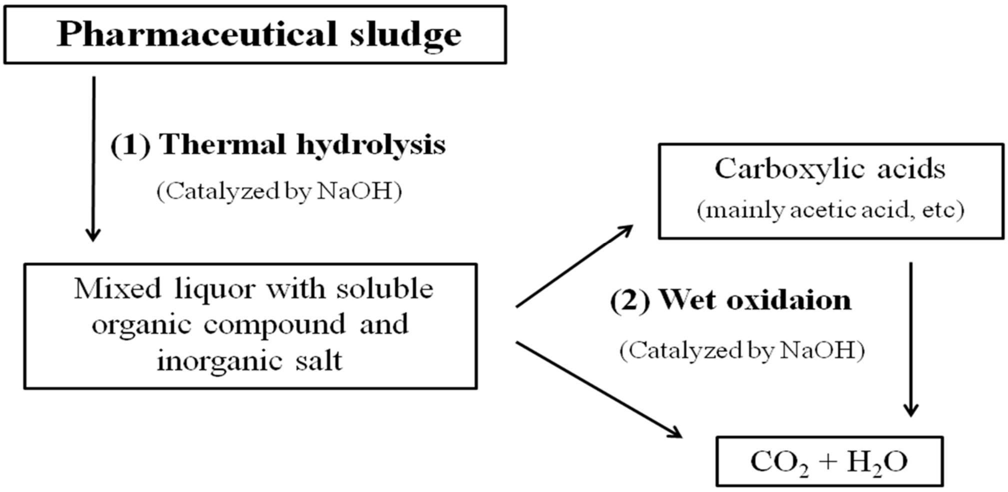


Figure 7. Diagram of the proposed degradation pathway.

3. Material and Methods

3.1. Materials

The raw pharmaceutical sludge was selected for the study from a synthetic pharmaceutical factory, located in Zhejiang Province, China. The characteristics were as follows. Total COD value of the sludge solution: from 19,000 to 20,000 $g \cdot L^{-1}$; the VSS value: from 15.5 to 15.8 $g \cdot L^{-1}$; the suspended solid value: from 15.8 to 16.9 $g \cdot L^{-1}$. pH was 7.5~8.5. NaOH and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All of the reagents used in this study were of analytical grade and were used as received without further purification. The gaseous oxygen (industrial gaseous oxygen, 99.5%) used as the oxidant was commercial industrial gas.

3.2. 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 [21]. 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 °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 sampled and analyzed.

3.3. Analysis

The analyses performed to characterize the sludge were VSS and COD. The detailed analysis information could be found elsewhere [21,22]. 3D-EEM analysis was used to assess the degradation of sludge. After the wet reactions, the liquid samples were collected and filtered with a 0.22 μm filter membrane. Identification and quantitative analysis for liquid samples were conducted to detect VFAs [33] using high-performance liquid chromatography (HPLC, Agilent 1200, Santa Clara, CA, USA) with refraction index (RI; RI-2031 plus; Jasco, Tokyo, Japan) and ultraviolet-visible (870-UV; Jasco, Tokyo, Japan) detectors. Sugar-SH1011 (Showa Denko, Tokyo, Japan) was used as the column medium. 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.

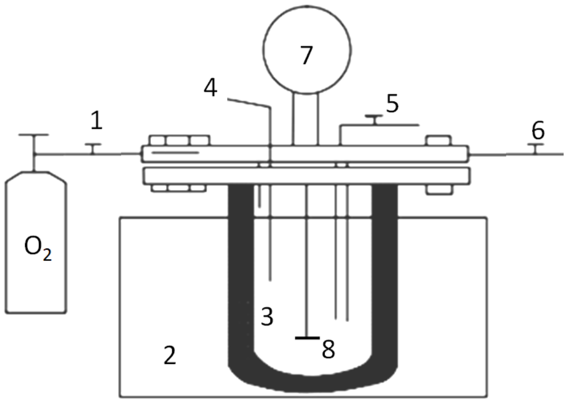


Figure 8. Diagram of wet oxidation reactor. 1—oxygen supply, 2—heating jacket, 3—oxidation reactor, 4—thermocouple, 5—discharge of gas, 6—bleeder valve, 7—pressure meter, and 8—stirrer.

4. Conclusions

In this study, enhanced wet oxidation of excess sludge from pharmaceutical wastewater by NaOH as an alkaline homogeneous catalyst was investigated. The effects of the catalyst amount, temperature, time, and oxidant amount were analyzed. The maximum value of VSS removal, 95.2%, was achieved at 260 °C within 60 min with an initial oxygen pressure of 1.0 MPa and NaOH of 0.5 $g \cdot L^{-1}$. Simultaneously, the COD removal rate reached 57.3%. The increase in VFA concentration demonstrated that NaOH acted as an effective catalyst. Interestingly, the production of acetic acid increased significantly, which could be used as a carbon source. Based on the detection of intermediate products, possible reaction pathways were discussed. The carboxylic acids were formed due to the oxidative decomposition of intermediate products such as butanedioic acid, levulinic acid, maleic acid, fumaric acid, etc. These results illustrated that the wet oxidation of sludge provided a promising method for industrial utilization. Furthermore, these results also indicated that NaOH is a promising alkaline catalyst in wet oxidation processes for the high-efficiency degradation of pharmaceutical sludge.

Author Contributions: X.Z. conceived and designed the experiments; K.F. performed the experiments; Y.Z. analyzed the data; X.Z. contributed reagents/materials/analysis tools; X.Z. and Y.Z. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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