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ARTICLE TYPE

Heterogeneous catalytic wet peroxide oxidation of simulated phenol wastewater by copper metal-organic frameworks

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Two different porous copper metal-organic frameworks (Cu-MOFs) named as $Cu_3(BTC)_2$ and Cu(BDC) were synthesized and applied as heterogeneous catalysts for catalytic wet peroxide oxidation (CWPO) of simulated phenol wastewater (100 mg/L). The characterization including X-ray Powder Diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX) were achieved. By comparison, Cu(BDC) exhibited better catalytic degradation performance. Then, Cu(BDC) was selected for further experiments. Several parameters including temperature, H_2O_2 dose, catalyst dose and initial pH of phenol wastewater which could affect the catalytic degradation efficiency by Cu(BDC) were investigated. Under optimum conditions, phenol conversion of 99% and COD (Chemical Oxygen Demand) removal of 93% were achieved. The degradation on different concentration of phenol solution (100 to 1000 mg/L) was also carried out. No matter small or large concentration of phenol solution, satisfactory results with the phenol conversion of 99% and COD removal of over 90% were obtained. After reused twice, the Cu(BDC) could still keep well catalytic performance with phenol conversion of 99% and COD removal of over 85%. Like other copper catalysts, the mechanism of degradation process was also hydroxyl radical mechanism. The leaching of Cu^{2+} was also monitored by Inductively Coupled Plasma-Atomic Emission Spectrum (ICP-AES) with a negligible release of copper (7 ppm). Overall, Cu-MOFs could be a kind of promising heterogeneous catalyst for catalytic oxidation of phenol with H_2O_2 as oxidant.

1. Introduction

With the development of industry satisfying people's increasing demands for chemical products, the problem of environmental pollution especially water pollution has become more and more serious at the same time. Phenol and its derivatives as common refractory contaminants in wastewater coming from herbicides, pesticides, paints, leathers, and the textile industries have become the focus of effluents treatment due to their high toxicity and poor biodegradability[1]. In order to obtain satisfactory degradation effect, numerous treatment technologies have been applied for removal of phenol and its derivatives mainly including physical methods[2], chemical treatment technologies[3, 4] and photocatalytic degradation[5].

In general, the physical methods are employing some porous adsorbents for absorption of phenol and its derivatives in the wastewater such as activated carbon[6], polymeric adsorbents[7] et al. However, after absorption, it is still needed further complicated post-treatment and the used absorbents are difficult to regenerate resulting in high cost and resources consumption[2] which restricted their wide application. The required conditions for photocatalytic degradation of phenol is rather rigorous especially the light condition making it be difficult to realize industrial application. Therefore, all kinds of the chemical treatment technologies especially Advanced Oxidation Processes (AOPs) which exploit highly active hydroxyl radicals[8] have been extensively developed in order to make phenol obtain complete mineralization by generating carbon dioxide and water[9].

Among all the AOPs, catalytic wet peroxide oxidation (CWPO) employing eco-friendly hydrogen peroxide as the oxidant has become a hot topic because of its outstanding degradation effect, low costs and mild operating conditions[10, 11]. The employed catalysts could be classified as homogeneous catalysts[12, 13] and heterogeneous catalysts[14, 15] in CWPO. The application of conventional homogeneous catalysts cause secondary pollution due to hard separation of metal ions from the treated wastewater which make them be replaced by the heterogeneous catalysts. Large varieties of heterogeneous catalysts with transition metals as active species have been reported in catalytic degradation of phenol wastewater[16-20]. Phenol conversion of 95% and TOC (total organic carbon) conversion of 45% were achieved when Fe-ZSM-5 zeolite membrane catalysts were applied in catalytic wet peroxide oxidation of phenol by Yan et al.[21]. Wang et al.[22] prepared composite nanospheres of hydrogel coated Fe_3O_4 magnetic and tested for catalytic wet peroxide oxidation of phenol with phenol conversion of 98% and COD removal of 76% reached. Liou et al.[23] reported catalytic oxidation of phenol with CuO impregnated activated carbon and found that over 90% COD removal was obtained. Among these transition metals catalysts, heterogeneous copper catalysts appears to be satisfactory catalysts for catalytic degradation of organic wastewater under moderate conditions. So, the catalytic oxidation of organic effluents was focused on large amounts of heterogeneous copper catalysts in the latest years including copper oxide[24], polymer-supported copper complexes[25], copper hydroxyl salts[26] and so on.

Metal-organic frameworks (MOFs) with two or three-dimensional porous structures developed by organic bridging ligands and metal ions or metal clusters have obtained intensive attention due to large pore volume, high specific surface area, tunable pore size and functionalities[27, 28]. They have been considerably applied in gas separations, gas storage, molecular sensing and catalysis[29-32] et al. Various kinds of MOFs were applied as catalysts for different reaction systems. And Salvatore De Rosa[33] regarded $Cu_3(BTC)_2$ as heterogeneous catalysts for treating olive oil mill wastewater and obtained satisfactory performance. But almost no MOFs were applied in CWPO for phenol wastewater treatment. In this work, two different types of Cu-MOFs including $Cu_3(BTC)_2$ and Cu(BDC) were synthesized and tried to take them as heterogeneous copper catalysts for simulated phenol wastewater treatment in CWPO.

