Preparation of CuO/HZSM-5 catalyst based on fly ash and its catalytic wet air oxidation of phenol, quinoline and indole

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Abstract
This work aims to use fly ash and the organic template of tetrapropyl ammonium bromide (TPABr) to synthesize the catalyst carrier of HZSM-5 and prepare the catalyst of CuO/HZSM-5 for catalytic wet air oxidation (CWAO) of phenol, quinoline and indole in aqueous solution. The carrier and the catalyst were characterized by x-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF) and Brunauer-Emmett-Teller (BET) tests and the results indicate HZSM-5 zeolite and CuO/HZSM-5 catalyst have been successfully synthesized. The specific surface area of catalysts with copper loading from 0 to 15% decreased from 310.1 m² g⁻¹ to 253.8 m² g⁻¹. The results of catalyst performance showed that the catalyst of CuO/HZSM-5 with copper loading of 10% has the best removal effect on the mixed aqueous solution containing phenol, quinoline and indole. When the total concentrations of phenol, quinoline and indole are 200 mg l⁻¹ (namely 120 mg phenol l⁻¹, 60 mg quinoline l⁻¹ and 20 mg indole l⁻¹), the catalyst with the copper loading of 10% can remove these organic matters with 100% efficiency after reaction for 4 h at 200 °C and the COD removal rate is more than 75%. Under the same experimental conditions, if the reaction temperature drops to 120 °C, the COD removal rate will rise to 86.2%. The CWAO experiments showed the optimum reaction temperature range for the Cu-10% catalyst is from 120 °C to 150 °C.

1. Introduction
Phenolic compounds and nitrogen heterocyclic compounds such as quinoline and indole are mainly derived from coal coking, coal gasification, coal liquefaction, petroleum and pharmaceutical industries [1–5]. Even at low concentrations, phenol can cause serious harm to the ecological environment and human health. Therefore, China’s drinking water standards require that phenol content must be less than 0.002 mg l⁻¹ (GB5749-2006). Phenol and quinoline are both priority pollutants for environmental protection [2, 4]. In addition, the standard (GB5749-2006) stipulates that drinking water is free from peculiar taste and odor. However, phenol, quinoline and indole cause taste and odor problems [2, 6–8]. Odor occurs when indole concentration reaches 0.1 μg l⁻¹ in water [7, 9]. Phenol, quinoline and indole with toxicity and carcinogenicity also have high solubility in aqueous solution, which makes them easy to migrate and transformation in ecological system. Because of the toxicity and harmfulness of the wastewater containing phenol, quinoline and indole, it must be fully treated before discharge.

The adsorption effect of different adsorbents such as activated carbon, zeolite, natural clay, fly ash, coal, sludge, sawdust and rice husk, etc on phenol in wastewater has been systematically reviewed [2]. Sarker et al. [10] have synthesized a kind of porous metal organic adsorbent and found that it has excellent adsorption efficiency for quinoline and indole. Many adsorbents such as coking coals, biochar, activated carbon, bagasse fly ash, guar gum derived carbon, lignite, anthracite, coal powder have been used to adsorb quinoline from aqueous solution [8, 11–15]. Our previous work also reported the adsorption of phenol, quinoline and indole from aqueous solution by ZSM-5 zeolite [16]. Although the adsorption technology has the advantages of simplicity and high efficiency, it only realizes the transfer of pollutants from solution to adsorbent, which cannot really solve the harmfulness of pollutants. In order to solve the problem of water pollution of phenol, quinoline and indole...
which have biological toxicity and are difficult to degrade, many advanced oxidation methods have been proposed. Photochemical oxidation, fenton oxidation, electrochemical mineralization, ozone oxidation, etc have been widely reported to remove the pollutants of phenol, quinoline and indole [4–7, 17–26]. As an advanced oxidation technology, wet air oxidation (WAO) process can be used to treat high concentration, toxic and refractory organic wastewater and remove organics like phenol, quinoline and indole effectively [3, 27–29]. Besides, WAO is very attractive for treating wastewater which is too toxic for biological technology and too dilute for incineration [30]. Wet air oxidation technology uses pure oxygen or air as oxidant to transform organic matters into carbon dioxide and water under high temperature and pressure conditions. However, its operating conditions are severe (0.5–20 MPa and 150 °C–350 °C) and its cost is usually expensive [27, 31–33]. CWPO (catalytic wet peroxidation) is a kind of advanced oxidation technology, which uses hydrogen peroxide as catalyst to promote the decomposition of hydrogen peroxide to form hydroxyl radical and oxidize organic matter. Zhang [34] prepared iron-containing (10 w/w%) MCM-41 catalysts and test for CWPO of phenol aqueous solutions in a fixed bed reactor. The experimental results showed that the conversion of TOC reached 72.5% and few Fe (0.01 mg l⁻¹) was detected under optimum condition. Huang [35, 36] prepared copper metal-organic frameworks and copper hydroxyl sulfates as heterogeneous catalysts for CWPO of simulated phenol wastewater. The results showed that both of the two catalysts have excellent removal efficiency (99% for phenol, 90% and 97% for COD). However, CWPO also have disadvantages such as low pH and the possibility of secondary contamination due to the dissolution of active components [37]. In order to avoid secondary pollution and increase oxidation rate, catalytic wet air oxidation (CWAO) technology has been widely reported for the treatment of refractory organic compounds [38]. The treatment of phenol and quinoline wastewater by CWAO process has been widely reported [1, 39–41]. However, the literatures on CWAO of indole are scarce.

