

Article

The Treatment of Antibiotic Excess Sludge via Catalytic Wet Oxidation with Cu-Ce/ γ -Al₂O₃ and the Production of a Carbon Source

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Abstract: In the present study, the effectiveness of catalytic wet oxidation triggered by using Cu-Ce/ γ -Al₂O₃ to degrade antibiotic excess sludge was investigated, during which some small molecule carboxylic acids were produced, which are valuable in biological wastewater treatment as an organic carbon source. The influence of reaction parameters on the degradation efficiency was explored through single-factor and orthogonal experiments, including catalyst amount, reaction temperature and time, and oxygen supply amount. The results illustrated that the treatment system can achieve 81.2% COD and 93.8% VSS removal rates under optimized reaction conditions. Carboxylic acids produced after the sludge degradation mainly included acetic acid, propanoic acid, etc. The results of wastewater biological treatment experiments exhibited that the degraded solution after catalytic wet oxidation has potential to be used as a carbon source to meet the demand of biological treatment, which helps the removal of COD and TN. This work confirms the effectiveness of catalyst for enhancing antibiotic excess sludge treatment, which provided a new idea for the rational disposal of antibiotic excess sludge.

Keywords: antibiotic excess sludge; catalytic wet oxidation; carboxylic acid; carbon source



Citation: Chu, S.; Lin, H.; Zeng, X. The Treatment of Antibiotic Excess Sludge via Catalytic Wet Oxidation with Cu-Ce/ γ -Al₂O₃ and the Production of a Carbon Source. *Water* **2024**, *16*, 1249. <https://doi.org/10.3390/w16091249>

Academic Editor: José Alberto Herrera-Melián

Received: 2 March 2024

Revised: 21 April 2024

Accepted: 22 April 2024

Published: 27 April 2024



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1. Introduction

Wastewater treatment plants have been employed throughout the world to treat wastewater and are a key part of the residential water cycle [1]. Due to the increase in the production and consumption of drugs, an increasing concentration of pharmaceutical compounds has gained much attention. However, due to the complex composition of sewage wastewater admitted to sewage treatment plants, antibiotic substances are difficult to be degraded effectively. At the same time, microorganisms in the sewage treatment system develop resistance under the influence of antibiotics, which not only deteriorates its treatment effect, but also may be discharged with the effluent water to cause a risk of polluting the natural water environment [2–4]. Pharmaceutical wastewater contains various high toxicity pollutants, including refractory antibiotics. Some antibiotics are adsorbed in pharmaceutical sludge. Therefore, it is important to adopt effective methods to dispose of antibiotic-containing sludge. Usually, the disposal methods of residual sludge include landfilling and incineration, among which incineration has certain economic benefits, while landfilling poses the risk of environmental leakage, which is not suitable for the treatment of hazardous sludge [5–7]. With regard to the incineration method, secondary pollutants can be released, for example, dioxins, sulfur, and nitrogen oxides [8]. In recent years, advanced oxidation technology has demonstrated a large application potential in sludge treatment [9–11]. Antibiotic sludge safety issues and resource utilization could be solved at the same time by choosing a reasonable disposal method. Catalytic wet oxidation technology has been widely studied due to its strong oxidizing properties for

organic pollutants [12,13]. In this process, the solid was transferred to liquid through thermal hydrolysis, which happened during the solubilization process. This process provides high volume reduction efficiency and stabilization of heavy metals. Some small molecule organics, produced after the oxidation process, may be utilized for the growth of microorganisms. Furthermore, compared with expensive incineration technology, this process is cheaper, because it can be conducted with a self-sustaining condition and heat can be resource-utilized. However, there is a lack of detailed study on the treatment and utilization of antibiotic-containing sludge using catalytic wet oxidation, and the degradation mechanism is still unclear. The biochemical performance of the reaction solution after oxidative degradation of sludge and its performance as a carbon source for reuse in wastewater treatment systems are not clear. The antibiotic excess sludge can be degraded efficiently to improve its safety, and, at the same time, the degraded material can be used as a carbon source to replenish the sewage treatment system to improve the biochemical properties of the system, which is extremely favorable to save treatment costs and begin a new process.

