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ARTICLE TYPE

Copper hydroxyl sulfate as heterogeneous catalyst for the catalytic wet peroxide oxidation of phenol

Kai Huang*, Jiejie Wang, Dongfang Wu and Sheng Lin

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Copper hydroxyl sulfates: $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were successfully synthesized by simple hydrothermal method and applied as heterogeneous catalysts to degrade phenol wastewater in a batch reactor in the presence of hydrogen peroxide (H_2O_2). The influence of temperature, H_2O_2 dosage, initial pH and catalyst dosage on phenol and COD removal efficiencies was investigated to get optimum conditions and to understand degradation process more clearly. The Cu^{2+} concentrations in the solutions after three hours reaction were also measured to prove the catalysts were stable. Excellent results, phenol removal efficiency of 99% and COD removal efficiency of 97%, had been achieved when treating 100 and 500 mg/L phenol wastewater. Even though the catalysts had low specific surface area, mesopores were mainly existed to decrease diffusion control of H_2O_2 and organics.

1. Introduction

Phenol and its derivatives are broadly applied in petrochemical, chemical, pharmaceutical, oil refineries, dyes, and plastics industries as raw materials, resulting in contaminants in effluent inevitably. [1] The treatment of phenolic wastewater is necessary before discharging it directly, due to the hazard to human health and aquatic life. [1] There are many methods to deal with phenolic wastewater, but biological treatment is ineffective at a phenol concentration of 50 mg/L or higher or need long time because of the biorefractory and toxic phenolic compounds [2]. Some physical technologies, such as adsorption [3, 4], coagulation [5, 6], and membrane separation, are only suitable for wastewater of higher concentration. The wastewater after treated is not easy to meet emission standards, still requiring biological or chemical treatment [7]. Advanced oxidation processes (AOPs) [8-10] of chemical technologies which can eventually oxidize organic pollutants to water, carbon dioxide, and other harmless small molecules non-selectively, are the main alternatives for wastewater treatment, especially for refractory pollutants.

AOPs based on extraordinarily reactive species such as hydroxyl radicals mainly include Fenton process [11, 12], photocatalysis [13, 14], electrocatalysis [15] and catalytic wet peroxide oxidation (CWPO) [16]. The classic Fenton process has two major disadvantages: strictly controlled pH which is around 3.5 and further treatment of much iron sludge [11, 12]. A great amount of energy and special apparatuses are needed when applying photocatalysis and electrocatalysis. Whereas catalytic wet peroxide oxidation (CWPO), which almost operates under the ambient conditions (atmospheric pressure and T⩽323 K) has been extensively and intensively investigated as one of the most effective, environmentally friendly and economical methods for treating refractory organics [17].

Copper based materials are preferred catalysts for the oxidation of phenol [18] because of good catalytic effect in transition metals. However, in most cases, low phenol conversions or COD removal efficiencies are reported. In order to improve catalytic effect, copper based materials are loaded on some supports such as activated carbon [19] and polymers [20, 21] through complicated methods to increase the specific surface areas. In recent years, a few copper hydroxyl salts with low specific surface area were proposed as promising catalysts in azo dyes removal via catalytic wet peroxide oxidation (CWPO). In 2010, Zhan and Chen reported the degradation of azo dyes over copper hydroxyphosphate, $Cu_2(OH)PO_4$, and it performed well only under near-neutral pH condition [22]. They also pointed out that diffusion resistance associated with microporous materials may result in low activity and, consequently, non-porous catalysts with low surface area may also exhibit satisfactory activity, but specific data of pores were not provided. Copper hydroxide nitrate, $Cu_2(OH)_3NO_3$, is an effective CWPO catalyst for oxidative degradation of azo dyes in a wide pH range [23], and $Cu_2(OH)_3NO_3$ synthesized by solvothermal method showed higher catalytic activity, than the control sample synthesized hydrothemally by the direct reaction of $Cu(NO_3)_2$ with NaOH in the catalytic wet peroxide oxidation of Direct Blue15. It could be seen from the above examples that different copper hydroxyl salts and the same copper hydroxyl salts synthesized by two methods had different performances. According to Li's report [24], up to now, the excellent efficiency catalyzed by 150 mg $[C_{16}H_{33}(CH_3)_3N]_4H_2SiV_2W_{10}O_{40}$ was obtained with the maximum 91.6% phenol (0.53 mM 50 mL) removal efficiency at pH 2.8 and 93.2% COD removal efficiency after 90 min. 300 mg $H_5PV_2Mo_{10}O_{40}$@SBA-15 hybrid [25] are need to degrade phenol

(0.53 mM 100 mL), though the TOC removal could achieved 100%. However, 20 mg $Cu_4(OH)_6SO_4$-A can remove 99% phenol (1.06 mM 150 mL) and 97% COD in a wide pH range (4.88-7.88). The synthesis of $Cu_4(OH)_6SO_4$-A is simple and its dosage is fairly small compared to the above polyoxometalate. The purpose of this work was to prove the high catalytic activity of copper hydroxyl salts was because of mesopores. Copper hydroxyl sulfates which had variance in pore diameter, one of the copper hydroxyl salts, were applied to explain how they weaken diffusion resistance for organics thoroughly.

Copper hydroxyl sulfates are atmospheric corrosion products of copper surface[26]. Brochantite $Cu_4(OH)_6SO_4$, one of the most common copper hydroxyl sulfates, have been synthesized by many methods. Typical synthetic process is mixing sulfates and hydroxides [27-29] at low temperature, and hydroxides can be replaced by urea [30], carbonate [31], ammonia and metal oxides [32]. Hydrothermal treatment has been utilized for preparing large and better crystals. Different morphologies of $Cu_4(OH)_6SO_4$ have been synthesized by Recep Kas using copper salt and sodium peroxydisulfate under the assistance of ultrasound [33]. Ultrasound assisted method can mix the solution uniformly and decrease the diffusion control on the reaction kinetics.

