Influence of Surface Modification on Catalytic Activity of Activated Carbon Toward Decomposition of Hydrogen Peroxide and 2-Chlorophenol

Hsu-Hui Huang [a] , Ming-Chun Lu [b] , Jong-Nan Chen [a] & Cheng-Te Lee [a]

[a] Institute of Environmental Engineering , National Chiao Tung University , Hsinchu, Taiwan, R.O.C.

[b] Department of Environmental Engineering and Health , Chia Nan University of Pharmacy and Science , Tainan, Taiwan, R.O.C.
Published online: 06 Feb 2007.

PLEASE SCROLL DOWN FOR ARTICLE

Influence of Surface Modification on Catalytic Activity of Activated Carbon Toward Decomposition of Hydrogen Peroxide and 2-Chlorophenol

Hsu-Hui Huang,[1] Ming-Chun Lu,[2,*]
Jong-Nan Chen,[1] and Cheng-Te Lee[1]

[1]Institute of Environmental Engineering, National Chiao
Tung University, Hsinchu, Taiwan, R.O.C.
[2]Department of Environmental Engineering and Health,
Chia Nan University of Pharmacy and Science,
Tainan, Taiwan, R.O.C.

ABSTRACT

The objective of this research was to investigate the influence of the activated carbons modified by chemical treatment on the surface catalyzed loss of H_2O_2 and 2-CP. The characteristics of the modified activated carbons were examined by several techniques including nitrogen adsorption, SEM, and EDS. The H_2O_2 decomposition rate would be suppressed significantly either by the change of surface properties modified with chemical treatment or the reduction of active sites occupied with the adsorption of 2-CP. In addition, the H_2O_2 decomposition rate with activated carbons within a specific time can be described by a second-order kinetic expression with respect to the concentration of GAC and H_2O_2 in the absence or presence of 2-CP. The catalytic activities of the three activated carbons toward 2-CP reduction followed the inverse sequence of those toward H_2O_2 loss, implying that acidic surface functional group could retard the H_2O_2

*Correspondence: Ming-Chun Lu, Department of Environmental Engineering and Health, Chia Nan University of Pharmacy and Science, 60 Erh-Jen Rd., Sec. 1, Pao-An, Jen-Te, Tainan Hsien 717, Tainan, Taiwan, R.O.C.; E-mail: mmclu@mail.chna.edu.tw.
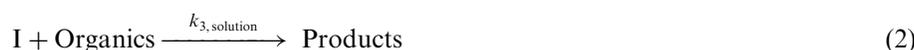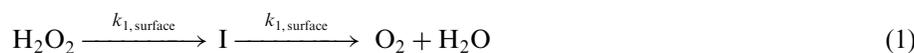
1233

loss and reduce the effect of surface scavenging resulting in increasing the reduction efficiency of 2-CP. By the detection of chloride ions in reaction mixture, it can be demonstrated that the reduction of 2-CP was not only attributed to the advanced adsorption but also the oxidation of the 2-CP with effective radicals. The real oxidation efficiency of 2-CP for the activated carbon modified with hot nitric acid was observed between 0.04 and 0.01 (mol/mol), offering a comparable efficiency to that of the other oxidation system using metal oxide as catalyst.

INTRODUCTION

The application of Fenton-like chemical oxidation process for remediation of contaminated soils and treatment of wastewater has gained more attention in last decade.[1–6] Recently, the practical application of this kind of oxidation process, such as supported iron oxides or granular size solid catalysts were studied for their catalytic properties.[6,7] These investigators indicated that the catalytic decomposition of hydrogen peroxide and target pollutants would depend on the specific characteristics of the organic compounds and catalysts. A general simplified mechanism proposed to describe the catalyzed organics with H_2O_2[4] is quoted as

$$H_2O_2 \xrightarrow{k_{1,\text{surface}}} I \xrightarrow{k_{1,\text{surface}}} O_2 + H_2O \tag{1}$$

$$I + \text{Organics} \xrightarrow{k_{3,\text{solution}}} \text{Products} \tag{2}$$

where I is intermediate (e.g., $\cdot OH$ or O_2^-) produced from the reaction of H_2O_2 with catalyst surface, $k_{1,\text{surface}}$ and $k_{2,\text{surface}}$ are the surface rate constants, and $k_{3,\text{solution}}$ is the rate constant in the reaction solution.

Granular activated carbon (GAC), used as a catalyst as well as adsorbent in this study, has been applied for a long time in the heterogeneous catalysis and adsorption for its enormous surface area, porous structure, and characteristic flexibility.[8] A number of studies have been carried out on the interaction of oxidizing agents (e.g., H_2O_2 or O_3) with carbon and carbon-supported materials.[9,10] Recent works[7,11] indicated that surface catalyzed reaction of GAC induced by oxidizing agent may lead to contaminants decay in water system. Although GAC adsorption method is effective to the removal of organic compounds, the GAC can get saturated easily in the process, which requires regeneration or complete replacement. Combination of both adsorption and heterogeneous catalysis into a single process could offer an attractive alternative in the wastewater treatment. Due to the complex role of GAC, the catalytic decomposition of contaminants with GAC deserves further investigation.

