Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons

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Abstract

The objective of this research was to examine the heterogeneous catalytic decomposition of H_2O_2 and 4-chlorophenol (4-CP) in the presence of activated carbons modified with chemical pretreatments. The decomposition of H_2O_2 was suppressed significantly by the change of surface properties including the decreased pH_{pzc} modified with oxidizing agent and the reduced active sites occupied by the adsorption of 4-CP. The apparent reaction rate of H_2O_2 decomposition was dominated by the intrinsic reaction rates on the surface of activated carbon rather than the mass transfer rate of H_2O_2 to the solid surface. By the detection of chloride ion in suspension, the reduction of 4-CP was not only attributed to the advanced adsorption but also the degradation of 4-CP. The catalytic activity toward 4-CP for the activated carbon followed the inverse sequence of the activity toward H_2O_2, suggesting that acidic surface functional group could retard the H_2O_2 loss and reduce the effect of surface scavenging resulting in the increase of the 4-CP degradation efficiency. Few effective radicals were expected to react with 4-CP for the strong effect of surface scavenging, which could explain why the degradation rate of 4-CP observed in this study was so slow and the dechlorination efficiency was independent of the 4-CP concentration in aqueous phase. Results show that the combination of H_2O_2 and granular activated carbon (GAC) did increase the total removal of 4-CP than that by single GAC adsorption.
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Keywords: Granular activated carbon; Hydrogen peroxide; 4-Chlorophenol; Heterogeneous catalysis

1. 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 (Ravikumar and Gurol, 1994; Kong et al., 1998; Lu et al., 2002). However the disadvantage of Fenton's reagent is that the homogeneous catalyst cannot be retained in the process thus causing additional water pollution. A number of researchers (Valentine and Wang, 1998; Miller and Valentine, 1999) with attempt to minimize the leaching of iron ion focused on the efficiency of heterogeneous catalysis for pollutant oxidation. Recently, considering the practical application of the oxidation process, supported iron oxides or granular size solid catalysts, such as graphite and activated carbon, were also studied for their catalytic characteristics (Lucking et al., 1998; Chou and Huang, 1999). In addition, the potential for applying H_2O_2 to Fenton-like water treatment is primarily restricted to the supply and stability of H_2O_2. Therefore, understanding the fate of H_2O_2 is still an important topic (Lin and Gurol, 1998; Huang et al., 2001).

Granular activated carbon (GAC), used as a catalyst as well as adsorbent in this study, has been applied for a

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Nomenclature

C_H	H$_2$O$_2$ concentration in bulk solution (mM)
DOC	dissolved organic carbon
d_p	diameter of particle (cm)
E	stoichiometric efficiency; E_R is the ratio for 4-CP reduction (loss) to H$_2$O$_2$ decomposition; E_D is the ratio for 4-CP dechlorination to the H$_2$O$_2$ decomposition
GAC	granular activated carbon
k	rate constant
k_c	mass transfer coefficient (cm/s)
k_{mass}	(observed rate constant)/(catalyst mass per unit volume of solution)
k_{suf}	(observed rate constant)/(catalyst total surface area per unit volume of solution)
k_H	equilibrium binding constant (mM^{-1})
m	catalyst dosage (g/cm^3)
pH$_{pzc}$	point of zero charge
pH$_f$	pH at the end of reaction
Q	adsorption capacity
R_H	decomposition rate of H$_2$O$_2$ (mM/time); R_{Hi} for initial decomposition rate
ρ_p	particle density (g/cm^3)
[]	concentration of solute in aqueous phase (mM); []$_0$ denotes initial concentration; [4-CP]$_S$ is 4-CP concentration remaining in solution after isotherm adsorption

long time in the heterogeneous catalysis and adsorption for its enormous surface area, porous structure and characteristic flexibility (Francisco, 1998). A number of studies have been carried out on the interaction of oxidizing agents (e.g. H$_2$O$_2$ or O$_3$) with carbon and carbon-supported materials (Heisig et al., 1997; Khalil et al., 2001). These investigations were not only concerned with the factors affecting the catalytic rate, but also directed toward applying this type of reaction for practical purposes, especially in environmental impacts. Recent studies (Lucking et al., 1998; Lin and Lai, 2000) indicated that surface catalyzed reaction of GAC induced by oxidizing agent may lead to contaminant decay in aqueous 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 H$_2$O$_2$ and contaminants with GAC deserves further investigation.

In this study, we examined and compared the surface catalyzed transformation of the model pollutant, 4-chlorophenol (4-CP), by H$_2$O$_2$ in the presence of GAC with different surface properties modified by various chemical processes. The factors including H$_2$O$_2$ concentration, GAC dosage, and GAC types affecting the decomposition behavior of H$_2$O$_2$ and 4-CP are discussed.