2. Experimental

2.1. Materials and reagents

Copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), 1,3,5-benzenetricarboxylic acid (H_3BTC), 1,4-benzenedicarboxylic acid (H_2BDC), N,N-dimethylformamide (DMF), ethanol (C_2H_5OH), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), phenol (C_6H_6O), hydrogen peroxide (H_2O_2, 30%, w/w) et al. were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemical reagents were of analytical reagent (AR) grade and directly employed without further purification. During the experiment, deionized water was used to prepare all the aqueous solutions.

2.2. Synthesis of $Cu_3(BTC)_2$ metal-organic framework

The $Cu_3(BTC)_2$ metal-organic framework which is also called HKUST-1 was synthesized by solvothermal method, as reported elsewhere[34] with some modification. In typical experiments, copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$) (1.94 g) was dissolved in 30 mL deionized water. 1,3,5-benzenetricarboxylic acid (H_3BTC) (0.84 g) was dissolved in a mixed solvent including 15 mL DMF and 15 mL ethanol. Then, the two solutions were mixed and then stirred for 10 minutes in order to obtain homogeneous suspension. After that, the suspension was transferred into a 100-mL Teflon-lined stainless steel autoclave. Further, the autoclave was sealed and heated at 110 °C in an oven for 24 hours. After reaction, the autoclave was naturally cooled to room temperature. Subsequently, the resulting deep blue crystals were separated by centrifugation and washed with ethanol, N,N-dimethylformamide and chloroform several times, respectively. Finally, the obtained material was dried at 60 °C under vacuum for 24 hours. The prepared catalysts was grounded to powders and used for the following experiments.

2.3. Synthesis of Cu(BDC) metal-organic framework

Solvothermal method is the typical method for preparing Cu(BDC) metal-organic framework. In this work, the Cu(BDC) was synthesized according to a modified literature procedure[35]. Firstly, Copper(II) nitrate trihydrate (2.42 g, 8 mmol) was dispersed in 75 mL N,N-dimethylformamide with continuous stirring at room temperature. 1,4-benzenedicarboxylic acid (0.8050 g, 4mmol) was put into the solution with further stirring for 10 minutes. Then, 10 minutes' ultrasound was conducted so that the mixture could be evenly mixed. After that, the mixture was loaded into a Teflon-lined stainless steel autoclave before the autoclave was sealed. The crystallization was conducted at 100 °C for 24 hours in the drying oven. Subsequently, the autoclave was cooled to room temperature in natural conditions. The obtained suspension was centrifuged and blue solid was separated from the suspension. The solid sample was washed in N,N-dimethylformamide for 3 days, then washed with ethanol and dichloromethane, respectively. Finally, the solid sample was dried under vacuum at 60 °C overnight. After cooling to room temperature, the solid catalysts was grounded to desired powders and used for further experiments.

2.4. Characterization of catalysts

The X-ray diffraction (XRD) analysis of the two synthesized Cu-MOFs was carried out on a Bruker D8 diffractometer using Cu K_α radiation with 2θ range = 5-60°. Fourier-transform infrared (FT-IR) spectra was conducted to obtain further structure of the synthesized Cu-MOFs by a Perkin Elmer fourier-transform infra-red spectrometer. And the microtopography of the Cu-MOFs was observed on FEI ESEM Quanta 400 scanning electron microscope. Energy dispersive X-ray (EDX) spectrum was performed to analyze the chemical composition of the two Cu-MOFs. The leaching of Cu^{2+} after catalytic degradation of phenol was monitored by ICP-AES.

2.5. Catalysis tests

In the experiments of catalytic oxidation of phenol, 150 mL 100 mg/L of simulated phenol wastewater was poured into a 250-mL three-necked round-bottomed glass reactor which was equipped with continuous mechanical stirring for each test. A total reflux system was equipped to avoid the loss of phenol vapor. All over the experiments, thermostatic water-bath was employed to keep the reaction temperature at desired value. The percentage conversion of phenol and removal efficiency of COD were two important indexes to evaluate the catalytic degradation process. The phenol conversion efficiency was measured by 4-aminoantipyrine spectrophotometric method[36]. And the COD removal efficiency was detected by a standard method after reflux with K_2CrO_7. They are calculated over the following equations

$$Phenol\ conversion(\%) = (\frac{C_0 - C_t}{C_0}) \times 100\%$$

$$COD\ removal(\%) = (\frac{COD_0 - COD_t}{COD_0}) \times 100\%$$

where C_0 and COD_0 are the initial phenol and COD concentration (mg/L) of the phenol effluents, C_t and COD_t are the phenol and COD concentration (mg/L) after time (t).

The effect of different variables including reaction temperature (40-70 °C), H_2O_2 dose (0.58-1.15 mL), catalyst loading (10-60 mg), initial pH values (3.66-9.64) and initial phenol concentration (100-1000 mg/L) on catalytic degradation reaction were investigated. In the experiments, ter-butanol was used to investigate the catalytic degradation mechanism. And the experiments of catalyst reutilization were also conducted in order to evaluate the reusability of the catalyst.