As a solid waste from coal-fired power plants, the utilization rate of fly ash is only 70%, about 80% of fly ash is used by the construction industry and only 5% are used for industrial, environmental and high-value applications [42]. The composition of fly ash is similar to that of zeolite. Preparing zeolite with fly ash is considered to be an effective method [43]. The main objectives of this work are (i) prepare the catalyst of CuO/HZSM-5 with precipitation and calcination method, (ii) investigate the catalyst performance on the wet air oxidation of phenol, quinoline and indole wastewater. and (iii) study the influence of operating conditions (such as temperature, time, catalyst dosage and organic matter concentration) on the CWAO of the wastewater containing phenol, quinoline and indole.

2. Experimental

The raw material of fly ash is from a heating company in Tianjin, China, and its chemical compositions have been reported by Liu et al [44–46]. The main chemicals utilized in this study are sodium carbonate (Na₂CO₃, AR), hydrochloric acid (HCl, AR), tetrapropyl ammonium bromide (TPABr, 99%), copper nitrate (Cu(NO₃)₂·3H₂O, AR), phenol (C₆H₅OH, GC), quinoline (C₉H₇N, GC), indole (C₉H₇N, GC), oxygen (O₂, 99.5%), sodium hydroxide (NaOH, AR) and sulphuric acid (H₂SO₄, AR).

2.1. Catalyst preparation

2.1.1. Pretreatment of fly ash and the synthesis of ZSM-5 zeolite

The pretreatment of fly ash and the synthesis of ZSM-5 zeolite have been reported in our previous work [46]. During the pretreatment of fly ash, the mass ratio of Na₂CO₃ to fly ash is 1.2, and the other treatment steps are the same as those reported in our previous work [46].

2.1.2. Preparation of CuO/HZSM-5

The CuO/HZSM-5 catalyst was prepared by precipitation/calcination with the fly ash synthesized zeolite as carrier. A certain amount of zeolite was dispersed in distilled water. Then according to the mass proportion of 10 w/w%, 5 w/w%, 10 w/w% and 15 w/w% of copper ions on carrier, the corresponding mass of Cu(NO₃)₂·3H₂O is dissolved in distilled water of the same volume and fully mixed. The pH of mixed solution was adjusted to 6 ~ 7 with 0.1 M sodium hydroxide and shaken in a thermostatic oscillator for 4 h. Then the samples were filtered, washed and dried. Finally, the samples were calcined at 200 °C in a muffle furnace for 2 h to produce copper oxide. The catalysts were respectively named as Cu-1%, Cu-5%, Cu-10% and Cu-15% according to the different amounts of Cu²⁺ during the preparation of catalysts.

2.2. Characterization

The crystal x-ray diffraction data of the sample in the range of 2θ = 5°–45° were collected by D/MAX-2500 x-ray diffractometer according to the scanning speed of 6° min⁻¹. Then crystal phases of XRD data were analyzed by jade 6.0 software. The chemical compositions of the samples were analyzed by S4Pioneer x-ray
fluorescence spectrometer. Nitrogen adsorption/desorption isothermal tests were carried out with bistatic automatic surface and pore size analyzer (AutosorbQ2-MP, USA), and the specific surface area and pore diameter of the samples were analyzed using density functional theory (DFT) and BET methods.