Recent studies have focused on the exploitation of new catalysts, which induced a decrease in the operating temperature and an increase in the reaction efficiency [14,15]. For instance, various solid catalysts and homogeneous catalysts exhibited high efficiency, including Cu^{2+} , Mn^{2+} , and Ni^{2+} [16,17]. In our previous studies, we reported on some catalysts, for example, $\text{CuO-CeO}_2/\gamma\text{-Al}_2\text{O}_3$, molecular sieve, etc. [18]. Aluminum oxides are commonly used as catalytic wet oxidation catalysts to enhance oxidation performance [19,20]. Among them, Al_2O_3 is widely used due to its good catalytic performance, high stability, low cost and is easy to obtain. $\gamma\text{-Al}_2\text{O}_3$ has a larger specific surface area than $\alpha\text{-Al}_2\text{O}_3$, with excellent heat resistance and high porosity; thus, higher-activity catalytic materials can be obtained with it. Doping modification with rare earth metals can not only obtain well-dispersed composite catalysts, but it also greatly optimizes the reaction conditions and reduces energy consumption [14,21]. For example, a Cu-loaded catalyst exhibited a notable enhancement of the oxidation of acetaldehyde under wet oxidation conditions [22]. In Chou's study, the oxidation of aromatic compounds was enhanced considerable with a Cu-based catalyst [23]. Taran et al. reported the noticeable effect of Cu in the catalytic wet peroxide oxidation for the treatment of formic acid and phenol [24]. In addition, a Ceria-based catalyst also attracted much attention in the catalytic wet oxidation of pollutants [25,26]. However, the catalytic wet oxidation of real industrial sludge has been rarely studied. Furthermore, the production of useful chemicals in the catalytic wet oxidation is not clear.

Some volatile fatty acids (VFAs), including acetic acid, propanoic acid, etc., can be generated in a considerable amount with in the wet oxidation solution of sludge [27]. These acids have the potential to be utilized as an organic carbon source for the biological treatment of wastewater. Gapes reported on the high yield of VFAs in the catalytic wet oxidation treatment of sludge [28]. Specifically, Chung reported that the concentration of propionic acid could be obtained with 13.5 mg/L at 240 °C in the catalytic wet oxidation of sewage sludge [29]. Up until now, a lot of the available literature has reported that acetic acid and other useful chemicals can be generated after the wet oxidation of organic pollutants [30,31]. Therefore, the study of the production and utilization of VFAs in the catalytic wet oxidation of sludge is very important.

Therefore, in the present study, we used the catalytic wet oxidation technique to treat antibiotic sludge in order to change its physicochemical properties and generate a microbially available organic carbon source. The degradation performance and influencing factors of the Cu-Ce-modified $\gamma\text{-Al}_2\text{O}_3$ catalyst on the antibiotic/sludge mixture were investigated. The organic acids produced during the degradation process were identified. Further, A/O processes were constructed to explore the effects of utilizing the degradation solution as a carbon source on the effluent indexes, and the effects of replacing the degradation solution by adding other carbon sources were compared. These results can provide a reference for the treatment of the antibiotic/sludge mixture and carbon source utilization.

2. Materials and Methods

2.1. Synthesis of Cu-Ce/ γ -Al₂O₃

The specific preparation method was as follows: γ -Al₂O₃ was used as a carrier, repeatedly washed with distilled water 3~5 times until the cleaning solution was clear, dried at 105 °C, and then roasted for 3 h at 550 °C. After cooling, it was placed in a mixed solution of Cu and Ce nitrate at a concentration of 2.0 mol/L. The pH value was adjusted to about 10.0 by adding NaOH; then, the solution was filtered and dried. Afterwards, it was baked in a muffle furnace at 700 °C for 3 h and cooled naturally to obtain a Cu-Ce/ γ -Al₂O₃-supported catalyst.

2.2. Characterization

The morphology and structure of the prepared catalyst were analyzed via scanning electron microscope (FESEM, SU8020, HITACHI, Tokyo, Japan) measurements with energy-dispersive X-rays spectroscopy (EDS). Brunauer–Emmett–Teller (BET) analysis was used for the acquisition of the surface area and pore size distribution information (America, XiGo Nanotools, Acorn Area, Freehold, NJ, USA). Temperature-programmed oxidation (TPO) was used to determine the carbon adsorption on the Cu-Ce/ γ -Al₂O₃'s surface.