3. Results and Discussions

3.1. Catalysts characteristics

The two synthesized Cu-MOFs catalysts were characterized by XRD, FT-IR, SEM and EDX determinations. Figure.1 (a and b) showed the XRD pattern of the as-prepared $Cu_3(BTC)_2$ and Cu(BDC). With regard to the sample of as-prepared $Cu_3(BTC)_2$, each diffraction peak was consistent with the atlas of $Cu_3(BTC)_2$ reported in the literature[34] as presented in Figure.1a. This demonstrated that what we have synthesized by solvothermal method was copper metal-organic framework $Cu_3(BTC)_2$. The high intensity of the peaks in XRD pattern manifesting that perfect crystallinity of $Cu_3(BTC)_2$ was developed[37]. Figure.1b represented the XRD pattern of Cu(BDC) with sharp peaks which were in accordance with those have reported in the literature[35]. This certified that the synthesized sample was the desired Cu(BDC) metal-organic framework.

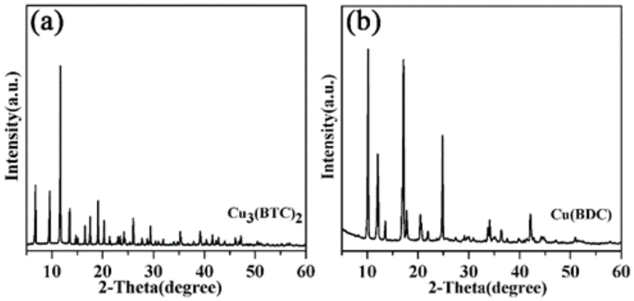

Figure.1. XRD pattern of the synthesized Cu-MOFs: (a) as-synthesized $Cu_3(BTC)_2$; (b) as-synthesized Cu(BDC)

FT-IR spectrums, as shown in Figure.2 (a and b), were conducted to obtain more detailed information about the structure of the two synthesized Cu-MOFs. For the sample of $Cu_3(BTC)_2$, the characteristic absorption peaks at 490 and 730 cm^{-1} could be assigned to Cu-O stretching vibration[34, 38]. The characteristic peak at 1373 cm^{-1} was attributed to the stretching vibration of C-O in the carboxyl. Compared with the absorption band of 1720 cm^{-1} in H_3BTC, the absorption peak at 1644 cm^{-1} which was in accordance with the stretching $V_{C=O}$ showed bathochromic effect suggesting that Cu^{2+} have coordinated with the oxygen atom. The O–H bending vibration at 1447 cm^{-1} indicated the presence of carboxylic acid group[38]. Figure.2b showed the FT-IR spectrum of H_2BDC and the synthesized Cu(BDC). The strong absorption peak emerged at 1667 cm^{-1} was a bit lower than the stretching vibration value of C=O in the spectrum of H_2BDC (1684 cm^{-1})[39]. It was due to deprotonation of carboxylic acid group. In addition, the stretching vibration peaks of C-O were also found at 471 and 563 cm^{-1}[40]. All these illustrated that Cu(BDC) has developed.

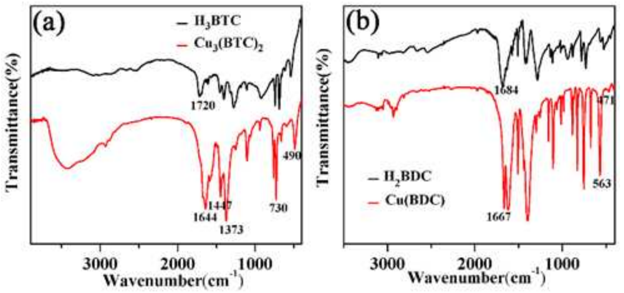

Figure.2. FT-IR spectrums of the synthesized Cu-MOFs: (a) H_3BTC and $Cu_3(BTC)_2$; (b) H_2BDC and Cu(BDC)

The SEM image of as-synthesized Cu-MOFs was demonstrated in Figure.3 (a, b, c and d). Figure.3 (a and b) showed the SEM image of $Cu_3(BTC)_2$ with perfect octahedral shape which was consistent with others reported[41]. And the size of the synthesized $Cu_3(BTC)_2$ was around 20 μm. However, the surface was covered by some fractionlet. Maybe it was because that the sample was not completely washed. The micrography of Cu(BDC) was clearly seen in Figure.3 (c and d) with regular hexahedral structure. But the crystal was not very symmetrical with most crystal of about 5 μm. The size of the large crystals could reach 10 μm.