In this work, $Cu_4(OH)_6SO_4$-A was prepared hydrothermally from $CuSO_4 \cdot 5H_2O$ and NaOH [34], and copper hydroxyl sulfate (denoted as $Cu_4(OH)_6SO_4$-B) was synthesized based on a modfication of the hydrothermal method [32, 35] from $CuSO_4 \cdot 5H_2O$ and ZnO under magnetic stirring. The catalysts were applied to degrade phenol, a model compound in wastewater, and the effects of temperature, catalyst dosage, hydrogen peroxide dosage and initial pH by $Cu_4(OH)_6SO_4$-A were investigated.

2. Experimental Section

2.1. Materials

Copper sulfate pentahydrate ($CuSO_4.5H_2O$), sodium hydroxide (NaOH), tert-butanol, phenol, ZnO and H_2O_2 were purchased from Shanghai Chemical Reagent Co. Ltd. All chemicals used in this work were commercially supplied as analytical grade reagents and used without further purification. De-ionized water was used throughout the experiments.

2.2. Synthesis of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B catalysts

2.2.1 Synthesis of $Cu_4(OH)_6SO_4$-A

$Cu_4(OH)_6SO_4$-A was synthesized hydrothermally from copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium hydroxide (NaOH) [34]. The 6.6 M sodium hydroxide aqueous solution (8.7 g NaOH in 33 mL water) was dropped slowly into the 1.4 M solution of copper sulfate (5.6 g $CuSO_4 \cdot 5H_2O$ in 25 mL water) under magnetic stirring. Next, the resulting mixture was stirred for 0.5 h and sonicated at 25℃ for 0.5 h, followed by a hydrothermal treatment at 110℃ in a 100 mL Teflon-lined stainless steel autoclave for 48 h. The solid product was centrifuged, washed with de-ionized water for three times, and dried at 80℃ for 10 h. The product is named as $Cu_4(OH)_6SO_4$-A.

2.2.2 Synthesis of $Cu_4(OH)_6SO_4$-B

7.2 g $CuSO_4 \cdot 5H_2O$ was dissolved in 80 mL water, and 0.5 g commercial ZnO powder was directly added to the above 0.6 M aqueous solution to form suspension. Next, the suspension was sonicated at 25℃ for 0.5 h and stirred for 0.5 h. The suspension was sealed in a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated up to 120℃ and maintained at the target temperature for 48 h. Then the autoclave was allowed to cool to ambient temperature. The product was centrifuged and washed with de-ionized water. Finally, the precipitates were dried at 80℃ for 10 h, and kept in a dry condition at room temperature. The obtained sample is hereafter referred to as $Cu_4(OH)_6SO_4$-B.

2.3. Characterization of the sample

The powder XRD data of as-prepared samples were characterized on a Bruker (AXS model D8 advance) powder X-ray diffractometer equipped with Cu K_α radiation, λ = 1.5419 Å, 2θ range = 10 – 80 °. The scanning electron microscopy of catalyst samples was examined on a JEOL (JSM-6400) scanning electron microscope. The pore diameter and specific surface area were studied by using Brunauer–Emmett–Teller method (BET Model Quantachrome/Autosorb-1).

2.4. Catalytic degradation experiments

All catalytic reactions were carried out in a 250 mL three necked round-bottomed flask with a mechanical stirrer. When the temperature was constant, the designed dosage of H_2O_2 and catalyst were added to the 150 mL 100 mg/L (1.06 mM, pH=6.88) solution, then, the reaction was started.

Many factors had influence on the phenol and COD removal efficiencies in the degradation of phenol wastewater, such as temperature, H_2O_2 dosage, catalyst $Cu_4(OH)_6SO_4$-A dosage and initial pH value. To get the optimal conditions of phenol wastewater degradation and to understand degradation process more clearly, complementary experiments were performed changing the above reaction conditions. Different temperatures (40–70℃), H_2O_2 dosages (0.35–0.92 mL), catalyst $Cu_4(OH)_6SO_4$-A dosages (0.02–0.05 g) and initial pH values (2.88–8.88) were tested. The desired pH values were adjusted by adding diluted ammonia water (NH_4OH) and sulfuric acid (H_2SO_4).

The phenol removal efficiency was monitored as a function of time by taking out a given amount phenol solution and measuring absorbance of the phenolic compounds using spectrophometic method [16, 24, 36] after catalytic treatment at given time intervals. The catalyst must be immediately centrifuged from the solution in order to avoid influence the results. The phenol removal efficiency (η_t, %) after 't' min degradation was calculated by using this equation:

$$\eta_t = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where A_0 was the initial concentration of phenol and A_t was the concentration of phenolic compounds (including hydroquinone and catechol) after 't' min. The COD (Chemical Oxygen Demand) was measured by a standard method after the oxidation with potassium dichromate ($K_2Cr_2O_7$) [16]. The COD removal efficiency after 't' min degradation was defined as:

$$COD_t(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (2)$$

where C_0 was the initial COD of phenol aqueous solution and C_t

was the COD of phenol aqueous solution after ‘t’ min.

The stability of catalysts was studied by measuring the concentration of Cu^{2+} in the solution after three hours’ reaction which was determined by using an atomic absorption spectrometer. The reusability of catalysts was tested through continuous experiments for three times under the above optimal conditions.

