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ORIGINAL PAPER

High-efficiency catalytic degradation of phenol based on the peroxidase-like activity of cupric oxide nanoparticles

Y.-B. Feng · L. Hong · A.-L. Liu · W.-D. Chen · G.-W. Li · W. Chen · X.-H. Xia

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Abstract Based on the recently discovered peroxidase-like activity, cupric oxide nanoparticles with diameters about 6 nm were synthesized and used to remove phenol from aqueous solution. As a kind of peroxidase mimetic substance, cupric oxide nanoparticles can be used as a promising catalyst for the total oxidation of phenol in aqueous solutions by peroxidation, which therefore avoids the need of secondary treatments. The mechanism study suggested that cupric oxide nanoparticles could catalyze hydrogen peroxide to form hydroxyl free radicals, which were mainly responsible for the removal of phenol. The catalytic conditions for the phenol degradation were extensively optimized among a range of pH as well as initial concentration of catalyst, H_2O_2 and phenol. High degradation efficiency of phenol can be achieved in relatively wide pH range from 3 to 7. Under optimized conditions, phenol (0.25 g/l) can be eliminated completely in 35 min. It can be potentially applied in treating the industrial wastewaters.

Keywords Phenol · Degradation · Cupric oxide nanoparticles · Enzyme mimic · Catalysis

Y.-B. Feng · L. Hong · A.-L. Liu · W.-D. Chen ·
G.-W. Li · W. Chen (✉)
Department of Pharmaceutical Analysis, Fujian Medical
University, Fuzhou 350004, China
e-mail: chenandhu@163.com

X.-H. Xia
State Key Laboratory of Analytical Chemistry for Life Science,
School of Chemistry and Chemical Engineering, Nanjing
University, Nanjing 210093, China

Introduction

Industrial processes generate a large diversity of wastewater containing organic pollutants, which has become a major social and economic problem. Phenol is one of the major organic pollutants in aqueous effluents generated by various industrial processes, such as refineries, resins and plastics processing, coal conversion, and manufacture of petrochemicals. Due to its high toxicity and hard degradation, phenol has been listed as one of the priority control pollutants by the environmental protection agency in many countries. A variety of techniques such as solvent extraction (Li et al. 2004), physical adsorption (Burleigh et al. 2002; Dabrowski et al. 2005), pervaporation (Hoshi et al. 1997), wet air oxidation (Joglekar et al. 1991; Chen et al. 2001), ozonolysis (Chedeville et al. 2007), wet peroxide oxidation (Barrault et al. 2000; Kang et al. 2002; Calleja et al. 2005; Gonzalez et al. 2008), electrochemical oxidation (Li et al. 2005; Pacheco et al. 2007), photocatalytic oxidation (Vione et al. 2005; Wang et al. 2005), supercritical water gasification (Dileo et al. 2007), electrical discharge degradation (Liu and Jiang 2005), and biodegradation (Jiang et al. 2006; Ucun et al. 2010) have been developed to remove phenol from industrial wastewaters. Each method has its own advantages and disadvantages and can be only applied in speculate conditions. Biological treatment is ideally for low concentration, typically around 50 ppm or lower for phenol. In addition, biodegradation processes are inherently slow and do not allow for high degrees of removal. Diluting wastewater to a suitable concentration and the disposal of sludge formed during the biological treatment can pose additional expenses and environmental problems. One more promising process is catalytic wet oxidation, which destroys a variety of organic pollutants and achieves a high conversion with the addition of catalyst.

Enzymes are promising candidates for catalysis and sensor owing to their chemo-, regio-, stereo-, and chiral-specificity as well as the mild reaction conditions that can be used (Schmid et al. 2001; Bornscheuer 2003; Schoemaker et al. 2003; Lu et al. 2011). In recent years, enzyme-catalyzed processes have been widely reported to play an important role in numerous waste treatment applications (Duran and Esposito 2000). Horseradish peroxidase is, by far, one of the most commonly used enzyme in waste treatment in order to remove phenols from aqueous solutions. In the presence of hydrogen peroxide, phenolic compounds are catalytically oxidized to phenoxy radicals and then polymerized to form insoluble high molecular weight polymers that could be easily removed by filtration or sedimentation (Klibanov et al. 1983). Such methods have several advantages due to their specificities and efficiencies. However, enzyme application was currently hampered by limited natural source, difficult and high-cost purification process, and inherent instability. In order to improve the active life of the enzyme, and thereby a reduction in treatment cost, various efforts have been devoted to find the alternative source, protecting reagent and immobilization method of enzyme on various supports (Cheng et al. 2006; Gonzalez et al. 2008).

