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Preparation of Cu_2O/AC Photocatalysts and Their Photocatalytic Activity in Degradation of Pyrocatechol[1]

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Abstract—Cu_2O on active carbon (Cu_2O/AC) catalysts were prepared by impregnation of support with aqueous solutions of $CuSO_4$ in various concentrations and then treated with a mixture of glucose and NaOH. Photocatalytic activity of the prepared catalysts was investigated in the photocatalytic degradation of pyrocatechol. The catalyst prepared by dipping of 0.5 g of AC into 25 ml of 0.04 mol/l $CuSO_4$ was found to exhibit the best activity. The effects of the reaction time and the amount of catalyst on the photocatalytic degradation of pyrocatechol were also studied.

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Nowadays, the adequate purification of industrial waste water is a problem of major concerns. New and more stringent regulations are being proposed, which demand to develop and implement treatment technologies capable of treating the existing hazardous pollutants in many industrial waste streams. Phenol and phenolic compounds are original and intermediate compounds in many industrial processes and they are present in effluents from coke ovens, oil refineries, petrochemical units and polymers production. Waste water from these activities contains variable concentrations of phenolic compounds (from 500 to 4000 mg/l) [1, 2].

Photocatalytic oxidation is an advanced oxidation process (AOP) which is based on the generating of hydroxyl radicals to degrade the pollutants. This technique has several advantages such as relatively short reaction time, the cheapest and most abundant oxidant, the simplicity of process, safety to environment, improvement of the biochemical quality of the organic waste water, etc. It was rapidly developing in recent two decades [3–5].

A number of catalysts have been proposed for the treatment of organic pollutants. Particularly, carbon-supported catalysts are highly active. Many catalysts such as Cu, MnO_2, Pt, Pd and Ni, etc. supported on carbon were studied by many researchers [6–11]. It is well known that the activity of the catalysts supported on activated carbon is strongly dependent on both the nature of active phase and the properties of support [12]. Activated carbon as a support has some advantages such as high surface area, relatively lower cost, possibility of easy recovering of the supported metal by simple combustion, good chemical stability and so on [13]. In the case of metallic active phases supported on activated carbon, the chemical property of surface plays an important role in the metal dispersion and the catalytic behavior. Surface oxygen complexes can act as anchoring sites that interact with metallic precursors to improve the dispersion of the system. The surface properties can be modified through thermal and/or oxidative treatments which may lead to increasing of the amount of surface oxygen complexes [14].

Cuprous oxide (Cu_2O) is a *p*-type semiconductor with a direct band gap of 2.17 eV, and it is widely used in the hydrogen production and superconductor technology [15]. Recently, it has been found that Cu_2O has good catalytic properties [16]. In this work, we prepared various carbon-supported Cu_2O catalysts, proposed the general process of the photocatalytic oxidation and reported on the photodegradation of pyrocatechol. In addition, the possible pathways and the kinetics of the photocatalytic process were discussed in detail.

EXPERIMENTAL

Preparation of Cu_2O/AC Catalysts

Prior to use, the active carbon (Coconut shell, China Activated Carbon Industries Ltd.) was activated with concentrated HCl to increase its physical adsorption capacity. The treatment processes were as follows. The active carbon was placed in the vessel with the

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adequate amount of distilled water (100 ml) and the suspension was stirred for several minutes. Afterwards, it was heated until boiling and then adjusted to pH ~2 with HCl. After 30 min, it was stewed for 24 h at room temperature. After filtration, the solid was washed with distilled water until pH 7 and then dried at 373 K for 4 h. The pretreated activated carbon was kept in dry conditions for further use.