2.3. CWAO experiments
Phenol, quinoline and indole are the main refractory organic compounds in coking wastewater. Usually, the order of concentration from high to low is phenol, quinoline and indole. The mass ratio (6(phenol):3(quinoline):1(indole)) of the three kinds of organic matter in this paper is similar to that of a real coal chemical wastewater. Then, a certain amount of catalyst was added into the artificial simulated wastewater, and the solid liquid mixture was transferred into a high-pressure reactor with 200 ml volume. After that, pure oxygen was injected into the reactant in the reactor with 0.2 l min⁻¹ for 2 min. After oxygen injecting, the reactor was sealed and placed in an oven with preset temperature for a period of time. After the reaction, the solution was sampled and filtered with 0.45 um membrane. The filtrate was analyzed by high performance liquid chromatography (HPLC) technology to investigate the residual concentration of the three organic pollutants. The analysis method of HPLC for phenol, quinoline and indole in aqueous solution has been reported in our previous study [16]. The removal rate of phenol, quinoline and indole was calculated by equation (1).

\[
y = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

Where \(y\) (\%), \(C_0\) (mg l⁻¹) and \(C_t\) (mg l⁻¹) represent the removal rate of organic matters, the initial organic concentration and the organic concentration at t moment, respectively. According to the Chinese national standard of GB1914-89, the chemical oxygen demand (COD) of filtrate was also measured. The COD removal rate can be calculated using equation (2).

\[
x = \frac{COD_0 - COD_t}{COD_0} \times 100\%
\]  

Where \(x\) (\%), \(COD_0\) (mg l⁻¹) and \(COD_t\) (mg l⁻¹) denote the COD removal rate, the initial COD and the COD at t moment, respectively.

3. Results and discussion

3.1. Characterization
3.1.1. XRD
The XRD results of the HZSM-5 are shown in figure 1(a). It can be seen that the typical MFI peaks appear at \(2\theta = 7.99^\circ, 8.86^\circ, 23.12^\circ\) and \(23.32^\circ\) [47, 48]. The matching of Jade 6.0 indicates that the synthesized product is very similar with H-type ZSM-5 zeolite (\(H_{1.65}Na_{0.32}(SiO_2)_{0.91.02}(AlO_2)_{4.97} \cdot 24H_2O\), PDF#49-0657). The XRD peaks of the product match that of HZSM-5 zeolite well. The sample peaks have very high strength at \(2\theta = 7.99^\circ, 8.86^\circ, 23.12^\circ\) and \(23.32^\circ\). The XRD results of the prepared catalyst are shown in figure 1(b). The characteristic diffraction peaks of HZSM-5 zeolite appear in all the four samples, which indicates that the catalysts have HZSM-5 zeolite structure. The XRD data of copper oxide in Cu-1% catalyst does not clearly
appear due to the small amount of copper loaded on the catalyst, however, the XRD data of copper oxide at $\theta = 35.5^\circ$ and $38.6^\circ$ in the other three catalysts are clear [49]. Moreover, the intensity of the diffraction peaks for CuO crystal increased with the increase of Cu$^{2+}$ content. The analysis of XRD data shows that iron oxide in the catalyst belongs to $\gamma$-Fe$_2$O$_3$ (PDF #39-1346), as shown in figure 1(b).

### Table 1. Chemical compositions by XRF for HZSM-5 and CuO/HZSM-5 (%).

| Samples | Al$_2$O$_3$ | SiO$_2$ | CaO | Fe$_2$O$_3$ | CuO | P$_2$O$_5$ | Si/Al molar ratio |
|---------|------------|---------|-----|-------------|-----|----------|-----------------|
| HZSM-5  | 5.20       | 83.86   | 1.92| 2.01        | 0   | 1.22     | 27.4            |
| Cu-1%   | 5.82       | 76.31   | 2.94| 4.66        | 2.79| 1.31     | 22.3            |
| Cu-5%   | 5.22       | 70.63   | 2.99| 3.89        | 10.13| 1.43     | 23.0            |
| Cu-10%  | 4.26       | 59.23   | 2.44| 3.68        | 23.90| 1.29     | 23.6            |
| Cu-15%  | 3.67       | 50.93   | 2.07| 3.21        | 34.22| 1.15     | 23.6            |

| Samples | CuO | Al$_2$O$_3$ | SiO$_2$ | CaO | Fe$_2$O$_3$ | Si/Al molar ratio |
|---------|-----|------------|---------|-----|-------------|-----------------|
| HZSM-5  | 5.20| 83.86      | 1.92    | 2.01| 0           | 27.4            |
| Cu-1%   | 5.82| 76.31      | 2.94    | 4.66| 2.79        | 22.3            |
| Cu-5%   | 5.22| 70.63      | 2.99    | 3.89| 10.13       | 23.0            |
| Cu-10%  | 4.26| 59.23      | 2.44    | 3.68| 23.90       | 23.6            |
| Cu-15%  | 3.67| 50.93      | 2.07    | 3.21| 34.22       | 23.6            |

