



## CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE AND 2-CHLOROPHENOL WITH IRON OXIDES

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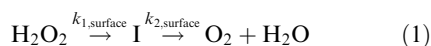
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**Abstract**—The aim of this study was to examine the catalyzed decomposition of hydrogen peroxide and 2-chlorophenol (2-CP) in the presence of iron oxides. Granular ferrihydrite, goethite, and hematite were selected as catalysts in this study. 2-CP was used as the model compound because it is a typical toxic compound and has not been investigated in the catalytic decomposition by iron oxides. The catalytic activity for hydrogen peroxide decomposition followed the sequence: granular ferrihydrite > goethite > hematite. However, hematite exhibited the highest activity in catalyzing 2-CP oxidation. The oxidation efficiency of 2-CP corresponded with the inverse sequence of specific area and  $pH_{pzc}$  of the iron oxides. The catalytic activity of granular ferrihydrite was affected significantly by the mixing speed and particle size for its large value of Thiele modulus ( $\varphi$ ) and Damkohler number (Da). The strong diffusion resistance for granular ferrihydrite was attributed either to its microporous structure or to the formation of oxygen in the pores of the iron oxide leading to the unexpected catalytic activity of granular ferrihydrite to hydrogen peroxide and 2-CP. © 2001 Elsevier Science Ltd. All rights reserved

**Key words**—hydrogen peroxide, iron oxides, heterogeneous catalysis, Fenton-like reaction, 2-chlorophenol, diffusion

### INTRODUCTION

The application of Fenton-like chemical oxidation process for remediation of contaminated soils and groundwater has gained more attention in recent years. Several studies observed that various organic contaminants in water or soil could be oxidized by hydrogen peroxide in the presence of iron oxide mineral (Ravikumar and Gurol, 1994; Kong *et al.*, 1998, Valentine and Wang, 1998). These investigators indicated that the catalytic efficiency for the decomposition of hydrogen peroxide and target pollutants would depend on the specific characteristics of the iron oxides. Miller and Valentine (1995) adapted the model proposed by Ono *et al.* (1977) to describe the oxidation of organic contaminants in the presence of aquifer sand. They suggested a mechanism including intermediate radicals from hydrogen peroxide and scavenging reaction shown as follows:



where I are intermediates (e.g.  $\cdot OH$  or  $O_2^-$ ),  $k_{1,surface}$  and  $k_{2,surface}$  are rate constants onto the iron oxide surface, and  $k_{3,solution}$  in the reaction solution. A number of earlier literatures have reported the decomposition of hydrogen peroxide over heterogeneous catalyst, such as the noble and transition metal, namely Ag, Cu, Fe, Mn, Ni, and Pt and their oxides on supported silica, alumina, and zeolites (Kitajima *et al.*, 1978; Krutikov *et al.*, 1984). Recently, Kakarla and Watts (1997) suggested that injection of hydrogen oxide or the use of *ex situ* slurry reactors may provide a more economical design for highly reactive, impermeable soils. Lin and Gurol (1998) proposed a new hydrogen peroxide decomposition mechanism that was similar to the classical Langmuir–Hinshelwood rate model, and could be modified as

$$R_H = -\frac{d[H_2O_2]}{dt} = \frac{k[FeOOH][H_2O_2]}{1 + k_H[H_2O_2]} \quad (3)$$

where  $k_H$  and  $k$  are the binding and rate constant, respectively. When  $k_H[H_2O_2] \ll 1$ , equation (3) could be reduced to a second-order kinetic expression shown as follows:

$$R_H = k_{mass}[FeOOH][H_2O_2] = k_{obs}[H_2O_2] \quad (4)$$

where  $k_{obs}$  is the observed first-order rate constant, and  $k_{mass}$  is equal to  $k_{obs}/\text{iron oxide concentration}$ .

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Chou and Huang (1999) observed that the oxidation rate of hydrogen peroxide in their catalytic fluidized-bed reactor (FBR) system was proportional to the outlet hydrogen peroxide concentration ( $C_H$ ) at low  $C_H$ , but declined at high  $C_H$ . They interpreted their results using the modified Langmuir–Hinshelwood equation by incorporating the substrate inhibition model. The potential for applying hydrogen peroxide to Fenton-like soil remediation or water treatment was primarily restricted to the supply and stability of hydrogen peroxide. Therefore, understanding the fate of hydrogen peroxide is still an important topic.

The objective of this paper was to investigate the decomposition of hydrogen peroxide and 2-chlorophenol (2-CP) on different iron oxide surfaces. Three iron oxides (hematite, granular ferrihydrite, and goethite) used in this study are the most common constituents in the subsurface environment. Goethite and hematite are the most thermodynamically stable iron oxide, therefore, they are the most widespread iron oxides in soils and sediments. Ferrihydrite that represents a freshly precipitated and amorphous iron oxide is considered as a possible precursor to the solid state formation of goethite and hematite (Schwertmann and Cornell, 1991). The factors including concentrations of iron oxide and hydrogen peroxide, disturbance, and organics affecting hydrogen peroxide decomposition were examined. Hence, this study can lead to a better understanding of the catalytic reaction of hydrogen peroxide and organics in the environment.

