



Short communication

CuO impregnated activated carbon for catalytic wet peroxide oxidation of phenol

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ABSTRACT

This paper presents an original approach to the removal of phenol in synthetic wastewater by catalytic wet peroxide oxidation with copper binding activated carbon (CuAC) catalysts. The characteristics and oxidation performance of CuAC in the wet hydrogen peroxide catalytic oxidation of phenol were studied in a batch reactor at 80 °C. Complete conversion of the oxidant, hydrogen peroxide, was observed with CuAC catalyst in 20 min oxidation, and a highly efficient phenol removal and chemical oxygen demand (COD) abatement were achieved in the first 30 min. The good oxidation performance of CuAC catalyst was contributed to the activity enhancement of copper oxide, which was binding in the carbon matrix. It can be concluded that the efficiency of oxidation dominated by the residual H₂O₂ in this study. An over 90% COD removal was achieved by using the multiple-step addition in this catalytic oxidation.

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1. Introduction

Recently, toxic organics in wastewater have become a more and more important issue. Phenol is one of the most common organics in wastewaters discharged from petrochemical, chemical and pharmaceutical industries [1].

Much research effort has been expended on the catalytic oxidation of phenol in wastewater with a view to the elimination or abatement of toxic organics in wastewater [2–6]. One system, wet air oxidation (WAO), is used primarily for the treatment of high strength industrial effluent and uses high temperature and pressure with oxygen or air to oxidize organics in aqueous solution. Noble metal oxides are used as catalyst in WAO and the reaction usually carried out with higher pressure and temperatures [7–10]. The cost of catalyst and deactivation problems limited the application of noble metal catalyst in WAO process. Improved or alternative systems are necessary, especially those that can be effective at milder operating conditions (i.e. pressure and temperature).

Wet hydrogen peroxide catalytic oxidation (WHPCO) has been developed in response to the noted drawbacks of WAO [11–14]. In catalytic wet peroxide oxidation (CWPO) processes, the redox properties of dissolved transition metals (e.g. Fe, Cu, Ce) are used to generate hydroxyl radicals under mild reaction conditions in the presence of hydrogen peroxide. Although WHPCO has been widely used for the oxidation of wastewater streams with high organic (TOC) content, the utility of this system is also limited because of the restricted viable pH range [3–5] and the need for the recovery

of the homogeneous catalyst. The use of heterogeneous catalysts overcomes these drawbacks. Several heterogeneous catalysts with Fe or Cu impregnated clay or other support have been prepared for WHPCO [15–20]. The high oxidative ability of these catalysts for the removal of phenol or TOC conversion was found to be directly related to the iron or copper content. Unfortunately, the presence of metal oxides can lead to metal leaching into the solution and consequent secondary pollution problems.

In this study, a new copper binding catalyst was synthesized for use in CWPO. Activated carbon was impregnated with copper at various concentrations and the resultant CuAC catalysts were used in the CWPO of phenol in aqueous solution. Catalyst activity and characteristics, particularly pore properties, were assessed in detail. XRD was used for the characterization of copper oxide and stability of the catalysts was also assessed.

2. Experimental

2.1. Preparation of catalyst

To prepare the CuAC catalysts, ground coconut shell, sieved to 4 × 12 mesh and dried in an oven at 105 °C, was immersed in a dominant Cu(NO₃)₂ aqueous solution (Merck Co.) reagent grade and used without further purification. Two hundred grams of coconut shell was mixed with various concentrations of Cu(NO₃)₂ solution (impregnation ratio, $W_{\text{Cu(NO}_3)_2} / W_{\text{coconut shell}} = 0-1.0$) in a water bath at 80 °C for 12 h. To achieve carbonation the mixture was heated from room temperature at a heating rate of 25 °C min⁻¹ with a nitrogen flow of 20 ml min⁻¹ until it reached 400 °C, at which temperature it was maintained for 30 min. The nitrogen was then stopped and the sample was activated at a heating rate

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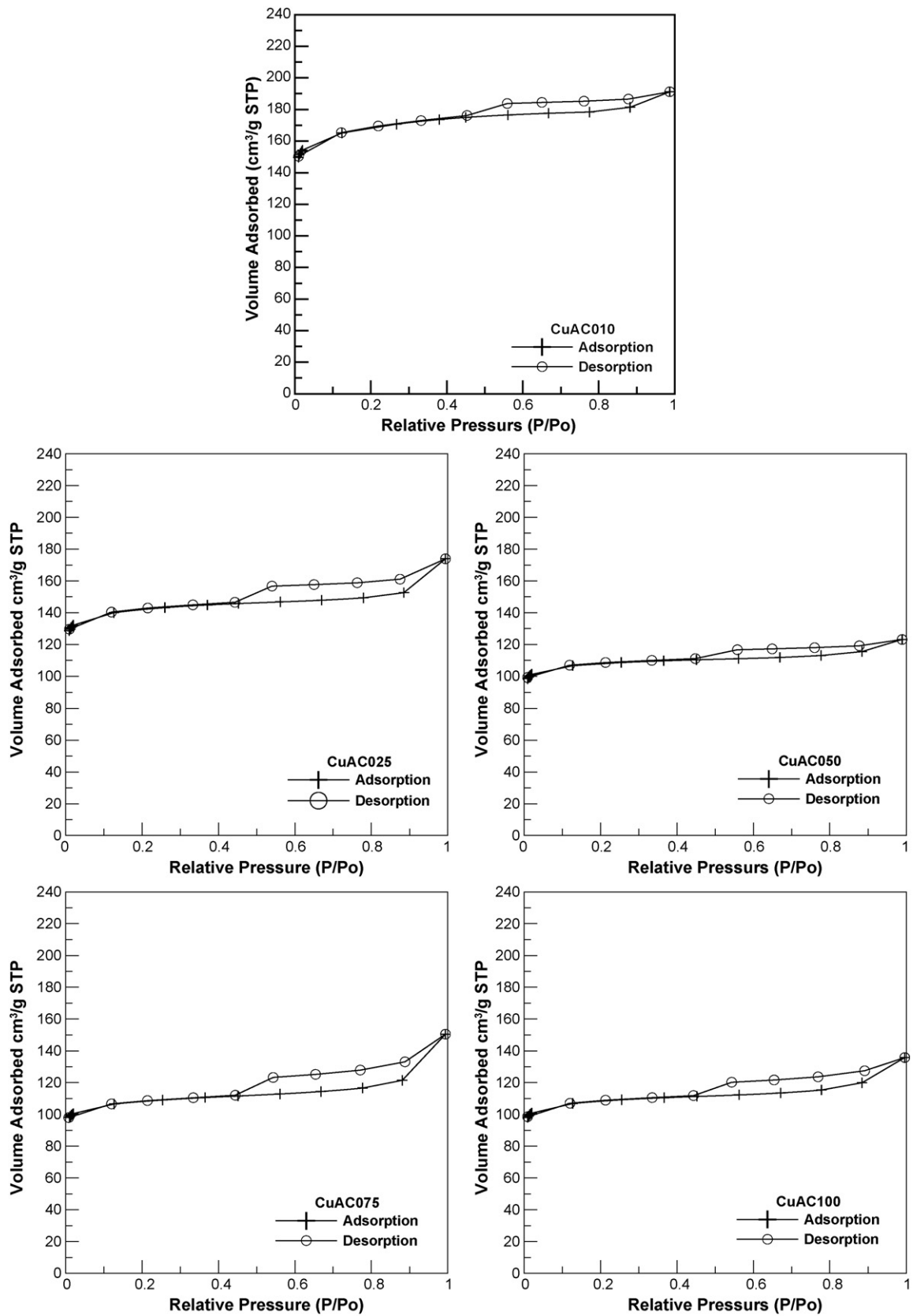