2.3. Catalytic Wet Oxidation Experiments

The sludge used in this study was acquired from a pharmaceutical factory which produced antibiotics, mainly cefaclor. The concentration of antibiotics was lower than 500 mg/L. In addition, the sludge contained other pollutants, such as chemical extractants and microbial fluid. The catalytic wet oxidation of the antibiotic/sludge solution was performed in an autoclave reactor. Specifically, 50 mL of the antibiotic/sludge mixture was added to the reactor, with an initial COD of 15,000~16,000 mg/L. The reaction temperature varied from 180 to 260 °C, the reaction time varied from 20 to 60 min, and the oxygen supply amount with the initial oxygen pressure varied from 0.2 to 1.0 MPa. A stirring speed of 300 r/min was chosen in the experiments. The reactor was cooled to room temperature once the desired reaction time was obtained. Then, the reacted liquid was collected to perform the COD and VSS analyses with a standard method [18]. Experimental reagents, including the catalyst carrier γ -Al₂O₃, were acquired from Shanghai Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. They were utilized in the experiments without any further treatment. The removal rates of COD and VSS were calculated based on the analytic results of the final liquid.

2.4. Experimental Setup of Oxidation Liquid as Organic Carbon Sources

The laboratory has built a small-scale experimental device with a processing capacity of 24 L/d, and the process flow diagram is shown in Figure 1. The device is made of organic glass material and can simulate the two-stage A/O series process. By adjusting the influent positions at different heights of the pool body, the residence time of the anoxic pool and the aerobic pool can be adjusted. By controlling the pump flow rate, adjustments are made to the reflux ratio of the mixed liquid and sludge. This reaction device can achieve primary A/O operation or secondary A/O series operation.

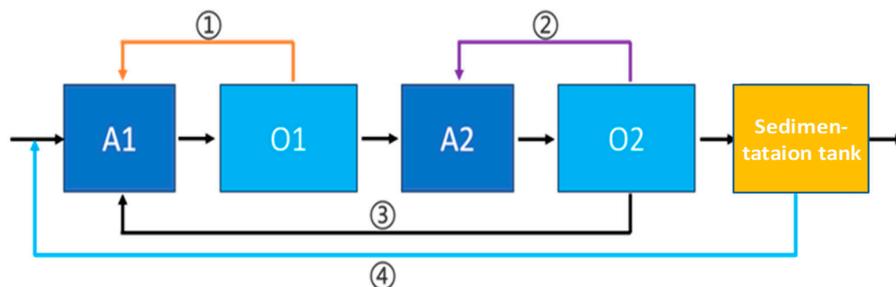


Figure 1. The process flow diagram of the simulated two-stage A/O process (① nitrification liquid reflux from primary aerobic tank to primary anaerobic tank; ② nitrification liquid reflux from secondary aerobic tank to secondary anoxic tank; ③ nitrification liquid reflux from secondary aerobic tank to primary anaerobic tank; ④ sludge reflux from sedimentation tank to primary anoxic tank).

3. Results and Discussion

3.1. Physicochemical Properties of the Cu-Ce/ γ -Al₂O₃

SEM analysis was conducted on the prepared catalyst. Figure 2a shows that the catalyst powder has good uniformity and uniform distribution of loaded particles on its surface. The EDS result (Figure 2b) shows that Ce and Cu elements were loaded on the surface of Al₂O₃. SEM photos show that the active component loading of the catalyst is relatively high, indicating that the introduction of Ce as an auxiliary agent has a positive effect on the morphology. The SEM-EDS spectrum indicated that the loading of the active components of the catalyst was successful. From the TPO spectrum (Figure 2c), it can be seen that according to the proportion change of the mixed gas caused by the consumption of oxygen via TPO, the oxygen consumption of the sample was detected by the detector. During the low-temperature reaction stage, which was 250~260 °C, the surface of the Cu-Ce/ γ -Al₂O₃ was not prone to carbon adsorption. The BET measurement results show that the catalyst had a large specific surface area (142.39 m²/g) (Figure 2d).