In this study, the surface catalyzed transformation of the model pollutant, 2-CP, by H_2O_2 in the presence of GAC and the difference of GAC surface properties modified by various chemical processes are examined. The factors including H_2O_2 concentration, pH, and GAC types affecting the oxidation behavior of 2-CP and H_2O_2 are discussed.

MATERIAL AND METHODS

The activated carbon was Filtrasorb-300 granular activated carbon supplied by the Calgon Carbon with an average particle density of 0.8 g/cm^3 and particle diameter of 0.64 mm (sieved with 20 × 40 US mesh size). GAC1 was the original carbon which was washed several times with deionized water until most of the fines were removed, and then dried in an oven at 50°C for preservation. GAC2 and GAC3 was the product of GAC1 which was oxidized with concentrated H$_2$O$_2$ (1 g GAC1 in 10 mL, 9.8 M H$_2$O$_2$) and HNO$_3$ (1 g GAC1 in 10 mL, 13.9 N HNO$_3$ heated at 80°C) solution for 24 h, respectively. Prior to the oxidation experiment, GAC1 and GAC2 was treated with diluted HCl solution (1 g GAC in 10 mL 1 N HCl) for 24 h in order to reduce the amount of metal ions on activated carbon. After the treatment, all the activated carbons were washed with deionized water several times until the pH value of supernatant did not change. In addition, the GAC treated with diluted HCl was washed with boiling deionized water twice more to clear off the chloride anion adsorbed on GAC. Specific surface area was calculated by N$_2$-BET meter (Micromeritics ASAP 2000). The morphology and surface components of activated carbons were examined using high-resolution scanning electron microscope and energy dispersive spectrometer (Hitachi S4700I). The value of pH$_{pzc}$ was measured by the mass titration method.[12]

The experiments were conducted in 250 mL flasks that were capped and shaken in a thermal oscillator tank at constant temperature of 30°C. The ionic strength was kept at 0.05 M by the addition of NaClO$_4$. The decomposition experiment of H$_2$O$_2$ was prepared by filling desired amount of GAC into the reaction mixture; the reaction mixture was 150 mL; the reaction was initiated by the addition of H$_2$O$_2$. The range of the pH variance observed in the H$_2$O$_2$ decomposition experiment was less than 0.5. In the oxidation experiment of 2-CP, the reactor was prepared by filling the desired amount of 2-CP and GAC; the reaction mixture was 200 mL. Prior to the oxidation experiment, the adsorption equilibrium of the reaction mixture (GAC and 2-CP) was achieved for three days. For the pH controlled experiment, the reaction mixture was adjusted several times to keep a constant pH during the adsorption. Samples taken from the reactor within certain time intervals were filtered through 0.45 μm membrane filters to separate GAC particles from the solution. H$_2$O$_2$ concentration was quantified by the peroxytitanic acid method with the addition of Ti(SO$_4$)$_2$ test solution.[13] Residual 2-CP was measured by an HPLC (Water LC module 1) with a reverse phase 3.9 × 150 mm Nova-Pak C$_{18}$ column (Waters). Total dissolved organic carbon (DOC) was determined using a TOC analyzer (Shimadzu 5000A). Concentration of chloride ion was measured with a chloride analyzer (Cole-Parmer U27502-13 plus WTW Ph 340/ion meter).

RESULTS AND DISCUSSION

Characterization of Modified Activated Carbons

The surface morphology and property of the three activated carbons are shown in Fig. 1 and Table 1. The total specific surface area of GAC is increased slightly