Supported catalysts were prepared by impregnation with aqueous $CuSO_4$ solutions. 0.5 g of pretreated activated carbon was mixed with 25 ml of aqueous $CuSO_4$ solutions of various concentrations (0.02, 0.04, 0.06 and 0.1 mol/l), then the sample was put into the shake incubator (SKY-2008, Shanghai Sukun industry and commerce Co., Ltd.) at 298 K with 90 rpm of the rotary speed for 24 h. After filtration, the wet solid was transferred to a mixture of adequate amounts of glucose (AR, Shanghai Shanpu chemical Co., Ltd.) and NaOH (AR, the chemical reagent factory of Hefei University of technology). Then the suspension was put into the shake incubator (303 K, 90 rpm) for 24 h followed by filtration and washing with distilled water until pH 7. The samples were dried in a vacuum drying oven at 373 K for 3 h. The calculated Cu_2O percentage on AC was 7.15, 14.3, 21.5 and 35.8 wt %. The catalysts were used after drying.

Photocatalysis

The photocatalytic reaction was carried out in a borosilicate flask (120 ml) that contained 50 ml of pyrocatechol (CP, Shanghai No 3 chemical reagent factory) aqueous solution (initial concentration 100 mg/l). The reactions were conducted with constant magnetic stirring and air bubbling. Before each reaction, the system was maintained in the dark for at least 150 min in order to reach the adsorption equilibrium. Thereafter, the mixture was irradiated with the visible light at room temperature. The visible light source was a 200 W electric incandescent lamp (PZ220-200, 18300 mW/cm^2, Institute of Electric Light Source, Beijing) which was located at 10 cm over the reaction solution. The samples were taken at preselected time intervals using a syringe and then centrifuged at 3000 rpm for 20 min. Evaluation of the photocatalytic activities of the samples was conducted by measuring the change in absorption of the pyrocatechol solution during the photocatalytic degradation at $\lambda = 275$ nm which is the maximum absorbance of pyrocatechol. The absorbance values were measured on a UV-Vis spectrometer (TU1901, Bejing Purkinje General Instrument Co Ltd, China). The removal rate (R) was calculated by the equation $R = (A_0 - A_t)/A_0$, where A_0 is the initial absorbance of pyrocatechol and A_t is the absorbance at time t.

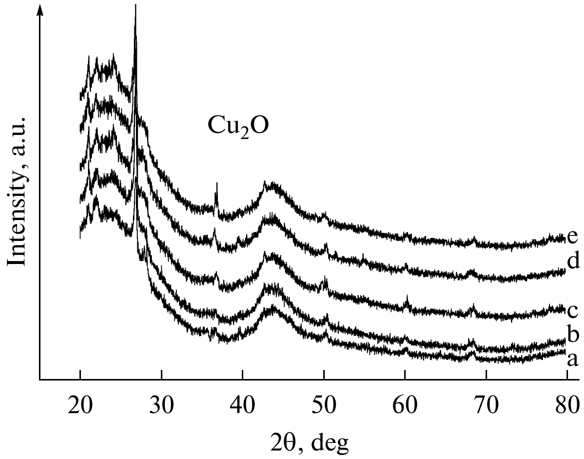


Fig. 1. The XRD patterns of the samples: a—AC, b—7.15 wt % Cu_2O/AC, c—14.3 wt % Cu_2O/AC, d—21.5 wt % Cu_2O/AC, e—35.8 wt % Cu_2O/AC.