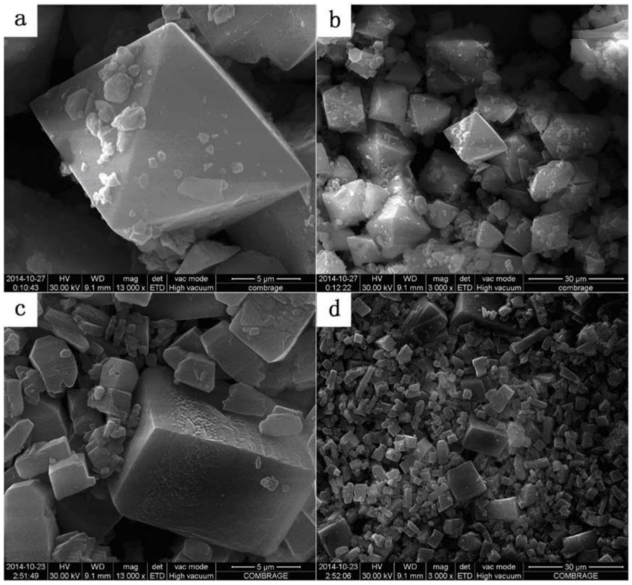

Figure.3. SEM spectrums of the two synthesized Cu-MOFs: $Cu_3(BTC)_2$ (a) and (b); Cu(BDC) (c) and (d)

The element included in the two Cu-MOFs was analyzed by EDX shown in Figure.4 and Table.1. Except C, O, Cu three element, the N element was found in the two different Cu-MOFs suggesting that the DMF participated in the coordination. The peak of copper was higher in $Cu_3(BTC)_2$ than in Cu(BDC) seen in Figure.4, revealing more Cu^{2+} was involved in $Cu_3(BTC)_2$ and the content of Cu^{2+} was shown in Table.1. The contents of copper element were 26.17wt%, 15.21wt% in $Cu_3(BTC)_2$ and Cu(BDC), respectively.

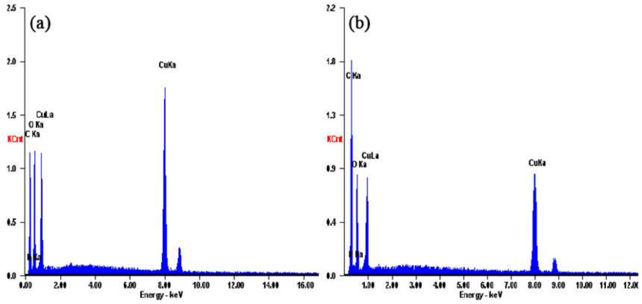

Figure.4. EDX analysis of the Cu-MOFs samples: (a) $Cu_3(BTC)_2$; (b) Cu(BDC)

Table.1. EDX analysis of the synthesized $Cu_3(BTC)_2$ and Cu(BDC)

MOFs	wt%			
	C	N	O	Cu
$Cu_3(BTC)_2$	47.90	2.47	23.46	26.17
Cu(BDC)	58.04	4.50	22.25	15.21

3.2. Phenol oxidation test

In each test, 150 mL simulated phenol effluents was added into a 250-mL three-neck bottom equipped with continuous mechanical stirring and the temperature was kept at desired value by a thermostatic water-bath. After adding the catalyst and H_2O_2, the reaction started. During the catalytic oxidation process, 5 mL liquid was taken out and centrifuged to remove the catalysts at different time. Bits of MnO_2 was added into the liquid in order to remove the residual H_2O_2. After removing MnO_2, the phenol conversion and COD removal efficiency were measured. Different parameters which could influence the degradation efficiency were investigated by single-factor control experiment.

3. 2.1. Comparison of the two Cu-MOFs

The two synthesized Cu-MOFs were applied as catalysts for catalytic oxidation of phenol, respectively. The initial reaction conditions and degradation performance were shown in Figure.5.

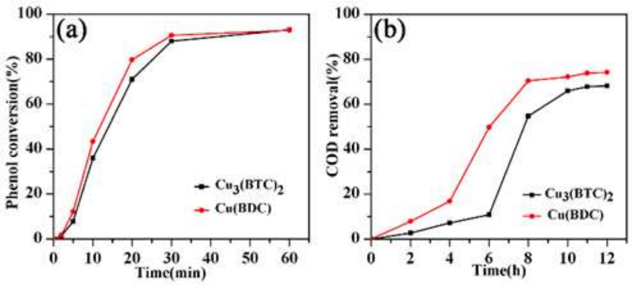

Figure.5. Comparison of $Cu_3(BTC)_2$ and Cu(BDC) on catalytic oxidation of phenol: (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 50 °C; H_2O_2: 0.80 mL; catalyst: 50 mg; pH: 6.65)