Fig. 1. Nitrogen adsorption isotherm of CuAC catalysts at 77.3 K.

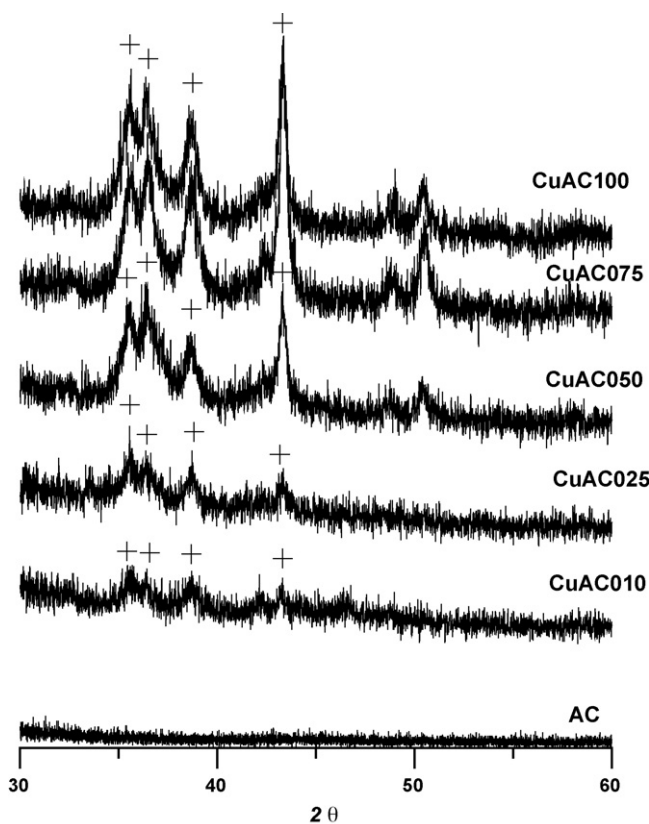


Fig. 2. XRD analyses of CuAC catalysts.

of $25^{\circ}\text{C min}^{-1}$ in a flow of 800 ml min^{-1} CO_2 until the temperature reached 800°C . This temperature was maintained for 1 h. The activated carbon was then cooled to room temperature in a CO_2 environment and the final product was washed with distilled water until solute copper ions could not be detected on atom adsorption spectra ($<1\text{ mg L}^{-1}$). It was then filtrated and dried at 100°C ready for use. Copper loadings were determined by soaking the catalyst in 65% HNO_3 solution for 24 h under stirring to dissolve the copper into the acid, and then analyzing the copper concentration using Atomic Absorption Spectroscopy. Catalysts were designated CuAC100, CuAC075, CuAC050, CuAC025 and CuAC010, representing an impregnated copper concentration of 1.0–0.10 M.

2.2. Properties, surface area and pore properties analysis

Specific surface areas and porosity properties of ready-to-use catalyst were determined by nitrogen adsorption (automated gas adsorption apparatus, Micromeritics Inc., ASAP 2010), performed at -196°C . Before gas adsorption measurement, all samples were degassed at 250°C in a vacuum 10^{-3} Torr for 8 h. By assuming all pores in the sample are parallel and cylindrical, the average pore diameter of samples can be determined by dividing the pore vol-

ume by the surface area. To enable this calculation, surface area and micropore volume of samples were determined using the Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (D–R) equations, respectively. The adsorption isotherms of nitrogen were produced at relative pressure of 0.04–0.2. The status of copper in the samples was analyzed by powder XRD analysis using a diffractometer (XRD, Rigaku D/MAX-2000) with $\text{Cu K}\alpha$ radiation (1.540 \AA). Samples were scanned at a speed of $0.05^{\circ}\text{ s}^{-1}$ and a step of 0.05° . The morphology and size distribution of copper oxides as well as elemental analyses of the CuAC were examined using scanning electron microscopy (SEM, Hitachi, S-4200) equipped with energy dispersive spectrometry (EDS). The copper contents of the catalysts were digested in nitric acid, and membrane filtration ($0.25\text{ }\mu\text{m}$). The copper contents of CuAC catalysts were analyzed by atomic absorption spectrometry (AAS) using a PerkinElmer 400 spectrophotometer.