### Table 2. BET result of zeolite and catalysts.

| Samples | $S_{BET}$/m$^2$ g$^{-1}$ | $S_{DFT}$/m$^2$ g$^{-1}$ | $V_{pore}$/cm$^3$ g$^{-1}$ |
|---------|-------------------------|--------------------------|---------------------------|
| HZSM-5  | 473.0                   | 467.033                  | 0.156                     |
| Cu-1%   | 310.1                   | 307.351                  | 0.154                     |
| Cu-5%   | 464.753                 | 431.463                  | 0.142                     |
| Cu-10%  | 431.463                 | 431.463                  | 0.142                     |
| Cu-15%  | 389.617                 | 389.617                  | 0.142                     |

3.1.2. XRF of ZSM-5 and catalyst

The composition of the zeolite and catalyst are shown in table 1. The results show that the molar ratio of silicon to aluminum in the HZSM-5 zeolite can reach about 27.4. In addition, the HZSM-5 zeolite contains iron, calcium and phosphorus, which are come from raw fly ash. It also shows that with the increase of Cu$^{2+}$ content, the mass fraction of CuO in samples is gradually increased, and other elements such as silicon, aluminum and ferrum and calcium are gradually reduced, indicating that copper is successfully loaded on HZSM-5 zeolite, which is also consistent with the XRD results (figure 1). In addition, the molar ratio of Si to Al in samples decreased to about 23 after copper oxide loading.

3.1.3. BET

Figure 2 shows nitrogen adsorption/desorption isothermal curves for the prepared catalysts. The specific surface area and pore volume of Cu-1%, Cu-5%, Cu-10% and Cu-15% catalysts determined by DFT methods are listed in table 2. It can be seen that the specific surface area of the catalysts decreases with the increase of the loading of Cu$^{2+}$, which is due to the covering of Cu$^{2+}$ on zeolite surface and the filling of Cu$^{2+}$ in internal channels of zeolite. The nitrogen absorption/desorption curve of the catalysts belongs to the I-type adsorption curve, but the area of hysteresis loop reduces with the rise of Cu$^{2+}$ loading. At the same pressure, the N$_2$ volume adsorbed by catalysts decreases with the increase of copper loading. These phenomena indicate that the loading
of copper oxide clearly affects the surface and pore properties of catalysts. The BET result has been reported in our previous work [46].

In our previous work [46], the SEM of HZSM-5 zeolite has been reported. The images of HZSM-5 are bulk crystals, and the size of the particles is less than 10 um. The data of the XRD of CuO/HZSM-5 catalyzer shown that CuO/HZSM-5 have the diffraction characteristics of HZSM-5 and CuO. This phenomenon indicates that CuO and HZSM-5 in the synthesis catalyst belong to physical mixing state, and no new crystal phase is produced. It indicates that the CuO produced is covered on the surface or in the void of HZSM-5 zeolite. It is for this reason, the BET data can show that the more the CuO is loaded, the smaller the specific surface area of the catalyst is.

3.2. Performance of catalyst

The experimental conditions for evaluating the performance of catalysts are as follows: the total organic matter concentration is 200 mg l\(^{-1}\) (namely 120 mg phenol l\(^{-1}\), 60 mg quinolone l\(^{-1}\) and 20 mg indole l\(^{-1}\)), the catalyst dosage is 5 g l\(^{-1}\), and reaction temperature and time are 200 °C and 4 h, respectively. In order to compare the organic removal efficiency of CWAO, the adsorption efficiency of HZSM-5 zeolite at 25 °C for 4 h was also studied. After CWAO or adsorption, the contents of the three target organic compounds in solution were.
analyzed by HPLC. The results of HPLC are shown in figure 3 and the removal effects of organic matters are shown in figure 4.

