



Hydrogen peroxide decomposition on manganese oxide (pyrolusite): Kinetics, intermediates, and mechanism

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ABSTRACT

The objective of this study is the kinetic interpretation of hydrogen peroxide decomposition on manganese oxide (pyrolusite) and the explanation of the reaction mechanism including the hydroperoxide/superoxide anion. The decomposition of hydrogen peroxide on manganese oxide at pH 7 was represented by a pseudo first-order model. The maximum value of the observed first-order rates constants (k_{obs}) was 0.741 min^{-1} at 11.8 of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ when $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ were ranged from 58.8 to 3.92. The pseudo first-order rate constants (k_{MnO_2}) approximated as the average value of $0.025 (\text{min mM})^{-1}$ with a standard deviation of 0.003 at $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ ranged from 39.2 to 11.8. When $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ was 3.92, the rate constants (k_{MnO_2}) was $0.061 (\text{min mM})^{-1}$ as maximum. Oxygen production showed that the initial rates increased with decreasing $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ and the total amounts of oxygen was slightly less than the stoichiometric value (0.5) in most experiments. However, oxygen was produced at more than 0.5 in low $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ (i.e. 3.92 and 9.79). The relative production of hydroperoxide/superoxide anion implied that the production increased with low $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$, and the existence of anions suggested that the mechanism includes propagation reactions with intermediates such as hydroperoxide/superoxide anion in solution. In addition, both $[\text{H}_2\text{O}_2]$ decomposition and the production of anion were accelerated in alkaline solution. Manganese ion dissolved into solution was negligible in neutral and alkaline conditions, but it greatly increased in acidic conditions.

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1. Introduction

There has been increasing interest in finding the physical/chemical characteristics of reaction intermediates from hydrogen peroxide decomposition, because of the high reactivity, which is highly effective for the removal of contaminants (Kwan and Voelker, 2003; Seol and Javandel, 2008). One of the most well-known intermediates, the hydroxyl radical, is generated from hydrogen peroxide decomposition on iron. Known as the Fenton reaction, it has been characterized, and the reaction has been modified (Peyton et al., 1995; Lin and Gurol, 1998; Laat and Gallard, 1999; Lipczynska-Kochany and Kochany, 2008). Moreover, it has been shown that the generation of various reaction intermediates (hydroxyl radical, hydroperoxyl radical, superoxide anion, hydroperoxide anion, oxide radical ion, etc.) is possible (Buxton et al., 1988; Gonzalez and Martire, 1997).

Besides the hydroxyl radical, hydroperoxide and superoxide anion have been investigated for their identification (Pignatello, 1992; Smith et al., 2004). It has been suggested that hydroperoxide anion and superoxide anion including a hydroxyl radical provide a

treatment matrix that desorbs, oxidizes, and reduces contaminants (Watts et al., 1999). In particular, hydroperoxide anion and superoxide anion have been proposed as candidates to improve the desorption of organic compounds from soils (Watts et al., 1999). Recently, superoxide anion generated from a modified Fenton system was proven to be a responsible species for carbon tetrachloride transformation (Smith et al., 2004). However, there has been no evidence for the physical role of hydroperoxide/superoxide anion for improving the desorption of contaminants.

In addition to hydrogen peroxide decomposition on iron to generate reactive reagents, hydrogen peroxide decomposition on manganese oxides has been studied to investigate the catalytic activity of manganese oxides (Zhou et al., 1998; Baldi et al., 1998), and the decomposition of hydrogen peroxide on the metals (i.e. both iron and manganese) coated filter showed that hydrogen peroxide decomposition rates mostly depend on manganese concentrations (Miller and Valentine, 1995). Moreover, it has been suggested that hydroperoxide/superoxide anions could be generated from the decomposition of hydrogen peroxide on manganese oxide including metals embedded manganese oxide catalysts (Hasan et al., 1999). However, the detection of hydroperoxide/superoxide anion produced from the reaction of hydrogen peroxide on manganese oxide (pyrolusite) has yet to be reported.