2. Material and methods

The activated carbon was Filtrasorb-300 GAC 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. GAC2 and GAC3 were the products of GAC1 which was oxidized with concentrated H$_2$O$_2$ (1000 mg GAC1 in 10 ml, 9.8 M H$_2$O$_2$) and HNO$_3$ (1000 mg 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 were treated with diluted HCl solution (1000 mg GAC in 10 ml, 1 N HCl) for 24 h to reduce the metal ions contained in GAC. After the treatment, all the activated carbons were washed with deionized water several times until the pH of the supernatant was constant. In addition, the GAC treated with diluted HCl was washed with boiling deionized water twice more to minimize the interference of chloride ions desorbed from GAC during the oxidation experiment. All GAC were dried in an oven at 50 °C for preservation. Specific surface area and average pore diameter were calculated by N$_2$-BET meter (Micromeritics ASAP 2000). The value of pH$_{pzc}$ was measured by the mass titration method (Noh and Schwarz, 1989). Table 1 lists the properties of the activated carbons. The specific surface area increased slightly after the treatment with concentrated H$_2$O$_2$ but decreased significantly by the heating

Table 1
Characteristics of the activated carbons

Parameters	GAC1	GAC2	GAC3
Specific surface area (m^2/g)	983	1023	556
Average pore size (Å)	17.1	17.0	18.1
Micropore volume (cm^3/g)	0.28	0.26	0.11
pH$_{pzc}$	4.2[a]	3.5[a]	3.2

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

treatment of concentrated HNO_3. This is due to the strong corrosive character of HNO_3 which makes the pore walls thinner resulting in widening of the microporosity and consequently diminishing of the BET value. In addition, the general range of pH_{pzc} for F-300 is 9.8–10.2. Therefore, the washing and chemical treatment has affected the surface acidity of activated carbon significantly.

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 kinetics of H_2O_2 decomposition was studied by examining the variables such as the concentration of H_2O_2 and GAC. The reactor was prepared by filling proper amount of GAC and adjusted to the desired pH value several times (equilibrium for one day); the reaction mixture was 150 ml; the reaction was initiated by the addition of H_2O_2. The range of the pH variance in the H_2O_2 decomposition experiment was less than unit. In the oxidation experiment of 4-CP, the reactor was prepared by introducing the proper amount of 4-CP and GAC; the reaction mixture was 200 ml. The adsorption equilibrium of the solution (GAC and 4-CP) was to be achieved for at last three days prior to the oxidation experiment. 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_2O_2 concentration was quantified by the peroxytitanic acid method with the addition of $Ti(SO_4)_2$ test solution (Schumb et al., 1955). Residual 4-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 pH340/ion meter).

3. Results and discussion

3.1. Hydrogen peroxide decomposition

3.1.1. Comparison of modified activated carbons

The decomposition of H_2O_2 with GAC in the presence and absence of 4-CP is shown in Fig. 1. The reaction behavior followed a first-order rate expression with respect to H_2O_2 concentration, which is consistent with the observation of the previous research (Khalil et al., 2001). The decomposition of H_2O_2 with the activated carbon of which surface has been saturated with 4-CP in advance is still found to follow a first-order reaction. However, the decomposition rate was reduced largely in comparison with that in the absence of 4-CP. This is attributed to the 4-CP adsorption which reduces the surface active sites available for the H_2O_2. Lucking et al.
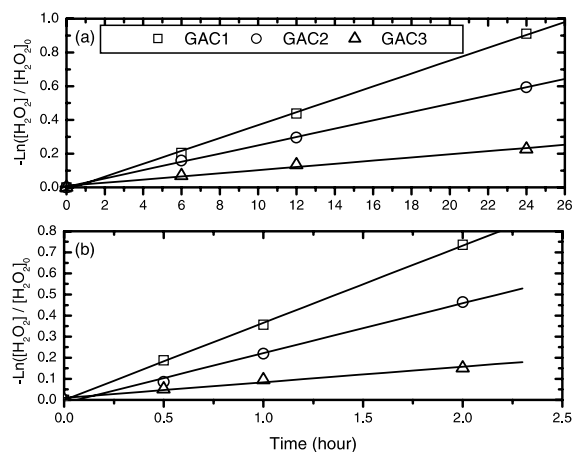

Fig. 1. Change of H_2O_2 concentration in presence and absence of 4-CP (a) 500 mg/l GAC with addition of 4-CP; (b) 1000 mg/l GAC without 4-CP ($[H_2O_2]_0$, 20 mM; temperature, 30 °C; ionic strength, 50 mM $NaClO_4$).

