

Mechanism of hydrogen peroxide decomposition by manganese dioxide

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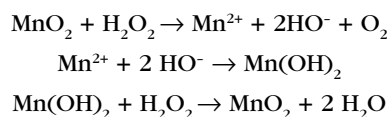
ABSTRACT: The Mn^{2+} , Mn^{3+} , and hydrogen peroxide concentrations were monitored during the MnO_2 -induced peroxide decomposition. Only a small amount of MnO_2 (less than 1.5%) is converted to Mn^{2+} and Mn^{3+} because of its limited surface area. The chemistry of MnO_2 -induced peroxide decomposition is similar to that of the Mn^{2+} - or Mn^{3+} -induced peroxide decomposition. At the same manganese concentration, the activity to decompose peroxide by Mn^{2+} was higher than it was to decompose peroxide by MnO_2 . The effect of the surface area of MnO_2 on the peroxide decomposition was studied, and the peroxide decomposition was found to increase with the increase in the surface area of the particles. Zeolite was effective in protecting Mn^{2+} against oxidation under alkaline conditions and hence in inhibiting peroxide decomposition.

Application: Manganese can decompose hydrogen peroxide under alkaline conditions, but the right combination of chemicals can make the solution more stable.

Hydrogen peroxide (H_2O_2) is widely used in the pulp and paper industry, especially in the brightening of mechanical pulps [1, 2]. Catalytic processes that involve transition metal ions, particularly manganese, lead to the decomposition of peroxide under alkaline conditions, which is not beneficial to the bleaching operation [3, 4]. Manganese dioxide (MnO_2) represents one of the more stable species among various oxidation states of manganese, and many efforts have been made to clarify the mechanism of decomposition of H_2O_2 by MnO_2 .

In a study of the chemistry of the colloidal MnO_2 in reaction with H_2O_2 , Baral *et al.* [5] proposed that the reaction is autocatalytic, involving Mn^{3+} and superoxide radical anion (O_2^-). However, the theory of the formation of the radical species is not consistent with the theories of others [6, 7]. In a study of the mechanism of the decomposition of H_2O_2 solutions by MnO_2 , Broughton and Wentworth suggested a mechanism in which MnO_2 is reduced by H_2O_2 to manganous ion, and then manganous ion in hydroxide form, $\text{Mn}(\text{OH})_2$, is oxidized to MnO_2 [8]. However, other researchers [9, 10] have reported that the MnO_2 -induced peroxide decomposition involves trivalent manganese.

Colodette *et al.* [6] proposed the following mechanism to account for the H_2O_2 - MnO_2 system:



However, the function of Mn^{3+} species and oxygen during the reaction is not apparent.

In this study, we carried out experiments to further elucidate the mechanism of alkaline H_2O_2 decomposition by MnO_2 . We also compared the catalytic ability of Mn^{2+} with that of MnO_2 in decomposing H_2O_2 .

EXPERIMENTAL

We used reagent-grade 30% H_2O_2 solution, manganese sulfate (MnSO_4), sodium silicate (Na_2SiO_3), manganese dioxide (MnO_2 , particle size 44 μm), 40% diethylene-triamine-pentaacetic acid (DTPA), ethylene-diamine-tetraacetic acid (EDTA), and sodium hydroxide (NaOH , 1 mol/L) from Fischer Scientific. Deionized and distilled water was used throughout the experiments.

The H_2O_2 decomposition runs, except those involving nitrogen or oxygen purge, were carried out in 250 mL Erlenmeyer flasks. Water, H_2O_2 , MnO_2 , and NaOH were added to the flask to reach specified conditions. Samples were taken during the course of the reactions for the determination of Mn^{3+} , Mn^{2+} , and H_2O_2 concentrations. In cases in which stabilizers were added to the system, the order of addition of chemicals was as indicated in the tables.

When nitrogen or oxygen purge was applied, the peroxide decomposition experiments were conducted in a 500 mL gas washing bottle with a side inlet and fritted disc at the bottom, with nitrogen or oxygen flowing through the solution continuously.