3. Results and Discussions

3.1. Characterization of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B

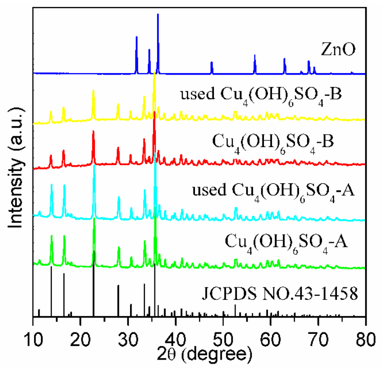

Fig.1. XRD patterns of the $Cu_4(OH)_6SO_4$-A (fresh and the used), $Cu_4(OH)_6SO_4$-B (fresh and the used), ZnO samples and the standard pattern of $Cu_4(OH)_6SO_4$.

X-ray diffraction patterns of commercial ZnO, the as-prepared $Cu_4(OH)_6SO_4$-A, $Cu_4(OH)_6SO_4$-B, the used $Cu_4(OH)_6SO_4$-A and the used $Cu_4(OH)_6SO_4$-B were shown in Fig.1. In this figure, the peak positions of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B are consistent with JCPDS card No. 43-1458 and no diffraction peaks for other phases or materials e.g. ZnO and CuO are observed in the XRD patterns, indicating a high purity of the final products. In this study the crystal forms of the formed products and commercial ZnO are monoclinic and hexagonal, respectively. It should be noted that the diffraction peak of ZnO in $Cu_4(OH)_6SO_4$-B is not observed. In previous literatures, ZnO was added into $Cu(NO_3)_2$ solution to produce $ZnCu_{1.5}(NO_3)_{1.13}(OH)_{3.88}$ [37] and $(CuZn)_5(SO_4)_2(OH)_6$ [38] was synthesized by mixing ZnO powder with $CuSO_4$ solution at room temperature. Zinc oxide was directly involved into the reaction and existed in the form of zinc ion in the basic salt in these examples. Thus, zinc ion was existed in the filtrate and the prepared basic salt was different based on different conditions probably. After our long and careful consideration, the residual ZnO content in the as-sample is too little to be detected due to the transformation of ZnO into $ZnSO_4$ according to the equation ($3ZnO + 4CuSO_4 + 3H_2O = Cu_4(OH)_6SO_4 + 3ZnSO_4$). In order to confirm the viewpoint, filtrate which is obtained after washing the catalyst is measured and the result proves the presence of a large amount of zinc ions.

In order to identify the structure of the synthesized catalysts, the FT-IR spectra of commercial ZnO, $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were measured, as shown in Fig.2.

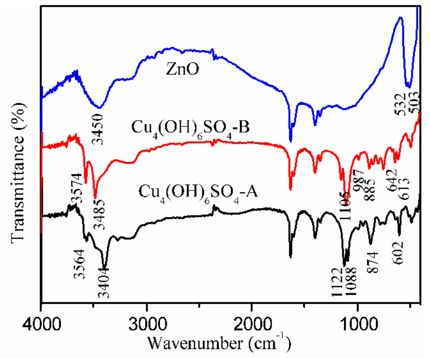

Fig.2. FT- IR spectra of $Cu_4(OH)_6SO_4$-A, $Cu_4(OH)_6SO_4$-B and ZnO samples.

The fundamental vibration frequency for OH is found at the range 3600-3200 cm^{-1} depending on the degree of H-bonding. The peaks at 3564 and 3404, 3574 and 3485 cm^{-1} indicate two different types of hydroxyl group in the $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B. Cu-O-H bending modes with different degree of H-bonding could be found in Fig.2. The peak at 987 cm^{-1} could be assigned to strong H-bonding in Cu-O-H. The peaks at 874 cm^{-1} and 885 cm^{-1} are corresponding to medium H-bonding in Cu-O-H. The IR bands at 1122(ν_3), 1088(ν_3), 1105(ν_3), 602(ν_4), 642(ν_4) and 613(ν_4) cm-1 are regarded as the stretching modes of $SO4^{2-}$ [31, 39]. The typical peaks of ZnO at 532 and 503 cm^{-1} are not obviously observed in $Cu_4(OH)_6SO_4$-B, agreeing with the result of XRD, and the same reason was discussed above.

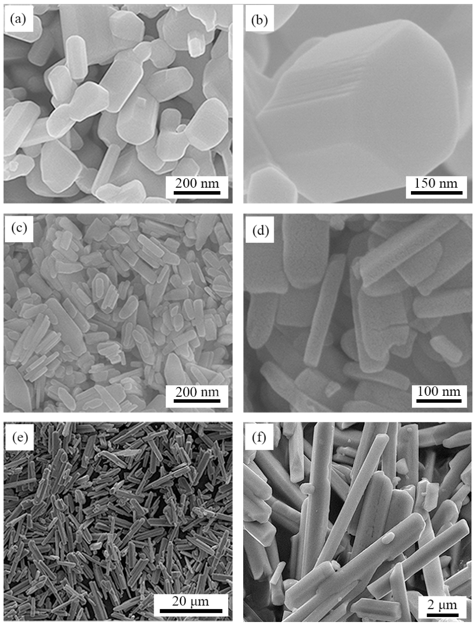

Fig.3. SEM images of commercial ZnO (a-b), $Cu_4(OH)_6SO_4$-A (c-d) and $Cu_4(OH)_6SO_4$-B (e-f) in high and low resolution.

