Supercritical water oxidation of dyeing sludge

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Abstract. Supercritical water oxidation (SCWO) of dyeing sludge has been conducted in a batch reactor, and experiments were investigated at reaction temperature of 520–600 °C, oxidation coefficient of 1–1.2, residence time of 120–600 s and a fixed pressure of 25 MPa. Experimental results indicated that most of the organic matters were degraded at 600 °C, 25 MPa, oxidation coefficient of 1.2 within residence time of 600 s, which reached up to 99.80% of COD removal efficiency. Reaction temperature, oxidation coefficient and residence time all play significant influences on the removal of organic matters, and the reaction temperature is the most influential factor while oxidation coefficient and residence time become less significant as they exceed fixed values. Moreover, the effects of different catalysts on the degradation of organic matters were further studied to enhance the removal efficiency of COD and NH3-N. It is suggested that all the tested catalysts (MnO2, CeO2, Al2O3, ZrO2) could degrade COD and NH3-N to a certain extent, but CeO2 has the highest activity compared with other catalysts.

1. Introduction
With the development of the textile dyeing industries, the discharge of dyeing wastewater becomes huger and huger in the world. And it will produce 10 tons wet sludge (moisture content of 97%) when dealing with 1000 tons of dyeing wastewater. The composition of dyeing sludge is complex and contains much refractory material such as dyes, sizing agents, auxiliaries and other ingredients [1]. What’s more, dyes are rich in considerable aromatic hydrocarbon, nitrogen compounds and heavy metals like chromium, arsenic which is harmful to both environments and people’s health. Therefore, dealing with dyeing sludge reasonably has become one of the most serious environmental problems.

The conventional sludge treatment technologies are incineration and landfill methods which both have numbers of inevitable problems. For example, the landfill can’t harmlessly and thoroughly achieve the degradation of sludge, and it will account for a large number of valuable land resources. Landfill leachate produced by landfills contains many types of highly toxic pollutants, which pollutes the surrounding environment seriously [2]. What’s more, incineration method has more worse influences. Although the incineration can treat sludge to a certain extent, the elements such as nitrogen, sulfur and chlorine are easily converted into toxic substances such as NOx, SOx, PM2.5 and dioxin during the incineration process. The fly ash and solid residue often contain heavy metals, so it is always regarded as a hazardous waste. Thus, the incineration brings serious secondary pollution. So, it is necessary to seek an efficient and environmental protection method for dyeing sludge treatment.

Supercritical water oxidation (SCWO) is an effective and green technique for treatment of organic wastes proposed by Professor Modell in 1980s [3], which has the advantages of high efficiency, environmental protection and energy conservation. Because of the special properties of supercritical water (SCW, Tc=647 K, Pc=22.1 MPa): low density, low dielectric constant and low ionization constant,
it can be used for homogeneous reaction medium which could completely dissolve organic matters and oxidant and rapidly initiate homogeneous free radical reaction. During the SCWO process, organic matters could rapidly and thoroughly be oxidized into small molecules such as CO$_2$, H$_2$O and N$_2$, heterocyclic atoms such as chlorine, sulfur and phosphorus are converted into corresponding acids or salts separately, and heavy metals are steadily mineralized into solid residues. Because of more than 99.9% organic matters can be removed by SCWO within less minutes and it will not produce secondary pollutants like NO$_x$ and SO$_x$ [4]. Therefore, amounts of wastewater as well as sludge has been successful and thoroughly degraded by SCWO, such as pesticide wastewater [5], oily sludge [6], municipal sludge [7] and phenol [8] et al.

This work aimed to investigate the effects of key operation parameters such as reaction temperature, oxidation coefficient, residence time and heterogeneous catalyst on the destruction of dyeing sludge in a batch reactor and analyses the reaction mechanism, thus building experimental and theoretical basis for the industrialized treatment of dyeing sludge by SCWO technology.

2. Apparatuses and procedures

2.1 Apparatus and Materials

The experimental system and process for SCWO reaction discussed here are the same as our previous study [9].

The dyeing sludge was collected from a textile wastewater treatment plant located in Jiangsu province, and the properties of tested sludge are showed in Table 1. What’s more, the oxidant we use in this work was 30 wt.% hydrogen peroxide (H$_2$O$_2$) solution obtained from Tianjin Fuchen Chemical Agent Co, Ltd (China), and the catalyst MnO$_2$, CeO$_2$, Al$_2$O$_3$, ZrO$_2$ were purchased from Hongyan Company.

| Moisture content (wt.%) | Viscosity (mPa·s) | COD (mg/L) | pH | NH$_3$-N (mg/L) | Colour |
|-------------------------|------------------|-----------|----|----------------|--------|
| 88                      | >100000          | 74388     | 7.5| 1352           | Black  |

2.2 Analysis methods

In this work, we mainly discuss the chemical oxygen demand (COD) and ammonia nitrogen (NH$_3$-N) remaining in the liquid effluents. COD was analysed by potassium dichromate method HJ 828-2017 and NH$_3$-N was determined by a multiparameter water analyser with Merck cell (Model NOVA60). What’s more, the pH was determined by a professional meter (Model PP-50). And residual organic matters in liquid effluents after SCWO reaction were detected by a gas chromatography–mass spectrometry analyzer (GC–MS, Model Agilent 6890-5973).