As described in Figure.5a, the conversion efficiency of phenol showed not much difference with final conversion efficiency of 90% after 1 h for the two catalysts. However, the COD removal efficiency was obviously higher when applying Cu(BDC) as catalyst than $Cu_3(BTC)_2$. (Figure.5b). This was due to large amounts of the intermediates generated by oxidation of phenol being not degraded. The better catalytic performance of Cu(BDC) than $Cu_3(BTC)_2$ might be attributed to the more complicated three-dimensional structure of $Cu_3(BTC)_2$. For $Cu_3(BTC)_2$, dimeric Cu paddle wheels were connected to BTC ligands to form complicated microporous framework[38] making it difficult for the larger organics and H_2O_2 molecules to enter into interior of the pores from the around of $Cu_3(BTC)_2$. Therefore, a portion of Cu^{2+} in the framework didn't play the role of catalysis. However, Cu(BDC) was developed by stack of overlapping sheets to form one-dimensional pores[42]. The organics and H_2O_2 molecules were easier to diffuse into the pores of Cu(BDC) compared with $Cu_3(BTC)_2$. As a consequence, Cu(BDC) showed much higher catalytic activity than $Cu_3(BTC)_2$ for catalytic oxidation of phenol wastewater. On the other hand, the content of copper in $Cu_3(BTC)_2$ was higher than in Cu(BDC) as described in Table.1. For 50 mg Cu(BDC), the amount of the active component was enough for catalytic oxidation of 150 mL 100 mg/L of phenol wastewater. When 50 mg $Cu_3(BTC)_2$ was applied as catalyst for catalytic degradation of identical phenol wastewater, the amount of the active component was much more than the required amount. However, too much active component was not beneficial to catalytic degradation of phenol wastewater as described in the following section (3.2.4). Considering the better catalytic performance, Cu(BDC) was selected for further experiments.

3.2.2. Effect of temperature

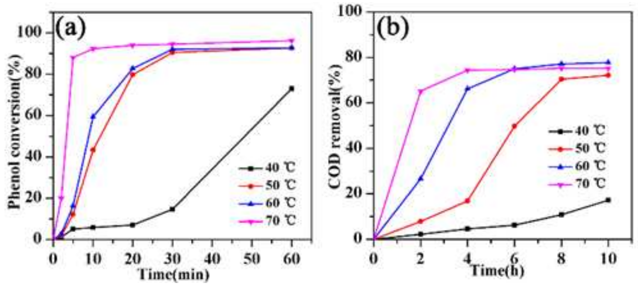

Figure.6. Effect of temperature on catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; H_2O_2: 0.80 mL; Cu(BDC): 50 mg; pH: 6.65)

The temperature is an important parameter which is directly related to the generation of ·OH in CWPO. The effect of temperature on degradation of phenol was shown in Figure.6 (a and b). Obviously, the phenol conversion and COD removal increased with the increase of temperature from 40 °C to 70 °C. The oxidation rate was also accelerated. This is due to that the generation of hydroxyl radicals by H_2O_2 (Eq.1) is much easier and faster at higher temperature[43], resulting in the oxidation of organics accelerated. On the other hand, the active sites of the catalysts were not only located on external surface, but also a large part of active sites existed in the inner pore surface. The increase in temperature was contributed to the diffusion of H_2O_2, phenol and the intermediates of degradation process into the inner pore surface of Cu(BDC)[44]. Therefore, higher temperature was beneficial to the degradation of phenol. Under the reaction temperature of 60 °C, phenol conversion and COD removal were nearly 93% and 78% after 60 minutes and 10 hours, respectively. For the temperature of 70 °C, though the phenol conversion (96%) was more satisfactory than at 60 °C after 60 minutes, the COD removal (75%) was lower than the temperature of 60 °C after reaction of eight hours. This could be attributed to that phenol was easily oxidized into the intermediates which were difficult to be mineralized. In the process of oxidation of the intermediates, the thermal decomposition of H_2O_2 (Eq.2) was serious which resulted in low utilization of H_2O_2[37]. Therefore, too high temperature was not contributed to improving the degradation performance. Furthermore, it not only resulted in high energy consumption but also leaded to the waste of resources. Considering all aspects including energy consumption, resources saving and the final degradation effect, 60 °C should be the best temperature for catalytic oxidation of phenol by Cu(BDC) with H_2O_2 as oxidant. By the way, the COD removal efficiency had almost no increase from the eighth hour to the tenth hour, which suggested that it should be not necessary to degrade phenol wastewater for ten hours. Consequently, the reaction time was decreased to eight hours at 60 °C in the later experiments.

$$H_2O_2 \rightarrow HO\cdot + HO\cdot \qquad (1)$$

$$H_2O_2 \rightarrow H_2O + O_2 \qquad (2)$$

3.2.3 Effect of H_2O_2 dosage

The generation of hydroxyl radicals closely depends on the dosage of H_2O_2. According to the stoichiometric ratio, the theoretical dose of H_2O_2 for complete oxidation of 150 mL 100 mg/L of phenol solution is 0.23 mL. In view of the added H_2O_2 being not fully utilized, more than the stoichiometric ratio of hydrogen peroxide is needed in most cases. Figure.7 (a and b) showed the effect of H_2O_2 concentration on the catalytic degradation of phenol wastewater. With the increase of the concentration of hydrogen peroxide from 0.58 mL to 1.15 mL, the phenol conversion (Figure.7a) and COD removal (Figure.7b) showed a consistent trend. As the H_2O_2 dosage was increased from 0.58 mL to 1.0 mL, an increased tendency of the phenol conversion and COD removal was observed with the phenol conversion rising from 90% to 95% and the COD removal aggrandizing from 59% to 81% after 60 minutes and 8 hours, respectively. This could be explained as higher dosage of H_2O_2 promoted to generate more hydroxyl radicals (Eq.1) to oxide phenol[45]. When the initial dosage of H_2O_2 was kept adding up to 1.15 mL, the degradation efficiency presented downward trend which was caused by two aspects. Firstly, it was mainly ascribed to the scavenging effect[46] as shown by Eq.3 and Eq.4. A good deal of hydroxyl radicals reacted with residual H_2O_2 producing $HO_2\cdot$ (Eq.3) which owned worse oxidizability than $\cdot OH$[47] being not beneficial to oxide organics. Furthermore, the generated $HO_2\cdot$ could continue to consume $\cdot OH$ to form oxygen gas (Eq.4) giving rise to severe loss of H_2O_2.