#### MATERIALS AND METHODS

The goethite was prepared by aging ferric hydroxide precipitates produced from ferric nitrate solution at pH 13 and 70°C for 60 h (Schwertmann and Cornell, 1991). The final synthesized goethite was separated from suspension by centrifugation, washed with deionized water till the pH value of supernatant was reduced below pH 7, and then dried at 40°C for 48 h. The synthesized goethite was examined by X-ray diffraction to confirm its crystal. The granular ferrihydrite with a size range of 0.3–0.6 mm was purchased from Aldrich Chemical Company. Hematite was also a commercial product purchased from the RDH Company. The commercial products were used without further purification. The values of  $pH_{pzc}$ , the pH at point of zero charge, were measured by the mass titration method (Noh and Schwarz, 1989). Physical characteristics of the iron oxides are summarized in Table 1. These values could compare with reported values in literatures (Schwertmann and Cornell, 1991; Kung, 1988).

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 reaction was then initiated by the addition of iron oxides. For 2-CP oxidation experiments, blank experiments were carried out to measure the amounts of 2-CP adsorbed on iron oxide in the absence of hydrogen peroxide. Samples taken from the reactor within certain time intervals were filtered through 0.45  $\mu m$  membrane filters to separate iron oxide particles from the solution. The filtrates were then analyzed for the concentrations of hydrogen peroxide, 2-CP, and pH. Hydrogen peroxide concentration was quantified by the peroxytitanic acid method with the addition of  $Ti(SO_4)_2$  test solution (Schumb *et al.*, 1955). Residual 2-CP was measured by an HPLC (Water LC module 1) with a reverse-phase 3.9  $\times$  150 mm Nova-Pak  $C_{18}$  column (Waters).

#### RESULTS AND DISCUSSION

##### Comparison of different iron oxides

The catalytic decomposition of hydrogen peroxide by metal oxides is believed to involve a radical chain mechanism and the reduction–oxidation conversion of the iron oxides. The decomposition of hydrogen peroxide followed a first-order rate expression with respect to hydrogen peroxide concentration. On the base of the single iron oxide dosage, a comparison of catalytic activity of common oxides in subsurface environment is shown in Table 2. The rate constant,  $k_{obs}$ , for granular ferrihydrite is about 1.5, which is 2 orders of magnitude greater than those for goethite and hematite, respectively. The difference of reaction activity between goethite and hematite largely disappeared when  $k_{obs}$  or  $k_{mass}$  was normalized with surface area described as follows (Valentine and Wang, 1998):

$$k_{suf} = \frac{k_{obs}}{SA_v} = \frac{k_{mass}}{SA_m} \quad (5)$$

where  $SA_v$  is surface area per unit of water volume, and  $SA_m$  is surface area per unit mass of oxide; they are defined as

$$SA_v = \frac{\text{Total surface area of iron oxide}}{\text{Volume of reaction mixture}}$$

and

$$SA_m = \frac{\text{Total surface area of iron oxide}}{\text{Mass of iron oxide}}$$

The result shown in Table 2 indicated that the  $k_{suf}$  of granular ferrihydrite was still four times greater than

Table 1. Characteristics of synthesized and commercial iron oxides

Type of iron oxide (formula) <sup>a</sup>	Granular ferrihydrite ( $Fe_5HO_8 \cdot 4H_2O$ )	Synthesized goethite ( $\alpha$ - $FeOOH$ )	Hematite ( $\alpha$ - $Fe_2O_3$ )
Structure	Amorphous	Crystalline	Crystalline <sup>a</sup>
Particle shape	Sphere	Needle	Plate <sup>a</sup>
Particle color	Reddish-brown	Yellow-brown	Deep-red
Dry density ( $g/cm^3$ )	3.89	4.26	5.11
$pH_{pzc}$	8.9	7.5	5.4
Specific surface area ( $m^2/g$ )	190.33	39.52	9.15

<sup>a</sup>Schwertmann *et al.* (1991).

Table 2. The values of  $k_{\text{mass}}$  and  $k_{\text{surf}}$  on hydrogen peroxide decomposition for different iron oxides

Oxide type	$k_{\text{mass}}$ ( $\text{min}^{-1}(\text{g/L})^{-1}$ )	$k_{\text{surf}}$ ( $\text{min}^{-1}(\text{m}^2/\text{L})^{-1}$ )	pH <sub>eq</sub>
Granular ferrihydrite <sup>a</sup>	$0.9 \times 10^{-2}$	$4.7 \times 10^{-5}$	8.4
Goethite <sup>a</sup>	$5.3 \times 10^{-4}$	$1.3 \times 10^{-5}$	6.4
Hematite <sup>a</sup>	$8.3 \times 10^{-5}$	$0.9 \times 10^{-5}$	5.9
Goethite <sup>b</sup>	$1.0 \times 10^{-3}$	$1.8 \times 10^{-5}$	7.7
Ferrihydrite <sup>b</sup>	$1.5 \times 10^{-2}$	$4.8 \times 10^{-5}$	7.7
Support-iron oxide <sup>c</sup>	$2.2 \times 10^{-4}$	$2.1 \times 10^{-6}$	5.4
$\gamma\text{-Al}_2\text{O}_3^{\text{a}}$	NA	—	8.6
Silica sand <sup>a</sup>	NA	—	5.8

<sup>a</sup>This study;  $[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$ ; iron oxide = 1.0 g/L; Temp. = 30°C.