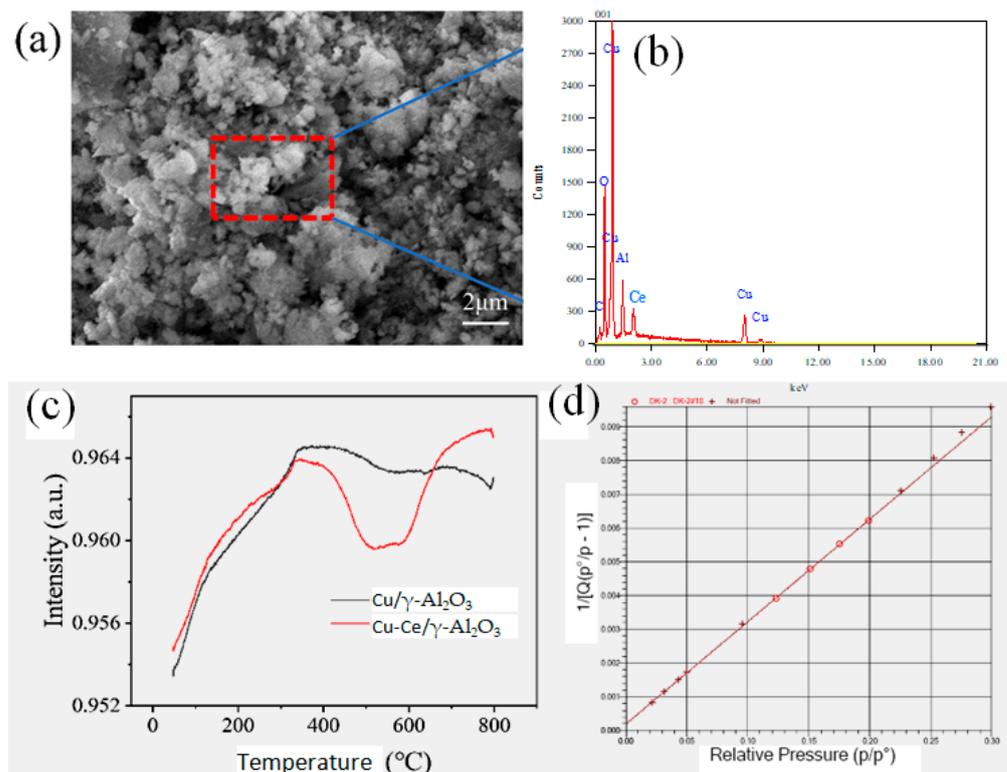


Figure 2. (a) SEM image of Cu-Ce/ γ -Al₂O₃ and (b) the corresponding content of elements; (c) temperature-programed oxidation spectra; (d) BET linear curve of Cu-Ce/ γ -Al₂O₃.

3.2. Influence of Experimental Parameters on Antibiotic/Sludge Degradation

3.2.1. Cu-Ce/ γ -Al₂O₃ Dosage

The influence of catalyst dosage was investigated by changing the additional amount of the catalyst by 1.0, 3.0, 5.0, and 7.0 g/L in the wet oxidation reaction system, with the reaction temperature 260 °C for 60 min and initial oxygen pressure 1.0 MPa. As shown in Figure 3, the removal of COD and VSS can reach its highest at 81.2% and 93.8%. With the increase after the addition of the Al₂O₃ catalyst, the removal of COD from the sludge gradually first increases and then remains basically unchanged, indicating that the catalyst plays an important role in shortening the reaction cycle. The removal rate of sludge VSS also increases with the addition of the catalyst, but the change increase is not significant, and the increase is not significant after the amount of the catalyst is changed to 5.0 g/L. Considering the industrial application of catalysts, this study did not consider adding too much of the catalyst, and it is believed that adding 5.0 g/L is sufficient.

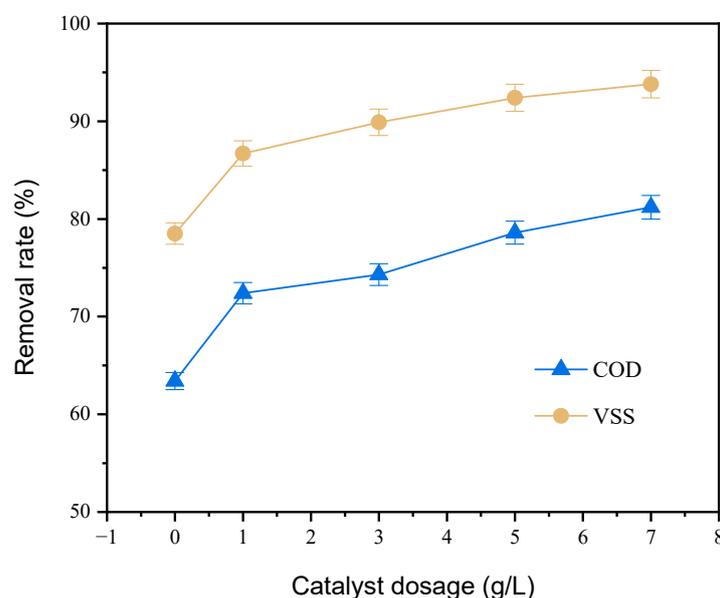


Figure 3. Influence of catalyst dosage on the sludge degradation.