The oxidant coefficient (OC) was defined by the following equation:

$$OC = \frac{[O_2]_{\text{init}}}{[O_2]_{\text{stoi}}}$$

where $[O_2]_{\text{init}}$ is actual concentration of O$_2$ fed into the reactor, forming from complete decomposition of hydrogen peroxide. And $[O_2]_{\text{stoi}}$ is the stoichiometric requirement concentration of O$_2$ for the theoretically complete oxidation of organic matters.

The COD removal efficiency $X_{COD}$ and NH$_3$-N removal efficiency $X_{NH_3-N}$ are defined as follows:

$$X_{COD} = \frac{[COD]_0 - [COD]_t}{[COD]_0} \times 100\%$$

(2)
\[
X_{\text{NH}_3-N} = \left( \frac{[\text{NH}_3-N]_0 - [\text{NH}_3-N]_1}{[\text{NH}_3-N]_0} \right) \times 100\% \tag{3}
\]

where \([\text{COD}]_0\) and \([\text{NH}_3-N]_0\) are the initial COD and NH\(_3\)-N concentration of the raw dyeing sludge with a moisture content of 88 wt.%, while \([\text{COD}]_1\) and \([\text{NH}_3-N]_1\) is the residual COD and NH\(_3\)-N concentration of liquid effluents after SCWO reaction.

3. Results and discussion

In order to investigate the effects of key operation parameters for the destruction of dyeing sludge, experiments were conducted at fixed pressure of 25 MPa, variable reaction temperature of 520–600 °C and oxidation coefficient of 1–2.2 within residence time of 120–600 s. Meanwhile, each experiment was repeated three times, then the average value was considered to be the true value.

3.1 Effect of reaction temperature

Figure 1 shows the influence of different reaction temperature (520 °C, 540 °C, 560 °C, 580°C, 600 °C) on the removal of COD. As we can see, reaction temperature has a significant influence on the removal efficiency of organic matters during SCWO process. What’s more, it illustrates that the removal of COD increased with the increase of temperature. The COD removal efficiency rose from 95.77% to 99.80% when the temperature increased from 520 °C to 600 °C at pressure of 25 MPa, oxidation coefficient of 1.2 and residence time of 600 s. What’s more, residual COD concentration was only 150.86 mg/L in liquid effluents under optimal reaction conditions without catalyst, which appears that most of the organic matters in the dyeing sludge are removed after SCWO process. However, the trend of COD removal efficiency tends to become slowly with the increase of temperature further, which implies that promoting methods should be taken to improve COD removal efficiency such as adding catalysts like MnO\(_2\) [10] or promoters like methanol [11].

![Figure 1. The effect of reaction temperature on the degradation of dyeing sludge at 25 MPa, 600 s, OC=1.2.](image)

3.2 Effect of oxidation coefficient

Figure 2 illustrates the effect of different oxidation coefficient on the COD removal efficiency at reaction temperature of 580 °C, pressure of 25 MPa within residence time of 600 s. It was obvious that the conversion of COD increased as oxidation coefficient increased, when the oxidation coefficient rose from 1 to 1.2, the COD removal efficiency drastically increased from 98.46% to 99.22%. But continuing to increase the oxidation coefficient, the COD removal efficiency varies gently. As can be seen, the COD removal efficiency only increased by 0.26% while the oxidation coefficient increased by 83.3%. Therefore, although high oxidation coefficient could improve the destruction of dyeing sludge to a
certain extent, too much oxidant not only effects a little for degradation of dyeing sludge, but also
decreases the economy of SCWO system.

The most possible explanation for this phenomenon is that SCWO follows the free radical
mechanism [12]. At the initial stage of the reaction, adding excess oxidant will produce high
concentration of OH· radicals to accelerate the oxidation rate. But with the process of reaction, increase
oxidant concentration further will have little influence on the degradation of refractory intermediate
products produced during the reaction. Therefore, there is an optimal value of oxidation coefficient
which is most beneficial for all of COD removal efficiency, initial investment and running costs.
Considering that we choose 1.2 as the oxidation coefficient in this research.