<sup>b</sup> $[\text{H}_2\text{O}_2]_0 = 14.7 \text{ mM}$ ; iron oxide = 0.5 g/L; Temp. = 20°C (Valentine *et al.*, 1998).

<sup>c</sup> $[\text{H}_2\text{O}_2]_0 = 23.5 \text{ mM}$ ; iron oxide = 10 g/L; Temp. = 24°C (Chou, 1999).

that of other iron oxides. Chou and Huang (1999) observed that the rate constant of supported-iron oxide to hydrogen peroxide decomposition increased with increasing the pH. Valentine and Wang (1998) demonstrated that the catalytic activity for hydrogen peroxide decomposition was similar for different crystalline iron oxides at a controlled pH condition. In this study, with the consideration of the effect of surface complex and ionic strength, the solution pH was not controlled with a buffer or acid–base titration during the experiments. The catalytic activities of iron oxides studied in other literatures are also shown in Table 2. Clearly, the value of  $k_{\text{surf}}$  had an increasing trend with equilibrium pH, pH<sub>eq</sub>. Therefore, it could be concluded that the effect of pH on the reaction activity of iron oxides was also important as well as the effect of surface active sites. Since granular ferrihydrite and goethite exhibited a higher activity for catalytic decomposition of hydrogen peroxide, they were selected for further study.

#### Effect of hydrogen peroxide and oxides concentrations

The decomposition of hydrogen peroxide performed in this study also followed a first-order rate expression, which is consistent with the observations of the other researches (Kitajima *et al.*, 1978; Kakarla and Watts, 1997). The results of the experiments conducted at different mixing speeds in the presence of granular ferrihydrite and goethite are presented in Fig. 1. In the figure, the solid straight lines are the average values of the mass normalized rate constants. For both iron oxides, although the average values of the  $k_{\text{mass}}$  varied with different mixing speeds, they were independent with different initial hydrogen peroxide concentrations, ranging from 0.98 to 9.8 mM. In addition, further experiments were conducted for goethite at higher hydrogen peroxide concentration, ranging from 9.8 to 17.8 mM. No significant difference was observed for the rate constant in these experiments, implying that the number of sites on iron oxide surface available for adsorption of hydrogen peroxide was still not limited under the range of hydrogen peroxide concentration in this study.

A plot of the observed first-order rate constant  $k_{\text{obs}}$  as a function of iron oxide concentration is shown in Fig. 2. Obviously, the values of  $k_{\text{obs}}$  were proportional to the iron oxide concentrations at higher mixing speed. The experiments conducted at such higher mixing speed could provide uniform distribution and full suspension of iron oxide particles. The fluid condition in this situation could be considered as a “microfluid” (Levenspiel, 1972). A “macrofluid” occurred when experiments were conducted at higher solid concentration and lower mixing speed. At this condition, the rate constant was no longer proportional to the solid concentration. Since goethite particle was small and easier to be suspended, the effect of macrofluid on goethite was smaller than that of granular ferrihydrite. However, no matter what the fluid condition was, the decay of hydrogen peroxide still followed a first-order kinetics with respect to hydrogen peroxide concentration.

#### Effects of mass transfer

The apparent rate of a heterogeneous catalytic reaction is usually dominated by either the rate of intrinsic reaction on the surface or the rate of diffusion of the solutes to the surface. In this section, the interphase (diffusion through liquid film) and intraphase (pore diffusion) transport phenomena between the interface of iron oxides and liquid was discussed. The effect of film resistance could be examined to see whether the conversion rate was changed at different mixing speeds (rpm) of oscillator tank in this study (Levenspiel, 1972). Figure 3 exhibits the effect of disturbance on the hydrogen peroxide decomposition with iron oxides. In this figure, we could found that the catalytic activity of goethite for hydrogen peroxide decomposition does not vary obviously with changing the mixing speed at the lower solid dosage. However, the catalytic activity of granular ferrihydrite was affected significantly with the mixing speed. In addition to the consideration of fluid segregation mentioned earlier, the extent of interphase transport should also be evaluated by estimating the value of Damkohler number (Da). The ratio of surface chemical reaction

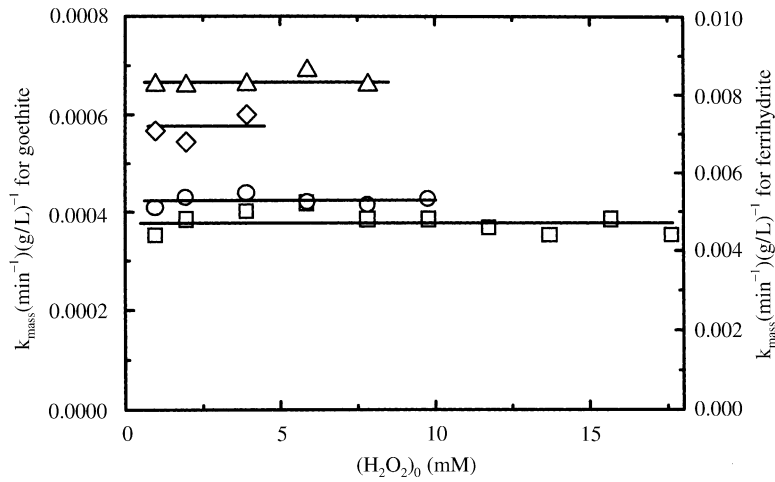


Fig. 1. Effect of hydrogen peroxide concentration on  $k_{\text{mass}}$  of hydrogen peroxide decomposition in the presence of goethite and granular ferrihydrite ( $\Delta$ : ferrihydrite = 1 g/L, 225 rpm;  $\diamond$ : ferrihydrite = 1 g/L, 160 rpm;  $\square$ : goethite = 1 g/L, 225 rpm;  $\circ$ : goethite = 1 g/L, 160 rpm).