after the treatment with concentrated H_2O_2 solution, but reduced significantly by the heating treatment of concentrated HNO_3 solution. The difference among activated carbons modified by different treatments can also be verified via the observation of SEM diagram. The oxidation treatment by concentrated H_2O_2 has moderate impact on the texture of the activated carbon, while the treatment by hot nitric acid makes the surface morphology quite different with that of the original activated carbon. This may be due to the strong corrosive property of hot nitric acid, which makes the
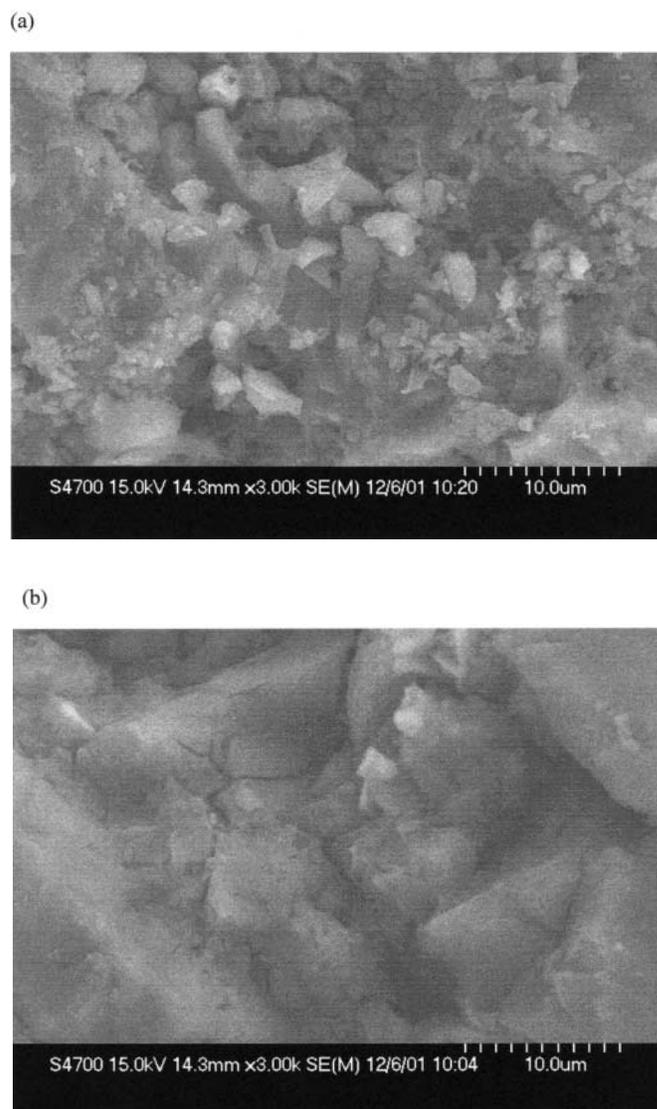

Figure 1. SEM images of modified activated carbons. (a) Original; (b) modified by H_2O_2; (c) modified by HNO_3.

(c)

S4700 10.0kV 13.4mm x3.00k SE(M) 14:38   10.0um
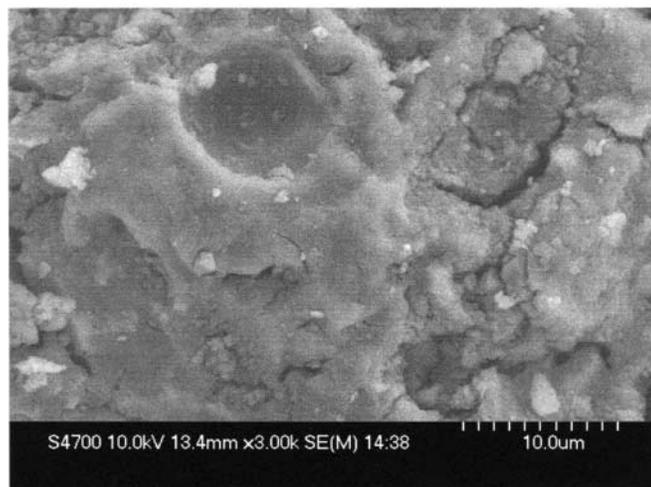
Figure 1. Continued.

Table 1. Properties of catalysts.

Catalyst	Specific surface area (m^2/g)	pH$_{pzc}$	Element composition (wt%)			
			C	O	Fe	Others
GAC1	983	4.16[a]	82.8	1.5	12.2	3.5
GAC2	1023	3.49[a]	96.7	1.2	0.3	1.8
GAC3	555.7	3.16	90.7	6.4	0.6	2.3

[a]After the treatment of diluted HCl and washing process.

pore walls thinner resulting in a widening of the microporosity and consequently a diminishing of surface area. The elements of C, O, Fe, and other metal ions were detected on the surface of activated carbons by EDS. It should be noted that the value of elemental analysis is not the absolute mass but the relative weight percentage of the surface composition. However, from the analysis, we still can observe the change of element composition. The washing treatment by diluted HCl solution could not extract the metal ions effectively, but the oxidation treatment by H$_2$O$_2$ and nitric acid removed large amount of the metal ions from the surface of GAC. Moreover, the higher weight percentage of oxygen was observed for GAC3, indicating that the functional group containing oxygen is higher on its surface. It was reported that acidic oxygen surface complexes would be introduced predominantly onto activated carbons when they were treated by strong oxidation process.[13] In addition, the values of pH$_{pzc}$ are much smaller than the general range of pH$_{pzc}$ (i.e., 9.8–10.2) reported for F-300.[14] Therefore, the washing and chemical treatment has increased the surface acidity of activated carbon significantly.

Hydrogen Peroxide Decomposition

The decomposition of H_2O_2 with the activated carbons in the presence and absence of 2-CP are shown in Fig. 2. The catalytic reaction in the absence of 2-CP (Fig. 2a) followed a first-order rate expression with respect to H_2O_2 concentration, which could be observed even the reaction time was over 24 h. The catalytic activity toward H_2O_2 loss for GAC2 and GAC3 is smaller than that for GAC1, indicating that the catalytic activity of the activated carbon has been affected apparently by the oxidation treatment. In addition, the catalytic activity toward H_2O_2 loss has a declining trend with the sequence of surface acidity (i.e., pH_{pzc}) for the three modified activated carbons, which could be explained by the description of Khalil et al.[9] that the H_2O_2 is easier to form complexes with basic groups or sites on the surface of activated carbon resulting in faster decomposition rate.