The Mn^{3+} concentration was measured in accordance with a method used earlier by Bodini and Sawyer [11]. Sodium gluconate was added to the sample, resulting in the formation of color complexes that can be determined by a UV/Vis spectrophotometer. The color intensity was correlated to the Mn^{3+} concentration. All reported values are averages of experiments carried out in triplicate.

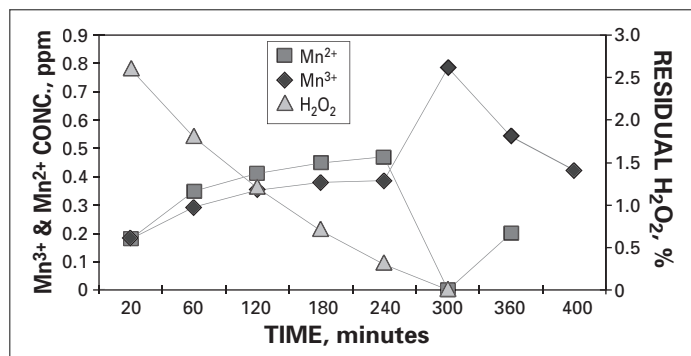
We used a UV/Vis spectrophotometer (model Milton Roy 1001 plus), interfaced to μ -Quant software, which runs on a personal computer. The Mn^{3+} gluconate complexes have maximum absorbances at 235 and 450 nm, and we chose a wavelength of 450 nm for this study. A linear relationship was predetermined to exist between the absorbance at 450 nm and the Mn^{3+} gluconate concentration in the range of 1.6–8.0 ppm. We quantified the Mn^{2+} by oxidizing both Mn^{2+} gluconate and Mn^{3+} gluconate to Mn^{4+} gluconate. The concentration of Mn^{4+} gluconate was determined at 510 nm. The difference between Mn^{4+} and Mn^{3+} gave the concentration of Mn^{2+} .

The H_2O_2 concentration was determined following CPPA testing method J.16P (1992).

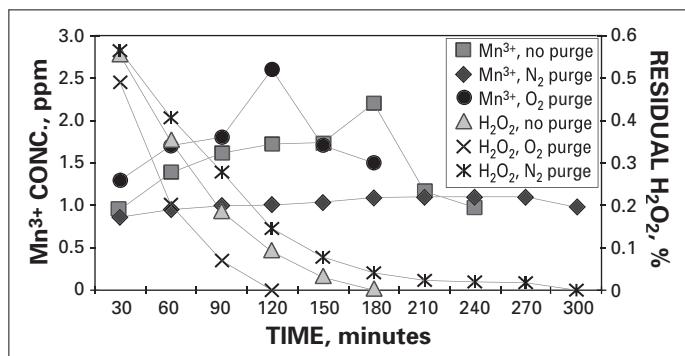
RESULTS AND DISCUSSION

Figure 1 presents results on the development of manganese species and peroxide concentrations in the MnO_2 - H_2O_2 system. Although MnO_2 was added as the only species at the start of the decomposition experiment, both Mn^{2+} and Mn^{3+} form rapidly. During the initial phase,

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1. In the H_2O_2 - MnO_2 system, the concentrations of Mn^{2+} and Mn^{3+} are steady until the peroxide is depleted (66.6 ppm MnO_2 , pH 10, 25EC, 3% H_2O_2).



2. Effects of purging with either N_2 or O_2 on the development of Mn^{3+} and H_2O_2 concentrations (84.3 ppm MnO_2 , pH 10, 0.75% H_2O_2 , 25EC).