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The objective of this study was to find supporting results to evaluate the role of hydroperoxide/superoxide anion for contaminant desorption. To accomplish this objective, hydrogen peroxide decomposition on manganese oxide (pyrolusite) was chosen instead of iron, because it can minimize the effect of the hydroxyl radical (strong oxidant). Hydrogen peroxide decomposition on manganese oxide (pyrolusite) was studied kinetically, and the mechanisms of this decomposition are suggested as being comprised of both the production of oxygen and the involvement of intermediates (hydroperoxide/superoxide anion). To date, the literature has shown little evidence of their existence.

2. Experimental

2.1. Materials

Double deionized water (DDW) was used with a deionization system (Milli-Q Model Gradient A 10). Manganese oxide (MnO_2) from near Pullman, WA was used below the size of 0.088 mm, and was identified to be pyrolusite by XRD analysis (Cu K-alpha1 X-ray radiation, 40 kV beam voltage, and 100 mA beam current). The specific surface area of MnO_2 measured by the BET method using nitrogen was $6.063 \text{ m}^2 \text{ g}^{-1}$.

Hydrogen peroxide (35%, Junsei Chemical Co.) was used. Titanium sulfate (Junsei Co.), hydroxylamine hydrochloride (Aldrich), sulphanilic acid (Aldrich), glacial acetic acid (J.T. Baker), and α -naphthylamine (Fluka) were used for spectrophotometer analysis. All of the reagents used in this research were reagent grade.

2.2. Experimental systems

All experiments were conducted at room temperature. The initial pH of solution was $\text{pH } 7.0 \pm 0.1$ except for the experiment of the pH effect. The final pH of solution increased to 9–10 after the completion of the reaction. Decomposition of hydrogen peroxide on manganese oxide and oxygen production was tested in a 250 ml Erlenmeyer flask filled with 200 ml volume of solution. Light was excluded by wrapping the container with aluminum foil. The pH was adjusted by NaOH and HCl if necessary. The reaction began when the manganese oxide was introduced into the hydrogen peroxide solution during mixing. Different concentration ranges of hydrogen peroxide and manganese oxide were tested for hydrogen peroxide decomposition and oxygen/anion (hydroperoxide/superoxide) production.

2.3. Analytical methods

Hydrogen peroxide was detected by a colorimetric method at 467 nm (Milton Roy Company, Spectronic 20*) (Kong et al., 1998). The reagent for detection was titanium sulfate and it was kept in a refrigerator at a temperature below 4°C . Aluminum foil was used for exclusion of light.

Oxygen produced by a reaction of hydrogen peroxide and manganese oxide was detected by gas chromatography with a thermal conductivity detector (GC-TCD (Shimadzu GC-8A), detector temp.: 120°C , carrier gas: He, software: Autochro-win chromatography data system). The GC-TCD was connected directly to the reaction vessel, which was stirred with a magnetic stirrer, to detect oxygen in real-time.

The production of the hydroperoxide/superoxide anion was also detected by a modified colorimetric method using a wavelength of 530 nm. The method (US Patent 4629696) used the oxidation of hydroxylamine hydrochloride to produce nitrite ion, and the nitrite ion was detected by a mixture of sulphanilic acid, α -naphthylamine reagent, and glacial acetic acid. The method was modified

as follows. Hydroxylamine hydrochloride (0.69 g) was dissolved in 100 mL of DDW and 1.6 mL of hydroxylamine hydrochloride solution was mixed with the reaction solution. The resultant nitrite ion was determined by the addition of both 0.4% (w/v) sulphanilic acid solution and 0.1% (w/v) α -naphthylamine solution in 25% glacial acetic acid. This mixture was stored in a dark place for 20 min to make reddish purple azo dye complex, and the absorbency of azo dye complex was measured by a colorimetric method at 530 nm. The measured absorbency of hydroperoxide/superoxide anion was calculated by subtracting the initial absorbency of control, which only contained hydrogen peroxide, from the absorbency of the sample. From the measured absorbency, the yield of hydroperoxide/superoxide anion was determined as a relative value compared to the reference condition (i.e. $[\text{H}_2\text{O}_2]_r = 294 \text{ mM}$ and $[\equiv\text{MnO}_2]_r = 7.5 \text{ mM}$).