(1998) reported the similar results in their adsorption/oxidation system using GAC as catalyst. But, slight influence of organics adsorption on H_2O_2 decomposition was observed in the previous researches using iron oxide as catalyst. Those were due to the low affinity of organics with the metal oxide surface (Valentine and Wang, 1998; Huang et al., 2001).

A comparison of catalytic activity toward H_2O_2 decomposition for the activated carbons is shown in Table 2. The k_{mass} and k_{suf} are the first-order decomposition rate coefficients modified on the basis of the mass and total surface area of catalyst per unit volume of reaction mixture, respectively (Valentine and Wang, 1998). Apparently, no matter the observed rate constant is modified with mass or surface area basis, the catalytic activity toward H_2O_2 decomposition is the highest for GAC1 and the least for GAC3 either in the presence or absence of 4-CP. In the majority of previous studies, H_2O_2 decomposition with activated carbon is considered to depend mainly on carbon porosity, slurry pH, and chemical properties of the surface (Khalil et al., 2001). Regarding the effect of porosity on the extent of H_2O_2 decomposition, the difference of micropore volume and pore size between GAC1 and GAC2 (Table 1) is insignificant; moreover, the effect of pore diffusion (i.e. reaction rate reduced by pore diffusion) for GAC3 with larger pore size is expected to be less than those for GAC1 and GAC2. This indicates that the effect of porosity on H_2O_2 decomposition for the three activated carbons is not the major factor. Although the H_2O_2 decomposition is dependent generally on the pH of the carbon slurry, the values of pH_f, pH at the end of the reaction, for the reaction mixtures containing GAC1 and GAC2 were controlled at the similar range from 6.8 to 7.2. This signifies that the variance of rate constant in

Table 2
The rate constant of k_{mass}, k_{suf} in the presence and absence of 4-CP

Catalyst type	k_{mass}[a]	k_{suf}[a]	pH_f[a]	k_{mass}[b]	pH_f[b]
GAC1	6.71×10^{-6}	6.83×10^{-6}	~7.0[c]	1.27×10^{-3}	~4.5
GAC2	4.87×10^{-6}	4.76×10^{-6}	~7.0[c]	8.21×10^{-4}	~4.3
GAC3	1.17×10^{-6}	2.12×10^{-6}	~3.9	3.33×10^{-4}	~3.5

k_{mass}: $min^{-1}(mg/l)^{-1}$; k_{suf}: $min^{-1}(m^2/l)^{-1}$.
[a] In the absence of 4-CP.
[b] In the presence of 4-CP; $[H_2O_2]_0 = 20$ mM; catalyst dosage = 1000 mg/l.
[c] With pH control; $[H_2O_2]_0 = 5$ mM; catalyst dosage = 500 mg/l.

such an oxidation system is attributed not only to the medium pH but also the surface characteristic of GAC. Additional experiments without pH adjustment also show the same decline trend of catalytic activity toward H_2O_2 decomposition with the decreased pH_{pzc} of the activated carbons. It was reported that acidic oxygen surface complexes (e.g. carboxylic, phenolic, and lactonic groups) would be introduced predominantly onto activated carbons when they were treated with oxidizing agents such as H_2O_2 and HNO_3 (Castilla et al., 1995; Figueiredo et al., 1999). Therefore, the lower pH_{pzc} of the modified activated carbon shown in Table 1 is probably due to the formation of acidic function groups on the surface.

It has been widely suggested that catalytic decomposition of H_2O_2 by activated carbon could be initiated by the exchange of a hydroxyl group with a hydrogen peroxide anion as shown below (Khalil et al., 2001),

$$\text{Carbon-surface)C}\frac{H^+}{H}O \cdots OH^- + H^+OOH^-$$
$$\rightarrow)C\frac{H^+}{H}O \cdots OOH^- + H_2O \qquad (1)$$
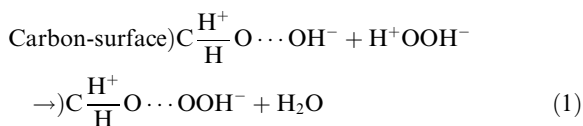
H_2O_2, meanwhile, can be thought as a weak acid ($pK_a = 11.6$) to proceed its dissociation to H^+ and OOH^-. The OOH^- anion, much less stable than H_2O_2 itself, decomposed readily. From the assumptions, it is reasonable to predict that the dissociation of H_2O_2 will be enhanced in alkaline medium. As the result, the acidic function groups of GAC2 and GAC3 treated with H_2O_2 and HNO_3 would retard the combination and dissociation of H_2O_2 resulting in suppressing the H_2O_2 decomposition rate considerably. Our results confirm again that the surface chemical nature of the GAC modified with oxidizing agent is the major factor in governing the catalytic action of GAC on H_2O_2 decomposition.