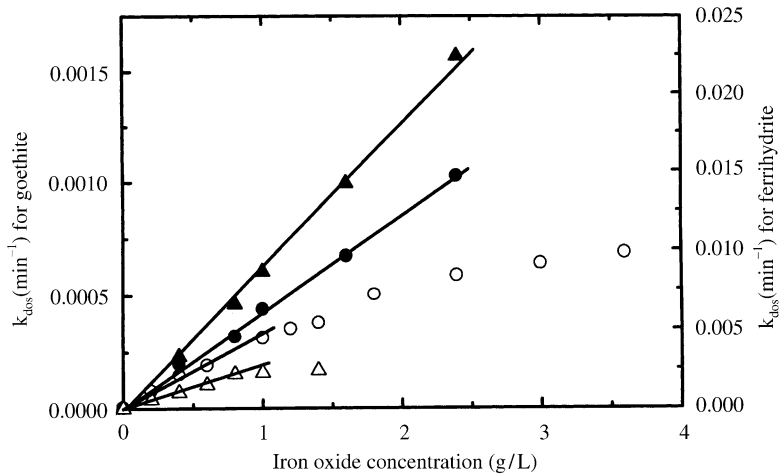


Fig. 2. Effect of iron oxide concentration and disturbance on the  $k_{\text{obs}}$  in the presence of granular ferrihydrite and goethite ( $[\text{H}_2\text{O}_2]_0 = 5.88 \text{ mM}$ ;  $\blacktriangle$ : ferrihydrite, 225 rpm;  $\triangle$ : ferrihydrite, 160 rpm;  $\bullet$ : goethite, 225 rpm;  $\circ$ : goethite, 160 rpm).

rate to bulk mass transfer rate is described as (Carberry, 1976)

$$\text{Da} = \frac{k_s C_{\text{H}}^{n-1}}{k_c} \quad (6)$$

where  $k_s$  is local surface rate constant with the units of length per time,  $k_c$  is mass-transport coefficient, and  $C_{\text{H}}^{n-1}$  is the bulk concentration. The decomposition of hydrogen peroxide was observed as the first-order kinetics, then  $n$  is equal to unity.

At steady state, the effect of interphase and intraphase transport could be combined as an equal equation (Levenspiel, 1972; Carberry, 1976):

$$R_{\text{H}} = k_c S_{\text{ex}} (C_{\text{H}} - C_{\text{HS}}) = k_{\text{int}} S_{\text{ex}} C_{\text{HS}} \eta \quad (7)$$

where  $S_{\text{ex}}$  is the exterior surface of catalyst particle,  $C_{\text{H}}$  is the bulk concentration,  $k_{\text{int}}$  is the intrinsic rate

constant (cm/min),  $C_{\text{HS}}$  is surface concentration, and  $\eta$ , the effectiveness factor, is the ratio of reaction rate with and without the effect of the pore diffusion in the particle volume. According to equation (7), the following equation is obtained:

$$C_{\text{HS}} = \frac{k_c C_{\text{H}}}{k_c + k_{\text{int}} \eta} \quad (8)$$

Rearranging equation (8) gives

$$C_{\text{HS}} = \left( \frac{1}{1 + k_{\text{int}}/k_c} \right) C_{\text{H}} \quad (9)$$

$R_{\text{H}}$  can also be expressed as

$$R_{\text{H}} = - \frac{1}{V_r} \frac{dN_{\text{A}}}{dt} \quad (10)$$

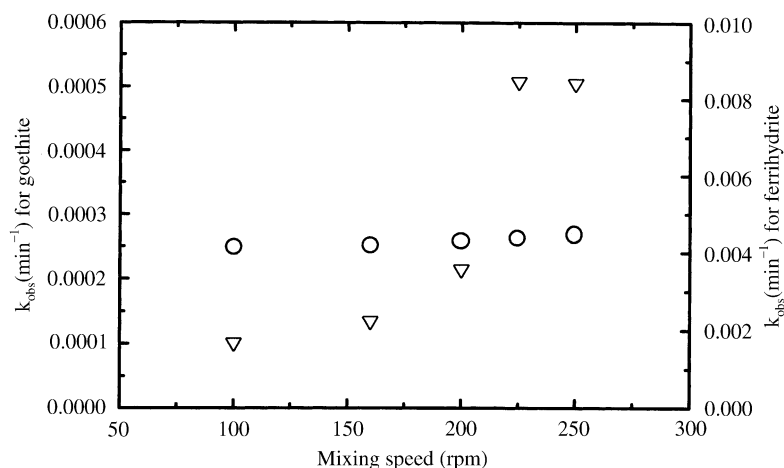


Fig. 3. Effect of mixing speed on the  $k_{obs}$  in the presence of granular ferrihydrate and goethite ( $[H_2O_2]_0 = 5.88$  mM; ▽: ferrihydrate = 1 g/L,  $pH_{eq} = 8.5$ ; ○: goethite = 0.6 g/L,  $pH_{eq} = 6.3$ ).