3.2.2. Reaction Temperature

As shown in Figure 4, the removal of COD and VSS from the sludge noticeably increased with a higher reaction temperature after the addition of catalysts. Therefore, the influence of the reaction temperature in catalytic wet oxidation is very important. The increase in COD and VSS removal rates significantly slowed down when the reaction temperature was elevated from 240 °C to 260 °C. Compared with the reaction in the absence of a catalyst, the addition of the catalyst significantly increased the reaction rate. Considering factors such as the effectiveness of catalytic wet oxidation treatment at various temperatures, the activity efficiency of the catalyst, the requirements of a temperature increase on the reactor material, and the safety and controllability of subsequent pilot experiments, 260 °C was selected as the reaction temperature for subsequent research.

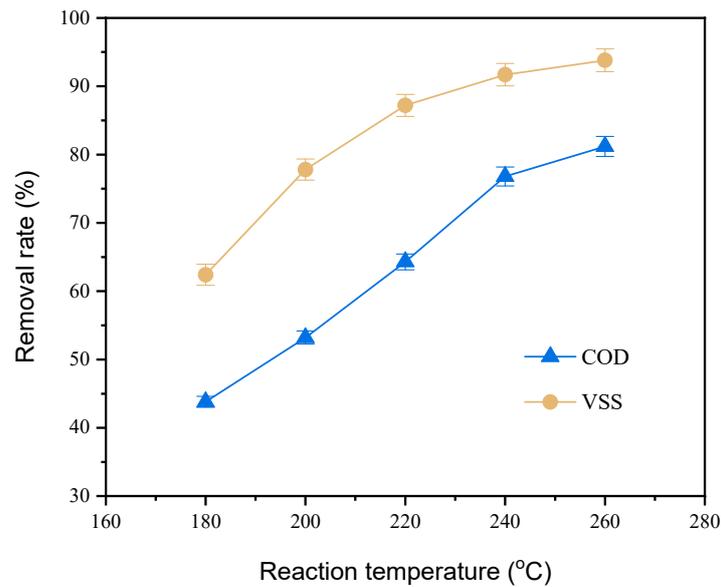


Figure 4. Influence of reaction temperature on sludge degradation.

3.2.3. Reaction Time

As can be seen from Figure 5, the results show that the removal of sludge VSS can achieve good results in a short time. The COD removal rate of sludge was low with a short time and gradually increased with the extension of the reaction time. The main reason for this is that the thermal hydrolysis of sludge is rapid under a reaction temperature of 260 °C, and the VSS in the solid phase of sludge can be quickly dissolved into the liquid phase via thermal hydrolysis; due to these reasons, a high removal rate of VSS can be achieved quickly. These phenomena show that in the process of catalytic wet oxidation, organic materials with low activation energy participate in the reaction and can be rapidly oxidized without the action of a catalyst under the reaction conditions, with an extended time. Moreover, the organic matter in the solid phase is transferred to the liquid phase, and the organic materials available for degradation in the liquid phase are accumulated. At this time, due to the presence of the catalyst, organic products with a higher activation energy also begin oxidize in large quantities; thus, the overall reaction speed increases greatly, the concentration of the reactants decreases, and the reaction rate decreases.