2.3. Catalytic oxidation of phenol

The catalytic performance of CuAC for the CWPO of phenol in solution was evaluated in a typical 500 ml batch reactor with stirring. An optimum amount (catalyst dosage: 1 g) of CuAC catalyst was tested under the same conditions at 80°C , with an initial phenol concentration of 1000 mg/L in 500 ml aqueous solution. For the purpose of eliminating residual H_2O_2 from the liquid samples, all the sampling solutions were well mixed with 0.1 g manganese oxide at least 15 min before measuring the concentration of phenol and COD titration. Phenol concentration was determined at intervals using liquid chromatography (Shimadzu Inc., model UV-2100 chromatograph with a UV detector). The analytical column (Supelco Co., Taiwan) was a 25 cm, ODS C-18 column at 254 nm. At the desired time interval thereafter, liquid sample was taken from the reactor. Sampling was continued for 180 min. TOC was analyzed by Shimadzu TOC-5000A and chemical oxygen demand (COD) was analyzed using the standard methods, Section 5220D, APHA, 1995 [21]. The concentration of H_2O_2 in solution was measured by a self-indicating potassium permanganate titration. Portion of sample was transfer to a 250-ml flask, and 100 ml and 10 ml H_2SO_4 (2 M) were added. Solutions were titrated using standard potassium permanganate solution (0.02 M) until the first permanent pink color appeared [22].

3. Results and discussion

3.1. Characterization of CuACs

The adsorption/desorption isotherms of N_2 at $T=77\text{ K}$ for the CuAC catalysts, shown in Fig. 1, reveal a hysteresis loop in each curve. The hysteresis loop area in isothermal curves is generally proportional to mesopore volume and structure [23–26] and the similarity in hysteresis loop appearance between catalysts seen in Fig. 1 is therefore suggestive of a similarity in these features in the activated carbon of each catalyst. On the other hand, the isotherm curves showed that the sorption area decreased with higher copper content.

Table 1
Properties of CuACs catalyst by nitrogen adsorption in reaction and the product yield.

Catalyst	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{micro} (cm^3/g)	V_{micro}/V_t	D_{BJH}^a (\AA)	Yield (%)	Copper ^b (%)
CuAC010	670	0.295	0.219	0.74	10.1	22.9	4.6
CuAC025	572	0.269	0.195	0.73	10.2	27.2	7.2
CuAC050	437	0.190	0.150	0.79	10.2	35.1	9.8
CuAC075	435	0.230	0.146	0.65	10.3	35.7	25.4
CuAC100	436	0.209	0.148	0.71	10.2	36.3	38.9

^a BJH adsorption average pore radius (2V/A by BET).

^b The copper contents in catalyst were determined by atomic absorption spectrometry (AAS).