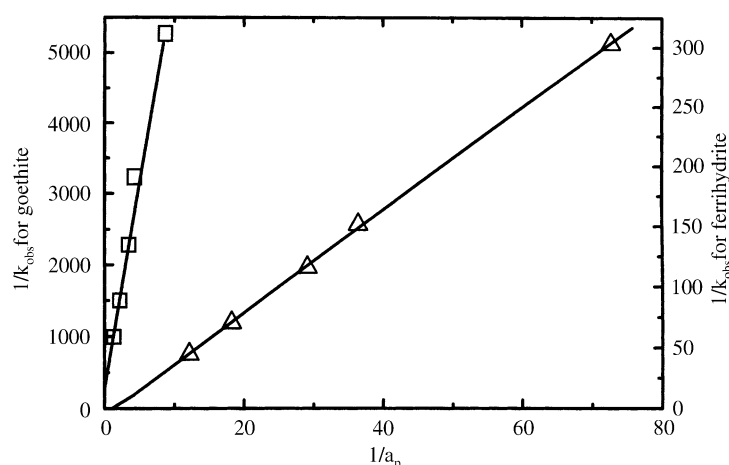


Fig. 4. Relationship between  $1/a_p$  and  $1/k_{obs}$  ( $[H_2O_2]_0 = 5.88$  mM; □: goethite; △: ferrihydrate).

where  $V_r$  is the volume of reaction mixture, and  $N_A$  is the moles of hydrogen peroxide. Therefore,

$$R_H = \frac{S_{ex}}{V_r} k_c (C_H - C_{HS}) \quad (11)$$

By defining  $a_p = S_{ex}/V_r$ , the exterior surface area of iron oxide per reaction volume, and substituting equation (9) into equation (11) give

$$R_H = a_p k_c C_H \left( 1 - \frac{1}{1 + \eta k_{int}/k_c} \right) \quad (12)$$

Rearranging the above equation gives

$$R_H = a_p \left( \frac{1}{1/\eta k_{int} + 1/k_c} \right) C_H \quad (13)$$

The iron oxides are assumed as spherical particles, and  $a_p$  can be calculated by the following equation:

$$a_p = \frac{4\pi(d_p/2)^2}{\frac{4}{\rho_p} \pi (d_p/2)^3} \times m = \frac{6m}{\rho_p d_p} \quad (14)$$

where  $\rho_p$  and  $d_p$  are dry density and particle size of the iron oxide, respectively, and  $m$  is solid concentration (g/L). According to equations (4) and (13), a plot of  $1/k_{obs}$  vs.  $1/a_p$  for iron oxides was then obtained by transforming data in Fig. 2 (solid symbol data) as shown in Fig. 4. The mass transfer coefficient  $k_c$  could be estimated as 0.01 cm/s, a typical value for particles falling in water (McCabe *et al.*, 1985). Therefore, the local surface rate constant  $k_s$  (e.g.  $\eta k_{int}$ ) could be calculated from the slope values as 0.00173 and 0.384 cm/min for goethite and granular ferrihydrate, respectively. It should be noted that for a wide distribution range of goethite particle size, it was difficult to analyze the mean particle size accurately. In this study, the value of  $k_s$  for goethite was measured by assuming the mean particle size as 0.05 mm that was much larger than the reported value (Valentine and Wang, 1998; Schwertmann and Cornell, 1991). The value of  $k_s$  was  $1.73 \times 10^{-5}$  cm/min if the mean particle size was assumed as reported value, 0.5  $\mu$ m (Valentine and Wang, 1998). Therefore,

the actual  $k_s$  of goethite should be less than the value of  $k_s$  predicted in Fig. 4.

For diluted hydrogen peroxide solution,  $Da$  was calculated as 0.0029 for goethite, implying that the film resistance could be neglected. On the contrary, the larger  $Da$ , 0.64, for granular ferrihydrite implied that interphase transport might affect the reaction and explained why the disturbance affected the catalytic activity significantly in the presence of granular ferrihydrite. The  $k_s$  could also be evaluated by means of the dimensionless diagram of  $\varepsilon$  vs.  $\varepsilon Da$  that was developed by Carberry (Carberry, 1976), where  $\varepsilon$  is the ratio of  $k_{obs}$  to  $k_s$ . From the dimensionless diagram, the values of  $\varepsilon$  for goethite and granular ferrihydrite (using the data of 1 g/L) were 1 and 0.6, respectively, and then  $k_s$  were measured as 0.00155 and 0.419 cm/min, respectively.