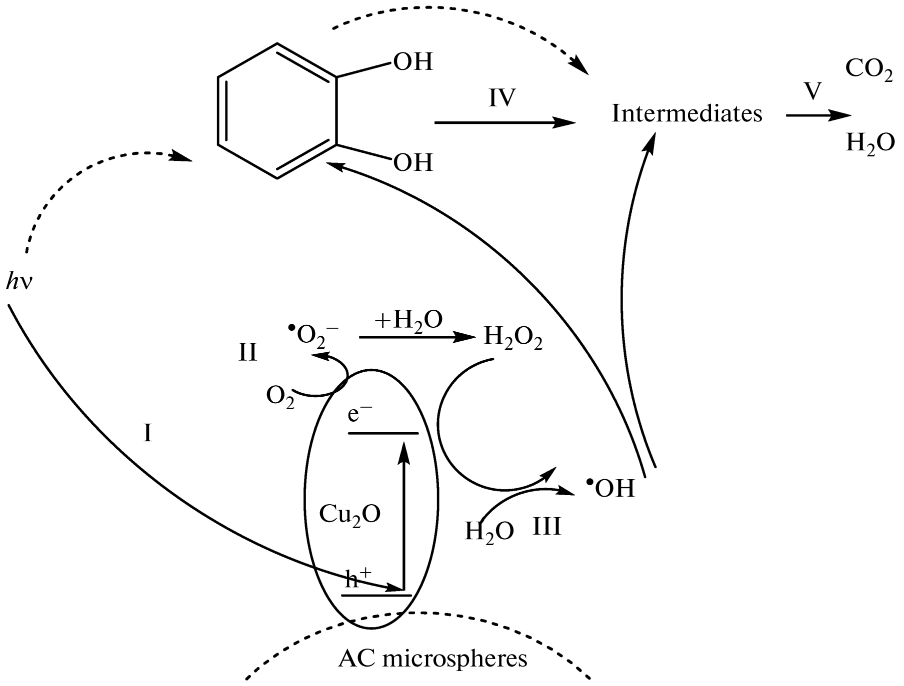
Characterization of Catalysts Prepared

The X-ray diffraction (XRD) of the catalysts prepared above was measured at room temperature using a DX-2000 X-ray powder diffractometer with CuK_α radiation and a scanning speed of 3°/min, where the accelerating voltage and emission current were 40 kV and 30 mA, correspondently.

RESULTS AND DISCUSSION

Catalysts Characterization

The XRD powder spectra of all samples are shown in Fig. 1. The XRD patterns of 7.15 wt % Cu_2O/AC is similar to that of AC. The characteristic peaks of Cu_2O have not been found in the two samples. With increase of Cu_2O quantity in the Cu_2O/AC catalysts, the small peaks corresponding to Cu_2O at $2\theta = 36.749$ and 42.686° emerge. The gradual increase of their intensity was observed with increasing Cu_2O content. That is related to the decrease of $CuSO_4$ amount supported on the carbon surface and the dispersion degree of cuprous oxide on the surface of the AC. The porous structure of AC makes the surface area larger. The ingredient is dispersed on the surface of AC. When the amount of dispersed $CuSO_4$ on the surface of AC is below or equals to the critical dosage of single molecular layer, the Cu_2O/AC catalysts showed the highest activity. However, when the amount of dispersed $CuSO_4$ exceeds the critical value, the larger particles are formed on the surface of AC so that the activity of the same dosage of the catalysts decreases. Thus, 0.04 mol/l was selected as the optimal concentration.



Scheme.

The Photocatalytic Process of Pyrocatechol Oxidization

The photocatalytic process is shown in the Scheme. When the catalyst adsorbs photons with energy equal or superior to its band gap, the valence band electrons are promoted to the conduction band energy level (Path I). On the one hand, the electrons in the conduction band (e^-) can recombine with the photogenerated vacancies (holes h^+) thus decreasing the efficiency of the photocatalytic process. On the other hand, electrons can migrate to the surface of the catalyst particle and being trapped by oxygen molecules form the superoxide anion ($^\bullet O_2^-$) and increase the efficiency of the photocatalytic process (Path II). In addition, the vacancies generated in the valence band (h^+) can be trapped on the catalyst surface promoting the splitting of water molecules or hydroxide anions generating hydroxyl radical $^\bullet OH$ (Path III). These hydroxyl radicals result in the oxidation of pyrocatechol due to their high oxidation capability. Then, the holes can directly oxidize the adsorbed pyrocatechol to oxidized intermediates (Path IV). Finally, the intermediates are further oxidized to inorganic matters (CO_2 and H_2O) [17, 18].