The morphologies of commercial ZnO, $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were characterized by SEM and shown in Fig.3. From Fig.3a, it could be seen clearly the morphology of commercial ZnO is hexagonal, and the $Cu_4(OH)_6SO_4$-A are short sheets observed from Fig.3d. Whereas, $Cu_4(OH)_6SO_4$-B are composed of many long slender rods ranging from 2 to 10 um in length (Fig.3e), which are different from $Cu_4(OH)_6SO_4$-A in size and shape. In addition, ZnO is also not observed cleraly in the SEM images of $Cu_4(OH)_6SO_4$-B, and it has been explained fully above.

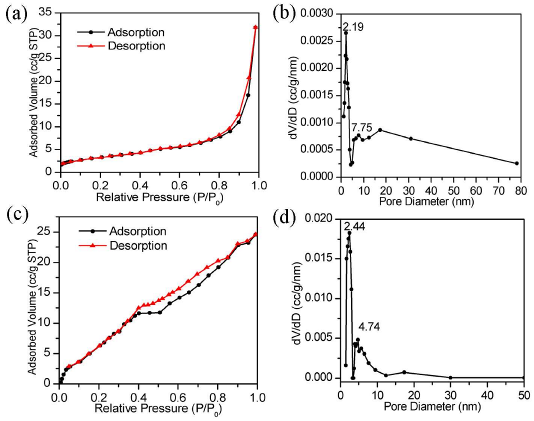

Fig.4. BET results of the products:(a) adsorption isotherm of $Cu_4(OH)_6SO_4$-A;(b) pore size distribution of $Cu_4(OH)_6SO_4$-A;(c) adsorption isotherm of $Cu_4(OH)_6SO_4$-B;(d) pore size distribution of $Cu_4(OH)_6SO_4$-B.

Table 1 Calculated data of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B.

Catalyst	V(cm^3/g)	d_1(nm)	d_2(nm)	SSA(m^2/g)
$Cu_4(OH)_6SO_4$-A	0.049	1.65	2.19	11.9
$Cu_4(OH)_6SO_4$-B	0.038	3.82	2.44	39.9

The adsorption isotherms and pore size distributions of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were described in Fig.4. The pore volume (V), the average pore diameter (d_1), the specific surface areas (SSA) and the most probable pore diameter (d_2) of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were shown in Table 1. As shown in Fig.4a, the adsorption isotherm of $Cu_4(OH)_6SO_4$-A is Type Ⅲ adsorption isotherm, declaring less pores in $Cu_4(OH)_6SO_4$-A because of little change of volume from 0.05-0.8 (P/P_0), and the pore size is mainly from 2.19 to 7.75 nm (Fig.4b) . The existence of macrospores maybe results from the gap between particles. The adsorption isotherm of $Cu_4(OH)_6SO_4$-B depicted in Fig.4c has Type Ⅳ adsorption isotherm which is characteristic for mesoporous materials. Micropores are existed because of the upside down line from 0-0.05 (P/P_0). However, mesopores are mainly existed from the sharp increased change of volume from 0.05-0.9 (P/P_0) and pore size distribution of $Cu_4(OH)_6SO_4$-B. The specific surface area values and the pore volume are measured as 11.9, 39.9 m^2/g and 0.049, 0.038 cm^3/g for $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B, which are significantly smaller than traditional catalysts'.

3.2 The influence of factors on the degradation effect

3. 2.1 Effect of temperature

It is well known that temperature was one of the important factors that influence the catalytic activity, thus temperature is selected as the first evaluated factor. The effect of temperature（40，50，60，70℃）used commonly in CWPO on the phenol and COD removal efficiency was given in Fig.5.

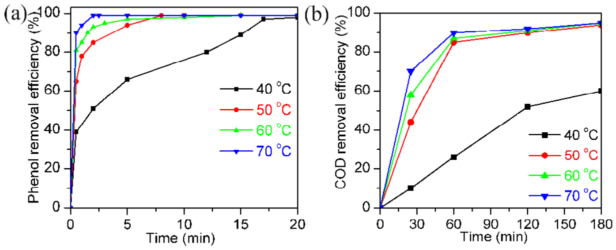

Fig.5. Effect of temperature on the catalytic degradation of phenol wastewater (catalyst $Cu_4(OH)_6SO_4$-A 50mg, pH=6.88, phenol concentration 100mg/L, H_2O_2 0.58mL): (a) phenol removal efficiency; (b) COD removal efficiency.

It could be seen that the phenol was easily removed by the catalyst from Fig.5a, and even at 40℃ the phenol removal efficiency after only 20 min could reach 98%. The excellent phenol removal efficiencies were related to the mesopores of the catalyst. The average pore diameter of $Cu_4(OH)_6SO_4$-A (1.65 nm) was much larger than the size of phenol (about 0.62 nm), so phenol was readily diffused into the inner pore of $Cu_4(OH)_6SO_4$-A to react with hydroxyl radicals [22]. Although all the final phenol removal efficiencies were nearly equal to 99%, the initial phenol removal efficiency was apparently increased and the time required was obviously shortened with the increase of temperature. Furthermore, the COD removal efficiencies at 40℃ were apparently lower than those at other temperatures. Like most of the catalysts, the catalytic activity was enhanced by rising the temperature [22，23]，therefore, more hydroxyl radicals were produced gradually to oxidize organics, especially from 40 to 50 °C. However, the higher temperature, the more energy consumption was need and catalysts might be sintered. The phenol removal efficiency at 50℃ could finally approach 99% and the COD removal efficiencies at 50, 60 and 70℃ were both around 94% after around 120 min, just a little bit higher than 90% at 50 ℃, thus 50 ℃ was chosen as the suitable reaction temperature for energy conservation. In addition, it was found that the removal of phenol and COD were dramatically different. It was illustrated that in this study phenol was easily oxidized to hydroquinone and catechol firstly [39] and they were easily oxidized to other intermediate products, but these intermediates were slowly mineralized [18].