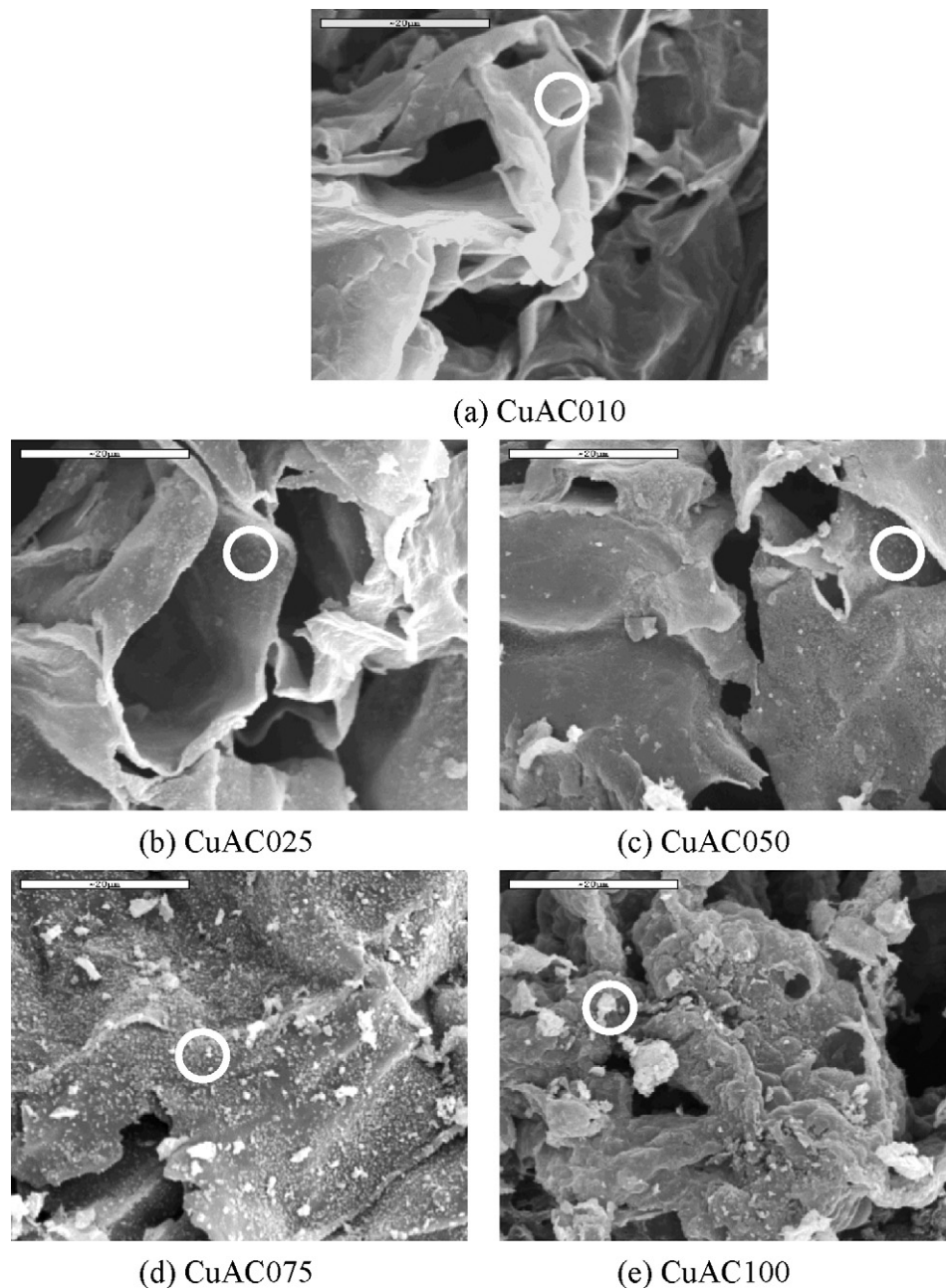


Fig. 3. SEM images of CuAC catalysts, bar scale in SEM images are 20 μm . (a) CuAC010; (b) CuAC025; (c) CuAC050; (d) CuAC075; (e) CuAC100.

In the case of catalytic oxidation, the pore volume and pore size of catalyst strongly affect the reaction rate in the oxidation. Pollutant adsorption on the active size will be reduced if pore size is smaller than the molecular size of pollutant, suppressing catalytic oxidation and, conversely, the adsorption, release and diffusion rate of pollutant is increased if pore size is larger than the size of pollutant. The optimum pore size of catalyst results the high oxidation rate in the reactor. In activated carbon, pores can be classified as either micropore (pore size < 1 nm) or mesopore (pore size about 2–3 nm). The effect of copper content on pore size of activated carbon is shown in Fig. 2. The main pore size distribution was in the micropore range for all loadings of copper, indicating that an increase in copper binding in activated carbons obtained the similar pore size distribution.

Surface area and micropore volume of CuACs were determined using the Brunauer–Emmett–Teller (BET) and Dubinin–

Radushkevich (D–R) equations, respectively [24]. Table 1 lists the results in terms of S_{BET} , V_{total} , V_{micro} , V_{meso} , D_{DR} , and Cu content (%), which showed that the surface area and micropore volume of activated carbon decreased with increasing the copper content up to impregnating concentration 0.05 M and then almost kept constant with further increasing the copper loading. As shown in Table 1, it can be seen that the micropore volume and BET area of CuACs decreased with increasing the copper loading. This phenomenon implied that the copper loading suppressed the gasification of carbon matrix during the activation. Therefore, the micropore of CuACs did not well develop to mesopore and showed the lower surface area.

In previous reports [24,27], impregnated metal in carbon matrix plays an important role on the carbon activation and dominates the final pore structure of activated carbon. Catalytic gasification of the matrix occurs during the activation stage of carbon catalyst

formation, thus the optimum levels of impregnated metal in the matrix enlarge the micropores of activated carbon to mesopores and hence increase its surface area. In this study, the S_{BET} values of CuACs were in the range 670–436 m²/g and gradually decreased with increasing impregnating concentration of nitro-copper. The micropore volume of activated carbon decreased with increasing impregnated copper content. Copper impregnation did not accelerate the gasification of the carbon matrix in the stream of CO₂. Table 1 shows that the pore volume decreased with increasing copper content in the carbon matrix (from 0.295 to 0.209 cm³ g⁻¹). It was indicated that the surface area and total pore volume decreased with increasing Cu loading due to the micropore blocking in activation. This result contradicts the results of chemical activation by ZnCl₂ in previous reports [28–30]. In our investigation, it was found that copper impregnation did not promote the formation of mesopores. Hayashi et al. [29] reported that impregnated ZnCl₂ in an activated carbon strongly affected the evolution rate of hydrogen during the activation and dominated the final pore size the pore size distribution of activated carbon. As shown in Table 1, the copper loading declined the surface area with increasing the impregnated copper up to 0.05. A higher copper loading showed the decline in the sorption area of activate carbon due to the less catalytic gasification and pores enlargement in activation stage. This result showed that the higher copper loading did not benefit the pore developing during the activation stage. The similar reports [31,32] were also evidenced in the similar cases of impregnated copper in carbon matrix. They had shown that the pore growth of activated carbons would be suppressed by impregnated copper in carbon matrix. On the other hand, it can be seen that the yield and copper content of the catalysts were not proportional to the impregnated copper concentration. The yield and copper content of catalysts first increased and then leveled off for copper concentrations higher than 0.5 M in impregnated solution. It was found that the increase in the viscosity of higher impregnated copper concentration inhibited the absorption of copper in the coconut shell and then limited the copper content in the catalyst. The yield of the catalysts was determined by the amount of carbonization of coconut shell and copper content. The catalytic gasification of coconut shell was determined by the amount of active metal in the carbon matrix during the carbonization.

In the case of catalytic oxidation, the activity was not only determined by the adsorption area of catalyst but also affected by the number of active sites on the catalyst. The effect of metal loading on catalytic activity of activated carbon was investigated by Calvo et al. [30] in the case hydrodechlorination system. They had also showed that the surface area of activated carbon did not contribute the oxidation activity in the catalytic oxidation. They implied that the characteristics of the metallic phase and surface area may be the key parameters to dominate the activity of carbon catalyst with transition metal loading.