In the presence of 2-CP, the H_2O_2 decomposition with GAC3 of which surface has been saturated with 2-CP in advance (Fig. 2b) can also be found to follow a first-order rate model within the first 12 h. Additional works shown in Fig. 3 establishes a linear relationship between the observed first-order decay coefficient, k_{obs}, and the mass of activated carbon with and without the addition of 2-CP. As the result, a second-order rate expression of H_2O_2 decomposition with GAC can be derived with a mass normalized rate coefficient, k_{mass}, as
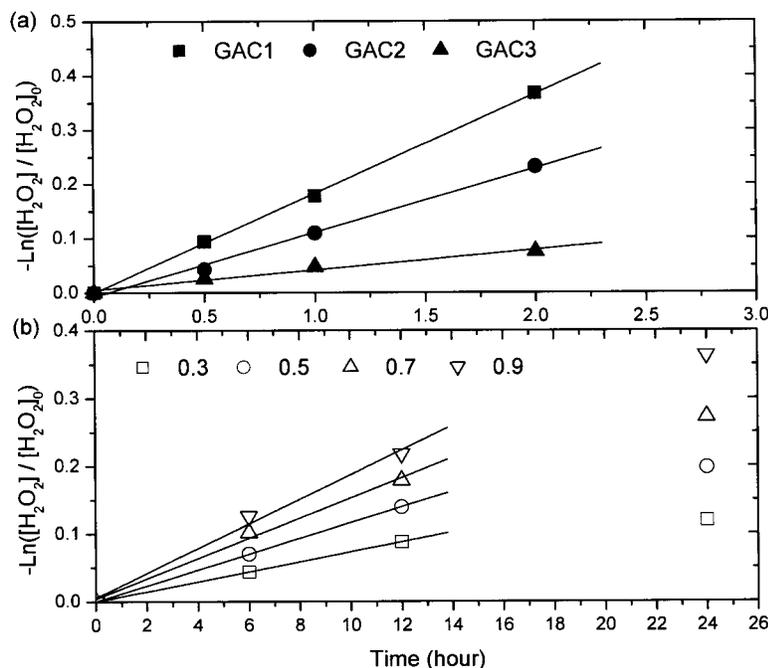

Figure 2. Change of H_2O_2 concentration in absence and presence of 2-CP. (a) 0.5 g/L GAC without 2-CP; (b) GAC3 with 1.13 mM 2-CP; (experimental condition: $[H_2O_2]_0 = 20$ mM; Temp. $= 30°C$).

Decomposition of H$_2$O$_2$ and 2-CP 1239

$$R_H = k_{\mathrm{mass}}[\mathrm{GAC}][\mathrm{H_2O_2}] = k_{\mathrm{obs}}[\mathrm{H_2O_2}] \qquad (3)$$

which is similar to the observations of the previous relative researches on the heterogeneous catalytic decomposition of H$_2$O$_2$.[1,3,9] However, unlike the slight influence of organics adsorption on H$_2$O$_2$ decomposition with metal oxide,[1,3] the H$_2$O$_2$ decomposition rate was reduced largely in the presence of 2-CP in comparison with that in the absence of 2-CP (Figs. 2 and 3). This is attributed to the 2-CP adsorption which reduces the surface active sites available for the H$_2$O$_2$. The surface of activated carbon is well known for its high affinity for organics. Lucking et al.[7] reported the similar result in their adsorption/oxidation system using carbon material as catalyst. Furthermore, a drop of the reaction rate in the presence of 2-CP over 12 h was also observed (Fig. 2b), which could be attributed to the advanced adsorption of the oxidative intermediates of 2-CP. The advanced adsorption of oxidative intermediate could change the number or property of active sites on GAC surface, resulting in that the rate model cannot be described by a first-order rate expression with respect to H$_2$O$_2$ concentration any more.

2-Chlorophenol Removal

Adsorption of Modified Activated Carbons

The experiments of 2-CP oxidation were conducted with various modified activated carbons. To exclude the competing adsorption of 2-CP which makes it difficult to differentiate the effect of adsorption and heterogeneous catalysis on the
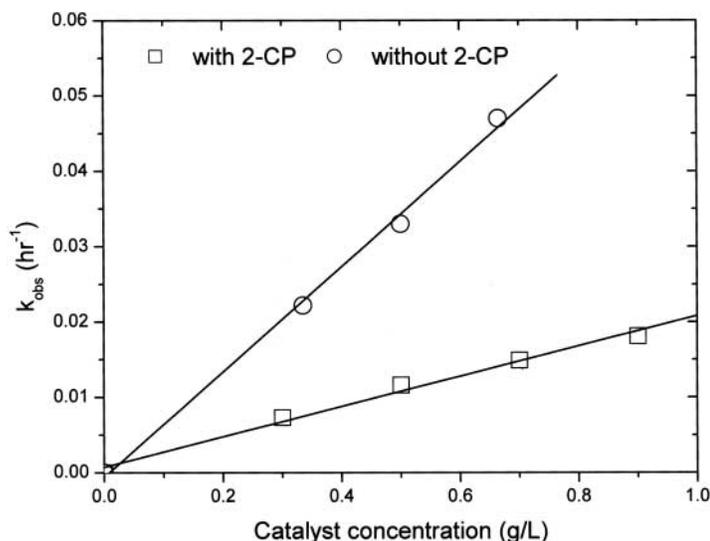