3.1.2. Decomposition kinetics

The decomposition behavior was clarified with the consideration of the effect of H_2O_2 concentration and catalyst dosage. Consistent with general observation on the heterogeneous catalytic decomposition of H_2O_2 (Lin and Gurol, 1998; Huang et al., 2001), the experiments conducted with various catalyst dosages establish a linear relationship between the observed first-order rate constant and the mass of activated carbon. However, the observed rate constants of H_2O_2 decomposition conducted with various initial H_2O_2 concentrations ($[H_2O_2]_0$: from 4 to 30 mM) in the presence of GAC were found to decline with the increasing $[H_2O_2]_0$. The phenomenon seems different from other studies using metal oxides as the catalyst (Lin and Gurol, 1998; Huang et al., 2001) in which observed rate constant was independent of the $[H_2O_2]_0$. To analyze the catalytic kinetics of H_2O_2 decomposition, a modified Langmuir–Hinshelwood (L–H) rate model with the consideration of catalyst dosage is used to approach the experimental data conducted with various $[H_2O_2]_0$. The rate model is described as

$$R_H = -\frac{d[H_2O_2]}{dt} = \frac{k[\text{catalyst}][H_2O_2]}{1 + k_H[H_2O_2]} \qquad (2)$$

where k_H and k are the binding and rate constant, respectively. The inverse initial decomposition rate of H_2O_2 (R_{Hi}) versus $[H_2O_2]_0$ is plotted in Fig. 2. In this
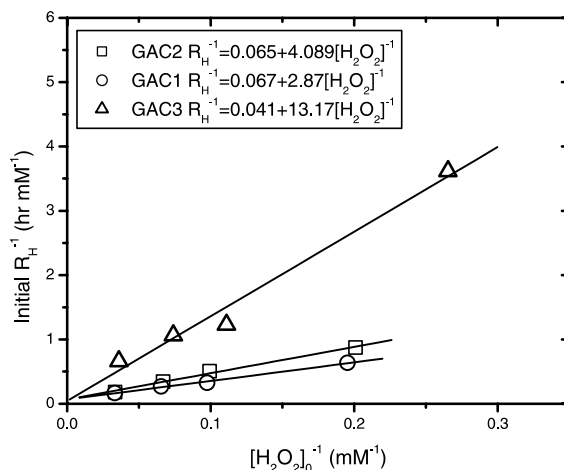
Fig. 2. Reciprocal of initial rate versus reciprocal of initial H_2O_2 concentration (GAC, 1000 mg/l; temperature, 30 °C; ionic strength, 50 mM $NaClO_4$).

Table 3
The parameters of k and k_H in L–H model

Catalyst type	k (min^{-1})	k_H (mM^{-1})	pH$_f$
GAC1[a]	5.93×10^{-3}	2.33×10^{-2}	~7.0
GAC2[a]	4.11×10^{-3}	1.71×10^{-2}	~7.0
GAC3	1.25×10^{-3}	0.31×10^{-2}	~3.9

[a] With pH control;[H$_2$O$_2$]$_0$ = 4–30 mM; catalyst dosage = 1000 mg/l.

figure, the reciprocal of the R_{Hi} is directly proportional to the reciprocal of the [H$_2$O$_2$]$_0$ ($R^2 > 0.98$). Hence, it can be concluded that the reaction behavior of H$_2$O$_2$ decomposition with the GAC can be well described by the modified L–H model. L–H kinetic rate model has been used empirically to describe many heterogeneous catalytic surface reactions (Lin and Gurol, 1998). From the intercept and the slope of the regression line, the initial rate constant k and binding constant k_H are listed in Table 3. The rate constants obtained from the L–H model are found to be a little less than but still similar to the values of k_{mass} shown in Table 2, indicating that the rate model could be simplified as a second-order rate expression with respect to the H$_2$O$_2$ concentration and catalyst dosage when the products of k_H and [H$_2$O$_2$] in the denominator are much smaller than unity. In addition, the binding constant k_H also follows the increased sequence of the catalytic activity for the activated carbons, implying the catalytic activity is dependent on the accessibility between the surface function groups and reactants. From the above discussion, it seems plausible that the surface phenomenon rather than mass transfer is the major factor, and the surface reaction is likely to control the overall reaction rate for the heterogeneous decomposition of H$_2$O$_2$ with GAC. In general, the apparent rate of a heterogeneous reaction is dominated by either the rate of intrinsic reaction on the surface or the diffusion rate of the reactant to the surface. The comparison of total molar flux can be used as a simple method to determine whether the film resistance or the surface reaction is the rate-controlling step. The maximum observed rate constant toward H$_2$O$_2$ decomposition for GAC1 is obtained as 1.19×10^{-4} s^{-1}. Hence, the product (i.e. R_H) of maximum rate constant and H$_2$O$_2$ concentration (e.g. 5 mM) is 5.95×10^{-4} mM s^{-1}. If the overall reaction rate were completely controlled by mass transfer, the surface concentration of the reactant would approach zero and the observed reaction rate could be calculated by the simplified rate equation (Satterfield, 1981)