Recently, the ferromagnetic nanoparticles have been found to be intrinsically active catalyst for oxidation reactions similar to that found in natural peroxidases (Gao et al. 2007). What is more, the peroxidase nanomimetics have a definite advantage compared with their protein-based counterparts because they are considerably more stable over a wide range of temperatures and various levels of acidity. Being inspired by the application of peroxidase, various nanomimetics, such as Fe_3O_4 nanoparticles (Zhang et al. 2008, 2009), gold nanoparticles (Han et al. 2008), iron oxide-based nanoparticles (Zelmanov and Semiat 2008), and γ-FeOOH nanosheets (Peng et al. 2011), have been used as catalysts for the catalytic oxidation of phenol. In the previous study, we have found that cupric oxide nanoparticle is a highly effective catalyst to peroxidase substrates, and the binding affinity for the substrate 3,3’,5,5’-tetramethylbenzidine (TMB) is higher than that of HRP and other peroxidase nanomimics (Chen et al. 2011). Based on this finding, we studied in this work the potential application of cupric oxide nanoparticles in phenol removal. The experimental results show that this process is highly efficient as compared to that using other peroxidase nanomimics. Complete phenol degradation can be achieved within about 30 min under mild conditions. This research was carried out in 2012 at Fujian Medical University, China.

Materials and methods

Chemicals and materials

All reagents used in the experiment were of analytical reagent grade and used without further purification. Cupric acetate, sodium hydroxide, glacial acetic acid, phenol, 4-aminoantipyrine (4-AAP), potassium ferricyanide, and 30 % (v/v) H_2O_2 were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). HPLC-grade methanol was obtained from Fisher Scientific Corporation (Fair Lawn, NJ, USA). Other reagents and chemicals were at least analytical reagent grade. The water used was purified by a Milli-Q system (Millipore, USA).

Preparation and characterization of cupric oxide nanoparticles

The cupric oxide nanoparticles with a diameter of 6 nm were prepared via a previously reported quick precipitation method (Chen et al. 2012). Briefly, 150 ml of 0.02 M copper acetate aqueous solution was mixed with 0.5 ml glacial acetic acid in a round-bottomed flask equipped with a refluxing device. The solution was heated to boiling with vigorous stirring. Then 10 ml of 40 g/l NaOH aqueous solution was rapidly added into the above boiling solution, where a large amount of black precipitate was simultaneously produced. The precipitate was centrifuged, washed three times with absolute ethanol, and dried in air at room temperature. About 85 mg cupric oxide nanoparticles can be obtained. The percentage of conversion of copper to cupric oxide nanoparticles is about 35 %.

The morphology and size distribution of the nanoparticles were studied by using a transmission electron microscope (TEM) of Tacnai-12 (Philip, Netherlands). The crystal phase was investigated by X’Pert Pro MPD X-ray diffractometer (Panalytical, Netherlands). As reported in our previous work, the average particle diameter is found to be approximately 6.3 nm, and the typical XRD pattern for the as-prepared nanoparticles is identical to the single-phase CuO with a monoclinic structure from the standard card JCPDS 72-0629 (Chen et al. 2012).

Catalytic reaction experiment procedure

Batch tests were carried out in aqueous solution at room temperature. Cupric oxide nanoparticles and phenol solution were added into the water in sequence, the final solution volumes were 25 ml. The reactions were initiated by adding H_2O_2 to a final concentration of 100 mM. At each checkpoint, the sample solution taken from the reaction batch was centrifuged to separate cupric oxide nanoparticles from solution. The phenol concentration was determined based on Emerson's method. The supernatant was mixed with 200 µl ammonia buffer (pH = 9.8), 20 µl 4-aminoantipyrine solution (2 %), and 20 µl potassium ferricyanide solution (8 %), and then diluted to a final solution volume of 4.0 ml. After incubated for 10 min, the absorbance at 510 nm was recorded using Shimadzu UV-2450 spectrophotometer.