3. Results and discussion

3.1. Reaction of hydrogen peroxide and manganese oxide

3.1.1. Decomposition of hydrogen peroxide

A study on kinetic decomposition of hydrogen peroxide on manganese oxide at the initial $\text{pH } 7.0 \pm 0.1$ was conducted in a batch reactor. The decomposition of hydrogen peroxide can be expressed with the observed first-order rate constants (k_{obs}). The observed first-order rate constants are calculated by non-linear regression using the least-square method. Fig. 1 shows the effect of initial hydrogen peroxide (29.4–441 mM) concentration on the decomposition of hydrogen peroxide in the presence of 7.5 mM of manganese oxide, and Fig. 2 shows the effect of manganese oxide (5–25 mM) concentration on the hydrogen peroxide (294 mM) decomposition as a function of time. Regression lines fit well with experimental data. The hydrogen peroxide decomposition rates (Table 1) increased with decreasing hydrogen peroxide concentration and increasing manganese oxide. The direct relation of both the concentration of the initial hydrogen peroxide and manganese oxide on the decomposition rates allows the first-order kinetics to be modified:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{\text{MnO}_2} [\equiv\text{MnO}_2] \cdot [\text{H}_2\text{O}_2] \quad (1)$$

$$k_{\text{obs}} = k_{\text{MnO}_2} [\equiv\text{MnO}_2] \quad (2)$$

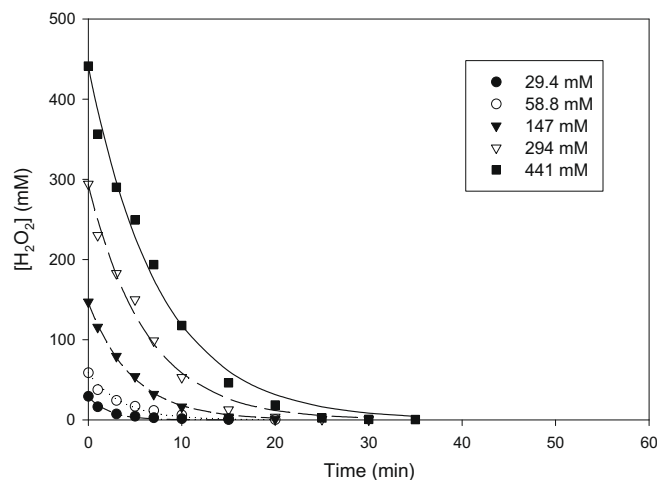


Fig. 1. Observed first-order rates constants at initial $\text{pH } 7.0 \pm 0.1$ and $[\equiv\text{MnO}_2] = 7.5 \text{ mM}$ under various initial hydrogen peroxide concentrations. Lines in figure represent regression fitting lines.

$[H_2O_2]$ is the concentration of hydrogen peroxide (mM), $[MnO_2]$ is concentration of manganese oxide in solution (mM), k_{obs} is the observed first-order rate constants (min^{-1}), and k_{MnO_2} is pseudo first-order rate constants ($(min\ mM)^{-1}$).

The linear regression for the observed first-order rate constant as a function of manganese oxide concentration (exp. 6–10) is $y = 0.033x - 0.097$ with $r^2 = 0.99$. It demonstrated that the observed rate constants gradually increased when $[MnO_2]$ were increased. The observed first-order rate constants (k_{obs}) as a function of $([H_2O_2]/[MnO_2])$ in Table 1 indicate the possible existence of the optimum ratio of $[H_2O_2]/[MnO_2]$.