Compared with the HPLC data for the simulated wastewater adsorbed by HZSM-5 zeolite (figure 3), new chromatographic peaks appear after CWAO treatment. The reason is that three kinds of organic substances are transformed or decomposed into small molecules. During oxidation reaction, the phenol can be oxidized to catechol, hydroquinone and benzoquinones, then the ring breaks into carboxylic acids such as oxalic acid, maleic acid, fumaric acid, malonic acid, etc of low molecular weight reported that oxidation process of quinoline and indole produces many low molecular weight intermediates such as nicotinic acid, formic acid, succinic acid and acetic acid. The adsorption process does not destroy the molecular structure of these organic compounds, thus there is no new chromatographic peak.

However, due to the less active components, the catalytic oxidation rate will be slow, which affects the removal rate decreases significantly, which is lower than that of the adsorption by HZSM-5 zeolite. Kim et al.[52] prepared CuO/Al₂O₃ catalysts with 1% to 25% copper loading, and it was found that 7% supported catalysts had the best removal rate of phenol in aqueous solution, which is similar to the phenomenon of our work. From the point of view of COD removal, Cu-10% catalyst has good catalytic oxidation effect. The reason is not only related to the content of active ingredients, but also to the specific surface area of the catalyst.

HZSM-5 is a kind of high silica zeolite with good adsorption capacity for phenol, quinoline and indole [46]. In CuO/HZSM-5 catalyst, the main role of HZSM-5 is to disperse CuO evenly and adsorb organic compounds and provide reactants for CuO catalytic oxidation. The role of CuO in the catalyst is catalytic active center. Both of them have great influence on the performance of the catalyst. When the content of CuO in the catalyst is small, the specific surface area of the catalyst is larger, which is conducive to the adsorption of organic matters. However, due to the less active components, the catalytic oxidation rate will be slow, which affects the removal
effect of organic matters. However, when the content of CuO in the catalyst is high, the specific surface area of the catalyst will be greatly reduced, and the concentration of reactants for CuO catalytic oxidation will be greatly reduced, which also leads to the unsatisfactory removal effect of organic matters. Therefore, there is always an optimal content of active components in the catalyst to achieve the best catalytic oxidation effect of organic matter. The synergistic effect between HZSM-5 and CuO for the removal of phenol, quinoline, indole can be illustrated by figure 6.

After CWAO treatment by four catalysts, the solution color is shown in figure 7. The solution color corresponding to Cu-1% catalyst is pale yellow, while the solution color corresponding to Cu-5% catalyst and Cu-15% catalyst is much lighter than that of Cu-1% catalyst, and the solution color for Cu-10% catalyst is almost colorless. According to the above analyses, Cu-10% catalyst is the best material and will be used in the following experimental research.

**Figure 6.** Diagram of CuO/HZSM-5 catalyst synergistic removal of organic matters.

**Figure 7.** The color of wastewater after CWAO treatment.
Figure 8. Effect of reaction time on COD and its removal rate.

Figure 9. Effect of total concentration of phenol, quinoline and indole mixed solution on COD and its removal rate.

Figure 10. Effect of catalyst dosage on COD and its removal rate.
3.3. Factors affecting CWAO

3.3.1. Effect of reaction time

The effect of reaction time on CWAO treatment of simulated refractory wastewater was investigated (figure 8). The experimental conditions are the same as those in the performance tests of catalysts. The change of COD and its removal rate with time is shown in figure 8. At different reaction time (1–4 h), COD and its removal rate are 254.7 mg l$^{-1}$, 191.0 mg l$^{-1}$, 175.1 mg l$^{-1}$, 108.5 mg l$^{-1}$ and 41.8%, 56.4%, 60.0%, 75.2%, respectively. The result suggested that the COD of the solution decreases with the prolongation of reaction time, and the removal rate of COD is more than 75% after 4 h. Therefore, for CWAO process of refractory wastewater, prolonging reaction time properly is beneficial to improving the removal efficiency of pollutants.