Analysis of the degradation intermediates

The degradation intermediates of phenol were determined with HPLC. The chromatographic conditions were as follows: C18 column (4.6 mm × 150 mm); samples were injected into a 20 µl loop; mobile phase was methanol–water containing 5 % H_3PO_4 (10:90) with a flow rate of 1 ml/min. UV detector wavelength was set at 280 and 215 nm.

Results and discussion

Catalytic degradation of phenol by cupric oxide nanoparticles

The effect of catalyst was investigated at room temperature and an initial phenol concentration of 0.25 g/l. The homogeneous reaction in the absence of catalyst is pronounced. Still, as shown in Fig. 1, the presence of the cupric oxide nanoparticles significantly enhances the oxidation rate of phenol in the reaction. In addition, it is clearly demonstrated that the degradation rate of phenol was improved by the increase in the concentration of cupric oxide nanoparticles. Complete removal of phenol can be achieved within 35 min when the concentration of cupric oxide nanoparticles exceeds 0.05 g/l. The experimental results show that this process is highly efficient as compared to that using other peroxidase nanomimics (Table 1).

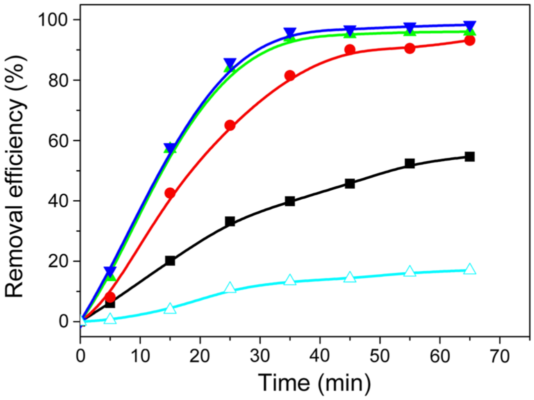


Fig. 1 Effect of the concentration of cupric oxide nanoparticles on removal efficiency of phenol. The concentration of phenol and H_2O_2 are 0.25 g/l and 100 mM, respectively. The concentration of cupric oxide nanoparticles (mg/ml): (*open triangle*) 0, (*filled square*) 0.001, (*filled circle*) 0.01, (*filled triangle*) 0.03, (*inverted filled triangle*) 0.05

Table 1 Removal efficiency of phenol in the presence of peroxidase nanomimics

Catalyst (g/l)	pH	Phenol/ H_2O_2 (ppm/ mM)	Time	Removal efficiency	Reference
Au/HAP (0.1)	6.8	100/490	2 h	82 %	Han et al. (2008)
Fe_3O_4 NPs (5)	6–7	94/1,200	6 h	~100 %	Zhang et al. (2009)
Fe_3O_4 NPs (0.1)	3.0	282/6	3 h	~85 %	Zhang et al. (2008)
γ-FeOOH nanosheets (0.12)		40/500	1 h	~80 %	Peng et al. (2011)
Iron(3) oxide-based NPs (0.015)	2–3	1,000/163	0.5 h	~100 %	Zelmanov and Semiat (2008)
CuO NPs (0.05)	3–7	250/100	35 min	~100 %	This work

To rule out the possibility that the observed catalytic activity is caused by copper ions leaching from cupric oxide nanoparticles in the solution, the reaction was conducted by using copper ions instead of cupric oxide nanoparticles. Even with the concentration of 0.625 mM (equivalent quantity to 0.05 g/l cupric oxide nanoparticles), copper ions have little effect on the reaction. The removal efficiency is about 32 % in 35 min in this case. These experimental results reveal that the observed catalytic activity is due to intact nanoparticles.

Studies performed by employing nanomaterials determined that the size of the catalytic species has a considerable effect on the catalyst performance (Zhou et al. 2006). Our further investigation reveals that the catalytic activity of cupric oxide nanoparticles is size-dependent. The removal efficiency of phenol is only about 27.9 % in 35 min even when 60-folds cupric oxide nanoparticles (3 mg/ml) with the diameter of 30 nm were used.