$$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \qquad (3)$$

$$HO_2\cdot + \cdot OH \rightarrow H_2O + O_2 \qquad (4)$$

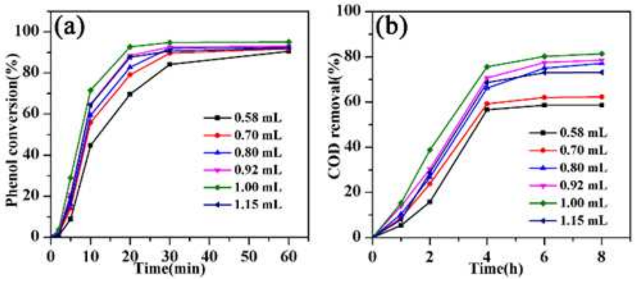

Figure.7. Effect of H_2O_2 dose on catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 60 °C; Cu(BDC): 50 mg; pH: 6.65)

For another, excess H_2O_2 competed with the organics leading to less organics diffusing into the interior of the pores of the catalysts. Thus, a large part of hydroxyl radicals generated in the pores were not utilized resulting in low phenol degradation efficiency. Therefore, to get better degradation effect, the dose of H_2O_2 should be strictly controlled. For this system, 1.0 mL of H_2O_2 which is 4.3 times of the theoretical dose was identified as the optimal value for CWPO of 150 mL 100 mg/L of phenol effluents. In the following experiments, the dose of H_2O_2 was 1.0 mL in each batch oxidation test.

3.2.4 Effect of catalyst dosage

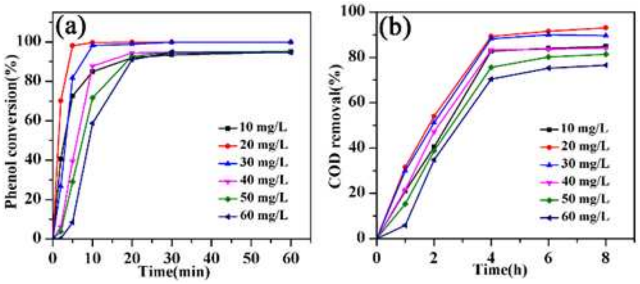

Figure.8. Effect of catalyst dose on catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 60 °C; H_2O_2: 1.0 mL; pH: 6.65)

In CWPO, catalyst dose is an extremely important factor for catalytic decomposition of H_2O_2 to form strong oxidizing hydroxyl radicals. The effect of catalyst dose on catalytic degradation of simulated phenol wastewater could be seen in Figure.8 (a and b). It was concluded that phenol conversion and COD removal efficiency were of great concern with catalyst dose. When the catalyst dose was increased from 20 mg to 60 mg, the phenol conversion and COD removal decreased from 99% to 94% and 93% to 76%, respectively. Therefore, 20 mg Cu(BDC) was enough for catalytic degradation of 150 mL 100 mg/L of phenol wastewater. More catalysts contributed to thermal decomposition of H_2O_2 to generate water and oxygen gas (Eq.2) resulting in less H_2O_2 to participate in the mineralization of phenol[48]. In addition, in the degradation process of phenol, the organics generated by the oxidation of phenol could be further oxidized into carbon dioxide, water and other intermediates as shown by Eq.5. After carbon dioxide dissolving into water, carbonic acid was formed (Eq.6) which could ionize to form bicarbonate (Eq.7). Moreover, bicarbonate is a kind of hydroxyl radicals elimination agent leading to decrease of hydroxyl radicals (Eq.8). At the beginning, more catalysts promoted to generate vast hydroxyl radicals (Eq.1) in a short time, and high concentration of hydroxyl radicals made these equilibrium equations move to the right so that less hydroxyl radicals were left to mineralize phenol. Hence, phenol conversion and COD removal efficiency decreased when too much catalysts were employed which have been certified by Zhang[44]. When the catalyst dose was decreased from 20 mg to 10 mg, the phenol conversion and COD removal efficiency decreased by 5% and 17% after 60 minutes and 8 hours, separately. This was because that when the catalyst concentration decreased, the number of active sites for catalytic production of hydroxyl radicals was less[49] resulting in the amount and rate of hydroxyl radicals generated by H_2O_2 declined at the same time and the conversion efficiency dropped. Therefore, properly adding catalysts not only economized the resources but also improved the degradation efficiency. 20 mg Cu(BDC) was applied for further experiments with other conditions kept constant.