3.2. XRD and SEM-EDS analysis of CuACs

The powder diffraction patterns of the CuAC catalysts, in Fig. 2, all show the characteristic peaks of CuO (Tenorite, syn, monoclinic, JCPDS # 41-254) around 35.9°, 39.0°, 49.1°, and 61.6°, and this intensity increased with increased copper content. This indicates that higher loading of copper in catalyst preparation led to form the higher levels of copper oxide on the activated carbon in the catalyst. Therefore, the SEM images and EDS analysis of CuAC catalysts were used to further investigate the distribution of copper oxides and copper content on the surface of activated carbon. The SEM images in Fig. 3 show that the carbonation did not destroy the fiber structure of coconut shell. It can be seen that higher copper loadings in the raw material led to enrichment of copper oxide formation on the surface of activated carbon, indicating that copper

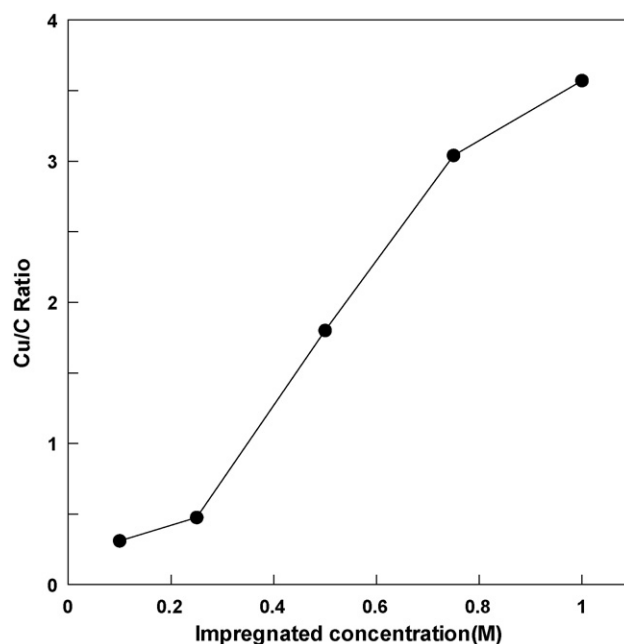


Fig. 4. Effect of impregnated nitrate copper concentration on copper/carbon ratio on carbon surface of CuAC catalysts (measured by SEM-EDS analysis).

salt loading acted to determine the amount of copper oxide product on the surface after carbonation had completed, with high copper salt loadings inducing high levels of copper oxides on the surface. The copper content on the surface of activated carbon was identified by SEM-EDS analysis and it was shown in Fig. 4. It was found that the copper/carbon ratio by SEM-EDS analysis increased with increasing the impregnating copper concentration. As described in the experimental method, the newly synthesized catalyst was washed with distilled water until no copper ion detecting in solution, hence it can be surmised that non-binding copper oxide was completely removed. Therefore, it is indicated that the binding of copper oxide was proportional to the impregnating copper concentration in preparation.

3.3. Catalytic activity of CuACs

Fig. 5 shows concentration over time of the oxidant, hydrogen peroxide, in the WHPCO reaction. As indicated in the experimental method, hydrogen peroxide was added into the reactor once only, at the start of the reaction. Decrease in hydrogen peroxide can therefore be attributed not only to catalytic reaction but also to thermal decomposition in the reactor. All the results show that the complete conversions of hydrogen peroxide were achieved in 15 min or less with all CuAC catalysts at 80 °C and initial phenol concentration of 1000 mg/L in 500 ml aqueous solution. This compared with complete conversion in 100 min with the non-impregnated activated carbon, indicating clearly that Cu impregnated in the carbon matrix accelerated the decomposition of hydrogen peroxide. Furthermore, the rate of decomposition of hydrogen peroxide with CuAC indicates a high catalytic ability for this catalyst in the WHPCO of organics. On the other hand, Fig. 6 shows phenol removal over time in aqueous solution at 80 °C with hydrogen peroxide only (phenol oxidized by H₂O₂), CuAC010 only (phenol adsorbed by CuAC), and with neither oxidant nor catalyst (blank). Low efficiency of phenol removal was observed in condition of either only hydrogen peroxide or only CuAC010, while a slight thermal decomposition of phenol was evident in the blank.

Fig. 7 shows concentration of TOC over time in aqueous solution at 80 °C with hydrogen peroxide only (oxidation test), CuAC010

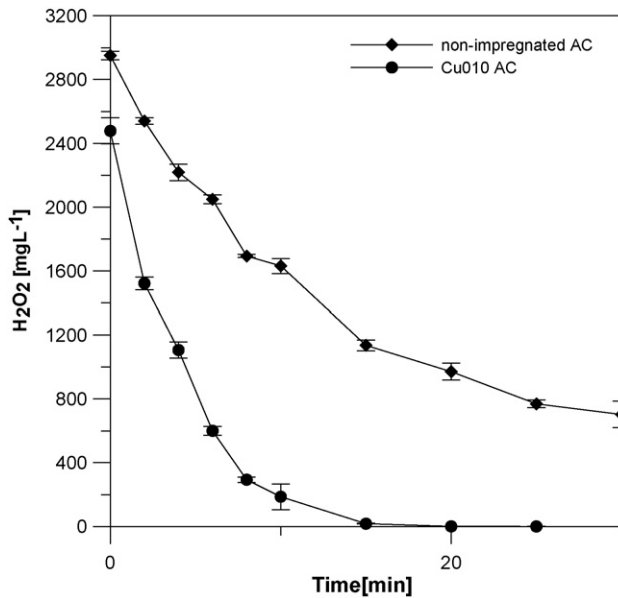


Fig. 5. Decomposition of hydrogen peroxide by CuACs catalytic oxidation at 80 °C. (◆: non-impregnated AC, ●: CuAC010, initial H₂O₂ concentration: 0.1 M), carbon dosage 1 g in 500 ml solution.

only (sorption test), and with neither oxidant nor catalyst (blank). Low efficiency of TOC removal was also observed in the case of both hydrogen peroxide and CuAC010 adsorption. A slight thermal decomposition of phenol was also observed in the blank. It is indicated that the phenol removal cannot be achieved by carbon adsorption and oxidation of hydrogen peroxide.