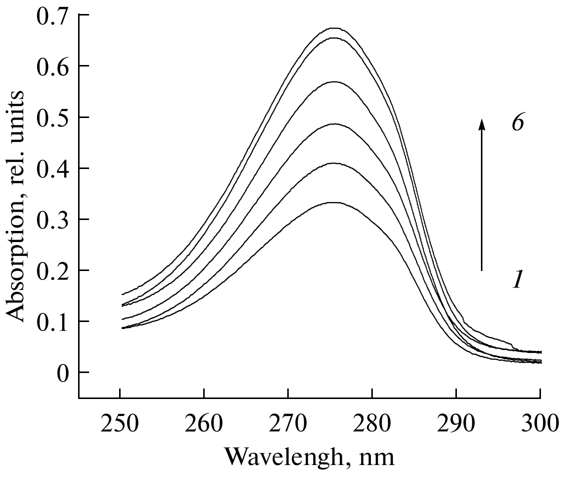


Fig. 2. The UV-vis spectra of pyrocatechol after 2.5 h degradation on 14.3 wt % Cu_2O/AC (*1*), 7.15 wt % Cu_2O/AC (*2*), 21.5 wt % Cu_2O/AC (*3*) and 35.8 wt % Cu_2O/AC (*4*), after 2.5 h of irradiation without catalyst (*5*) and after 2.5 h of dark adsorption on 14.3 wt % Cu_2O/AC (*6*).

Influence of Experimental Conditions

Effect of deposited amount of Cu_2O. Figure 2 shows the UV-vis spectra of the pyrocatechol on different catalysts after 2.5 h of degradation (curves *1–4*), after 2.5 h of irradiation (curve *5*) and after 2.5 h of dark adsorption (curve *6*). It can be seen that the pyrocatechol photodegradation activity is very low when the concentration of impregnation liquid of $CuSO_4$ is low, and the removal rate increases with increasing $CuSO_4$ concentration. The activity of degradation reaches the maximum when the $CuSO_4$ concentration in the impregnation liquid is 0.04 mol/l. However, the pho-

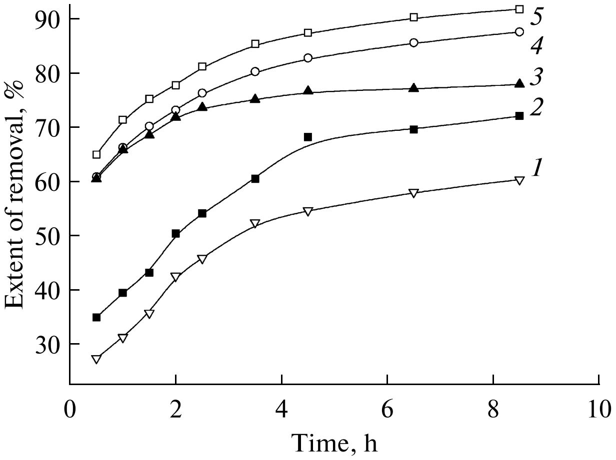


Fig. 3. Effect of initial pH of solution on pyrocatechol removal: *1*—4.0, *2*—5.0, *3*—9.0, *4*—8.0, *5*—7.0.

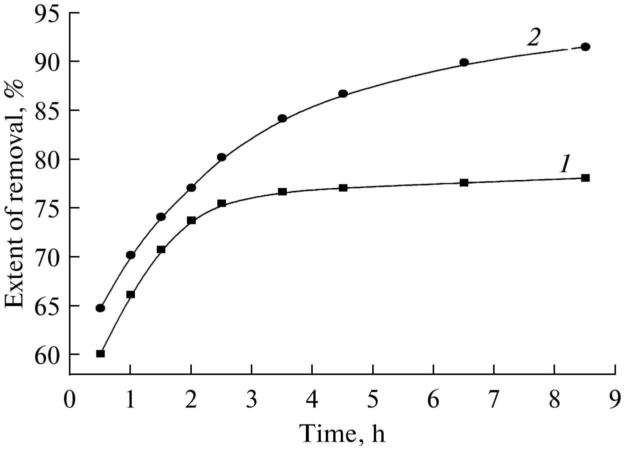


Fig. 4. The kinetic curves of the pyrocatechol removal on AC (*1*) and on 14.3 wt % Cu_2O/AC (*2*).

tocatalytic activity of catalysts drops again when $CuSO_4$ concentration exceeds 0.04 mol/l. This may be due to the large amount of Cu_2O jamming into pores so that it decreased the surface area of active carbon. In general, the surface area is the most important factor which influences the activity of catalyst. Thus the absorption of organic matter from the aqueous solution is reduced and the photodegradation activity of Cu_2O/AC descends. So 0.04 mol/l $CuSO_4$ was selected as the optimum concentration of impregnation liquid, and the 14.3 wt % Cu_2O/AC catalyst has the best degradation efficiency.