Figure 3. Effect of catalyst concentration on k_{obs} with and without 2-CP (experimental condition: [H$_2$O$_2$]$_0$ = 20 mM; [2-CP]$_0$ = 1.13 mM; Temp. = 30°C).

removal of 2-CP, the adsorption equilibrium of the solution is required prior to the oxidation experiment. Our preliminary experiment showed that the adsorption equilibrium of 2-CP with the modified activated carbons could be reached within 72 h. Table 2 lists the adsorption capacities of modified activated carbons obtained from the adsorption isotherm experiment. The adsorption capacity of GAC3 is much smaller than those of the other activated carbons, indicating that the adsorption property of activated carbon would be affected significantly by the surface modified pretreatment. Acidic oxygen-containing surface functional groups had been found to reduce the chemisorption of phenols on surface sites of activated carbons,[15] which is also verified by our result of element analysis that higher oxygen content was observed on the surface of GAC3.

Reduction and Dechlorination of 2-CP

The result of the experiment conducted with different H_2O_2 concentrations is shown in Fig. 4. The trend of 2-CP loss including reduction and dechlorination is observed to increase with the increase of H_2O_2 concentration for the three modified activated carbons, implying that the amount of 2-CP reduced would be proportional to that of H_2O_2 added. It should be emphasized that the term, reduction, in this study represents the loss amount of 2-CP which is attributed to the oxidation and advanced adsorption (if occurred) of 2-CP during oxidation experiment. In addition, for the same time interval, the 2-CP loss for GAC3 is higher but the H_2O_2 consumption is quite lower than those of the other activated carbons, indicating that GAC3 has the highest activity in catalyzing the pollute, 2-CP, by H_2O_2.

In general, the decomposition of H_2O_2 with activated carbons within a short time interval could be explained by a simple first-order relationship either in the absence or in the presence of 2-CP over a range of GAC concentrations, but the loss of 2-CP was much more complex than anticipated. To evaluate the catalytic ability of the modified activated carbons toward 2-CP degradation, two stoichiometric efficiencies, E_R and E_D, based on the hypothesis that the oxidation of pollutant

Table 2. The effect of modified activated carbons on the adsorption capacity and removal efficiency toward 2-CP.

		GAC1	GAC2	GAC3
Adsorption capacity[a]	Q (mmol/g)	1.57	1.65	0.73
	Q (mmol/m^2)	1.6×10^{-3}	1.61×10^{-3}	1.31×10^{-3}
	pH$_{eq}$	3.8 ± 0.2	3.8 ± 0.2	3.8 ± 0.2
Removal[b]	E_R (mol/mol)	0.011	0.013	0.036
	E_D (mol/mol)	0.0028	0.0045	0.011
	pH$_{eq}$	4.2	3.98	3.4

[a]Adsorption isotherm for 72 h; [2-CP]$_0$ = 1.13 mM; [GAC] = 0.5 g/L; 30°C.
[b]Catalytic oxidation for 96 h; [H$_2$O$_2$]$_0$ = 20 mM; [GAC] = 0.5 g/L; 30°C.
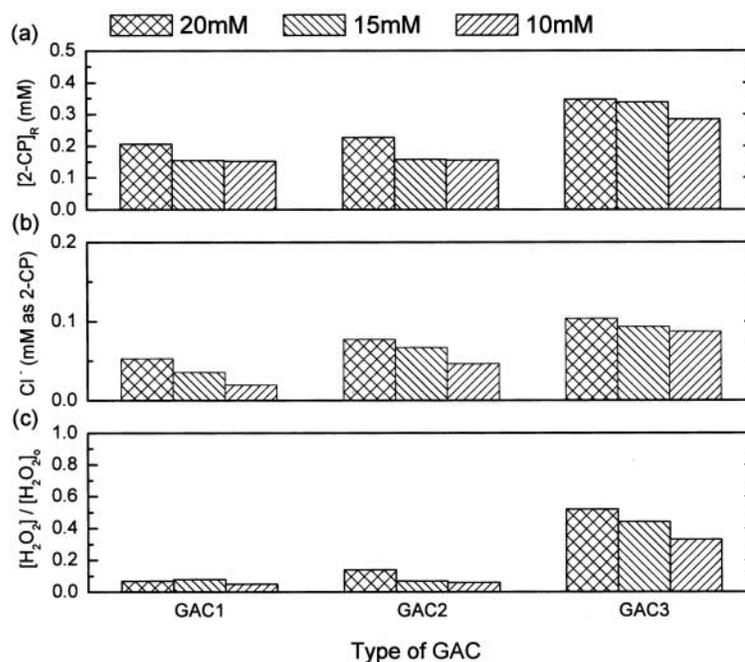
Figure 4. Effect of H_2O_2 concentration on reduction and dechlorination of 2-CP (experimental condition: GAC $= 0.5$ g/L; [2-CP]$_0 = 1.13$ mM; Temp. $= 30°$C).