Thiele modulus  $\varphi$  is usually used to estimate the effect of intraphase transport and could be expressed as the ratio of the reaction rate to the diffusion rate (Levenspiel, 1972; Carberry, 1976; Satterfield, 1981).

$$\varphi = L\sqrt{\frac{k_{int}}{D}} \quad (15)$$

where  $L$  is the pore length which can be estimated as  $d_p/6$  here, and  $D$ , diffusion coefficient, is generally  $10^{-5}$ – $10^{-6}$  cm<sup>2</sup>/s (Cussler, 1984). Since  $\varphi$  is dimensionless, the value of  $k_{int}$  is converted to the  $k'_{int}$  on the basis of catalyst volume ( $V_p$ ) with the relationship of  $k_{int}S_{ex} = k'_{int}V_p$ . The  $\varphi$  was calculated as 0.049–0.15 for goethite, indicating that the rate of hydrogen peroxide decomposition on goethite was far slower than its diffusion rate to the surface through the internal pores. It should be noted that the value of  $k_s$  is equal to  $k_{int}$  as  $\varphi$  is much small and then  $\eta$  approaches unity. The normal form of  $\eta$  is expressed as (Carberry, 1976; Satterfield, 1981).

$$\eta = \frac{k_s}{k_{int}} = \frac{3}{\varphi} \left( \frac{1}{\tanh \varphi} - \frac{1}{\varphi} \right) \quad (16)$$

The value of  $k_{int}$  for granular ferrihydrite on the base of particle volume could be obtained as 1.3–6.1 (s<sup>-1</sup>) by trial and error. Therefore,  $\varphi$  was estimated as 2.7–18.4, implying a strong liquid diffusion resistance. However, by comparing the results with the other researches on the catalyzed the decomposition of hydrogen peroxide in the presence of iron oxide or supported iron oxide, it was found that the effect of diffusion usually could be neglected (Lin and Gurol, 1999; Chou, 1999).

In general, the effect of diffusion was less important for liquid–solid catalytic system (Cussler, 1984). To verify the unexpected effect of pore resistance, the experiment carried out with various sizes of granular ferrihydrite is depicted in Fig. 5. The decomposition rate of hydrogen peroxide appeared much dependent on the granular ferrihydrite sizes. The ratios of the rate constant in Fig. 5 were nearly equal to the inverse ratios of their particle sizes, indicating a strong pore resistance (Levenspiel, 1972). The special crystal morphology of granular ferrihydrite could explain the strong diffusion behavior. Unlike clays, iron oxides, such as goethite and hematite, usually do not have an internal surface area. However, ferrihydrite with its small particle size (2–6 nm) frequently contains aggregates and has much internal area (Schwertmann and Cornell, 1991). In addition, the commercial granular ferrihydrite was prepared by binding porous ferrihydrite powder with proprietary material. Hence, there were large openings between the powder and small pores within each powder particles as observed from the image of scanning electron microscopy. Hansen *et al.* (1994) studied the surface equilibrium constants between ferrihydrite surface and silicate, and suggested that the equilibrium reaction was probably diffusion controlled.

Another possible reaction that surface scavenging of reactive intermediates resulting in the generation of oxygen (equation (1)) could also enhance the diffusion effect. Since the surface scavenging rate

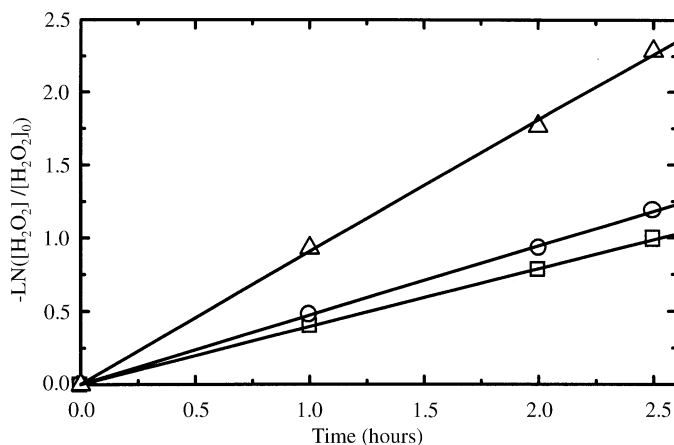


Fig. 5. Effect of particle sizes on hydrogen peroxide decomposition for granular ferrihydrite ( $[H_2O_2]_0 = 5.88$  mM; iron oxide = 1 g/L;  $pH_{eq} = 8.4$ ;  $\triangle$ :  $d = 0.074$ – $0.149$  mm,  $k_{obs} = 0.9023$ ;  $\circ$ :  $d = 0.149$ – $0.177$  mm,  $k_{obs} = 0.4708$ ;  $\square$ :  $d = 0.177$ – $0.21$  mm,  $k_{obs} = 0.3934$ ).

constant,  $k_2$ , was much larger than the rate constant of hydrogen peroxide decomposition,  $k_1$ , oxygen would be produced on the surface rapidly when hydrogen peroxide was decomposed (Miller and Valentine, 1995, 1999). Therefore, saturated dissolved oxygen concentration was then found during hydrogen peroxide decomposition in the presence of granular ferrihydrite. A large amount of oxygen bubbles were formed and covered on the solid surface when the experiment proceeded with lower mixing speed, implying that the amount of oxygen in solution exceeded its saturated dissolved concentration. Diffusion coefficient would be reduced when the Knudsen number (Kn) was large and then increased the  $\phi$  (Cussler, 1984). Knudsen number is a dimensionless ratio of mean free path of solute to pore diameter of particle. In liquid system, the Knudsen number is small for the mean-free path of solute being commonly a few angstroms. However, the mean free path for air at room temperature is over 600 Å which is much larger than the ferrihydrite particle size. Therefore, a larger Knudsen number was obtained when oxygen formed in the pores of granular ferrihydrite particles. In addition, the adsorption of oxygen would also retard the diffusion rate of solute into the pores and compete with hydrogen peroxide for the active sites of the iron oxide surface. Consequently, we could conclude that the effect of strong pore resistance in granular ferrihydrite/hydrogen peroxide catalytic system was probably attributed either to the microporous structure of granular ferrihydrite or to the formation of oxygen in the pores of the iron oxide.