Effect of the initial solution pH

From the practical point of view, pH is one of the most important parameters influencing heterogeneous liquid phase catalytic oxidation of phenol (Rokhina and Virkutyte 2011). In batch experiments, the effect of initial pH on removal efficiency of phenol was examined in the range from 2 to 13. It was shown in Fig. 2 that most of the phenol

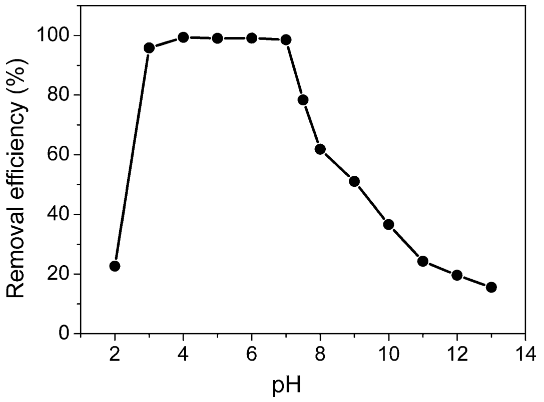


Fig. 2 Effect of initial solution pH on removal efficiency of phenol (0.25 g/l phenol, 100 mM H_2O_2, 0.05 g/l cupric oxide nanoparticles, 35 min)

was removed under acidic and neutral conditions, and the removal efficiency was low at alkaline conditions. The removal efficiency of phenol in 35 min was about 100 % under acidic and neutral conditions, and when pH above 7, the removal efficiency decreased sharply until to about 15 % at pH 13. It can be explained by the decomposition of hydrogen peroxide in alkaline solution to produce molecular oxygen instead of formation of appreciable amounts of hydroxyl radicals (Guo and Al-Dahhan 2003). High pH also favors the formation of carbonate ions, which are effective scavengers of hydroxyl ions and therefore can reduce the degradation efficiency (Kashif and Ouyang 2009). Moreover, the combination of OH^- with Cu^{2+} on the surface of the nanoparticles might inhibit the adsorption of hydrogen peroxide, and in turn negatively affecting the generation of hydroxyl radicals. The significant decline in the removal efficiency in strong acidic condition (pH < 2) can be attributed to the decomposition of cupric oxide nanoparticles (Chen et al. 2012). This can be confirmed by the low catalytic activity of copper ions mentioned above.

Effect of H_2O_2 concentration

Hydrogen peroxide is often the oxidant choice for chemical oxidation because of its simplicity of operation and the innocuous nature of its byproduct, water (Rokhina and Virkutyte 2011). Coupled with a sufficient catalyst, hydrogen peroxide exhibits excellent reactivity and high utilization efficiency. To test whether the catalytic activity of the cupric oxide nanoparticles is, like the conventional enzyme HRP, dependent on the concentration of H_2O_2, time dependence of phenol conversion at different H_2O_2 concentrations was performed. As shown in Fig. 3, the concentration of phenol did not change in the absence of H_2O_2, which suggests that H_2O_2 is necessary in phenol degradation system. In addition, a trace amount of oxygen dissolved in water or potential dissociation of phenol due to adsorption does not have any contribution to the conversion of phenol under the reaction conditions. Higher initial removal rate and degradation efficiency result from a

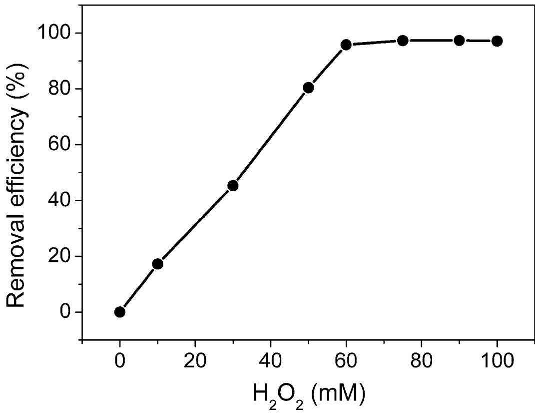


Fig. 3 Effect of the concentration of H_2O_2 on removal efficiency of phenol (0.25 g/l phenol, 0.05 g/l cupric oxide nanoparticles, 35 min)