The rate constant (k_{obs}) in Table 1 increased from 58.8 (mM/mM) of $[H_2O_2]/[MnO_2]$ to the maximum value ($0.741\ min^{-1}$) at 11.8 of $[H_2O_2]/[MnO_2]$, and it decreased when $[H_2O_2]/[MnO_2]$ was less than 11.8. According to the pseudo first-order rate constants, the rate constants (k_{MnO_2}) continuously increased in the range of 3.92–58.8 of $[H_2O_2]/[MnO_2]$. In detail, the pseudo first-order rate constants (k_{MnO_2}) approximated as the average value of 0.025 ($(min\ mM)^{-1}$) with a standard deviation of 0.003 when the ratios of $[H_2O_2]/[MnO_2]$ ranged from 11.8 to 39.2 (exp. 3, 4, and 7 to 10, $n = 6$). Moreover, when $[H_2O_2]/[MnO_2]$ was 3.92, the rate constant (k_{MnO_2}) was $0.061\ (min\ mM)^{-1}$ as maximum. This behavior suggests that $[H_2O_2]$ decomposition follows, not only on the surface of manganese oxide but also in the solution. The peak-shaped changes of k_{obs} with the slight increases of k_{MnO_2} on

$[H_2O_2]/[MnO_2]$ might imply the existence of intermediates (i.e. hydroperoxide/superoxide anion, or hydroperoxyl radical) and their reaction with $[H_2O_2]$. The peak-shaped changes of rate constants (k_{obs}) on $[H_2O_2]/[MnO_2]$ might also imply that the ratio of $[H_2O_2]/[MnO_2]$ needs to be considered as a parameter for hydrogen peroxide decomposition on manganese oxide.

3.1.2. Oxygen production

A mole of H_2O_2 , in stoichiometry, produces a one-half mole of oxygen on $[MnO_2]$. The GC-TCD analysis showed that the gas produced from the decomposition of hydrogen peroxide on manganese oxide was oxygen. The effect of variations in the concentration of hydrogen peroxide (0–73.5 mM) and manganese oxide (0–3.14 mM) on oxygen production was tested (Supporting material I and II). The dose of 1.88 mM manganese oxide was fixed for the effect of hydrogen peroxide, and 36.8 mM of hydrogen peroxide was used for the effect of the manganese oxide experiment. The amount of oxygen produced was recorded every 5 s. The time difference between the reaction starts and the first oxygen detection was 3 min. The amounts of oxygen detected in control samples ranged from 0.14 (without H_2O_2) to 0.16 mM (without MnO_2), and can be explained by oxygen dissolved in pure water.

The accumulative oxygen production per initial hydrogen peroxide ($O_2\ (g)/[H_2O_2]$) was estimated, and the estimation implied that the rates of initial oxygen production increased with a decrease in the ratio of $[H_2O_2]/[MnO_2]$ ranging from 3.91 to 39.1. According to the experimental results on the effect of manganese oxide, oxygen slowly accumulated with the lower doses of manganese oxide. The total amounts of oxygen production, which ranged from 0.45 to 0.49, was slightly less than the stoichiometric value, 0.5, except for the condition of the low ratio of $[H_2O_2]/[MnO_2]$ (i.e. 3.91 and 9.79). When the ratio of $[H_2O_2]/[MnO_2]$ (7.35 mM: 1.88 mM) was 3.91, the maximum production of oxygen was reached earlier and the produced oxygen per initial H_2O_2 was calculated to be as high as 0.53, which was obtained by subtracting the oxygen production of the control sample. This oxygen production in the low ratio of $[H_2O_2]/[MnO_2]$ might result from the existence of the other source for oxygen production. The oxide anion (O^-) can react with H_2O to produce both hydroxide ion and hydroxyl radical in the strong alkaline solution ($pK_a = 11.9$) (Buxton et al., 1988), and these intermediates (i.e. hydroxide ion and hydroxyl radical) are also involved in the propagation reaction to produce oxygen. The initial pH of 7.0 of the experiment system ended nearly at a pH of 10, and this increasing pH of the experimental system might favor the reaction between the oxide anion (O^-) and the H_2O .

Based on the results of oxygen production, it could be concluded that: (1) the total amount of oxygen produced was affected by the change of initial hydrogen peroxide and manganese oxide concentration, (2) the initial oxygen production rates were affected by the changes of $[H_2O_2]/[MnO_2]$, and (3) with increasing ratio of $[H_2O_2]/[MnO_2]$, the detection of oxygen was slowed or delayed (less than 9.79 of $[H_2O_2]/[MnO_2]$ and might develop under different conditions for production). This slow or delay behavior with high $[H_2O_2]/[MnO_2]$ could have been caused by: (1) the slow mass transfer, or (2) limited to the surface of manganese oxide to react with hydrogen peroxide.