$$R_H = \frac{6 m k_c C_H}{\rho_p d_p} \tag{3}$$

where k_c is mass transfer coefficient and can be estimated as 0.01 cm/s which is a typical value in agitated water

system, m is the catalyst dosage (g/cm^3), ρ_p is the particle density, and d_p is the particle diameter. Therefore, the observed rate estimated by Eq. (3) with the same H$_2$O$_2$ concentration (C$_H$ = 5 mM) for GAC1 is 5.8×10^{-3} mM s^{-1}. This is about 10 times the fastest rate observed in our experiment, indicating that the H$_2$O$_2$ concentration gradient between bulk liquid and catalyst outside surface, i.e. film resistance, could be neglected in this system. As the result, it is concluded that the catalytic reaction of H$_2$O$_2$ decomposition follows the L–H rate model; meanwhile, surface reaction is the rate-controlling step for the overall catalytic reaction.

3.2. Chlorophenol oxidation

3.2.1. Comparison of modified activated carbons

The decomposition of H$_2$O$_2$ could be described with a simple first-order rate expression either in the absence or in the presence of organics over the GAC. The experiment of 4-CP oxidation was conducted with the modified GAC. To exclude the competing adsorption of 4-CP which makes it difficult to differentiate the effect of adsorption and heterogeneous catalysis on the removal of 4-CP, the adsorption equilibrium of the solution is required prior to the oxidation experiment. The adsorption capacity of GAC obtained from the adsorption isotherm is listed in Table 4, indicating that the adsorption property of GAC is affected by the modified surface property. Acidic oxygen-containing surface functional groups were found to affect the adsorptive properties of activated carbons, and decrease the chemisorption of phenols (Tessmer et al., 1997).

Based on the mechanisms for the catalytic oxidation of contaminant by H$_2$O$_2$ proposed in the literatures (Miller and Valentine, 1995; Valentine and Wang, 1998), the oxidation loss of model pollutant, 4-CP, could be hypothesized to be proportional to the decomposition amount of H$_2$O$_2$. The stoichiometric efficiencies, E_R and E_D, are defined individually as the ratios of the reduction and dechlorination amount of 4-CP to the decomposition amount of H$_2$O$_2$.

$$E_R = \frac{\Delta[\text{4-CP}]_R}{\Delta[\text{H}_2\text{O}_2]} \quad \text{and} \quad E_D = \frac{\Delta[\text{4-CP}]_D}{\Delta[\text{H}_2\text{O}_2]} \tag{4}$$

where the Δ[4-CP]$_R$ and Δ[4-CP]$_D$ are the amount of 4-CP lost which are detected by HPLC and chloride analyzer, respectively. It should be emphasized that the term, reduction, in this study represents the loss of 4-CP attributed to the degradation and advanced adsorption (if occurred) of 4-CP during oxidation experiment.

The results of the preliminary experiments conducted with different H$_2$O$_2$ concentrations in the presence of GAC revealed a general trend that the degradation of 4-CP increased with the increase of H$_2$O$_2$ concentration (data not shown here). The values of catalytic efficiencies

Table 4
The effect of modified activated carbons on the adsorption capacity and removal efficiency toward 4-CP

		GAC1	GAC2	GAC3
Adsorption capacity[a]	Q (mmol/g)	1.66	1.61	0.77
	pH_f	5.7	4.7	3.8
Reduction[b]	E_R (mmol/mmol)	0.49×10^{-2}	0.63×10^{-2}	0.28×10^{-1}
	E_D (mmol/mmol)	0.41×10^{-2}	0.37×10^{-2}	0.12×10^{-1}
	pH_f	5.2	4.3	3.6

[a] Adsorption isotherm for 72 h, $[4\text{-}CP]_0 = 1.13$ mM; catalyst dosage = 500 mg/l; 30 °C.
[b] Catalytic oxidation for 24 h, $[H_2O_2]_0 = 20$ mM; catalyst dosage = 500 mg/l; 30 °C.