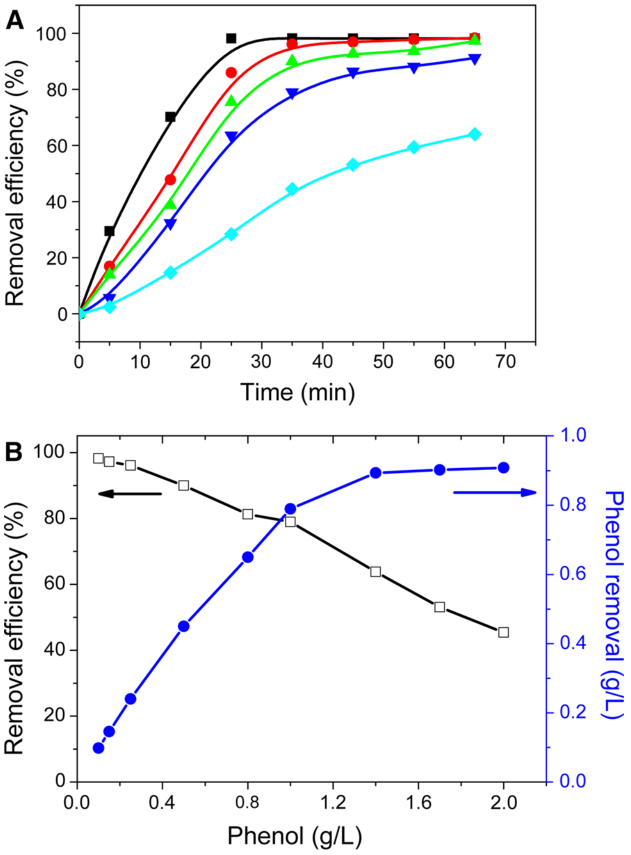


Fig. 4 **a** Degradation curves of phenol with different initial concentration (g/l). (*filled square*) 0.1, (*filled circle*) 0.25, (*filled triangle*) 0.5, (*inverted filled triangle*) 1, (*filled diamond*) 2. **b** Plot of phenol removal efficiency at 35 min versus initial concentration of phenol (100 mM H_2O_2, 0.05 g/l cupric oxide nanoparticles, 35 min)

higher H_2O_2 concentration. To reach the maximal level of phenol removal in 35 min, 60 mM H_2O_2 was required.

Effect of phenol concentration

The effect of the initial concentration of phenol was investigated in the range of 0.1–2 g/l. As shown in Fig. 4, the removal efficiency at 35 min was decreased with the increasing initial concentration of phenol. It took with 25, 35 and 65 min to totally destroy phenol with the initial concentration of 0.1, 0.25 and 0.5 g/l, respectively. It has been reported that high concentrations of organic pollutants usually inhibit free radical formation in the wet peroxide oxidation process (Kurian and Sugunan 2006). However, the conversion amount and the degradation rate are both proportional to the initial concentration of phenol in the range of 0.1–1 g/l, indicating that the inhibition of free radicals can be ignored in this case. When the initial concentration of phenol exceeds 1 g/l, the relative activity of the catalyst indeed decreased. It takes much longer to remove phenol when the solution is more concentrated. As for 2 g/l phenol solution, 80 % degradation can only be achieved after 4 h in presence of 100 mM H_2O_2. Since H_2O_2 is the origin of the hydroxyl radicals, higher degradation rate can be expected in the presence of sufficient amount of hydrogen peroxide. Over 78 and 90 % phenol can be successfully removed within 35 min for 2 g/l phenol solution in the presence of 200 and 400 mM H_2O_2, respectively.