3.3.2. Effect of initial concentration

The effect of initial organic matter concentration on CWAO of phenol, quinoline and indole mixed aqueous solution is shown in figure 9. The experimental conditions are: 5 g l$^{-1}$ catalyst, 200 °C and 4 h reaction time. The initial total organic concentrations are 200 mg l$^{-1}$, 250 mg l$^{-1}$, 500 mg l$^{-1}$ and 1000 mg l$^{-1}$, and the corresponding initial COD is 437.8 mg l$^{-1}$, 537.3 mg l$^{-1}$, 1090.5 mg l$^{-1}$ and 2133.0 mg l$^{-1}$, respectively. The experimental value of initial COD concentration in simulated wastewater is lower than its theoretical COD value, because potassium dichromate cannot completely oxidize aromatic and nitrogen-containing heterocyclic compounds. The COD and its removal rate after CWAO is shown in figure 10. After CWAO treatment, the residual COD in wastewater is 108.5 mg l$^{-1}$, 193.4 mg l$^{-1}$, 476.0 mg l$^{-1}$ and 1179.8 mg l$^{-1}$, respectively, and the corresponding COD removal rates are 75.2%, 70.0%, 56.4% and 44.7%. The higher the COD value of wastewater, and the lower the removal efficiency of COD. The similar phenomena were observed in CWAO of phenol over the catalyst of Ce/TiO$_2$ [53]. Although the COD removal rate decreases with the increase of initial organic concentration, the COD removal amount increases, and the corresponding value is 329.3 mg l$^{-1}$, 343.9 mg l$^{-1}$, 614.5 mg l$^{-1}$ and 953.2 mg l$^{-1}$, respectively. When the pollutant concentration increases, the degradation amount increases due to more adsorption of pollutant to available active surface and interaction to oxygen molecules [54]. The results show that under the same reaction conditions, unit mass catalyst has higher removal efficiency for high concentration wastewater.

3.3.3. Effect of catalyst dosage

The CWAO effect of catalyst dosage on the mixture of phenol and quinoline indole is shown in figure 10. The experimental conditions: total organic matter concentration of 200 mg l$^{-1}$, 200 °C and 4 h. Clearly, the increase of catalyst dosage is conducive to the removal of COD. When the catalyst dosage is 10 g l$^{-1}$, the COD removal rate is about 87.5%. The oxidation efficiency of pollutants increases with the increase of catalyst dosage is due to the increase of active sites for the reaction between organics and oxygen [55].

3.3.4. Effect of temperature

The effect of temperature on the removal of COD is shown in figure 11. When catalyst dosage is 5 g l$^{-1}$, and the mixed organic solution concentration is 200 mg l$^{-1}$, after 4 h reaction, the COD values corresponding to the order of reaction temperature from low to high (namely 80 °C, 100 °C, 120 °C, 150 °C, 180 °C and 200 °C) are 84.1 mg l$^{-1}$, 73.7 mg l$^{-1}$, 60.2 mg l$^{-1}$, 62.4 mg l$^{-1}$, 109.8 mg l$^{-1}$ and 108.5 mg l$^{-1}$, respectively, and the
corresponding COD removal rates are 80.8%, 83.2%, 86.2%, 85.8%, 74.9% and 75.2%. With the increase of reaction temperature, COD removal rate first increases and then decreases, and the best removal rate is 86.2% at 120 °C. When the temperature is low, the number of activated molecules is less so the reaction rate is low and when the temperature is too high, the dissolved oxygen content of the system decreases, which leads to less free radical production and a decrease in oxidation effect. When the reaction temperature is between 120 °C and 150 °C, the corresponding COD removal rate is between 85.8% and 86.2%. Therefore, for CWAO treatment of phenol, quinoline and indole in simulated wastewater with Cu-10% catalyst, too low or too high temperature is not conducive to the removal of these organic compounds.

4. Conclusion

Through the above research, the following conclusions can be drawn.

(1) HZSM-5 zeolite can be synthesized from treated fly ash with TPABr template using hydrothermal method. CuO/HZSM-5 catalyst was successfully synthesized by precipitation and calcination methods.

(2) There is a positive correlation between the amount of copper oxide supported on catalyst and its XRD peak intensity. If the amount of copper oxide in catalyst is larger, the specific surface area of catalyst will be smaller.

(3) The catalyst with a copper loading of 10% has the best effect for wet air oxidation of phenol, quinoline and indole. Under the conditions of 200 °C, 5 g l⁻¹ catalyst, 200 mg l⁻¹ total concentration of phenol, quinoline and indole, the three organic compounds in aqueous solution can be completely removed after 4 h CWAO treatment and its COD removal rate is about 75%. Under the same conditions, if the reaction temperature drops to 120 °C, the removal rate of COD can exceed 86%.

(4) Too low or too high reaction temperature is not conducive to COD removal of phenol, quinoline and indole mixture. The optimum reaction temperature range for the CWAO of Cu-10% catalyst is 120 °C–150 °C.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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