#### Effect of 2-CP

The adsorption and oxidation of 2-CP onto the surface of iron oxides were investigated in this study to compare the catalytic performance of iron oxides. A stoichiometric efficiency,  $E$ , is described as

$$E = \frac{\Delta[2 - CP]_{\text{ox}} - \Delta[2 - CP]_{\text{ad}}}{\Delta[H_2O_2]} \quad (17)$$

where  $\Delta[2 - CP]_{\text{ox}}$  and  $\Delta[2 - CP]_{\text{ad}}$  are the reduced amounts of 2-CP in oxidation and adsorption reactions, respectively. A comparison of 2-CP oxidation in the presence of the different oxides is shown in Table 3. Little reduction of 2-CP (less than 4%) was observed in the presence of granular ferrihydrite, while a 9% reduction in 2-CP concentration was observed with goethite. Hematite showed the greatest catalytic effect on 2-CP degradation, causing a reduction of approximately 15%. The loss amounts of 2-CP for adsorption and oxidation experiments were measured at the sixth hour. The catalytic activity of granular ferrihydrite was further examined at the hydrogen peroxide and solid concentration up to 17 mM and 2.5 g/L, respectively. Even at this concentration, no significant loss in 2-CP (less than 5%), but great decay of hydrogen peroxide was observed.

Table 3. Comparison of  $\text{pH}_{\text{eq}}$ , reduction ( $R$ ), and stoichiometric efficiency ( $E$ ) in the adsorption and oxidation experiment for various iron oxides

Type of iron oxide (surface area, $\text{m}^2/\text{g}$ )	Granular ferrihydrite <sup>a</sup> (190)	Goethite <sup>a</sup> (39.5)	Hematite <sup>a</sup> (9.15)	Goethite <sup>b</sup> (58)	Ferrihydrite <sup>b</sup> (290)	Supported-iron oxide <sup>c</sup> (48.3)
$\text{pH}_{\text{eq}}$	8.00	6.45	5.94	—	—	—
Adsorption	8.45	5.91	4.36	7.7	7.7	4.3
Oxidation	1.3	3.3	7.2	—	—	—
Adsorption <sup>d</sup>	3.2	8.4	14.9	—	—	—
Oxidation <sup>d</sup>	$2.3 \times 10^{-4}$	$2.2 \times 10^{-2}$	$1.69 \times 10^{-3}$	$\sim 10^{-4}$	$2 \times 10^{-2}$	—
$E$ (mol/mol)	$9 \times 10^{-3}$	$2.2 \times 10^{-2}$	$1.69 \times 10^{-3}$	$\sim 10^{-4}$	$2 \times 10^{-2}$	—

<sup>a</sup>This study;  $[H_2O_2]_0 = 9.8 \text{ mM}$ ; iron oxide = 1 g/L; 2-CP = 15 mg/L.

<sup>b</sup> $[H_2O_2]_0 = 14.7 \text{ mM}$ ; iron oxide = 0.5 g/L; quinoline = 10 mg/L (Valentine *et al.*, 1998).

<sup>c</sup> $[H_2O_2]_0 = 23.5 \text{ mM}$ ; iron oxide = 10 g/L; Benzoic acid = 116 mg/L (Chou, 1999).

<sup>d</sup>Triplicate experiments ( $n=3$ ).

Compared with the result of  $k_{\text{suf}}$  in Table 2, hematite had lower  $k_{\text{suf}}$  but higher  $E$  value. Hematite had less ability in degrading hydrogen peroxide but more efficiency in catalytic decomposition of 2-CP than goethite and ferrihydrite.

The catalytic activities of iron oxides studied in other literatures are also shown in Table 3 and can be compared with our results. It was found that stoichiometric efficiency,  $E$ , had a decline trend with the increase in pH and specific surface area of iron oxide, which could be explained with the scavenging model (equations (1) and (2)). The values of  $k_2$  and  $k_3$  were specific to different property of crystalline and chemical compounds, respectively. Since  $k_2$  is several orders of magnitude larger than that for hydrogen peroxide decomposition, the consumption rate of radicals on iron oxide surface would increase largely with increasing the surface area. In addition, the  $\cdot\text{OH}$  would react with  $\text{OH}^-$  to produce  $\text{O}^-$  and  $\text{H}_2\text{O}$  with a high-rate constant  $\sim 10^{10}$  M/s. In other words, with the competition reaction of  $\text{OH}^-$  at high pH, less amounts of radicals could react with the target compounds. Therefore, a smaller  $E$  value was observed at higher pH condition. It should be noted that when experiments proceeded at lower pH condition, a reductive dissolution could occur and then create a homogeneous catalytic reaction (i.e., Fenton reaction). To determine the importance of liquid phase reaction, samples were taken from the solid-liquid mixture by filtering through 0.2  $\mu\text{m}$  membranes. The filtrates were then aged for 24 h, and no significant liquid-phase reaction was observed.