The similar results were reported by Zhao et al. [33] and Hu et al. [34] with the impregnation using an aqueous copper salt solution supported on commercial granular activated carbon for Cu/AC catalyst preparation. They had concluded that the high oxidation activities of those catalysts were obtained in the case of wastewater treatment and phenol oxidation. Due to the limitation of preparing procedure, the low copper loading in carbon matrix

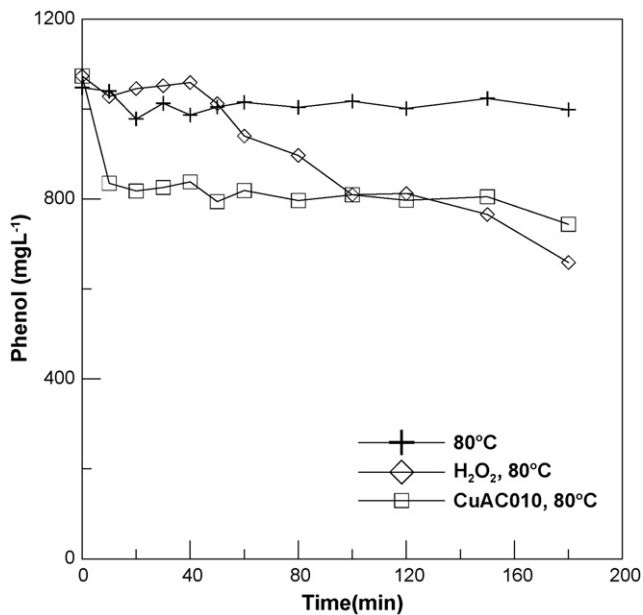


Fig. 6. Phenol removal in aqueous solution at 80 °C with hydrogen peroxide only (oxidation test), CuAC010 only (sorption test), and with neither oxidant nor catalyst (blank), carbon dosage 1 g in 500 ml solution.

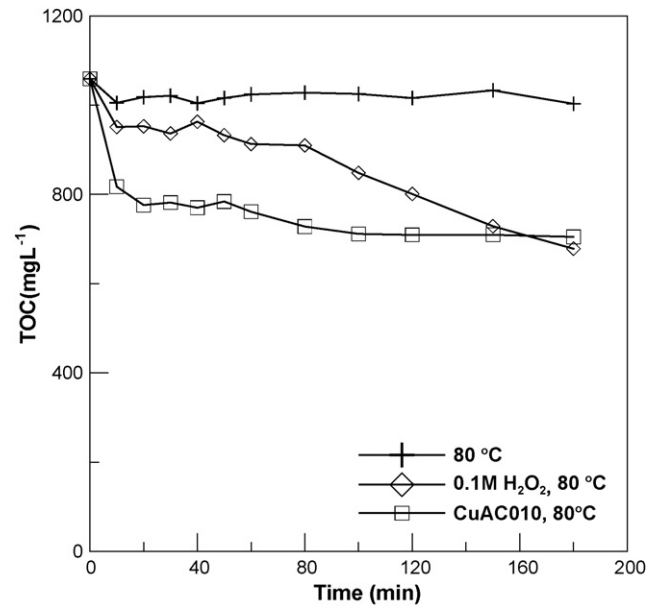


Fig. 7. TOC removal in aqueous solution at 80 °C with hydrogen peroxide only (oxidation test), CuAC010 only (sorption test), and with neither oxidant nor catalyst (blank), carbon dosage 1 g in 500 ml solution.

was obtained in the above report. In this study, a higher copper loading and oxidation activity can be obtained by the raw coconut shell immersion with Cu(NO₃)₂. As was noticed in previous works, a commercial activated carbon was selected in a reaction condition of high temperature (160 °C) and oxygen pressure (16 bar) [35] and activated carbon-supported copper catalyst prepared from sulfonated styrene-divinylbenzene resin [36] showed deactivation since large copper leaching for high concentration (1000 mg L⁻¹) of phenol oxidation. The CuAC catalyst shows high oxidation performance to treat phenol with low energetic cost and in a mild reaction condition.

3.4. Influence of copper impregnation on phenol oxidation

One gram of CuAC and 0.1 mol/L of hydrogen peroxide were added to a 500 ml aqueous solution together with phenol at a concentration of 1000 mg/L to start the catalytic reaction. At the experimental temperature of 80 °C complete degradation of phenol was achieved in less than 15 min with all catalysts (Fig. 8A). Over 98% of phenol was removed in this reaction. Observations of TOC over time (Fig. 8B) show that near-maximum abatement efficacy was achieved after approximately 40 min, by which time high copper content catalysts (CuAC100, CuAC075) had produced about 80% abatement and low copper content catalysts (CuAC050, CuAC025, CuAC010) had produced about 60%.

The similar results were reported by Zhao et al. [33] and Hu et al. [34] with the impregnation using an aqueous copper salt solution supported on commercial granular activated carbon for Cu/AC catalyst preparation. They had concluded that the high oxidation activities of those catalysts were obtained in the case of wastewater treatment and phenol oxidation. Due to the low copper loading in carbon matrix, the incompletely phenol removal was found in the above cases. However, the high copper loading and oxidation activity can be obtained in our study. It is indicated that the different preparation method in this study resulted a stable and high oxidation activity carbon catalyst for catalytic phenol oxidation.

Assuming an oxidation mechanism of adsorption-oxidation-desorption, the active sites on the surface of activated carbon play a dominating role in the catalytic oxidation and degradation rate of