3.1.3. Production of hydroperoxide/superoxide anion

Hydroperoxide/superoxide anion was detected and represented by relative value (absorbency of sample/absorbency of reference value). Hydroperoxide/superoxide anion production from 294 mM of hydrogen peroxide ($[H_2O_2]_r$) reacted with 7.5 mM of manganese oxide ($[MnO_2]_r$) and was used as the reference value for the effect of hydrogen peroxide (Fig. 3) and manganese oxide experiment (Fig. 4). The ratios of $[H_2O_2]/[H_2O_2]_r$ were from 0.10

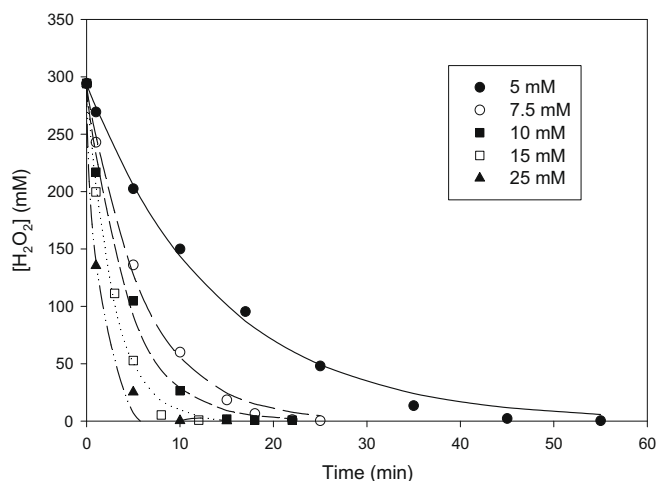


Fig. 2. Observed first-order rates constants at initial pH 7.0 ± 0.1 and $[H_2O_2] = 294\ mM$ under various $[MnO_2]$ concentrations. Lines in figure represent regression fitting lines.

Table 1

Observed and pseudo first-order rate constants of hydrogen peroxide decomposition on manganese oxide (pyrolusite).

Experiments	$[H_2O_2]$ (mM)	$[MnO_2]$ (mM)	Ratio of $[H_2O_2]/[MnO_2]$	$k_{obs} (\pm r.a.e.)^a$ (min^{-1})	$k_{MnO_2}^b$ ($mM^{-1} min^{-1}$)
1	29.4	7.5	3.92	0.461 (± 0.11)	0.061
2	58.8		7.48	0.275 (± 0.11)	0.037
3	147		19.6	0.212 (± 0.03)	0.028
4	294		39.2	0.162 (± 0.08)	0.022
5	441		58.8	0.132 (± 0.08)	0.018
6	294	5	58.8	0.072 (± 0.05)	0.014
7		7.5	39.2	0.166 (± 0.06)	0.022
8		10	29.4	0.232 (± 0.07)	0.023
9		15	19.6	0.352 (± 0.05)	0.023
10		25	11.8	0.741 (± 0.05)	0.030

^a Relative average error (average absolute error/average measured value).

^b Pseudo first-order rate constants ($k_{MnO_2} = \frac{k_{obs}}{[MnO_2]}$).

