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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 $[H_2O_2]/[\equiv MnO_2]$ when $[H_2O_2]/[\equiv MnO_2]$ 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 $(min\ mM)^{-1}$ with a standard deviation of 0.003 at $[H_2O_2]/[\equiv MnO_2]$ ranged from 39.2 to 11.8. When $[H_2O_2]/[\equiv MnO_2]$ was 3.92, the rate constants (k_{MnO_2}) was 0.061 $(min\ mM)^{-1}$ as maximum. Oxygen production showed that the initial rates increased with decreasing $[H_2O_2]/[\equiv MnO_2]$ 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 $[H_2O_2]/[\equiv MnO_2]$ (i.e. 3.92 and 9.79). The relative production of hydroperoxide/superoxide anion implied that the production increased with low $[H_2O_2]/[\equiv MnO_2]$, and the existence of anions suggested that the mechanism includes propagation reactions with intermediates such as hydroperoxide/superoxide anion in solution. In addition, both $[H_2O_2]$ 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.

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 desorbes, 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 $m^2\,g^{-1}$.

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 pH 7.0 ± 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. $[H_2O_2]_r = 294$ mM and $[\equiv MnO_2]_r = 7.5$ 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 pH 7.0 ± 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:

$$-\frac{d[H_2O_2]}{dt} = k_{MnO_2}[\equiv MnO_2] \cdot [H_2O_2] \tag{1}$$

$$k_{obs} = k_{MnO_2}[\equiv MnO_2] \tag{2}$$

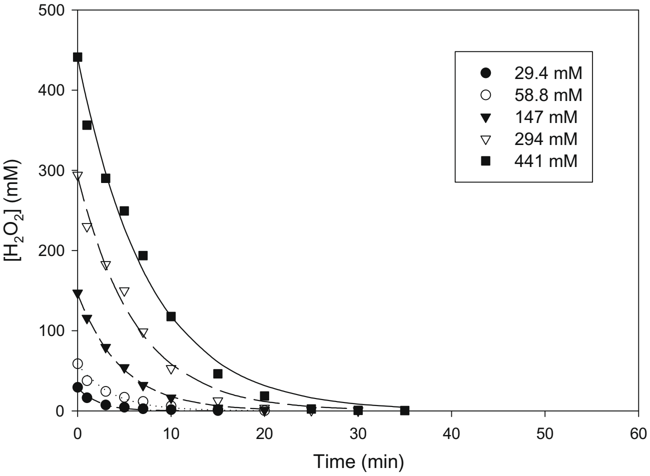

Fig. 1. Observed first-order rates constants at initial pH 7.0 ± 0.1 and $[\equiv MnO_2] = 7.5$ mM under various initial hydrogen peroxide concentrations. Lines in figure represent regression fitting lines.