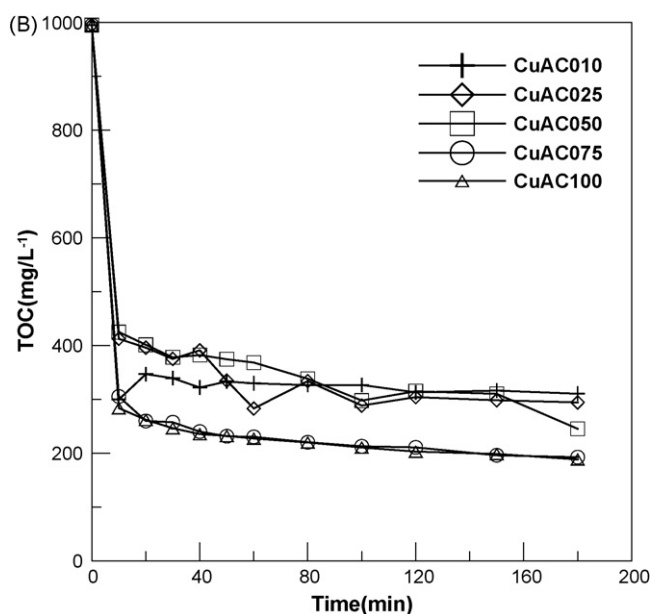
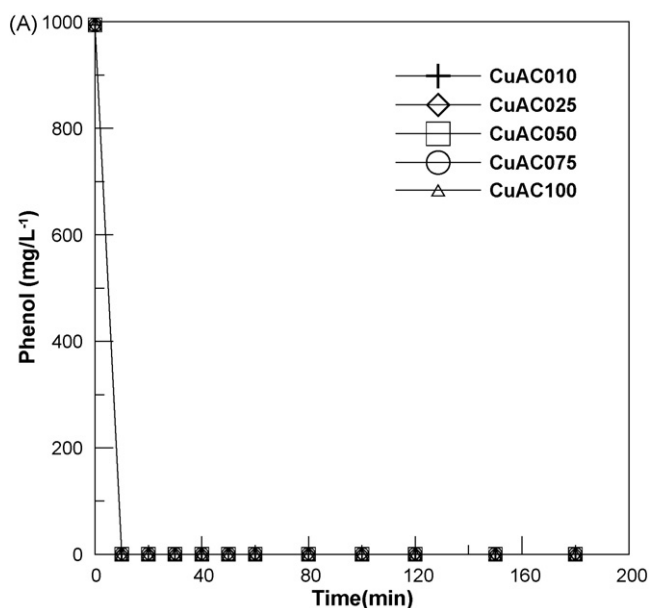
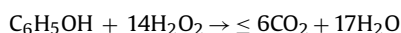


Fig. 8. Effect of copper loading of CuACs on phenol (A) and TOC (B) removal by catalytic wet oxidation. (reaction conditions: catalyst 1 g, phenol 1000 mg L⁻¹, 0.1 M H₂O₂, 80 °C).

phenol. The complete mineralization of phenol by hydrogen peroxide occurs according to the following reaction:



It is possible to estimate the theoretical phenol abatement achievable with optimal assignment of hydrogen peroxide, calculating the stoichiometric amount of hydrogen peroxide required using the above equation. In this study, excess of stoichiometric amount of hydrogen peroxide was added in the initiation stage of phenol oxidation, and therefore the significant phenol abatement and TOC removal were also found in the reaction. The results presented in Fig. 8 clearly show that under the described conditions phenol conversion was complete was achieved in less than 15 min. However it is necessary to make sure that the complete conversion of phenol was achieved with the original excess of H₂O₂ and further oxidation of intermediate products had ceased. Therefore, it is suggested that maintaining the concentration of H₂O₂ in the reac-

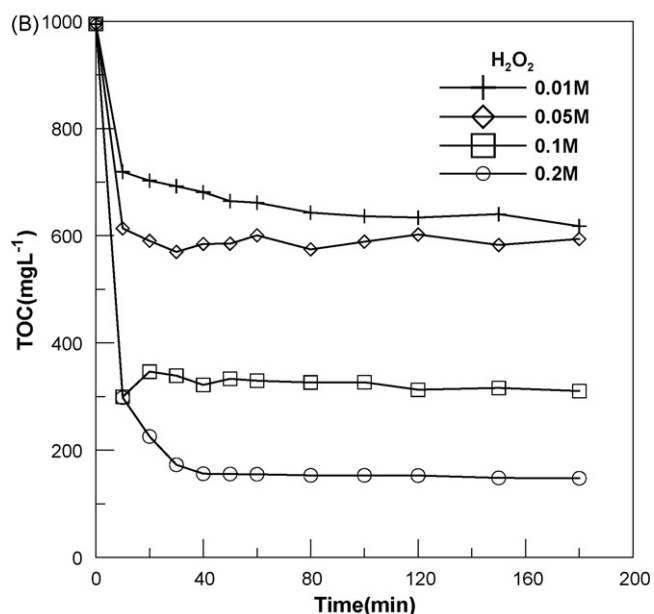
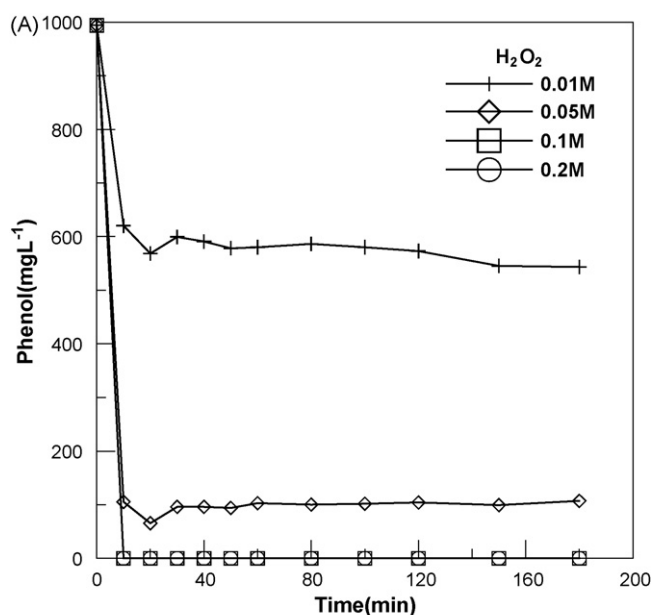


Fig. 9. Effect of H₂O₂ concentrations on phenol (A) and TOC (B) removal by catalytic wet oxidation. (reaction conditions: CuAC010 1 g, phenol 1000 mg L⁻¹, 80 °C).

tor may be helpful to the further abatement of COD and complete decomposition of phenol to carbon dioxide and water.