3.2.2 Effect of H_2O_2 dosage

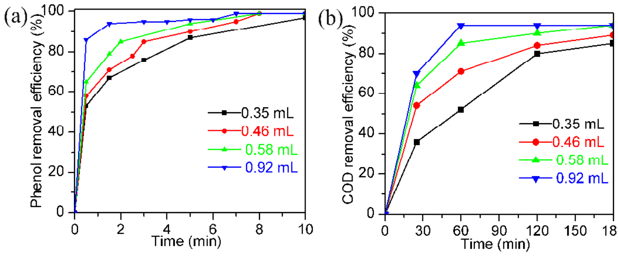

Fig.6. Effect of H_2O_2 dosage on the catalytic degradation of phenol wastewater (catalyst $Cu_4(OH)_6SO_4$-A 50mg, pH=6.88, phenol concentration 100mg/L, T=50℃): (a) phenol removal efficiency; (b) COD removal efficiency.

Phenol and COD removal efficiency affected by hydrogen peroxide dosage directly related to hydroxyl radicals was shown in Fig.6. The abatement of phenol was not occured nearly with 0 mL H_2O_2 and 50 mg $Cu_4(OH)_6SO_4$-A, proving H_2O_2 was the oxidizer beyond doubt and the absorption of $Cu_4(OH)_6SO_4$-A was negligible. With 0.58 mL H_2O_2, the same amount of catalyst and ter-butanol (scavenger of hydroxyl radical) [35] at the same time, the phenol was not oxidized during 180 min. Whereas, the phenol removal efficiency was 91% after 5 min and COD_{180} was 94% with the same H_2O_2/ $Cu_4(OH)_6SO_4$-A. It was declared that the organics were only oxidized directly by hydroxyl radicals coming from H_2O_2 in this study, and it was known that more hydroxyl radicals were produced quickly from more H_2O_2 in the presence of catalyst. So the initial phenol and COD removal efficiencies were increased with the increase dosage of H_2O_2. However, it was noted that the final COD removal efficiency with 0.92 mL H_2O_2 was equal to that with 0.58 mL H_2O_2, though the H_2O_2 dosage was increased dramatically to four times of theoretical value. It was due to the decrease of hydroxyl radicals in generation and the increase of their elimination. Finally, the residual hydroxyl radicals to be utilized were same. The chemical equation for complete oxidation of phenol by H_2O_2 was demonstrated as equation 1.

$$C_6H_5OH + 14H_2O_2 \longrightarrow 6CO_2 + 7H_2O \quad (1)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (2)$$

$$HO\bullet + H_2O_2 \longrightarrow HO_2\bullet + H_2O \quad (3)$$

$$HO_2\bullet + H_2O_2 \longrightarrow H_2O + O_2 \quad (4)$$

$$HO\bullet + HCO_3^- \longrightarrow OH^- + HCO_3\bullet \quad (5)$$

$$HO\bullet + HO\bullet \longrightarrow H_2O_2 \quad (6)$$

According to the equation 1, 14 mol H_2O_2 was needed to completely oxidize 1mol phenol, so 0.23 mL H_2O_2 (30%, wt%) was theoretically needed to oxidize 150 mL 100 mg/L phenol water. However, 0.23 mL H_2O_2 was not enough to oxidize phenol because of incomplete utilization [40], e.g. decomposition of H_2O_2 (equation 2), elimination of hydroxyl radicals (equation 3, 5 and 6) and generation of hydroperoxyl radicals ($HO_2\cdot$) [18], so more H_2O_2 dosage was needed to obtain better result. The hydroperoxyl radicals ($HO_2\cdot$) were not only less reactive but also reacted with H_2O_2 to consume the resource of $HO\cdot$. The hydroxyl radicals were also consumed by bicarbonate ions from carbonic acid generated from CO_2. The lifetime of hydroxyl radicals was especially short, and they would be recombined by themselves if they were not contacted with organics in time. Consequently, more organics must be diffused into pores of catalyst rapidly to react with hydroxyl radicals before hydroxyl radicals were reacted with H_2O_2, bicarbonate ions and themselves. The diffusion of organics could be readily occurred in the mesopores of $Cu_4(OH)_6SO_4$-A. The good degradation performance was attributed to cumulative hydroxyl radicals after generation and consumption. But the final COD removal efficiencies with 0.58 and 0.92 mL H_2O_2 were similar, thus, 0.58 mL H_2O_2 (2.5 times of theoretical H_2O_2 dosage) was beneficial for the removal of COD.