TIME, min	RESIDUAL PEROXIDE, % OF INITIAL PEROXIDE CONC.	
	Mn^{2+}	MnO_2
15	27	93
30	11	91
45	0	80

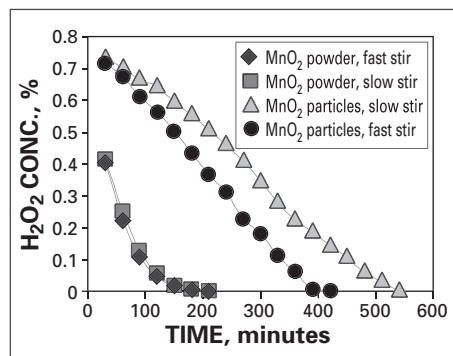
Initial H_2O_2 concentration = 0.75%. Manganese added (as MnSO_4 or MnO_2) = 13.3 ppm. Temp. = 25°C, pH = 10.

I. Comparison of the catalytic activities of Mn^{2+} and MnO_2 in decomposing alkaline peroxide solutions.

Y-zeolite, %	RESIDUAL PEROXIDE CONC., %		
	RUN 1	RUN 2	RUN 3
Time, min	0.0	1.5	4.0
15	0.09	0.70	0.74
30	0.02	0.69	0.74
45	0.00	0.68	0.74
60	0.00	0.66	0.74

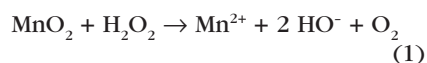
Initial H_2O_2 concentration = 0.75%. Manganese added (as MnSO_4 or MnO_2) = 13.3 ppm. Temperature = 25°C, pH = 10.

II. The catalytic activity of precipitated MnO_2 to decompose alkaline H_2O_2 solution with and without Y-zeolite added.

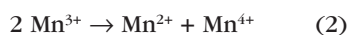


3. Effects on peroxide decomposition caused by differences in the surface area of MnO_2 and the speed of stirring (33.3 ppm MnO_2 , 0.75% H_2O_2 , pH 10, 25EC).

the Mn^{3+} and Mn^{2+} concentrations increased slightly and then stabilized. We propose that Mn^{2+} is formed from MnO_2 according to Reaction 1:



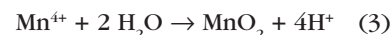
The hypothesis that MnO_2 is reduced to Mn^{2+} under alkaline conditions is in keeping with results of other studies [6, 8, 9]. Vasilenko has quantified Mn^{2+} ions in the H_2O_2 - MnO_2 system and correlated



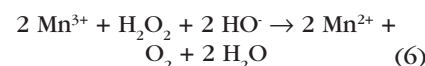
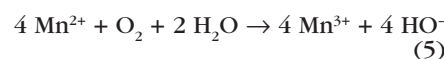
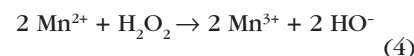
Y-zeolite, %	RESIDUAL PEROXIDE CONC., %	
	RUN 1	RUN 2
Time, min	300	1050
15	0.71	0.75
30	0.67	0.75
45	0.63	0.75
60	0.59	0.75

Initial H_2O_2 concentration = 0.75%. Manganese added (as MnSO_4 or MnO_2) = 13.3 ppm. Temperature = 25°C, pH = 10.

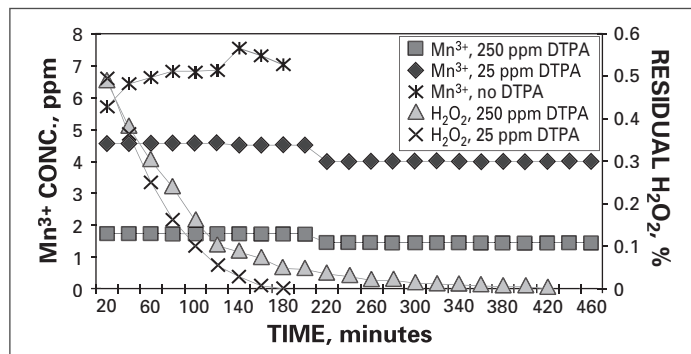
III. Catalytic activity of MnO_2 in decomposing H_2O_2 at temperatures of 300°C and 1050°C.