3.5. Influence of hydrogen peroxide concentration on phenol oxidation

To assess the impact of hydrogen peroxide in the reaction, it was added at different concentrations (0.01, 0.05, 0.1 and 0.2 M/L) in separate runs, with the remainder of components and conditions as described. The result is shown in Fig. 9A, higher molar concentrations of hydrogen peroxide were associated with increased phenol removal, and it was found that almost complete conversion of phenol was achieved with concentrations of 0.1 M and above. The removal/abatement occurred rapidly in the first 20 min irrespective of the dosage of H₂O₂ and this may be due to H₂O₂ was completely consumed by this time or because of intermediate compounds interfering with oxidation by H₂O₂. Higher molar concentrations of

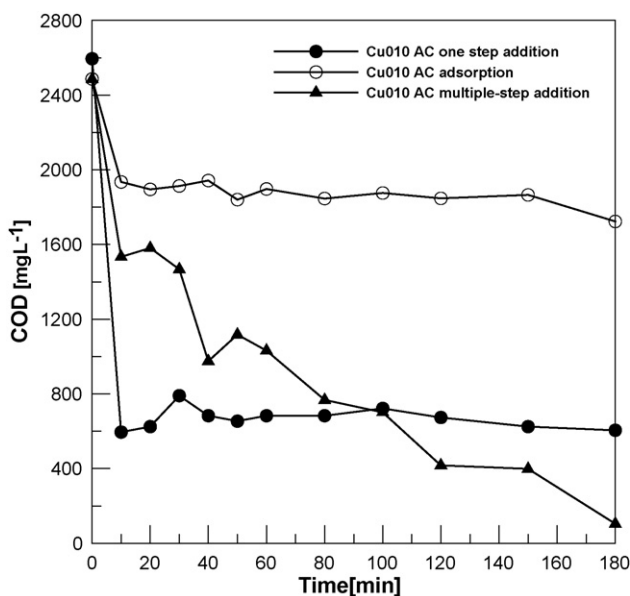


Fig. 10. Effect of the H_2O_2 additions on COD removal by catalytic wet oxidation. (reaction conditions: CuAC010 1 g, phenol 1000 mg L^{-1} , 80°C , total H_2O_2 dosage 0.1 M).

hydrogen peroxide were also associated with increased TOC abatement (Fig. 9B), it was found that markedly TOC removals were observed for H_2O_2 concentrations of 0.1 and 0.2 M. Based on the results of previous works on the mechanism of phenol decomposition in catalytic oxidation [37–39], it is suggested that the phenol was degraded into low molecular weight organic products (e.g. hydroquinone, organic acid), whereupon oxidation terminated, and the residual intermediate compounds were responsible for the still elevated TOC values after the termination of oxidation.

It can be seen that the time for complete decomposition of H_2O_2 was found in the case of copper content catalyst in the WHPCO reaction (Fig. 8), and this implies that the increase in copper oxide on the surface of catalyst could be enhancing the catalytic oxidation. However, with no residual hydrogen peroxide remaining after 20 min, it is possible that incomplete phenol removal and TOC abatement in oxidation were due to the complete decomposition of H_2O_2 in the reaction. It is proposed that it would be more efficient to process a multiple-step addition of H_2O_2 rather than the single-step addition at the beginning of the reaction to maintain the residual concentration of H_2O_2 at an optimal level allowing complete decomposition of the organic pollutants.

3.6. Influence of multiple-step H_2O_2 addition on phenol oxidation

One gram of CuAC010 and hydrogen peroxide were added into a 500 ml aqueous solution in every 15 min with total concentration 0.1 M and together with phenol at a concentration of 1000 mg/L to start the catalytic reaction. At the experimental temperature of 80°C complete degradation of phenol was achieved in less than 15 min with all catalysts (Fig. 9). Over 90% of COD removed in this reaction can be observed in oxidation. As shown in Fig. 6, the adsorption of phenol showed a 10–15% removal in TOC value and the one-step addition of H_2O_2 in this reaction showed incomplete degradation of phenol in oxidation. This result indicated that the hydrogen peroxide is one of the most important factors to dominate the degradation of phenol in the oxidation. Maintaining residual hydrogen peroxide in solution is helpful to generate more free radical in oxidation. Therefore, the continuous adding procedure of H_2O_2 is necessary to clarify the above viewpoint and further improving the COD removal in oxidation. As shown in Fig. 10, the low initial dosage of H_2O_2 in the case of multiple adding processes, the COD removal decreased slowly than the one-step H_2O_2 addi-

tion in the beginning stage of oxidation. However, the final COD removal of multiple additive methods significantly enhanced the COD removal than the one step addition. This result evidenced that the residual H_2O_2 dominated the final COD and phenol removal in oxidation. It is concluded that the residual hydrogen peroxide is a dominant factor to degrade phenol to final products in oxidation. Therefore, it was suggested that the completely oxidation of pollutant can be obtained with the optimum dosage and adding way of hydrogen peroxide in the WHPCO process.

4. Conclusions

CuAC catalysts presented an effective activity in oxidation at high concentration of phenol solution, achieving over 98% phenol removal and over 90% COD abatement in WHPCO process. COD abatement was strongly dependent on the residual concentration of oxidant (hydrogen peroxide). The powder diffraction patterns of the CuAC catalysts verified that the copper oxide was formed by impregnating copper salt in carbon matrix. The SEM/EDX observation also identified the copper oxides were well dispersed and the copper was binding in the carbon matrix. The residual concentration of H_2O_2 is the important factor to determine the removal ratio of phenol by a WHPCO process. The experimental results also showed that the addition step of hydrogen peroxide strongly dominated the efficiency of COD removal in oxidation. It is suggested that the completely oxidation of pollutant can be obtained with the multiple-step addition of hydrogen peroxide in the WHPCO process.

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