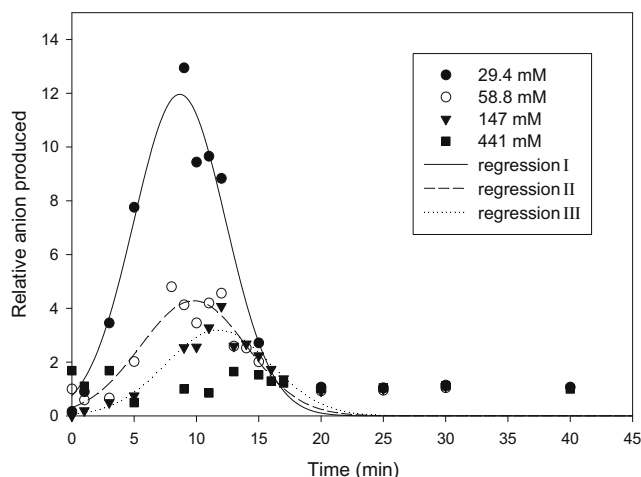


Fig. 3. Relative hydroperoxide/superoxide anion production at initial pH 7.0 ± 0.1 and $[\text{MnO}_2] = 7.5 \text{ mM}$ under various initial hydrogen peroxide concentrations. Lines represented non-linear regression using Gaussian equation ($y = a \exp[-0.5(x - x_0)^2/b^2]$). Parameters were $a = 12.0$, $b = 3.68$, $x_0 = 8.67$ for regression I, $a = 4.28$, $b = 4.26$, $x_0 = 9.77$ for regression II, and $a = 3.19$, $b = 4.18$, $x_0 = 11.7$ for regression III.

to 1.50 in Fig. 3, and the ratios of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$, as from 0.67 to 3.33 in Fig. 4. Experiments on the effect of hydrogen peroxide ($[\text{H}_2\text{O}_2] = 29.4, 73.5, 147$, and 441 mM) on manganese oxide ($[\text{MnO}_2] = 7.35 \text{ mM}$), and the effect of manganese oxide ($[\text{MnO}_2] = 5, 10, 15$, and 25 mM) for the decomposition of hydrogen peroxide ($[\text{H}_2\text{O}_2] = 294 \text{ mM}$) were conducted to determine whether the concentration range affects the anion production. Therefore, the ratios of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ for the effect of hydrogen peroxide were from 4 to 60, and 11.8 to 58.8 for the effect of manganese oxide experiment. Non-linear regression using a Gaussian equation was presented in Fig. 3 (regressions I, II, and III for $[\text{H}_2\text{O}_2] = 29.4, 58.8$ and 147 mM) and Fig. 4 (regressions I–III for $[\text{MnO}_2] = 10, 15$ and 25 mM).

The results showed that the relative production of hydroperoxide/superoxide anion increased when the ratio of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ was decreased. Especially, when the ratio of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ was 11.8 (in the condition of 294 mM $[\text{H}_2\text{O}_2]$ decomposed on 25 mM

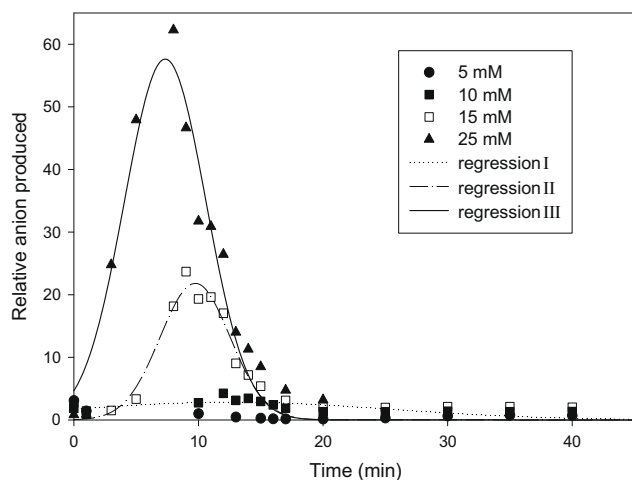


Fig. 4. Relative hydroperoxide/superoxide anion production at initial pH 7.0 ± 0.1 and $[\text{H}_2\text{O}_2] = 294 \text{ mM}$ under various $[\text{MnO}_2]$ concentrations. Lines represented non-linear regression using Gaussian equation. Parameters were $a = 2.84$, $b = 12.6$, $x_0 = 12.6$ for regression I, $a = 21.8$, $b = 2.81$, $x_0 = 9.74$ for regression II, and $a = 57.6$, $b = 3.27$, $x_0 = 7.33$ for regression III.