This observation is supported by results obtained under other conditions (different MnO_2 charges and H_2O_2 concentrations), and these results are similar to those we obtained in Mn^{2+} -induced peroxide decomposition [13]. Therefore, it is reasonable to assume that the chemistry of the MnO_2 -induced peroxide decomposition is similar to that of the Mn^{2+} -induced system. The consumption of peroxide is rapid as a result of the redox cycle via Reactions 4, 5, and 6:



Therefore, we draw the conclusion that the MnO_2 -induced peroxide decomposition proceeds via an initiation reaction (Reaction 1) and the redox cycle involving Mn^{2+} and Mn^{3+} (Reactions 4, 5, and 6). Bodini and Sawyer [11], in their effort to elucidate the MnO_2 - H_2O_2 system under



4. Development of Mn^{3+} and H_2O_2 concentrations with and without DTPA (96.0 ppm MnO_2 , pH 10, 0.75% H_2O_2 , 25EC).

alkaline conditions, also found that Mn^{2+} and Mn^{3+} are formed during the course of the reaction. The presence of Mn^{3+} species in such a reaction system is further supported by the experimental evidence of Baral *et al.* [5].

Figure 2 presents the effects of purging with either N_2 or O_2 on the development of Mn^{3+} and H_2O_2 concentrations. Evidently, purging with O_2 speeds up the reactions, whereas N_2 slows them down. Interestingly, the higher the peroxide decomposition, the higher the Mn^{3+} concentration. Again the experimental evidence is similar to that obtained in the study of Mn^{2+} - or Mn^{3+} -induced peroxide decomposition, further supporting the hypothesis that the chemistry in these three systems is similar.

Table I compares the catalytic activity of Mn^{2+} and MnO_2 . In the case of Mn^{2+} , the residual H_2O_2 is zero after 45 min, whereas 80% of the initially charged peroxide still remains in the case of MnO_2 . Therefore, MnO_2 is much less active than Mn^{2+} in decomposing the alkaline peroxide solution. This difference arises because of the limited surface area of MnO_2 , which leads to a slow initiation reaction. The assertion that Mn^{2+} has a higher catalytic activity than MnO_2 is consistent with the work of Jiang *et al.* in their study of homogeneous and heterogeneous catalytic processes in the decomposition of H_2O_2 by MnO_2 and $Mn(OH)_2$ [14].

Figure 3 shows the effects of the surface area of MnO_2 and the speed of stirring on peroxide decomposition. By grinding MnO_2 to smaller particles (powder), we increased the surface area for the reaction, and the rate of peroxide decomposition increased. Increasing the speed of stirring does not have much effect on the rate of peroxide decomposition by MnO_2 in powder form. However, for MnO_2 in particulate form, the rate of peroxide decomposition was higher for the fast-stirring run than for the slow-stirring run.

Table II shows more results pertaining to the effect of the surface area of MnO_2 on peroxide decomposition. In Run 1, Mn^{2+} solution was made alkaline and was left standing overnight. Under this condition, the Mn^{3+} formed from the oxidation of Mn^{2+} was completely hydrolyzed to precipitated MnO_2 [12]. The catalytic activity of precipitated MnO_2 was found to be much higher than MnO_2 in particulate form and was comparable to Mn^{2+} in Table I. This outcome arises because precipitated MnO_2 has a very large surface area, and Reaction 1 occurred extensively here. These results again support the conclusion that the surface area of MnO_2 is an important factor during MnO_2 -induced peroxide decomposition.