$$HO\cdot + \text{organics} \rightarrow \text{intermediates} + CO_2 + H_2O \qquad (5)$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (6)$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (7)$$

$$HO\cdot + HCO_3^- \rightarrow OH^- + HCO_3\cdot \qquad (8)$$

3.2.5. Effect of initial pH

The initial pH of effluents also played a critical role in CWPO of organic compounds. In this study, the initial pH of simulated phenol wastewater was adjusted by diluted nitric acid and ammonia solution ranging from 3.66 to 9.64 to evaluate the influence of pH on degradation performance. The effect of the initial pH on degradation process was clearly presented in Figure.9 (a and b). It was obvious that, the catalytic performance of Cu(BDC) closely depended on the initial pH of the phenol solution. The optimal degradation efficiency was obtained at the pH of 6.65 and the phenol conversion and COD removal efficiency reached 99% and 93% after 60 minutes and 8 hours, respectively. Lower and higher pH were not beneficial to the degradation of phenol. Especially, when the initial pH of phenol solution was too low (3.66) or too high (9.64), the degradation of phenol was severely prevented. This could be interpreted as that, in the basic conditions, H_2O_2 was more inclined to break down into H_2O and O_2 at high speed (Eq.2) instead of generating hydroxyl radicals[50] accounting for only a tiny part of H_2O_2 participating in the mineralization of organics. This not only resulted in waste of resources but also weakened the degradation effect. In consequence, the alkaline circumstance was not suitable for the degradation of simulated phenol wastewater by as-synthesized Cu(BDC). For the acidic environment especially heavily acidic conditions, the poor degradation efficiency could be attributed to leaching of Cu^{2+} in the catalysts[37]. The loss of Cu^{2+} was equivalent to the reduction of active sites which were directly related to the catalytic activity of Cu(BDC). In other words, acidic circumstance rendered deactivation of the catalysts to a certain degree leading to poor mineralization of phenol. Thus, near-neutral pH conditions were more suitable for catalytic oxidation of phenol wastewater. Considering the natural pH of 100 mg/L of phenol solution was 6.65, subsequent experiments were conducted at the pH of 6.65.

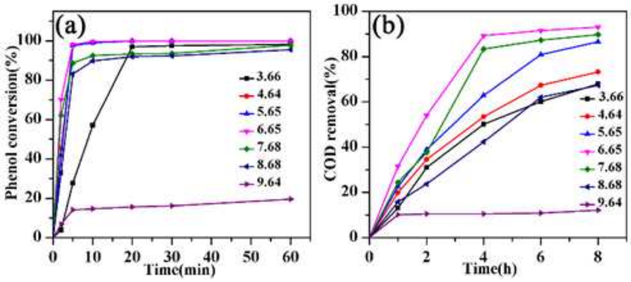

Figure.9. Effect of initial pH on catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 60 °C; H_2O_2: 1.0 mL; Cu(BDC): 20 mg)

3.2.6. Effect of initial concentration of simulated phenol wastewater

In view of the wide source and different concentration of phenol effluents discharged from all kinds of industries, satisfactory catalysts for catalytic degradation of phenol wastewater should adapt to these hostile environment especially to the concentration conditions. In order to investigate the adaptability of the as-synthesized Cu(BDC), different concentration of simulated phenol wastewater ranging from 100 mg/L to 1000 mg/L was used for catalytic oxidation experiments by Cu(BDC).

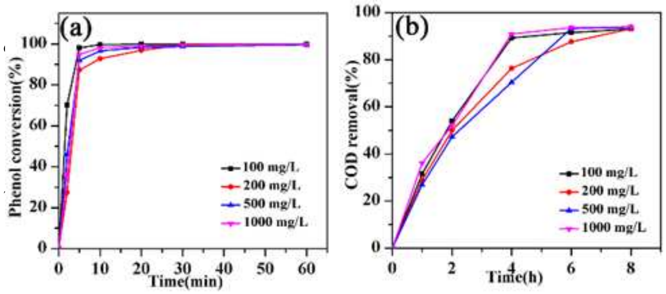

Figure.10. Effect of initial concentration on catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (temperature: 60 °C)

Figure.10 (a and b) showed the phenol conversion and COD removal of these different phenol wastewater embracing 100 mg/L, 200 mg/L, 500 mg/L and 1000 mg/L. With regard to the four different concentration of phenol wastewater, the final phenol conversion all reached 99% nearly complete conversion. And the COD removal were 93%, 93%, 93% and 94%, respectively. Although the phenol was almost removed after 60 minutes, the final COD data illustrated that a portion of intermediates generated by phenol oxidation were not degraded. But, this has achieved better degradation performance than Yavuz[51] having reported. So the as-synthesized Cu(BDC) could be a kind of satisfactory catalyst for CWPO of different phenol wastewater.