Possible reaction mechanism

Under the typical reaction conditions as described in experimental section, control teats were implemented in the case of phenol oxidation. There is almost no conversion of phenol in the absence of both cupric oxide nanoparticles and H_2O_2 after incubation for 65 min. Also, under the similar conditions in a H_2O_2-free solution, phenol was not

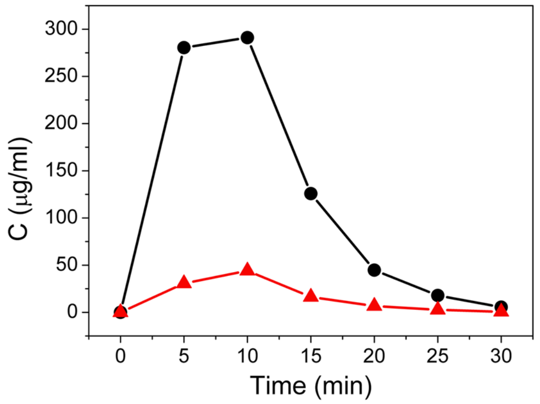


Fig. 6 Concentration variation of (*filled circle*) catechol and (*filled triangle*) hydroquinone in the degradation process of phenol

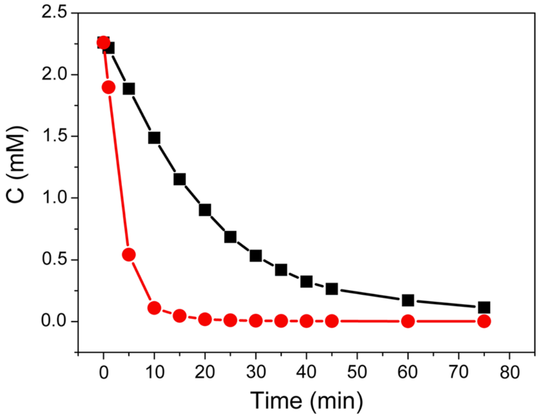
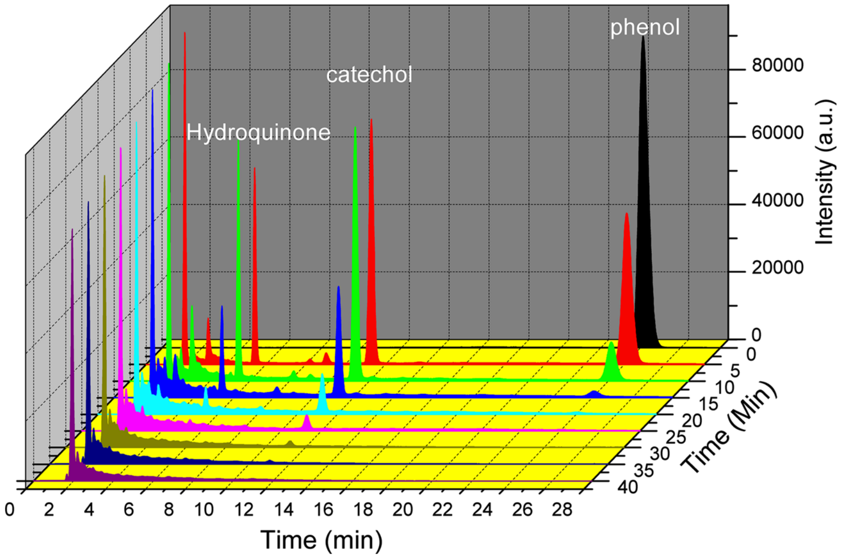


Fig. 7 Degradation curve of (*filled square*) catechol and (*filled circle*) hydroquinone (100 mM H_2O_2, 0.05 g/l cupric oxide nanoparticles)

