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To cite this article: Jianna Li *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **219** 012022

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Enhancement of Supercritical Water Oxidation for Municipal Sludge Degradation

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Abstract. Different measures to enhance the removal efficiency of municipal sludge by supercritical water oxidation were further studied in a batch reactor, including catalytic supercritical water oxidation, co-oxidation with methanol and multi-injection of oxidant experiments at 580 °C, 25 MPa within a total residence time of 10 min and a total oxidant coefficient of 1.1. The experimental results showed that splitting the same amount of oxidant and feeding into reactor at two different residence time had a significant enhancement on the removal of COD compared with NH₃-N, and the optimal second injection time of oxidant was 7.5 min in this investigation. Meanwhile, CuO catalyst could increase the degradation efficiency of both COD and NH₃-N, and it increased with the amount of CuO added, which was better than methanol. Moreover, combining CuO with injecting oxidant multi-stage experiment produced the maximum organics degradation efficiency of 99.9% and 83.47% for COD and NH₃-N, respectively, it demonstrates lower COD degradation of 99.58% and NH₃-N degradation of 35.69% utilizing methanol at fixed reaction condition.

1. Introduction

Recently, supercritical water oxidation (SCWO) has been widely applied for treating different types of hazardous wastes worldwide, which benefits from the advantages of high efficiency, environmental protection and energy conservation. Numbers researches have been done to degrade organic matters such as pesticide wastewater [1], landfill leachate [2], coking wastewater [3], textile sludge [4] and sewage sludge [5] et al, and ideal dispose results were obtained. As we all know, all these wastes contain high concentration of organic matters and ammonia. However, although most of the organic pollutants are removed during the SCWO process, there are still some residual refractory organic matters like complex heterocyclic aromatic hydrocarbons which are difficult to destruct completely. What's more, NH₃-N is considered to be one of the most refractory intermediates during SCWO of nitrogen-containing compounds, and degrading NH₃-N further is regarded as a key rate-determining step during the whole reaction process [6]. Unfortunately, complete transformation from NH₃-N to harmless N₂ requires extremely-severe reaction conditions [7].

Thus, numbers of different efforts have been taken to overcome these drawbacks recently. For instance, Ding et al. reported that MnO₂/CeO₂ catalyst could improve the conversion of NH₃-N up to 96% in the packed-bed reactor at the condition of 450 °C, 27.6 MPa [8]. Oe et al. indicated that the presence of methanol strongly affected the SCWO of NH₃. When the methanol-ammonia ratio is three at 590 °C, 25 MPa, the pure ammonia is completely destructed [9]. What's more, the existence of



methanol not only could improve the degradation of NH_3 , but also remove the organic matters further. Zhang et al. researched the effects of methanol on the degradation of acetic acid and phenol during SCWO process, and experimental results showed that methanol accelerated the removal rate of COD apparently by methanol-derived $\text{HO}_2\cdot$ and $\text{OH}\cdot$ radicals [10]. In addition to adding catalysts and methanol to improve the treatment efficiency of wastes, some researchers have improved new reactor with a multi-injection of oxidant. García-Jarana et al. improved SCWO system with oxidant multi-injection to degrade nitrogen-containing compounds, proving that multi-oxidant experiments enhance both TOC and $\text{NH}_3\text{-N}$ removal efficiency compared with single entry experiments. At 400 °C, 25 MPa within a residence time of 6 s and an oxidant coefficient of 1, achieving the maximum TOC removal efficiency of 89.2% and the lowest NH_4^+ concentration of 42 ppm compared with lower TOC removal efficiency of 79.8% and higher NH_4^+ concentration of 59.42 ppm obtained in single entry experiments of SCWO [11].

The aim of this study here is to take various measures to improve the treatment efficiency of municipal sludge based on maximum COD and $\text{NH}_3\text{-N}$ removal efficiency ultimately, including catalytic supercritical water oxidation, co-oxidation with methanol, multi-injection of oxidant and the combination of the other two methods mainly. All these experiments were conducting at 580 °C, 25 MPa within a total residence time of 10 min and a total oxidant coefficient of 1.1.

2. Apparatuses and procedures

2.1 Materials

The municipal sludge used in this study was obtained from sewage treatment plant located in Jiangsu province, and the basic properties of tested sludge are showed in Table 1. Meanwhile, we use 30 wt.% hydrogen peroxide (H_2O_2) solution as oxidant obtained from Tianjin Fuchen Chemical Agent Co, Ltd (China). The catalyst CuO was purchased from Hongyan Company while methanol was acquired from Sinopharm Chemical Reagent Co. And all the experimental equipment was cleaned by deionized water in the study.

Table 1. The basic properties of municipal sludge.