for the three activated carbons with the addition of 20 mM H_2O_2 are shown in Table 4. 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 loss of 4-CP, resulting in a lower value of catalytic efficiency. Therefore, not only the adsorption capacity but also the catalytic efficiency of 4-CP would be affected significantly by the modification of GAC. The reduction and dechlorination efficiency for GAC3 is 0.028 and 0.012 (mol/mol). This offers a comparable efficiency to those obtained from the other heterogeneous oxidation systems using metal oxides as catalyst. The majority of the stoichiometric efficiency reported earlier for catalytic oxidation of organics by H_2O_2 with iron oxide fell in the range of $10^{-2} \sim 10^{-4}$ (mol/mol) (Huang et al., 2001).

In addition, the loss of 4-CP could involve both heterogeneous and homogeneous catalytic reactions. Lucking et al. (1998) investigated the catalytic role of various activated carbons, certain amount of dissolved iron ion was observed to enhance the oxidation rate of 4-CP in the reaction volume during the oxidation experiment. To determine the importance of homogeneous reaction, the filtrate samples were aged for 24 h and the 4-CP concentration was monitored. No significant homogeneous loss was observed, which is attributed to the pretreatment of the GAC by strong acidic solution.

3.2.2. Sequential oxidation process

To further clarify the relative reactivity of each modified GAC, three sequential dosages of H_2O_2 were added into the reaction suspensions. The reduction of 4-CP and H_2O_2 concentration in the presence of GAC is shown in Fig. 3. It should be noted that the starting concentration of 4-CP, $[4\text{-}CP]_S$, represents the 4-CP concentration remaining in the solution after the isotherm adsorption experiment. The effect of starting 4-CP concentration on catalytic efficiency will be discussed later. The overall reduction of 4-CP is obviously higher than that with the single dosage of H_2O_2, indicating that the loss of 4-CP increases with the increase of H_2O_2 decomposition. This is coincident with the hypothesis suggested by Miller and Valentine (1995) mentioned
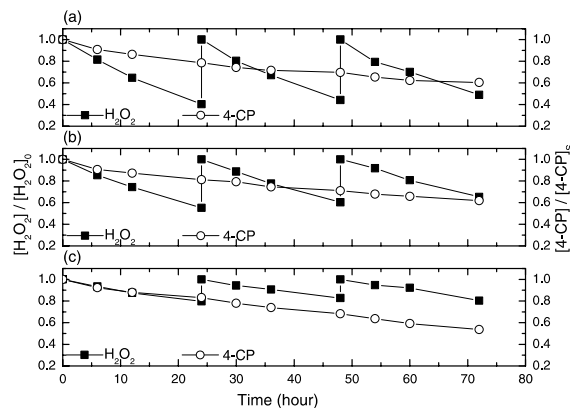

Fig. 3. Change of 4-CP and H_2O_2 concentrations with three sequential additions of 20 mM H_2O_2 in presence of activated carbons (GAC, 500 mg/l; $[H_2O_2]_0$, 20 mM; temperature, 30 °C; ionic strength, 50 mM $NaClO_4$).

earlier. It is shown that the higher reduction of 52% occurred with GAC3, and similar loss of 40% occurred in the presence of GAC1 and GAC2. However, an inverse trend of H_2O_2 decomposition is observed; the smallest loss of H_2O_2 for GAC3, a medium loss for GAC2, and the largest decomposition of H_2O_2 occurred with GAC1. As the result, the surface characteristic of activated carbons could be considered as the major factor affecting the 4-CP degradation as well as the H_2O_2 decomposition discussed earlier. Fig. 4 shows the accumulative reduction and dechlorination of 4-CP as the function of H_2O_2 decomposition for the sequential H_2O_2 dosage in the presence of GAC. The trend of dechlorination of 4-CP is observed being similar to that of reduction but the efficiency of dechlorination (i.e. E_D) is general one-third of that of reduction (i.e. E_R). This phenomenon could be attributed to the uptake of chloride ion which decreases the real dechlorination amount of 4-CP. Chloride ion could form an outer-sphere complex outside the surface of the metal oxide (Stumm, 1992). As the result, the detection of chloride ion can not represent the total degradation of 4-CP. Nevertheless, it is apparent that the real catalytic efficiency of 4-CP falls in the range between the observed values of reduction and dechlorination.
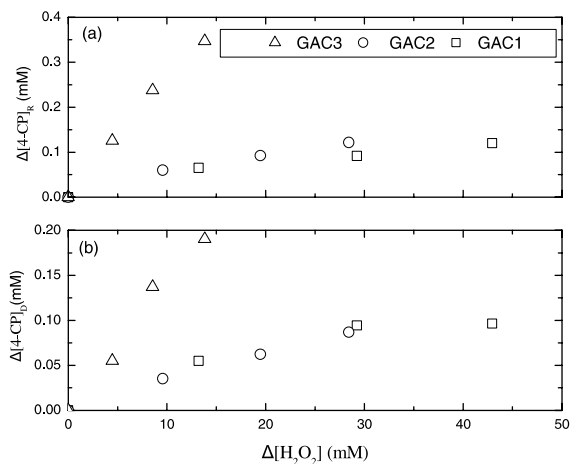
Fig. 4. Relationship between loss of 4-CP and decomposition of H_2O_2 in presence of activated carbons (a) reduction; (b) dechlorination (GAC, 500 mg/l; $[H_2O_2]_0$, 20 mM; temperature, 30 °C; ionic strength, 50 mM $NaClO_4$).