Valentine and Miller (1998) compared the catalytic activity of iron oxides for quinoline oxidation and demonstrated that ferrihydrite had no effect on quinoline loss. This may be due to the fact that ferrihydrite has more OH group and vacant Fe sites to consume radicals than other iron oxides. The

estimation of the reaction–diffusion modulus could also be used to explain the catalytic behavior. Lin and Gurol (1998) estimated the value of the  $\phi$  of the granular goethite for the OH radicals was greater than 5, implying that the reaction rates of radicals with surface sites were much faster than their diffusion rates. The estimation could be corresponding to the  $\phi$  value of granular ferrihydrite used in this study for its strong intraphase effect. Thus, the reactions of radicals with 2-CP in the liquid phase were expected to be negligible in the presence of granular ferrihydrite, which was coincident with our result. Although goethite and hematite with less internal surface were not expected to be much affected by the diffusion phenomena, strong surface scavenging of intermediates has led to low efficiency for these oxidation reactions.

The oxidation of 2-CP would affect the decomposition behavior of hydrogen peroxide as shown in Fig. 6. The addition of 2-CP did not affect the decomposition rate of hydrogen peroxide, because no significant 2-CP reduction was observed in the presence of granular ferrihydrite for the oxidation and the adsorption experiments. However, 2-CP decreased the decomposition rate of hydrogen peroxide in the presence of goethite and hematite. The decline of rate constants for hydrogen peroxide decomposition with the addition of 2-CP was primarily due to the decrease of  $\text{pH}_{\text{eq}}$  value. The higher  $\text{pH}_{\text{eq}}$  of the oxidation experiment was attributed to the enormous formation of oxygen that reduced the dissolved amount of carbonic acid. Although Valentine and Miller (1998) suggested that the adsorption of quinoline could result in deactivation of the catalytic sites, however, the amount of 2-CP adsorbed on iron oxides was small during the reaction time. As discussed earlier in Fig. 1, the active sites were not the limitation for hydrogen peroxide decomposition even at a

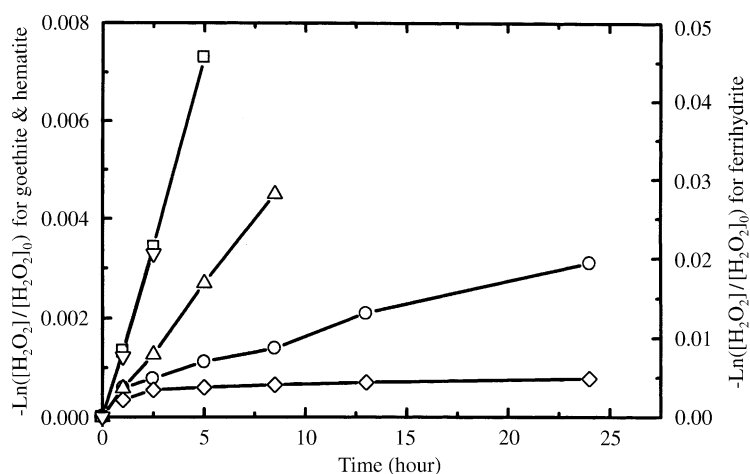


Fig. 6. Effect of 2-CP oxidation on  $\text{H}_2\text{O}_2$  decomposition for various iron oxides ( $[\text{H}_2\text{O}_2]_0 = 9.8$  mM; iron oxide = 1 g/L;  $[\text{2-CP}]_0 = 1.17 \times 10^{-4}$  M;  $\square$ : ferrihydrite with 2-CP;  $\nabla$ : ferrihydrite without 2-CP;  $\triangle$ : goethite without 2-CP;  $\circ$ : goethite with 2-CP;  $\diamond$ : hematite with 2-CP).



considerable hydrogen peroxide concentration. Therefore, even if 10% of 2-CP adsorbed onto the surfaces of iron oxides, no significant reduction of the available active sites would be expected. Consequently, the effect of the 2-CP adsorption on hydrogen peroxide decay was less important than the variation of  $\text{pH}_{\text{eq}}$  value.

### CONCLUSIONS

The catalytic activity for hydrogen peroxide decomposition was the highest for granular ferrihydrite, less for goethite, and much less for hematite based on mass and surface area basis. However, the catalytic activity for 2-CP oxidation exhibited a converse series for these three iron oxides. Therefore, we could propose that hematite was the most likely to be involved in the degradation of contaminants in the subsurface environment. Furthermore, the oxidation efficiency of 2-CP was corresponding to the inverse sequence of specific area and  $\text{pH}_{\text{pzc}}$  of the iron oxides, suggesting a guideline on selecting materials as catalyst in application. The extent of fluid segregation would affect largely on the decomposition kinetics of hydrogen peroxide. Consequently, the extent of mixing should be taken into consideration when applying such the Fenton-like reaction for *in situ* remediation or *ex situ* slurry reactor design. Unlike goethite and hematite, a strong diffusion resistance was observed for granular ferrihydrite, which was attributed either to the microporous structure of granular ferrihydrite or to the formation of oxygen in the pores of iron oxide.

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