Moisture content (wt.%)	Viscosity (mPa·s)	COD (mg/L)	pH	$\text{NH}_3\text{-N}$ (mg/L)	Colour
84	120000	106463.8	7.2	55.47	Black

2.2 Apparatus and Experimental Procedures

The experimental system and process for catalytic supercritical water oxidation and co-oxidation reaction employed in this work are the same as our previous study [2] while the process within multi-injection of oxidant is different.

In this passage we discussed, the multi-injection of oxidant to the reactant was achieved by injecting oxidant secondly into the batch reactors at different residence time while the total residence time for each experiment maintain the same during the SCWO process. And each experiment was repeated three times, the average value was regarded as the true value.

2.3 Analysis methods

The measurement of chemical oxidant demand (COD) was conducted by multi-parameter water analyser (NOVA60) with Merck cells in the liquid samples, while the ammonia nitrogen ($\text{NH}_3\text{-N}$) was determined by silver nitrate titration GB 11896-89. And the pH was evaluated by means of a professional meter (Model PP-50).

The oxidant coefficient (OC) was defined as :

$$OC = \frac{[\text{O}_2]_{\text{actual}}}{[\text{O}_2]_{\text{stoich}}} \quad (1)$$

Here $[O_2]_{\text{actual}}$ is the concentration of O_2 added into the reactor actually which completely producing from the decomposition of hydrogen peroxide, and $[O_2]_{\text{stoich}}$ is the stoichiometric requirement concentration of O_2 to theoretically oxidize all the organic matters.

Additionally, the COD removal efficiency X_{COD} and $NH_3\text{-N}$ removal efficiency X_{NH_3-N} were given as follows:

$$X_{\text{COD}} = \frac{[COD]_0 - [COD]_t}{[COD]_0} \times 100\% \quad (2)$$

$$X_{NH_3-N} = \frac{[NH_3-N]_0 - [NH_3-N]_t}{[NH_3-N]_0} \times 100\% \quad (3)$$

Here $[COD]_0$ and $[NH_3-N]_0$ are the initial COD and $NH_3\text{-N}$ concentration of the municipal sludge with a moisture content of 84 wt.%, respectively, while $[COD]_t$ and $[NH_3-N]_t$ is the residual COD and $NH_3\text{-N}$ concentration of liquid products.

3. Results and discussion

3.1 Effect of oxidant multi-injection in SCWO

The experiments discussed here were conducted at 580 °C, 25 MPa within a residence time of 10 min and an oxidant coefficient of 1.1. As been reported, the organic matters degraded thoroughly when injecting 75% of oxidant at the inlet of reactor and the remaining added into the second point which was treated as the optimum split-ratio [11]. To destruct the municipal sludge further, we also chosen 75% oxidant as the first injection while the rest was injected at the second time. All experiments studied this part were carried out with three different residence time for second injection of oxidant. It means that the first injection of oxidant at the beginning of reaction and the second injection time of oxidant was shown in Table 2.

Table 2. The subsection of oxidant injection.

Experiments	1	2	3	4
1 st injection time	0 min	0 min	0 min	0 min
2 nd injection time	/	2.5 min	5 min	7.5 min

The results of all experiments were presented in terms of residual COD and $NH_3\text{-N}$ concentration in the liquid effluents and were represented in Figure 1. It was indicated that the best residence time to inject oxidant secondly seems to be 7.5 min, which acquired the lowest COD concentration of 445 mg/L and the highest COD removal efficiency of 99.58% compared with injecting all the oxidant before the reaction started which obtained 1234.8 mg/L COD and 98.84% COD removal efficiency. A possible explanation for this improvement may be that oxidant multi-injection changed the degradation pathway of organic pollutants in municipal sludge, causing the intermediate products produced with an oxidant deficiency in the first part became more easily to be destructed by injecting oxidant twice [11]. Moreover, it appears that the $NH_3\text{-N}$ concentration in liquid products was higher than original sludge when the oxidant was injected into the reactor once at 580 °C, because municipal sludge contains amounts of nitrogenous compounds and most nitrogenous organics transform to ammonia during SCWO process, and $NH_3\text{-N}$ is widely considered as a refractory immediate product. However, the results indicate that oxidant multi-injection has less significant effects on the removal of $NH_3\text{-N}$ and the concentration after SCWO is still higher than raw fresh sludge. It may be due to that the effective degradation of $NH_3\text{-N}$ requires high temperature more than 650 °C without catalysts [6], changing the reaction path by injecting oxidant segmentally makes little sense.