Substances that adsorbed to aquifer sand surface could affect the degradation of H_2O_2 and organics (Miller and Valentine, 1995; Valentine and Wang, 1998). To examine the role of adsorption in the oxidation experiment, the relationship between the total reduction of 4-CP and DOC (dissolved organic carbon) in suspension is shown in Fig. 5. The decrease of DOC could be attributed to the advanced adsorption of 4-CP and its oxidation intermediates. The loss of DOC caused from the mineralization could be ignored for the weak catalytic activity toward the destruction of 4-CP in this system. For GAC1 and GAC2, the decrease of DOC is
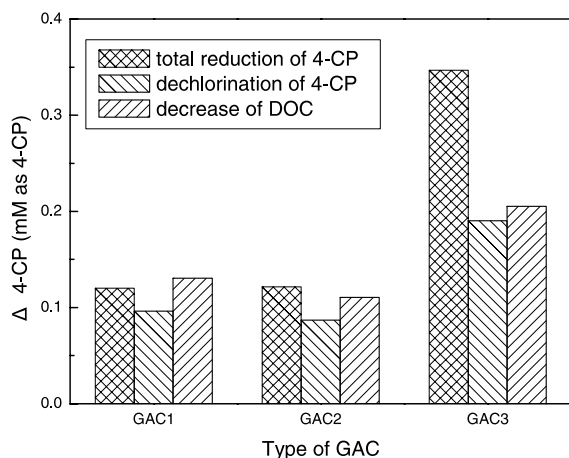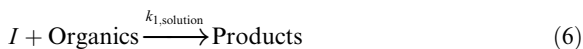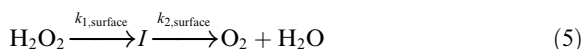

Fig. 5. Total change of 4-CP and DOC in presence of activated carbons (GAC, 500 mg/l; $[H_2O_2]_0$, 20 mM; temperature, 30 °C; ionic strength, 50 mM $NaClO_4$).

similar to the total reduction of 4-CP, indicating that 4-CP and its oxidation intermediates are almost adsorbed further onto GAC surface. However, GAC3 shows a stronger catalytic activity but weaker adsorption capacity toward 4-CP and its oxidation intermediates. The adsorption capacity of activated carbon toward phenolic compounds would be enhanced as the adsorption isotherm conducted in an oxic condition, i.e. oxidative coupling adsorption (Vidic et al., 1993). Therefore, the oxygen produced from H_2O_2 decomposition in oxidation experiment would increase the adsorption capacity of activated carbon even the real adsorption equilibrium had been achieved. The portion of adsorption caused from different substances is difficult to be divided. However, for the data of GAC3, even the decrease of DOC is entirely contributed from the oxidative-coupling adsorption, the total reduction of 4-CP is still much larger than that of DOC, indicating that the catalyzed degradation of 4-CP did occur in this system. In addition, no matter the reduction of 4-CP is attributed to the oxidative adsorption or catalytic oxidation, the combination of H_2O_2 and GAC has increased the reduction of 4-CP than that contributed by single GAC adsorption.

To explain why the three modified activated carbons exhibited different catalytic activity toward 4-CP oxidation, a general simplified mechanism proposed to describe the catalyzed organics with H_2O_2 is quoted as (Miller and Valentine, 1995)

$$H_2O_2 \xrightarrow{k_{1,surface}} I \xrightarrow{k_{2,surface}} O_2 + H_2O \qquad (5)$$