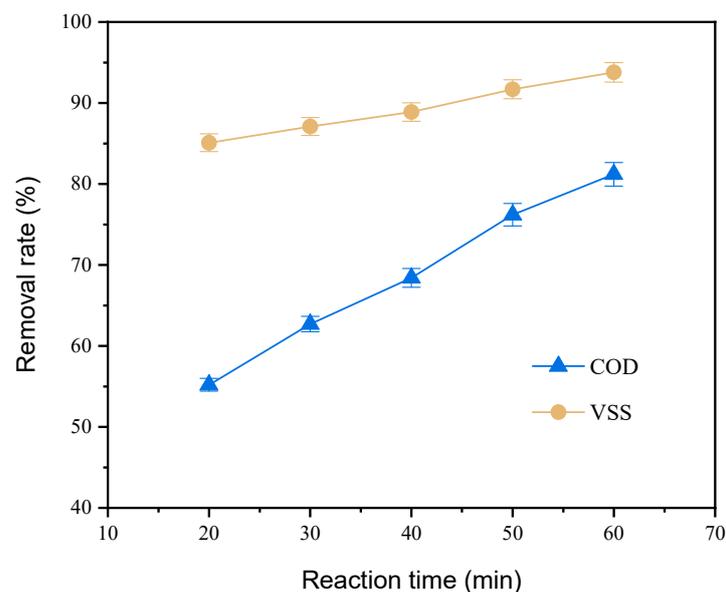


Figure 5. Influence of reaction time on sludge degradation.

3.2.4. Supplement of Oxygen

As can be seen from Figure 6, the initial oxygen pressure has a great influence on the removal rate of COD and VSS in the antibiotic/sludge mixture treated via catalytic wet oxidation. In Figure 6, due to the limitation of the amount of oxygen added to the oxidant, the COD removal rate increased most significantly when the initial oxygen pressure increased from 0.2 to 0.8 MPa. Compared to the experiment with or without a catalyst, the removal rate of VSS was affected by the initial oxygen pressure by more than 15% when the pressure was 1.0 MPa compared to a pressure of 0.2 MPa, in which it was affected to a lesser extent. When the reaction pressure increased from 0.8 MPa to 1.0 MPa, the increase in the COD removal rate slowed down. The reason for this may be that acetic acid is formed during the oxidation process, with it being difficult to further oxidize, which hinders the promotion of the oxidant with regard to an improvement in the COD removal rate.

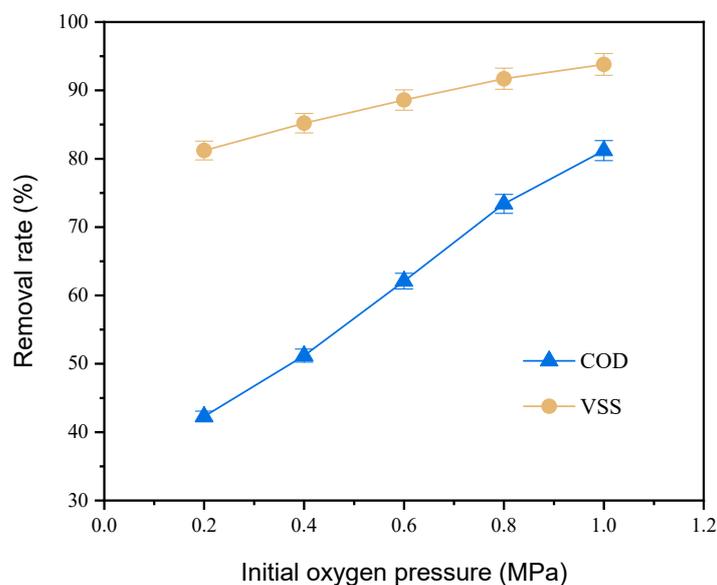


Figure 6. Influence of initial oxygen pressure on sludge degradation.

3.3. Optimization of Reaction Parameters

Based on the above experimental results, four factors, namely catalyst addition, reaction temperature, reaction time, and initial oxygen pressure, were selected to conduct orthogonal experiments at three research levels to investigate the optimal operating conditions of the catalyst for treating antibiotic/sludge liquid. The details are shown in Table 1.

Table 1. Orthogonal experimental parameters.

Level	Factors			
	(A) Catalyst Dosage (g)	(B) Temperature (°C)	(C) Time (min)	(D) Pressure of Oxygen (MPa)
1	4.0	220	30	0.6
2	5.0	240	45	0.8
3	6.0	260	60	1.0