$[\text{MnO}_2]$), the production of hydroperoxide/superoxide anion was relatively higher than other conditions. This observation agreed with the results of hydrogen peroxide decomposition, which showed the maximum observed rate constant (0.741 min^{-1}) using the same concentration of reactants. It was also coincident with the increases of initial oxygen production rates when the ratio of $[\text{H}_2\text{O}_2]/[\text{MnO}_2]$ was decreased. Interestingly, hydroperoxide/superoxide anion produced relatively high when the higher concentration of manganese oxide was used. To check whether there was interference of manganese oxide, a $0.45 \mu\text{m}$ membrane filter was used for filtration. It showed no interference of manganese oxide for the measured absorbency of anion. The overall reaction, including the production of hydroperoxide/superoxide anion and oxygen from $[\text{H}_2\text{O}_2]$ decomposition on $[\text{MnO}_2]$ indicated that anion was produced before oxygen was produced (Supporting material III). The retention time of hydroperoxide/superoxide anion in solution was tested, and it stayed for at least 24 h. It suggests that: (1) hydroperoxide/superoxide anion can be involved for oxygen production, and (2) the anion can be remained with a certain value for further application like physicochemical regeneration of absorbents.

3.1.4. The effect of pH for manganese oxide surface

The effect of pH (pH of 3, 7, and 9) was tested for H_2O_2 decomposition and oxygen/anion production. In the pH of 3 and 7, there was no difference in H_2O_2 decomposition and relative hydroperoxide/superoxide anion production. However, in the pH of 9, H_2O_2 decomposed rapidly, and the relative anion produced was higher than other conditions. Oxygen production was not affected when the pH of the solution ranged from 3 to 9.

It was mentioned above that manganese oxide did not interfere with the detection of anion. In addition, it is reported that manganese ion can leach from manganese oxide that is reacted with hydrogen peroxide in acidic condition (US Patent 4872909). Fortunately, manganese ion leached only 5 ppb at the initial pH of 7, which is negligible. However, in the initial pH of 3, manganese ion leached 3.1 ppm, while it leached 1 ppb at the initial pH of 9. Therefore, it can be assumed that the interference of manganese ion at the initial pH of 7 was not significant, and it is important to be aware of the possibility of second-contamination if manganese oxide is used in acidic conditions.

3.2. Mechanism of the reaction

A suggested mechanism of hydrogen peroxide decomposition on manganese oxide is presented in Table 2.

Table 2

Possible reaction mechanisms of manganese oxide and hydrogen peroxide.

Reaction mechanism	Eq.
$\text{H}_2\text{O}_2 + [\text{M-O}] \rightarrow [\text{M-O}]\text{H} + \text{H}_2\text{O}_2$	(3) ^a
$[\text{M-O}]\text{H} + \text{H}_2\text{O}_2 \leftrightarrow [\text{M-O}] + \text{OOH} + \text{H}_2\text{O}$	(4) ^a
$[\text{M-O}] + \text{OOH} \rightarrow [\text{M-O}]\text{H} + \text{O}_2(\text{g})\uparrow$	(5)
$[\text{M-O}]\text{H} + \text{H}_2\text{O}_2 \rightarrow [\text{M-O}]\text{OH} + \text{H}_2\text{O}$	(6)
$[\text{M-O}] + \text{H}_2\text{O}_2 \rightarrow [\text{M-O}]\text{H} + \text{OOH}^-$	(7)
$[\text{M-O}] + \text{H}_2\text{O}_2 \rightarrow [\text{M-O}]\text{O} + \text{H}_2\text{O}$	(8)
$[\text{M-O}]\text{O} + \text{H}_2\text{O}_2 \rightarrow [\text{M-O}]\text{OH} + \text{OOH}^-$	(9)
$2[\text{M-O}]\text{O} \rightarrow 2[\text{M-O}] + \text{O}_2(\text{g})\uparrow$	(10) ^b
$[\text{M-O}]\text{OH} + \text{OOH}^- \rightarrow [\text{M-O}] + \text{H}_2\text{O} + \text{O}_2^-$	(11)
$\text{H}_2\text{O}_2 + \text{OOH}^- \rightarrow \text{O}_2^- + \text{H}_2\text{O} + \text{OH}^-$	(12)
$\text{OOH}^- \leftrightarrow \text{O}_2^- + \text{H}^+ \text{ p}K_a = 4.8$	(13) ^c
$\text{OH}^- + \text{OOH}^- \leftrightarrow \text{O}_2^- + \text{H}_2\text{O}$	(14) ^d
$\text{OOH}^- + \text{O}_2^- \rightarrow \text{HOO}^- + \text{O}_2(\text{g})\uparrow$	(15) ^c

^a Lin and Gurol (1998).