could be proportional to the decomposition amount of H_2O_2 (3, 4) and the relationship between 2-CP reduction and H_2O_2 concentration observed in our experiments, are defined individually as the ratios of the reduction and dechlorination amount of 2-CP to the decomposition amount of H_2O_2.

$$E_R = \frac{\Delta[\text{2-CP}]_R}{\Delta[\text{H}_2\text{O}_2]} \quad \text{and} \quad E_D = \frac{\Delta[\text{2-CP}]_D}{\Delta[\text{H}_2\text{O}_2]} \tag{3}$$

where the $\Delta[\text{2-CP}]_R$ and $\Delta[\text{2-CP}]_D$ is the loss amount of 2-CP obtained by the detection with the HPLC and chloride analyzer, respectively. The reduction and dechlorination efficiencies of 2-CP with single H_2O_2 dosage for the three activated carbons are shown in Table 2. GAC3 shows the highest catalytic efficiency either in terms of reduction and dechlorination. However, the highest catalytic ability toward H_2O_2 decomposition for GAC1 cannot induce a relative high reduction of 2-CP, resulting in a lower value of catalytic efficiency. Therefore, not only the adsorption capacity but also the catalytic efficiency of 2-CP would be affected significantly by the modification of activated carbons.

In addition, the 2-CP loss could involve both heterogeneous and homogeneous catalytic reaction. To determine the importance of homogeneous reaction, the filtrate samples were aged for one day. No significant homogeneous loss was observed. Therefore, the 2-CP reduction could be attributed mainly to the heterogeneous reaction. The reduction efficiency of 2-CP for GAC3 (i.e., 0.036 mol/mol) offers a

comparable efficiency to those obtained from the other heterogeneous oxidation systems using metal oxide as catalyst. The majority of the reduction efficiency reported earlier for heterogeneous catalytic oxidation of organics by H_2O_2 with iron oxide fell in the range of 10^{-2}–10^{-4} (mol/mol).[1]

Sequential Oxidation Process

To further clarify the relative reactivity of each modified activated carbon, three sequential dosages of H_2O_2 were added into the reaction suspensions. The residual percentages of 2-CP and H_2O_2 in the presence of various activated carbons with three sequential H_2O_2 dosages are shown in Fig. 5. It should be noted that the starting concentration of 2-CP, $[2\text{-CP}]_s$, represents the 2-CP concentration remaining in the solution after the isotherm adsorption experiment. The similar trend of the 2-CP loss is observed as the single H_2O_2 dosage is applied, but the overall rate of 2-CP reduction only increased a little. However, no matter by single or sequential dosages of H_2O_2, GAC3 has the smallest ability in the consumption of H_2O_2.

Figure 6 shows the accumulative reduction of 2-CP as the function of H_2O_2 decomposition with sequential H_2O_2 dosages at various pH conditions. For GAC1 and GAC2, higher values of E_R (i.e., 0.008 and 0.007) at controlled pH ($pH_f \sim 3.3$) is observed than those (i.e., 0.0043 and 0.0046) at uncontrolled pH (pH_f above 4.0). The decrease in E_R at higher pH is mainly caused by an increase in k_{obs} which is due to the stronger binding between H_2O_2 and base sites at higher pH condition as discussed earlier. However, for GAC3, reduction efficiency of 2-CP (i.e., ~ 0.04) is much larger than those of the other activated carbons regardless of the pH condition. This phenomenon implies that the decrease of catalytic activity toward H_2O_2 decomposition (i.e., $k_{1,\text{surface}}$ in Eq. (1)) for the modified activated carbon would also lower the surface activity (i.e., $k_{2,\text{surface}}$) to scavenge the intermediate radicals of H_2O_2, and then induce to increase the collision probability for the effective radicals and 2-CP. As the result, the surface characteristic of activated carbons and pH condition could be considered as the important factors affecting the 2-CP reduction as well as the H_2O_2 concentration.