It can be concluded from the experimental results that the influence of each factor is different depending on whether the COD or VSS removal rates are used to evaluate the index. In one of the results, when the COD removal rate was used as the experimental index, the primary and secondary influencing order of each factor was B (reaction temperature) > C (reaction time) > D (initial oxygen pressure) > A (catalyst addition), and the extreme difference of reaction temperature was the most influential factor, with catalyst addition

being the least important factor. When the VSS removal rate was taken as the experimental index, the primary and secondary influencing orders of each factor were D (initial oxygen pressure) > B (reaction temperature) > A (catalyst addition) > C (reaction time), and the difference between the initial oxygen pressure and the reaction temperature was large and similar, indicating that in the presence of catalyst, temperature and oxygen pressure played a huge role in the VSS removal in the reaction, which was the most important factor. Moreover, the reaction time was very small, which was the least important factor, and the amount of catalyst added was the second most important factor. The results show that in the sludge catalytic wet oxidation reaction system, the reaction temperature is the most important influencing factor for degradation, and it can be said that it plays a decisive role. Considering the role of various influencing factors, reactor design requirements, and economic costs, it is recommended to select appropriate process parameters for adjusting the reaction temperature to 260 °C, the reaction time to 60 min, the initial oxygen pressure to 1.0 MPa, and the catalyst addition to 5.0 g/L.

3.4. Production of Carboxylic Acids

In this study, the effect of the reaction temperature on the production of carboxylic acids was investigated, and the results are shown in Table 2. The VFAs were identified and quantitatively analyzed using gas chromatography (G5, Persee General Analytical Instrument Co., Ltd., Beijing, China) with bonded polyethylene glycol capillary columns. The results show that the reaction temperature had a positive effect on the formation of acetic acid, mainly because with the increase in the reaction temperature, the intermediate product oxidized to form acetic acid; however, acetic acid is difficult to oxidize and decompose under high temperature conditions, so the yield increases because of this. Propionic acid and isobutyric acid were not stable under a high reaction temperature; therefore, the yields gradually decreased with the increase in the reaction temperature. In general, the organic components of sludge are basically oxidized and degraded into small molecule organic carboxylic acids after the wet oxidation reaction, mainly including acetic acid, propionic acid, and isobutyric acid, which are easily biodegradable substances—especially acetic acid, which can be used as an organic carbon source to achieve resource utilization.

Table 2. Production of VFAs.

Reaction Temperature (°C)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	Isobutyric Acid (mg/L)	Isovaleric Acid (mg/L)
200	1620	90	50	70
220	2680	140	80	90
240	3470	180	90	100
260	3620	150	60	40

3.5. Oxidation Solution as an Organic Carbon Source for Sewage Treatment

In this study, the effect of the wet oxidation reaction solution as an organic carbon source in a wastewater treatment system was verified by using a A/O tandem process through laboratory trials. The operating parameters of the first level A/O process were based on a retention time of 24 h in the anaerobic tank and 72 h in the aerobic tank, with a mixed liquid reflux of 300% and a sludge reflux of 100%. The water quality of the influent and effluent were recorded after allowing for a period of stability (Figure 7).

The results showed that the total nitrogen in the influent was about 235 mg/L, and the concentration of the effluent decreased gradually to lower than 30 mg/L with an increase in time. Due to the poor biochemical properties of some organic compounds in wastewater, they are difficult to be utilized by denitrifying bacteria. In order to improve the removal of total nitrogen, it is necessary to add organic carbon sources with good biochemical properties, such as carbohydrates, alcohols, and organic acids. Compared with the results in the absence of oxidation solution, the total nitrogen in the effluent was still above 100 mg/L. These results indicate that wet oxidation solution served as an organic

carbon source in the wastewater treatment system, providing a reference for the resource utilization of organic carbon.

As shown in Table 2, the produced VFAs mainly comprised acetic acid. The reason for this may be that the acetic acid was stable and was not easily oxidized or decomposed under wet oxidation reaction conditions. In fact, the VFAs produced by the wet oxidation of sludge included more than ten types of carboxylic acids. After the oxidation process, the B/C value of the liquid increased noticeably up to 0.68, which shows that the liquid was easily adopted by the microorganisms. It should be noted that acetate sodium has always been chosen as the organic carbon source in the biological wastewater treatment process. Therefore, the wet oxidation liquid has the potential for being used as a liquid organic carbon source, which is proved to save expenses with regard to the purchase of organic carbon sources. Thus, catalytic wet oxidation could be developed as an economic method that could be accepted and used within this field. We checked the concentration of antibiotics after the wet oxidation process using the HPLC analysis method, which demonstrated that the antibiotics were totally decomposed and removed.