3.2.3 Effect of initial pH

The degradation of phenol was significantly influenced by the initial pH and the experiment results were showed in Fig.7. As the initial pH values were adjusted widely from 2.88 to 7.88, the final phenol removal efficiencies were nearly 99% after only 15 min. However, the final phenol removal efficiency was 90% after 15 min at the initial pH=8.88. The initial phenol removal efficiencies in acid environment (pH from 2.88 to 6.88) were dropped with the decrease of initial pH because of the dissolution of catalyst [41]. The less catalyst, the less active sites, hydroxyl radicals would also be less from the same H_2O_2 dosage at the same time. The initial phenol removal efficiency in alkaline environment decreased (pH from 7.88 to 8.88) as the initial pH arose. The decomposition of some H_2O_2 in alkaline environment [1] led to the reduction of hydroxyl radicals' resource. The phenol removal efficiencies in acid environment (pH=2.88)were better than those in alkaline environment (pH=8.88), the total amount of hydroxyl radicals was not changed as the hydroxyl radicals were generated gradually, even if the catalyst was less in acid environment. In consideration of activity of the copper ions though homogenous reaction, an additional experiment was performed using 10 mg/L Cu^{2+}. The low COD removal efficiency of 2% indicated that the excellent performance in acid environment was not resulted from the dissolved copper ions. The tendency of COD removal efficiency was similar to that of phenol removal efficiency in acid and alkaline environment, respectively. However, the removal of COD needed longer time than the removal of phenolic compounds and its reason was discussed in the above part "effect of temperature". It was noted that COD_{180} still could achieve 71% at pH=8.88, illustrating that the decomposition of H_2O_2 was not seriously and many hydroxyl radicals were continually produced slowly within 180 min. So the COD removal efficiency was related to the cumulative amount of hydroxyl radicals during the period of intermediates were generated and degraded. In conclusion, the pH of phenol wastewater suitable for treatment was widely from 2.88 to 7.88, and it would be best at natural pH 6.88 regardless of phenol removal efficiency or COD removal efficiency which was most close to neutral, meaning less loss of catalyst and less decomposition of H_2O_2.

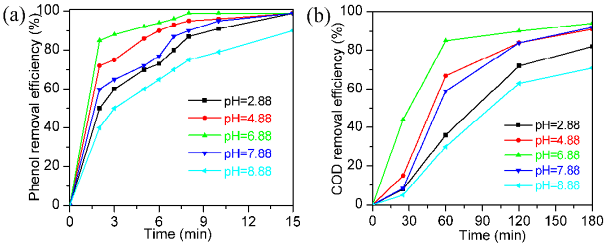

Fig.7. Effect of initial pH on the catalytic degradation of phenol wastewater (T=50 ℃, catalyst $Cu_4(OH)_6SO_4$-A 50mg, phenol concentration 100mg/L, H_2O_2 0.58 mL): (a) phenol removal efficiency; (b) COD removal efficiency.

3.2.4 Effect of catalyst dosage

Fig.8 presented the effect of catalyst dosage on the catalytic degradation of phenol. Revealed by the above figure, the phenol removal efficiency could achieve 32% and 99% at 25 and 180 min without catalyst. Whereas, the phenol removal efficiency of 99% was obtained after 25 min with only 10 mg catalyst.

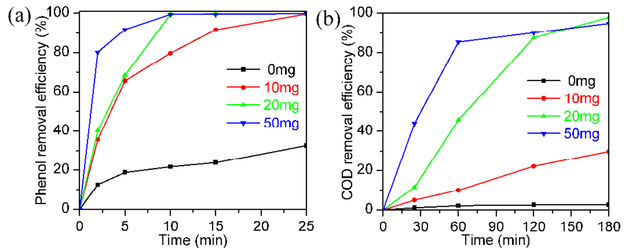

Fig.8. Effect of catalyst $Cu_4(OH)_6SO_4$-A loading on the catalytic degradation of phenol(T=50℃, pH=6.88, phenol concentration 100mg/L, H_2O_2 0.58mL): (a) phenol removal efficiency; (b) COD removal efficiency.

Using small amount of catalyst not only could shorten the time of degradation greatly, but also improved the phenol and COD removal efficiency markedly. Without catalyst, the COD removal efficiency only reached to 2% after 180 min, illustrating phenolic compounds were only translated to intermediates which were hardly further degraded to carbon dioxide and water because few hydroxyl radicals were produced in the absence of catalyst. The η_2 arrived 35%, 40% and 44% and the COD_{25} achieved about 5%, 11% and 44% when catalyst was added from 10 to 50 mg. It was inferred that more hydroxyl radicals were generated quickly from H_2O_2 in the presence of more catalyst which was equivalent to more active sites. Although the phenol and COD removal efficiencies were both lower with 20 mg catalyst than that with 50 mg at beginning, they could reach the similar results and even better at last. Less hydroxyl radicals were produced when adding 20 mg catalyst, resulting in a lower degradation rate. At the same time, less hydroxyl radicals were wasted compared to 50 mg catalyst as the aforementioned cause, hence the COD removal efficiency at 180 min could reach the best effect of 97%. Considering the COD removal efficiency and catalyst dosage, 20 mg (0.13 g/L) catalyst was enough to degrade 150 mL 100 mg/L phenol wastewater.

3.3 Catalytic activity of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B

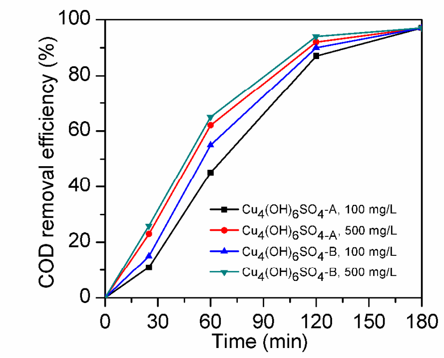

Fig.9. The COD removal efficiencies of degrading 100 mg/L and 500 mg/L model phenol wastewater under the optimal conditions with $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B.

In order to compare the activity of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B, 150mL 100 mg/L and 500 mg/L model phenol wastewater was degraded under the optimal conditions (50℃, pH=6.88, 0.13g/L catalyst, 2.5 times of theoretical H_2O_2 dosage) with the same amount of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B, respectively. The experiment results were showed in Fig.9.