The relationship between the loss of 2-CP and DOC in suspension is shown in Fig. 7. The amount of dechlorination is much smaller than those of total reduction and DOC, implying that the catalytic oxidation of 2-CP could undergo the reaction pathway via the attack on the ring structure by radicals, not the substitution of chloride (dechlorination). Therefore, the detection of chloride ions cannot be used to represent the total oxidation of 2-CP. Nevertheless, it is unambiguous that the really catalytic oxidation of 2-CP falls in the range between the values of total reduction and dechlorination. In addition, the decrease of DOC is observed to be similar to the total reduction of 2-CP. The decrease of DOC caused from the mineralization could be ignored for the weak catalytic oxidation power toward the dechlorination of 2-CP in this study. As the result, for the three modified activated carbons, the decrease of DOC could be attributed to the advanced adsorption of 2-CP and its oxidation intermediates onto the GAC surface. It was reported that the adsorption capacity of activated carbon toward phenolic compounds would be

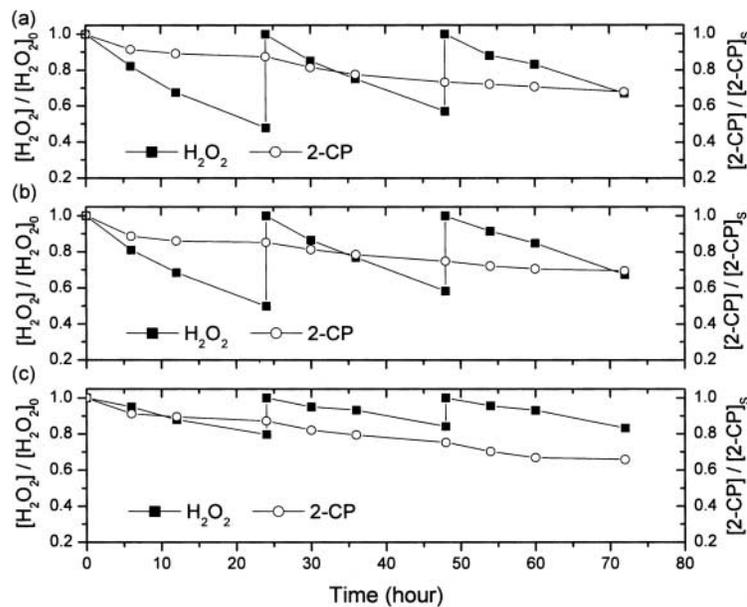**Decomposition of H₂O₂ and 2-CP**   **1243**

Figure 5. Change of 2-CP and H_2O_2 concentrations with three sequential additions of H_2O_2 in presence of activated carbons. (a) GAC1; (b) GAC2; (c) GAC3 (experimental condition: $GAC = 0.5\,g/L$; $[2\text{-}CP]_0 = 1.13\,mM$; $[H_2O_2]_0 = 20\,mM$; Temp. $= 30°C$).
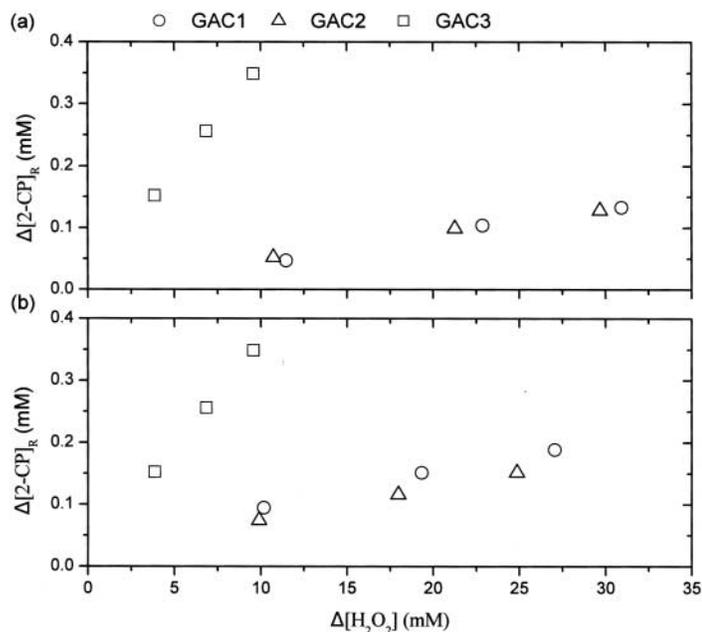

Figure 6. Change of [2-CP] vs. change of [H_2O_2] at various pH conditions. (a) pH uncontrolled; (b) pH controlled at pH 3.5 ± 0.3 (experimental condition: $GAC = 0.5\,g/L$; $[2\text{-}CP]_0 = 1.13\,mM$; $[H_2O_2]_0 = 20\,mM$; Temp. $= 30°C$).
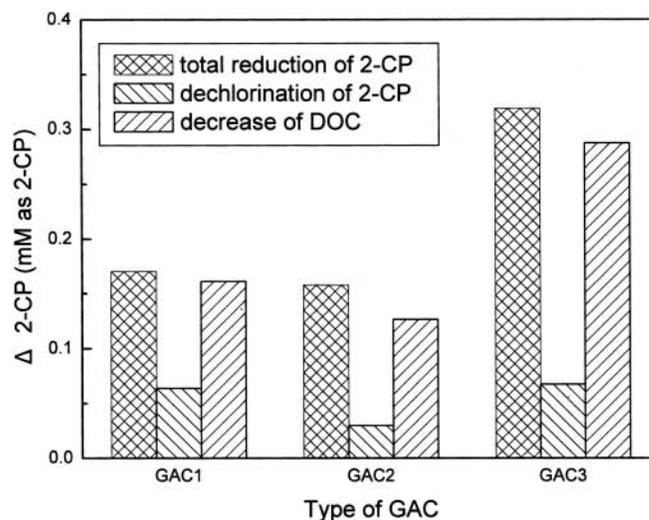
Figure 7. Total change of 2-CP and DOC in presence of activated carbons. (experimental condition: GAC = 0.5 g/L; $[2\text{-CP}]_0 = 1.13$ mM; $[H_2O_2]_0 = 20$ mM; Temp. = 30°C).