Fig. 5 Chromatograms of the degradation solution of phenol



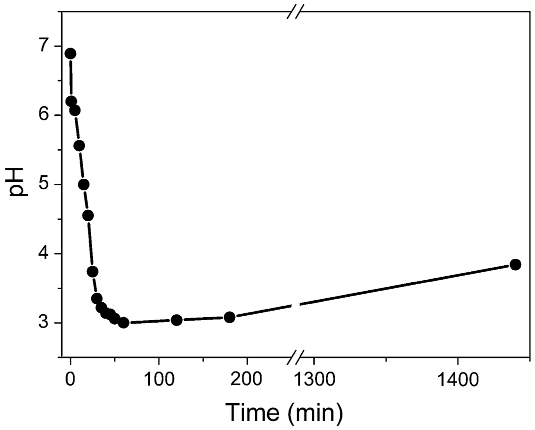


Fig. 8 pH change along the degradation reaction of phenol

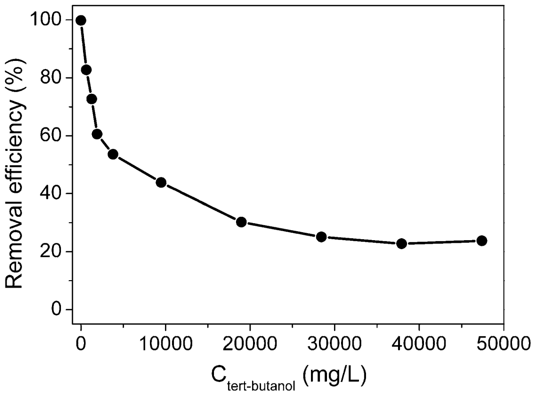


Fig. 9 Influence of tert-butanol on removal efficiency of phenol (0.25 g/l phenol, 100 mM H_2O_2, 0.05 g/l cupric oxide nanoparticles, 35 min)

converted. In the case of without cupric oxide nanoparticles in the reaction solution, only 16.4 % of phenol was removed. These results suggest that adsorption by cupric oxide nanoparticles and direct oxidation by H_2O_2 or dissolved oxygen do not mainly contribute to the removal of phenol under reaction conditions. So the loss of phenol was caused mainly by catalytic oxidation of cupric oxide nanoparticles in the presence of H_2O_2.

In order to investigate degradation intermediates of phenol, the reaction solution was analyzed by HPLC. The main detected intermediates in the product effluent were hydroquinone, catechol, maleic acid, and oxalic acid. For the existence of mineralization and intermediates detected, the degradation of phenol could be divided into two stages (Rokhina and Virkutyte 2011). During the first stage, hydroxylation of aromatic ring and formation of dihydroxybenzenes such as hydroquinone and catechol are observed. The existence of maximum points for hydroquinone and catechol can be observed in Figs. 5, 6. These profiles exhibit a common characteristic of the consecutive reaction pathway in which hydroquinone and catechol are formed from phenol and degraded progressively to simpler compounds. The degradation of hydroquinone and catechol in the presence of cupric oxide nanoparticles were further proved by using hydroquinone and catechol as initial reactants (Fig. 7). In the second oxidation stage, the aromatic rings open to form carboxyl acids. Similar to dihydroxybenzenes, the existence of maximum points for carboxyl acids can also be observed, indicating that they are further oxidized to water and carbon dioxide. After 35 min, phenol, hydroquinone, and catechol are completely degraded. Only small amount of oxalic acid can be detected in the solution.

Obvious pH change can be observed along the reaction. As shown in Fig. 8, in the initial stage, the pH value decreased rapidly to about 3, which can be contributed to the formation of acidic intermediates. Then in the next stage, the pH value of the reaction system increased slowly to 3.9, which is consistent with that of carbon dioxide saturated solution.

To confirm the existence of hydroxyl free radical, tert-butanol was introduced into the reaction system. As a strong radical scavenger, tert-butanol remarkably decreased the removal efficiency of phenol (Fig. 9). The results suggested that cupric oxide nanoparticles could catalyze H_2O_2 to form hydroxyl free radicals, which were mainly responsible for the removal of phenol.

Application in the treatment of waste water from ink production

The proposed method was applied for the degradation of phenol in waste water from ink production. The initial concentration of phenol in the samples was in the range of 0.1–0.5 g/l. The experimental results show that over 90 % phenol can be successfully removed within 1 h in the presence of 400 mM H_2O_2 and 0.05 g/l cupric oxide nanoparticles.

Conclusion

As a kind of peroxidase mimetic substance, cupric oxide nanoparticles can be used as a promising catalyst for the total oxidation of phenol in aqueous solutions by peroxidation, which therefore avoids the need of secondary treatments. High degradation efficiency of phenol can be achieved in relatively wide pH range from 3 to 7. Under optimized conditions, phenol can be eliminated completely in a short period. It can be potentially applied in treating the industrial wastewaters.

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