4. Degradation mechanism and reusability of Cu(BDC)

In general, the degradation process was proceeded by hydroxyl radical mechanism from the perspective of radical when copper-based catalysts were applied for catalytic wet peroxide oxidation of organic effluents. However, it was unclear that whether the catalytic degradation mechanism was the same as other copper-based catalysts for catalytic oxidation of phenol by Cu-MOFs. Ter-butanol as a kind of common hydroxyl radical scavenger was employed for investigating the mechanism. As ter-butanol was added into the reaction system, there was almost no change in color all over the experimental process. It seemed that the phenol was not degraded at all. Then, the conversion efficiency of phenol and COD removal efficiency were measured as presented in Figure.11 (a and b). It was obvious that ter-butanol severely inhibited the catalytic degradation of phenol. The conversion of phenol was less than 10% and the COD removal was only around 5% indicating negligible degradation of phenol. The negligible decrease of phenol and COD was resulted of absorption by Cu(BDC). This was because that the hydroxyl radicals generated by H_2O_2 were consumed by the added ter-butanol certifying the catalytic oxidation of phenol by Cu(BDC) did follow the hydroxyl radical mechanism which was in accordance with other copper-based catalysts[24-26].

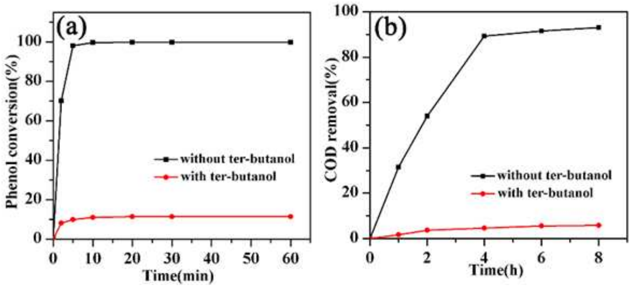

Figure.11. Effect of hydroxyl radical elimination agent on

catalytic oxidation of phenol by Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 60 °C; H_2O_2: 1.0 mL; Cu(BDC): 20 mg)

For industrial application, the key point was the reusability of catalyst. To evaluate the long term reusability of Cu(BDC), recycling study was conducted for catalytic oxidation of phenol by three runs. In the recycling study, the degradation process was controlled under the optimum conditions. The phenol conversion efficiency could still reach nearly 100% after reaction of 1 hour except that the conversion rate showed downtrend compared with the first run (Figure.12a). However, the final COD removal efficiency showed obvious decrease with each run (Figure.12b). Maybe, the collapse of a part of framework resulted in the declining trend. After three runs, more than 85% of COD removal efficiency was still achieved, indicating preferable reusability of Cu(BDC).

The content of Cu^{2+} after degradation 8 hours was 7 ppm indicating a negligible leaching. Maybe, the stable structure of Cu-MOFs inhibited the leaching of Cu^{2+}. The synthesized Cu(BDC) was really a kind of satisfactory heterogeneous catalyst for wastewater treatment.

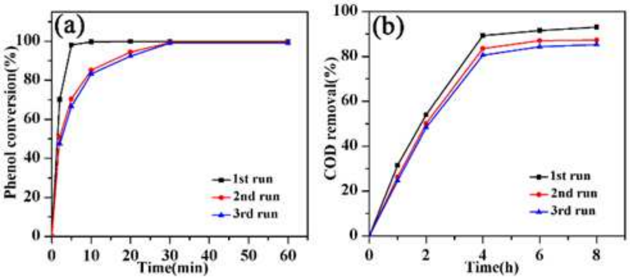

Figure.12. Catalytic oxidation of phenol in CWPO reaction with regenerated Cu(BDC): (a) phenol conversion; (b) COD removal. (phenol: 100 mg/L; temperature: 60 °C; H_2O_2: 1.0 mL; Cu(BDC): 20 mg)

5. Conclusions

This work describes the catalytic wet peroxide oxidation of simulated phenol wastewater by two different Cu-MOFs. Under the same conditions, Cu(BDC) showed higher catalytic activity than $Cu_3(BTC)_2$ which was mainly ascribed to the special structure of Cu(BDC) leading to easy entrance into the pores for the organics. The parameters affecting the catalytic oxidation of phenol were investigated and the optimal degradation conditions were obtained. Satisfactory degradation performance was achieved with phenol conversion efficiency of 99% and COD removal efficiency of 93%, respectively. After reused twice, Cu(BDC) still kept satisfactory catalytic activity. The catalytic oxidation of phenol was closely depended on the highly active hydroxyl radicals. The synthesized Cu(BDC) reflected strong ability to adapt to the simulated phenol wastewater of different concentration. Therefore, Cu-MOFs can be a kind of promising heterogeneous catalysts for catalytic wet peroxide oxidation of organic effluents. However, the catalytic oxidation of phenol by Cu(BDC) was confined to near neutral pH. Strong acid condition resulted in the loss of stability of Cu(BDC). Considering the wide pH range of the real effluents, improving the acid and alkali resistance of Cu-MOFs is significant for catalytic degradation of organic wastewater. In consequence, further work is devoted to modifying Cu-MOFs in order to make Cu-MOFs adapt to the wicked environment of the wastewater.

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Notes and references

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