^b Zhou et al. (1998).

^c Watts et al. (1999).

^d Buxton et al. (1988).

$[\equiv\text{MnO}_2]\text{OH}\cdot\text{H}_2\text{O}_2$ represented the initial transition state of manganese oxide bonding with hydrogen peroxide, and it could produce a hydroperoxyl radical (Eq. (4)). Eq. (3) though Eq. (6) explains that one-half mole of oxygen is produced from the reaction of hydrogen peroxide on manganese oxide. In high concentrations of hydrogen peroxide (Eqs. (7), (9), (11)), $[\text{H}_2\text{O}_2]$ decomposition on the surface of various transition forms of manganese oxide (i.e. $[\equiv\text{MnO}_2]$, $[\equiv\text{MnO}_2]\text{O}$, and $[\equiv\text{MnO}_2]\text{OH}$) could produce hydroperoxide/superoxide anion. In the middle of the reaction, if $[\text{H}_2\text{O}_2]$ decomposes on specific transition forms of manganese oxides (i.e. $[\equiv\text{MnO}_2]$ and $[\equiv\text{MnO}_2]\text{O}$), superoxide anion can be produced through certain steps (i.e. Eqs. of (7), (6), and (11) or (8), (9), and (11)).



Eq. (16) could occur in the middle of the reaction, and the residual superoxide ion might remain in solution. Moreover, H_2O_2 decomposition in solution by hydroperoxide/superoxide anion is also possible (Eqs. (12–15)). In Eq. (14), hydroxide ion reacts with the hydroperoxyl radical to produce superoxide anion and H_2O reversibly. It might imply that, in specific conditions like a low ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ (i.e. 3.91), superoxide anion could react with H_2O to produce other intermediates, and their complex reaction could possibly lead to the production of oxygen. This could explain the result of oxygen produced over a stoichiometric value with a low ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$.

4. Conclusion

The kinetics of decomposition of hydrogen peroxide on manganese oxide (pyrolusite) at initial pH 7 can be represented by a pseudo first-order rate model. The ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ needs to be considered as an important parameter to describe $[\text{H}_2\text{O}_2]$ a decomposition rate on manganese oxide. The observed increasing first-order rate constant (k_{obs}) and constant pseudo first-order rate constant (k_{MnO_2}) with certain ranges of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ (from 11.8 to 39.2) could imply the existence of $[\text{H}_2\text{O}_2]$ decomposition with reaction intermediates, mostly hydroperoxide/superoxide anion. In general, as the ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ was decreased, the decomposition rates of $[\text{H}_2\text{O}_2]$, initial production rates of oxygen, and the relative amounts of hydroperoxide/superoxide anion were increased. When the ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ was 11.8 (i.e. $[\text{H}_2\text{O}_2] = 294 \text{ mM}$ and $[\equiv\text{MnO}_2] = 25 \text{ mM}$), the measured first-order H_2O_2 decomposition rate constants (k_{obs}) was 0.741 min^{-1} at its maximum, and the relative production of hydroperoxide/superoxide anion at the same ratio of $[\text{H}_2\text{O}_2]/[\equiv\text{MnO}_2]$ reached the highest point compared to others. The study on the change of initial pH in solution showed that $[\text{H}_2\text{O}_2]$ decomposition and production of anion were accelerated under alkaline conditions. Manganese ion dissolved as high as 3.1 ppm in acidic conditions. The acidic condition should be avoided to prevent second-contamination. The existence of hydroperoxide/superoxide anion implies that the

suggested reaction mechanism could be explained by hydrogen peroxide being decomposed, not only directly on the surface of manganese oxide, but also through a propagation reaction involving intermediates such as hydroperoxide/superoxide anion in solution. Later, this result will be used to evaluate the physical characteristics of hydroperoxide/superoxide anion to regenerate absorbent in a separate paper.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.11.075.

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