$$I + \text{Organics} \xrightarrow{k_{1,solution}} \text{Products} \qquad (6)$$

where I is intermediate (e.g. ·OH or O_2^-) produced from the reaction of H_2O_2 with catalyst surface, $k_{1,surface}$ and $k_{2,surface}$ are the surface rate constants, and $k_{3,solution}$ is the rate constant in the reaction solution. In this study, the catalytic activity toward 4-CP loss is corresponded to the inverse sequence of that toward H_2O_2 decomposition for the three activated carbons. This phenomenon implies that the decrease of catalytic activity available for H_2O_2 (i.e. $k_{1,surface}$) by the oxidizing treatment would also reduce the surface activity ($k_{2,surface}$) to scavenge the intermediates of H_2O_2, and then induce to increase the collision probability for the effective radicals and organics (e.g. 4-CP). As discussed in H_2O_2 decomposition earlier, it could be concluded that the acidic functional groups would decrease the catalytic activity toward H_2O_2 and its intermediates but increase the degradation efficiency of 4-CP. Miller and Valentine (1995) found that the modified aquifer sand by acid-hydroxylamine decreased the rate of H_2O_2 decay while increased the degradation efficiency of quinoline significantly. Lin and Lai (2000) suggested an adsorption/ozonation mechanism that the destruction of organic was not only due to

Table 5
The comparison of dechlorination efficiency for each sequential H_2O_2 dosage

Parameter	GAC1 (20 mM)	GAC2 (20 mM)	GAC3 (20 mM)	GAC3 (15 mM)	GAC3 (10 mM)
E_{D1} ($\times 10^2$)	0.38	0.35	1.26	1.11	1.29
E_{D2} ($\times 10^2$)	0.32	0.32	1.65	1.11	1.06
E_{D3} ($\times 10^2$)	0.24	0.32	1.41	2.59	2.09
Average ($\times 10^2$)	0.31	0.33	1.44	1.60	1.47
pH range	5.6–3.9	4.9–3.6	3.9–3.3	3.8–3.2	3.9–3.4

Catalyst dosage = 500 mg/l; $E_{D1,2,3}$ is the ratio of 4-CP loss to H_2O_2 loss in each H_2O_2 dosage.

the direct ozonation but also the adsorbed pollutant oxidized catalytically on GAC surface.

Some additional results conducted with various activated carbons and H_2O_2 concentrations are shown in Table 5. A similar average efficiency for the different addition of H_2O_2 concentrations (10–20 mM) is observed, indicating that the degradation efficiency of 4-CP is independent of the H_2O_2 concentration for the same starting 4-CP concentration. Furthermore, according to the mechanism (Eq. (6)), it is plausible that the degradation efficiency of 4-CP should be the function of 4-CP concentration. If the 4-CP concentration in aqueous phase would affect the degradation efficiency, the decrease of efficiency should occur because of the decrease in 4-CP concentration at the time of each H_2O_2 addition during oxidation experiment. No obvious declining trend of dechlorination efficiency (i.e. $E_{D1,2,3}$) is observed for each H_2O_2 dosage in Table 5. The effect of pH should be taken into consideration. The variance of pH in oxidation experiment for GAC1 and GAC2 is larger than unit which could affect the degradation efficiency. However, with a small variance of pH, the effect of pH on degradation efficiency could be ignored in the presence of GAC3. Therefore, it could be concluded that the degradation efficiency toward 4-CP for GAC3 is independent of 4-CP amount remaining in aqueous phase. This unexpected result could be attributed to the excess concentration of 4-CP in comparison with the relative small amount of effective radicals which is consistent with the low oxidation rate of 4-CP observed in this study.

4. Conclusions

The modified surface property of the GAC by oxidizing agent indeed affect not only the decomposition of H_2O_2 but also the oxidation of 4-CP significantly. The catalytic activity toward H_2O_2 follows an increased sequence of pH_{pzc} for the three activated carbons. The decomposition kinetics of H_2O_2 over GAC can be well described by the L–H rate model. The rate constant increases with the increase of equilibrium constant (k_H), indicating the binding of H_2O_2 on the surface of catalyst could be an important factor on H_2O_2 decomposition.

In comparison with the mass transfer rate, the reaction rate of H_2O_2 decomposition is mainly dominated by the surface reaction. The acidic functional group may play a major role in this catalytic oxidation system, which would decrease the catalytic activity toward H_2O_2 and its intermediates inducing the increase of the 4-CP degradation efficiency. The degradation efficiency of 4-CP is independent of the initial H_2O_2 concentration, but the amount of 4-CP lost is proportional to the decomposition of H_2O_2. The efficiency relating 4-CP loss and H_2O_2 decay is independent of 4-CP concentration, which could be attributed to the small amount of effective radicals. The degradation efficiency of 4-CP for the modified activated carbon is comparable to those of the other oxidation systems using metal oxides as catalyst, suggesting an attractive alternative for the removal of organic pollutant in wastewater treatment.

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