Effect of pH on removal of pyrocatechol. In the photocatalytic process, pH influences on the pyrocatechol degradation rate and the product yields. The initial pH of solution for this study was adjusted at 4.0, 5.0, 7.0, 8.0 and 9.0 by adding NaOH or HCl. Figure 3 shows that the removal rate increases slightly with increasing pH up to 7.0. That can be attributed to the formation of $^\bullet$OH. At a high pH more hydroxide ions on the surface of catalyst can be easily oxidized and form more $^\bullet$OH [19], which rise the pyrocatechol degradation rate. On the other hand, the reaction rate constant decreases significantly at pH 8.0, mainly due to surface ionization of the catalysts. As the zero charge point of Cu_2O is at pH 4.7, Cu_2O surface is positively charged in an acidic media ($pH < 4.7$), whereas it is negatively charged under alkaline conditions ($pH > 4.7$).

Thus, an increase in pH (e.g., to 7.0) gradually increases the electrostatic repulsion between the catalyst surface and pyrocatechol, which is negatively charged at pH above 7.0, and further reduces already poor adsorption of pyrocatechol. Hence, it is not surprising that the degradation rate of pyrocatechol decreases at pH higher than 7.0. In addition, at a high pH, the formation of superoxide radical anion ($^\bullet O_2^-$) through oxygen reduction by electrons can be suppressed, and this results in the formation of less H_2O_2 and $^\bullet$OH. Based on these results, pH 7.0 was chosen as the optimal value and used in the subsequent experiments.

Effect of degradation time. Figure 4 (curve *2*) illustrates the effect of time on the photocatalytic degradation in the experiment, where 0.02 g of 14.3 wt % Cu_2O/AC was submerged in 50 ml of the pyrocatechol solution (100 mg/l). The removal rate increases with increasing irradiation time, and reaches 80.13% at 2.5 h. Beyond 2.5 h, the increasing of the removal rate becomes very slow. Considering the power consumption and waste water retention time which will increase with increasing oxidation time, 2.5 h was used as the optimum degradation time.

Comparison of Pyrocatechol Removals on AC and Cu_2O/AC. Comparison of the effects of AC and Cu_2O/AC on pyrocatechol removal is shown in Fig. 4. The 0.02 g of AC and 0.02 g of 14.3 wt % Cu_2O/AC were put into 50 ml of pyrocatechol (100 mg/l). The results indicate that the extent of removal on 14.3 wt % Cu_2O/AC increases with increasing reaction time, and reaches 91.4% at 8.5 h. The AC does not catalyze oxidation of pyrocatechol, but it is a good adsorbent. Therefore, the activated carbon removes pyrocatechol from aqueous solution only by adsorption. The process on Cu_2O/AC catalysts may be divided into two stages—pyrocatechol adsorption on activated carbon and its subsequent degradation on the Cu_2O photocatalysts. Since the adsorption process on the surface of the activated carbon proceeds much faster than the degradation by the photocatalysis, the removal of pyrocatechol in the first 2.5 h occurs mainly through the adsorbtion. Beyond 2.5 h, the extent of removal is influenced by both oxidation processes [20]. So the removal extent on 14.3 wt % Cu_2O/AC exceeds that on AC only by about 5% at the initial reaction stage. At

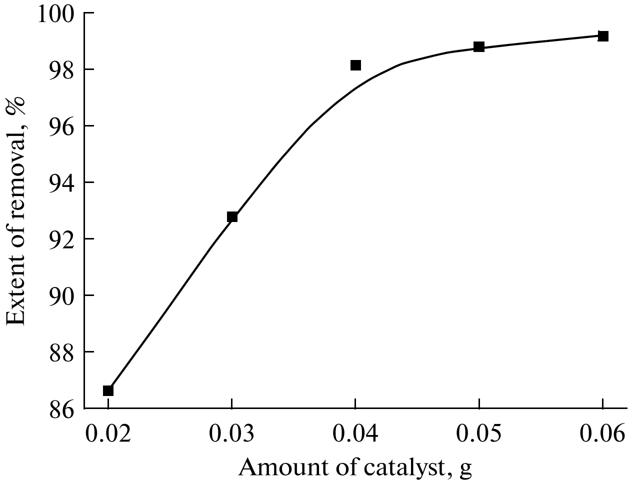


Fig. 5. The effect of the catalyst amount on the extent of pyrocatechol removal.