enhanced as the adsorption isotherm conducted in an oxic condition, i.e., oxidative coupling adsorption.[16] The oxygen produced from H_2O_2 decomposition in oxidation experiment would increase the adsorption capacity of activated carbon even the really adsorption equilibrium had been achieved in advance. The portion of oxidative coupling adsorption is difficult to be divided; however, from the observation of free chloride, the catalyzed oxidation of 2-CP occurred in this oxidation system. As the result, no matter the reduction of 2-CP is attributed to the oxidative adsorption or catalytic oxidation, the combination of H_2O_2 and GAC has increased the removal amount of 2-CP than that contributed by single GAC adsorption.

CONCLUSION

This work has demonstrated that GAC acts not only as an adsorbent but also a catalyst in promoting H_2O_2 and 2-CP oxidation. Of the various modified treatments carried out, it was observed that hot nitric acid significantly changed the surface properties of activated carbon and, consequently, promoted the catalytic activity toward H_2O_2 decomposition and 2-CP reduction. The acidic functional group on the activated carbon may be considered as the major role in this catalytic oxidation system, which would decrease the catalytic decomposition of H_2O_2 and its intermediates resulting in the increase of reduction efficiency of 2-CP. The reduction efficiency of organics for the activated carbon is comparable to that for iron oxide. The combination of H_2O_2 and GAC did increase the total removal of 2-CP than that by single GAC adsorption, suggesting an attractive alternative for the removal of organic pollutant in wastewater treatment.

ACKNOWLEDGMENT

REFERENCES

1. Huang, H.H.; Lu, M.C.; Chen, J.N. Catalytic decomposition of hydrogen peroxide and 2-chlorophenol with iron oxides. Wat. Res. **2001**, *35* (9), 2291–2299.
2. Lu, M.C.; Chen, J.N.; Huang, H.H. Role of goethite dissolution in the oxidation of 2-chlorophenol with hydrogen peroxide. Chemosphere **2002**, *46* (1), 131–136.
3. Valentine, R.L.; Wang, H.C.A. Iron oxide surface catalyzed oxidation of quinoline by hydrogen peroxide. J. Environ. Eng. **1998**, *124* (1), 31–38.
4. Miller, C.M.; Valentine, R.L. Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material. Wat. Res. **1995**, *29* (10), 2353–2359.
5. Miller, C.M.; Valentine, R.L. Mechanistic studies of surface catalyzed H_2O_2 decomposition and contaminant degradation in the presence of sand. Wat. Res. **1999**, *33* (12), 2805–2816.
6. Chou, S.; Huang, C. Application of a supported iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide. Chemosphere **1999**, *38* (12), 2719–2731.
7. Lucking, F.; Koser, H.; Jank, M.; Ritter, A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. Wat. Res. **1998**, *32* (9), 2607–2614.
8. Francisco, R.R. The role of carbon materials in heterogeneous catalysis. Carbon **1998**, *36* (3), 159–175.
9. Khalil, L.B.; Girgis, B.S.; Tawfik, T.A. Decomposition of H_2O_2 on activated carbon obtained from olive stones. J. Chem. Technol. and Biot. **2001**, *76* (11), 1132–1140.
10. Heisig, C.; Zhang, W.; Oyama, T. Decomposition of ozone using carbon supported metal oxide catalysts. Appl. Catal. B: Environ. **1997**, *14* (1), 117–129.
11. Lin, S.H.; Lai, C.L. Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds. Wat. Res. **2000**, *34* (3), 763–7722.
12. Noh, J.S.; Schwarz, J.A. Estimation of the point of zero charge of simple oxides by mass titration. J. Colloid Interf. Sci. **1989**, *130* (1), 157–164.
13. Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A. Modification of the surface chemistry of activated carbons. Carbon **1999**, *37* (9), 1379–1389.
14. Corapcioglu, M.O.; Huang, C.P. The surface acidity and characterization of some commercial actibated carbons. Carbon **1987**, *25* (4), 569–578.
15. Tessmer, C.H.; Vidic, R.D.; Uranowski, L.J. Impact of oxygen-containing surface functional groups on activated carbon adsorption of phenols. Environ. Sci. Technol. **1997**, *31* (7), 1872–1878.

16. Vidic, R.D.; Suidan, M.T.; Brenner, R.C. Oxidative coupling of phenols on activated carbon: impact on adsorption equilibrium. Environ. Sci. Technol. **1993**, *27* (10), 2079–2085.