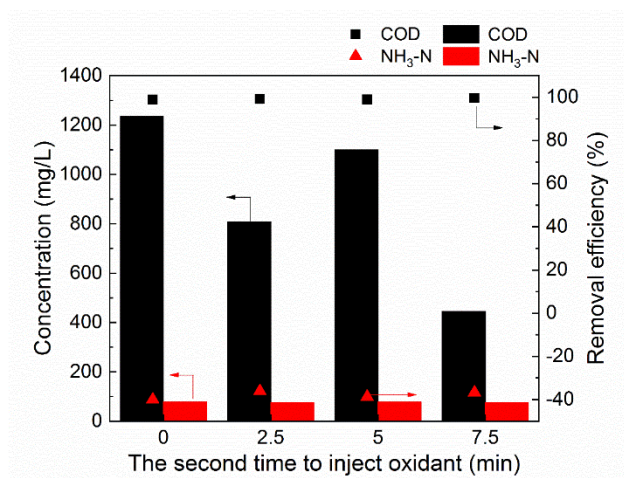


Figure 1. The effect of oxidant multi-injection on the degradation of municipal sludge at 580 °C, 25 MPa, the first injection is 75% oxidant (OC=1.1) and the total residence time of 10 min.

3.2 Effect of catalyst in SCWO

Figure 2 and Figure 3 expressed the influence of CuO catalyst on the conversion of COD and NH₃-N respectively at 580 °C, 25 MPa within a residence time of 10 min and an oxidant coefficient of 1.1. And the amount of CuO added to reactor is 0.2 wt.%, 0.5 wt.%, 1 wt.%, 2 wt.% and 3 wt.% of the dry sludge for each experiment. In this part, the oxidant was fed into the reactor once.

As can be seen, CuO can greatly accelerate the degradation of municipal sludge compared with the results obtained without catalyst. It was obvious that both COD and NH₃-N removal efficiency increased with the existence of CuO, and the conversion of COD reached up to 99.89% while NH₃-N removal efficiency was 82.6% when the CuO is 3 wt.% of the dry sludge. However, the increasing trend for COD removal efficiency gradually slowed down when the amount of CuO over 1 wt.%, which means that most of the organic matters are already destructed. Relatively, it still played a significant influence on the conversion of NH₃-N when the CuO rose from 1 wt.% to 3 wt.%. Although CuO improved the destruction of sludge to a certain extent, the problem is that CuO is instable under the supercritical water condition. It has been proved that Cu²⁺ in the liquid products would be detected while adding excess CuO as a result of dissolution or erosion for CuO, but the Cu²⁺ in the liquid products still retains its catalytic properties and simply functions as a homogeneous catalyst [12].

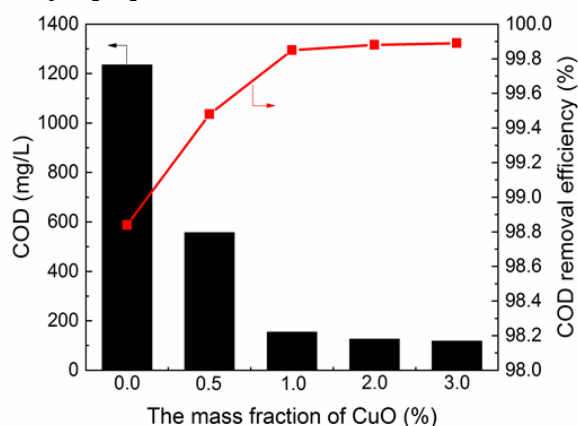


Figure 2. The effect of CuO catalyst on the COD degradation of municipal sludge at 580 °C, 25 MPa, 10 min, OC=1.1.

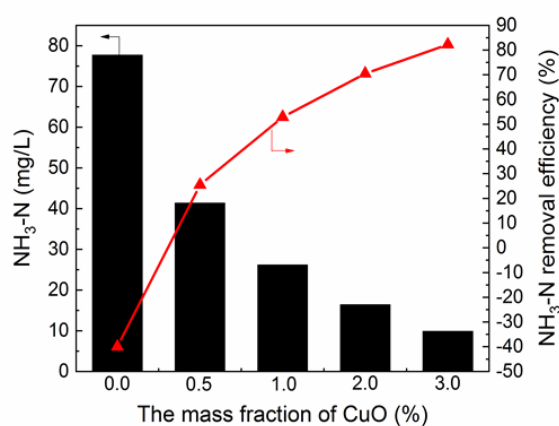


Figure 3. The effect of CuO catalyst on the NH₃-N degradation of municipal sludge at 580 °C, 25 MPa, 10 min, OC=1.1.