The COD removal efficiencies of degrading 100 mg/L and 500 mg/L phenol solutions by $Cu_4(OH)_6SO_4$-B were better than that by $Cu_4(OH)_6SO_4$-A. This was resulted from the bigger pore diameter (the most probable pore diameter and the average pore diameter) of $Cu_4(OH)_6SO_4$-B and more pores in $Cu_4(OH)_6SO_4$-B in Fig.4. The more pores were equal to more active sites, resulting in the more H_2O_2 reacting with catalyst, so more hydroxyl radicals were produced. On the other hand, the diffusion resistance for organics could be reduced because of the bigger pore diameter. The performance of 500 mg/L phenol solution was superior to that of 100 mg/L phenol solution because of the increasing collision frequency of molecules [23].

3.4 Stability and reusability of $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B

Table 2 The Cu leaching (mg/L) in low and high concentration solutions for three hours treatment by $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B.

concentration of phenol solution (mg/L)	$Cu_4(OH)_6SO_4$-A	$Cu_4(OH)_6SO_4$-B
100	6	5
500	30	30

The stability of catalyst is very essential for actual industrial application as one of the catalyst parameters. In order to illustrate the stability of catalyst, the Cu^{2+} concentration after catalytic wet peroxide oxidation for 180 min was measured. The Cu^{2+} leaching (mg/L) in treated 100 and 500 mg/L phenol solutions by $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were listed in Table 2. The low Cu^{2+} leaching proved that the copper hydroxyl sulfates were sable in the 100 mg/L phenol solution. It was further seen that the Cu^{2+} leaching was increased with the increasing concentration of phenol solutions. It was the combined results of the surface-catalyzed reaction [42] and the less acidic conditions [43] attributed to more organic acids. More active sites of catalyst were needed to react with H_2O_2 to produce more hydroxyl radicals as the increasing concentration of phenol solutions, and at the same time, catalyst was contaminated by more acid intermediates generated unavoidably.

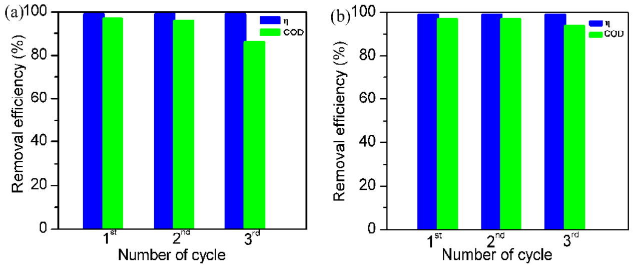

Fig.10. The phenol and COD removal efficiencies of degrading 100 mg/L phenol solution in three recycled runs by $Cu_4(OH)_6SO_4$-A (a) and $Cu_4(OH)_6SO_4$-B (b).

The phenol and COD removal efficiencies of degrading 100 mg/L phenol solution in consecutive three experiments with recycled $Cu_4(OH)_6SO_4$-A and $Cu_4(OH)_6SO_4$-B were described in

Fig.10. It was found that phenol removal efficiency in Fig.10a and Fig.10b could be maintained at 99% because of the easy conversion of phenol, and COD removal efficiency in Fig.10a was 97%, 96% and 86% for three consecutive runs. However, in Fig.10b the COD removal values were 97%, 97% and 94%, respectively. The decrease of COD removal efficiency was only associated with the change of catalyst under the same conditions. The XRD pattern of used catalyst was showed in Fig.1, indicating the catalysts' structures do not change. So the corrosion from intermediate acids formed during the degradation process and the dicarboxyli acids (the typical by-product) may lead to the reduction of pore diameter. The grayish green colour of the reused catalyst (the catalysts before using were green) indicated the adsorption of acids was one of the possible reasons. The COD removal efficiency with $Cu_4(OH)_6SO_4$-B in the third run was higher than that with $Cu_4(OH)_6SO_4$-A. It was mainly because that the pore diameter of reused $Cu_4(OH)_6SO_4$-B still belongs to size of mesopore even it might be decreased after reusing .

4 Conclusions

Copper hydroxyl sulfates were prepared by two different hydrothermal methods and showed considerable catalytic activity in oxidizing phenol solutions of low and high concentration at mild conditions (50 ℃ and atmospheric pressure). Phenol removal efficiency of 99% and COD removal efficiency of 97% were obtained under the optimal conditions (pH=6.88, 0.13g/L catalyst, 2.5 times of theoretical H_2O_2 dosage). The degradation efficiency was directly related to the utilized hydroxyl radicals which were equal to generation minus consumption. The generation and consumption were affected by these factors including experiment conditions and pore of catalyst, so a maximum utilization rate of hydroxyl radicals could be achieved under the optimal conditions. The mesopores of $Cu_4(OH)_6SO_4$-A were in favor of the diffusion of organics, and this was also confirmed by the better catalytic performance of $Cu_4(OH)_6SO_4$-B . Copper hydroxyl sulfates are effective and stable catalyst with low specific surface area in CWPO. Hence, the catalysts for the degradation of phenol may not be restricted to those with high specific surface area.

Notes and references

School of Chemistry and Chemical Engineering, Southeast University,
Nanjing, 211189, P.R. China.
Fax: +86 02552090620; Tel: +86 025 52090621;
E-mail: huangk@seu.edu.cn (Prof. K. Huang),