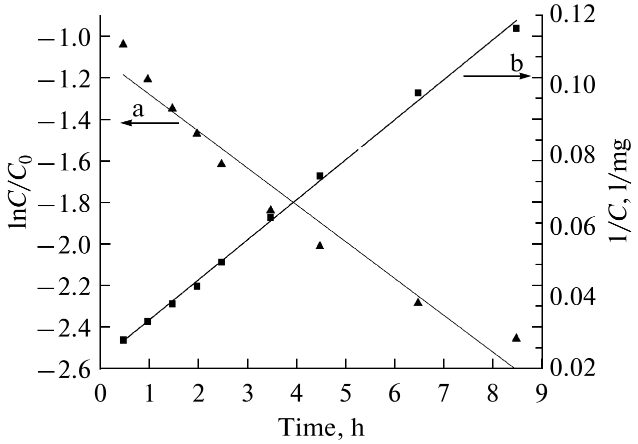


Fig. 6. Kinetics of the pyrocatechol photocatalytic degradation: the plots of $\ln C/C_0$ (a) and $1/C$ (b) vs. irradiation time. C is pyrocatechol concentration.

the next stage, the removal extent increases rapidly with time, and the degradation extent on 14.3 wt % Cu_2O/AC reaches 91.4% at 8.5 h. Thus, one can conclude that the carbon-supported cuprous oxide is the active and efficient catalyst.

Effect of the photocatalyst amount. The dosage of the catalyst plays an important role in catalytic oxidation reactions during the removal of organic pollutants. Accordingly, the effect of the photocatalyst amount on pyrocatechol removal was studied (Fig. 5). The experiments consisted in adding of different amounts (0.02, 0.03, 0.04, 0.05 and 0.06 g) of the 14.3 wt % Cu_2O/AC in the solution of pyrocatechol. The photocatalytic ability of pyrocatechol degradation was measured after irradiation for 2.5 h. It is seen that the removal extent markedly increases when the quantity of catalyst is under 0.04 g. However, the removal extent increases slower, when the quantity of catalyst exceeds 0.04 g. Considering the cost of catalyst and the removal efficiency, 0.8 g/l was chosen as the optimum catalysts content.

Kinetics

A linear relationship of $1/C$ (C is pyrocatechol concentration) vs. irradiation time was established in the experiments with 14.3 wt % Cu_2O/AC (Fig. 6b). Hence, the pseudo-second order model is found to be applicable for the photocatalytic degradation processes with the correlation coefficient $R^2 = 0.999$. From the slope and intercept in Fig. 6b, the values of k' and b' in the equation

$$\frac{1}{C} = k't + b'$$

were calculated to be 0.0113 l mg^{-1} min^{-1} and 0.0223, respectively. The plot of $\ln C/C_0$ vs. time is not linear (Fig. 6a) and consequently the first order model is not operative in this case.

In this study, using a 200 W incandescent lamp, the photocatalytic degradation of the organic pollutant (pyrocatechol) on the photocatalyst Cu_2O/AC was studied. The kinetics and the influence on different factors on the photocatalytic degradation of phyrocatechol were discussed in detail. We can conclude that 14.3 wt % Cu_2O/AC is the best photocatalyst among all prepared samples. Considering the various factors, we choose pH 7.0 as the optimum pH of solution, 2.5 h as the optimum degradation time, and 0.8 g/l as the optimum quantity of catalyst. The results show that the photocatalytic degradation processes may be described by pseudo-second order model.

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