3.3 Effect of co-oxidation with methanol in SCWO

Similarly, we also explored the influence of co-oxidation between municipal sludge and methanol in different condition of injecting oxidant by stages or in single entry. And the amount of methanol added to reactor at the beginning of reaction occupied 1 wt.% of the sludge. The results for the decomposition of municipal sludge are presented in Figure 4. It demonstrated that a greater increase was obtained because of the presence of methanol, making the COD and $\text{NH}_3\text{-N}$ concentration separately decrease from 1234.8 mg/L and 77.66 mg/L to 182 mg/L and 46.42 mg/L when oxidant was injected in single entry. Furthermore, a much higher COD and $\text{NH}_3\text{-N}$ removal efficiency achieved during the process of injecting oxidant multi-stage, which reached up to 99.58% and 35.69%, making residual COD and $\text{NH}_3\text{-N}$ concentration only 126 mg/L and 35.67 mg/L respectively. Obviously, methanol accelerates the removal rate of sludge, it may be due to that methanol acts as a reactive species, is oxidized at a shorter reaction time and produces a higher concentration of reactive intermediates such as $\text{HO}_2\cdot$ and $\text{OH}\cdot$ [10], which could attack the refractory organic matters in sludge.

However, at the fixed condition of injecting oxidant multi-stage, adding CuO plays more significant influences on the COD and $\text{NH}_3\text{-N}$ degradation of sludge than methanol which are shown in Figure 5. On the one hand, although the residual COD concentration in the liquid effluents was almost the same (COD removal efficiency of 99.9% for CuO and 99.58% for methanol), the difference in the conversion rate of $\text{NH}_3\text{-N}$ is large, where $\text{NH}_3\text{-N}$ removal efficiency is 83.47% with adding CuO but it is only 35.69% with methanol. Therefore, it is more efficient to degrade COD and $\text{NH}_3\text{-N}$ in the sludge simultaneously by choosing CuO as catalyst rather than methanol during SCWO reaction process.

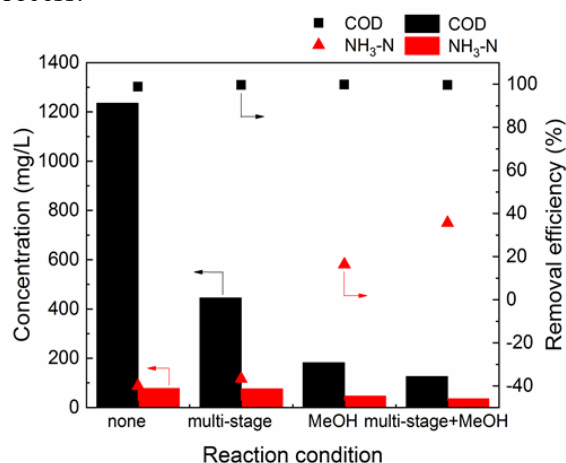


Figure 4. The effect of combining methanol co-oxidation with oxidant multi-injection on the degradation of municipal sludge at 580 °C, 25 MPa, 10 min, OC=1.1.

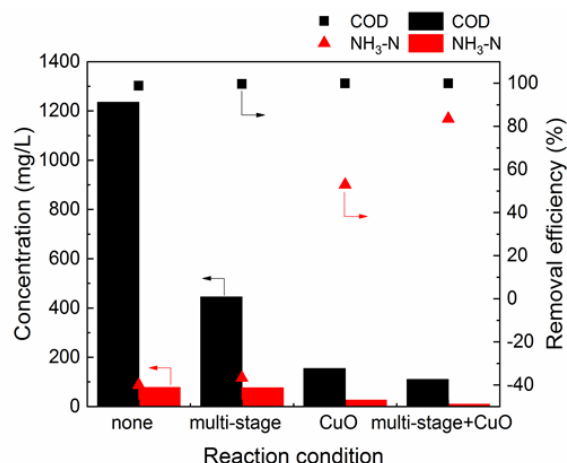


Figure 5. The effect of combining CuO catalyst with oxidant multi-injection on the degradation of municipal sludge at 580 °C, 25 MPa, 10 min, OC=1.1.

4. Conclusion

In this work, different measures were conducted to enhance the degradation of COD and $\text{NH}_3\text{-N}$ in municipal sludge. Experimental results indicated that catalytic supercritical water oxidation with CuO, co-oxidation with methanol, multi-injection of oxidant all could improve the destruction of organic pollutants. Methanol and multi-injection of oxidant played little effects on the removing of $\text{NH}_3\text{-N}$ while CuO catalyst made greater sense. Meanwhile, a better removal efficiency obtained on COD and $\text{NH}_3\text{-N}$ while combined CuO or methanol with injecting oxidant multi-stage. And it has proved that the optimal concentration of COD and ammonia nitrogen in the liquid effluents were received at 580 °C, 25 MPa, and the first injection of oxidant was 75% of the total (the oxidant coefficient of 1.1) with 1 wt.% CuO, and the rest oxidant was injected at 7.5 min (the total residence time of 10 min),

which will reach up to 99.9% COD removal efficiency and 83.47% $\text{NH}_3\text{-N}$ removal efficiency. Eventually, all these improvement measures would provide a theoretical basis for the optimization of SCWO system for degrading municipal sludge to a certain degree.

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