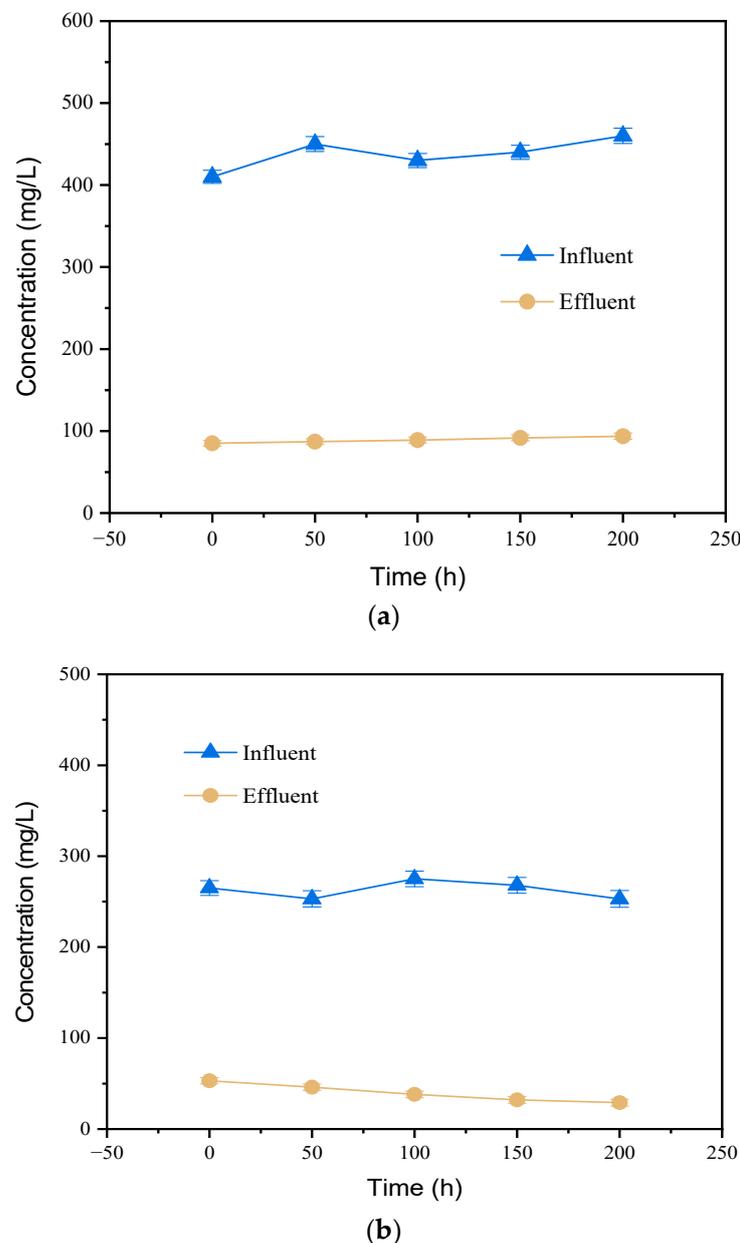


Figure 7. COD (a) and TN (b) concentrations in the influent and effluent.

4. Conclusions

In summary, a supported Cu-Ce/ γ -Al₂O₃ catalyst was investigated in the catalytic wet oxidation of excess antibiotic/sludge. The results showed that the removal rates of COD and VSS could reach 81.2% and 93.8%, respectively, with the initial COD of the sludge solution being 15,000~16,000 mg/L at 260 °C after 60 min, with an initial oxygen pressure of 1.0 MPa. Due to the effective catalytic performance of catalyst, it improved the degradation of sludge. The results show that the contents of small molecular carboxylic acids, such as acetic acid, propionic acid, and isobutyric acid, in the oxidation solution were high. Thus, this solution can be used as an organic carbon source in biological wastewater treatment. The results exhibited that the degraded solution, after catalytic wet oxidation, has the potential to be used as a carbon source to meet the demand of biological treatment, helping in the removal of COD and TN. This work confirms the effectiveness of this catalyst for enhancing excess antibiotic/sludge treatment, providing new ideas for the rational disposal of excess antibiotic/sludge.

Author Contributions: X.Z. contributed to the creation of this article; S.C. prepared the materials, conducted the experiments, collected the data, and performed the analyses; S.C. wrote the first draft of this manuscript; X.Z. and H.L. edited and revised this manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the support provided to them by the National Natural Science Foundation of China (51978499).

Data Availability Statement: The data can be made available upon request.

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

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