3.3 Effect of residence time
Figure 3 demonstrates the change rule of COD removal efficiency with the variety of residence time at
reaction temperature of 580 °C, pressure of 25 MPa and oxidation coefficient of 1.2. It can be confirmed
that extending residence time could receive a higher removal efficiency of COD, but the growing trend
of COD removal efficiency is gradually slowing down with the increase of residence time. For instance,
the COD removal efficiency rose from 97.80% to 98.90% rapidly while the residence time increased
only from 120 s to 300 s, but then the changing tendency varied slightly after 300 s. It is likely due to
more OH· radicals will be produced within long residence time which provide more opportunities for
the reaction between molecules and free radicals in the system. However, the concentration of reactants
will become lower and lower with the process of reaction, which gradually causing the effect of
residence time become less significantly. Moreover, excessive residence time will increase the length
of tubular reactor and cause expensive investment of reactor for large scale industrial application. It is
obvious that choosing an appropriate residence time plays an important influence on the industrial design
of SCWO system.
3.4 Effect of catalyst

Although the COD removal efficiency has reached 99.22% at reaction temperature of 580 °C, pressure of 25MPa, oxidation coefficient of 1.2 within residence time of 600 s, the residual COD and NH$_3$-N concentration was still 579.06 mg/L and 1250.81 mg/L in the liquid effluents. It has proved that the residual organic compounds in the effluents are complex heterocyclic aromatic hydrocarbons by GC-MS detection. Furthermore, ammonia is the refractory immediate product of nitrogenous compounds in the SCWO process and is especially hard to remove, to completely degrade ammonia requires higher reaction temperature exceeded than 650 °C [13].

Therefore, different kinds of catalysts were added to improve the degradation efficiency of organic pollutants in this research, the effects of catalysts for the COD and NH$_3$-N removal efficiency were displayed in Figure 4. And the amount of catalyst added for each experiment was 5 wt.% of the dry sludge. Compared with noncatalytic SCWO of dyeing sludge, it is clear that adding catalyst enhance both COD and NH$_3$-N removal efficiency at the same reaction condition. Among all tested catalysts, CeO$_2$ catalyst has the most positive effects than other catalysts while ZrO$_2$ plays the slightest impact. Therefore, the catalytic activity here is CeO$_2$>MnO$_2$>Al$_2$O$_3$>ZrO$_2$.

Figure 4 shows that the residual COD and NH$_3$-N concentration were up to 579.06 mg/L and 1250.81 mg/L from noncatalytic SCWO, and the COD and NH$_3$-N removal efficiency were 99.22% and 7.48%. Contrarily, the residual COD and NH$_3$-N concentration were only 253.9 mg/L and 762.72 mg/L due to the presence of the CeO$_2$ catalyst, causing the COD and NH$_3$-N removal efficiency increased to 99.66% and 44.33%. It is indicated that more refractory organic matters are degraded further, but the NH$_3$-N concentration is still not meet the discharging standard and needed to be treated again. The mechanism advanced for CeO$_2$ catalyst organic matters might be that CeO$_2$ forms favorable oxygen vacancies on the surfaces [14] which play an important rule during SCWO process. On the other hand, CeO$_2$ could store oxygen [15] and act as an oxygen donor [16], the desorption of oxygen leads to the formation of ‘active oxygen’, which is postulated to significantly accelerate the oxidation rate of organic matters [15]. Meanwhile, MnO$_2$ catalyst also improves the removal efficiency of COD and NH$_3$-N a lot. It is possible that MnO$_2$ plays the rule of oxidant which participates in and accelerates the oxidation reaction because of the lattice oxygen in MnO$_2$ and the absorbed oxygen on the surface of MnO$_2$ [17]. Therefore, adding suitable catalyst is an effective way to improve the degradation of organic matters during SCWO process.

![Figure 4. The effect of different catalysts on the degradation of dyeing sludge at 580 °C, 25 MPa, 600 s, OC=1.2.](image)

4. Conclusion

The SCWO of dyeing sludge was investigated in a batch reactor at different reaction conditions. It is proved that reaction temperature, oxidation coefficient and residence time all play positive effects on the degradation of organic matters. And the most remarkable operating parameter on COD removal efficiency was reaction temperature, which could reach up to 99.80% at the temperature of 600 °C, pressure of 25 MPa, oxidation coefficient of 1.2 within residence time of 600 s. Meanwhile, the effects
of oxidation coefficient and residence time became less significant as they exceeded a fixed value, which means that oxidation coefficient and residence time both have an effective and economic parameter for the design of large-scale treatment of dyeing sludge. Furthermore, catalytic supercritical water oxidation strongly enhances the removal efficiency of COD and NH$_3$-N compared with conventional noncatalytic SCWO of dyeing sludge under the same reaction conditions. Moreover, CeO$_2$ has the highest activity on the degradation of COD and ammonia which could dramatically decrease COD and NH$_3$-N concentration, followed by MnO$_2$. Even though, ammonia considered as the refractory immediate product in the SCWO process still needed to be treated deeply.

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