1 J. Guo and M. Al-Dahhan, *Ind. Eng. Chem. Res.*, 2003, **42**, 2450-2460.
2 Y. Yavuz, A. S. Koparal and Ü. B. Ögütveren, *Chem. Eng. Technol.*, 2007, **30**, 583–586.
3 S. S. Lin, C. L. Chen, D. J. Chang and C. C. Chen, *Water. Res.*, 2002, **36**, 3009-3014.
4 W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capala and I. Ostrowska, *Desalination*, 2004, **163**, 287–296.
5 G. K. Nesseris and A. S. Stasinakis, *J. Chem. Technol. Biotechnol.*, 2012, **87**, 540-545.
6 M. Tomaszewska, S. Mozia and W. Morawski, *Desalination*, 2004, **162**, 79–87.
7 G.. Busca, S. Berardinelli, C. Resini and L. Arrighi, T, *J. Hazard. Mater.* 2008, **160**, 265-288.
8 R. Andreozzi, V. Caprio, A. Insola and R. Marotta, *Catal. Today.*, 1999, **53**, 51–59.
9 M. Pera-Titus, V. García-Molina, M.A. Ba˜ nos, J. Giménez and S. Esplugas, *Appl. Catal. B: Environ.,* 2004, **47,** 219–256.
10 A. Vogelpohl and S. M. Kim, *J. Ind. Eng. Chem.,* 2004, **10**, 33-40.
11 E. Neyens and J. Baeyens, *J. Hazard. Mater.*, 2003, **98,** 33–50.
12 J. J. Pignatello, E. Oliveros and A. Mackay, *Crit. Rev. Environ. Sci. Technol.*, 2006, **36**， 1–84.
13 X. C. Ruan and H. Zhong, *Catal. Commun.*, 2013, **40**, 76–79.
14 T. L. Hewer, B. C. Machado, R. S. Freire, and R. Guardani, *RSC Adv.*, 2014, **4**, 34674-34680.
15 Q. Shi, H. Wang, S. L. Liu and Z. Y. Bian, *RSC Adv.*, 2014, **4**, 56263-56272.
16 P. Massa, F. Ivorra, P. Haure and R. Fenoglio, *J. Hazard. Mater.*, 2011, **190**, 1068–1073.
17 N. S. Inchaurrondo, P. Massa, R. Fenoglio, J. Font and P. Haure, *Chem. Eng. J.*, 2012, **198**,426-434.
18 N. S. Inchaurrondo, J. Cechini, J. Font and P. Haure, *Appl. Catal. B.: Environ.*, 2012, **111**, 641-648.
19 R.M. Liou and S.H. Chen, *J. Hazard. Mater.*, 2009, **172,** 498–506.
20 I. U. Castro, F. Stüber Font J, A. Fortuny and C. Bengoa, *J. Hazard. Mater.*, 2009, **163,** 809-815.
21 I. U. Castro, D.C. Sherrington, A. Fortuny, A. Fabregat, F. Stüber, J. Font and C. Bengoa, *Catal. Today.*, 2010, **157,** 66–70.
22 Y. Zhan, H. Li and Y. Chen, *J. Hazard. Mater.*, 2010, **180**, 481-485.
23 Y. Zhan, X. Zhou, B. Fu and Y. L. Chen, *J. Hazard. Mater.*, 2011, **187**, 348-354.
24 H. C. Li, X. Yu, H. W. Zheng, Y.M. Li, X. H. Wang and M. X. Huo, *RSC Adv.*, 2014, **4**, 7266-7274.
25 X. W. Wu, X. F. Chen, H. Y. Guan, X. H. Wang and L. Chen, *J. Sol-Gel. Sci. Technol.*, 2014, **72**, 663–667.
26 T. L. Woods, R. M. Garrels, *Appl. Geochem.*, 1986, **1**, 181-187.
27 S. V. S. Prasad, V. S. Rao, *J. Therm. Anal.*, 1985, **30**, 603-609.
28 N. Koga, J. M. Criado, *J. Therm. Anal.*, 1997, **49**, 1467-1475.
29 H. Tanaka, N. Koga, *J. Chem. Educ*., 1990, **67**, 612-614.
30 S. Kratohvil, E. Matijević. *J. Mater. Res*., 1991, **6**, 766–777.
31 F. Bakhtiari, E. Darezereshki. *Mater Lett*., 2011, **65**, 171-174.
32 H. Strandberg, V. Langer and L. G. Johansson, *Acta. Chem. Scan.*, 1995, **49**, 5-10.
33 R. Kas and Ö. Birer, *Ultrason. Sonochem.*, 2012, **19**, 692–700.
34 S. Vilminot, M. Richard-Plouet, G. André, D. Swierczynskia, F. Bourée-Vigneron, E. Marino and M. Guillot, *Cryst. Eng.*, 2002, **5**, 177-186.
35 A. Srikhaow and S. M. Smith, *Appl. Catal. B.: Environ.*, 2013, **130-131**, 84-92.
36 P. Xu, G. Zeng, D. Huang, L. Liu, C. Lai, M. Chen，C. Zhang, X. X. He, M. Y. Lai and Y. B. He, *RSC Adv.*, 2014, 4, 40828-40836.
37 M. Meyn, K. Beneke and G. Lagaly, *Inorg. Chem.*, 1993, **32**, 1209-1215.
38 M. Xue, R. Chitrakar, K. Sakane, K. Ooi, S. Kobayashi, M. Ohnishi, and A. Doi, *J. Solid State Chem.*, 2004, **177**, 1624–1630.
39 E. A. Secco, *Can. J. Chem.*, 1988, **66,** 329.
40 E. V. Rokhina, J. Virkutyte, *Crit. Rev. Env. Sci. Tec.*, 2010, **41**, 125-167.
41 T. Granato, A. Katovic, K. Maduna Valkaj, A. Tagarelli, G. Giordano, *J. Porous Mater.*, 2009, **16**, 227–232.
42 S. W. Zhou, C. B. Zhang, X. F. Hu, Y. H. Wang, R. Xu, C. H. Xia, H. Zhang and Z. G. Song, *Appl. Clay. Sci.*, 2014, **95**, 275–283.
43 M. L. Luo, D. Bowden, P. Brimblecombe, *Appl. Catal. B: Environ.*, 2009, **85**, 201–206.