In Run 2, Zeolite was added to Mn^{2+} solution, which was then made alkaline and left standing overnight. As shown, the

	MgSO ₄ + Na ₂ SiO ₃	DTPA	EDTA	RESIDUAL H ₂ O ₂ CONC., %
<i>With and without stabilizers</i>				
Run 1	—	—	—	41
Run 2	yes ^a	—	—	79
Run 3	—	yes ^b	—	68
Run 4	—	—	yes ^c	71
<i>With combinations of stabilizers</i>				
Run 1	yes ^a	yes ^b	—	80
Run 2	yes ^a	—	yes ^c	79
Run 3	—	yes ^b	yes ^c	75
Run 4	yes ^a	yes ^b	yes ^c	81

^a3.3 mmol/L MgSO₄ + 3.3 mmol/L Na₂SiO₃. ^b0.65 g/L EDTA. ^c0.65 g/L DTPA.
Order of addition: $H_2O + H_2O_2 +$ stabilizer(s) + NaOH + MnO_2 .
Initial H_2O_2 concentration = 0.75%. MnO_2 added = 63.3 ppm.
Temperature = 25°C, pH = 10.

IV. The decomposition of alkaline H_2O_2 by MnO_2 with and without stabilizers and with different combinations of stabilizers.

peroxide decomposition is much lower. One possible reason is that Zeolite can trap Mn^{2+} , so the oxidation of Mn^{2+} is much slower under alkaline conditions. This hypothesis is supported by the experimental observation that only a light brown color appeared during the oxidation process.

Run 3 was similar to Run 2, except that the concentration of Zeolite was increased to 4%. This increase was made to ensure that all the Mn^{2+} ions would be trapped by Zeolite. When the solution was made alkaline, no oxidation of Mn^{2+} to Mn^{3+} occurred, and there was no peroxide decomposition. Therefore, we conclude that Zeolite is effective in protecting Mn^{2+} against oxidation under alkaline conditions.

Table III presents the catalytic activity of precipitated MnO_2 in decomposing H_2O_2 when the alkaline peroxide solution is subjected to a high temperature. In Run 1, we prepared the precipitated MnO_2 by adding NaOH to a solution containing Mn^{2+} (to pH 11). This solution was left standing overnight and was then heated at 300°C for 4 h to drive off water and decrease its surface area through the formation of solid particles [15]. This heat reduced the extent of peroxide decomposition, which was comparable to that shown in Table I where MnO_2 was used in particulate form. In Run 2, the precipitated MnO_2 was prepared under the same conditions as in Run 1, except that the solution was heated at 1050°C for 4 h. In Run 2, there was no peroxide decomposition at all.

Figure 4 presents the development of Mn^{3+} and H_2O_2 concentrations with and without DTPA. The addition of DTPA (25 ppm) leads to a lower Mn^{3+} concentration. We also found that Mn^{3+} concentration decreases with an increase in DTPA charge (25 ppm to 250 ppm). These results can be explained by the formation of a complex between DTPA and manganese species, so that less Mn^{3+} is available for the redox cycle. As a result of the decrease in Mn^{3+} concentration, the peroxide decomposition decreases.

The results support the conclusion that the Mn-induced peroxide decomposition rate depends on the Mn^{3+} concentration: the higher the Mn^{3+} concentration, the higher the decomposition rate. The results also support the conclusion that the MnO_2 -induced peroxide decomposition proceeds via the Mn^{2+} - Mn^{3+} redox cycle. As a result, any additives that can suppress the Mn^{2+}

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or Mn^{3+} concentration are effective in decreasing the MnO_2 -induced peroxide decomposition.

In one set of experiments, we used Na_2SiO_3 , DTPA, and EDTA to suppress the Mn^{2+} and Mn^{3+} concentrations. **Table IV** presents the results. Without any stabilizer, the control run had the lowest residual peroxide concentration at 41%. When stabilizers were added, the peroxide decomposition fell. With a mixture of MgSO_4 and Na_2SiO_3 , Run 2 had the best stability, with a residual peroxide concentration of 79%.

Since the charge of additives in these experiments was quite large, we did not attempt to improve the peroxide stability by further increasing the additive charge. Instead, we studied the potential to improve the H_2O_2 stability by using more than one stabilizer. Table IV also presents these results. A combination of stabilizers improved the stability of H_2O_2 , as the data show. A mixture of MgSO_4 and Na_2SiO_3 , DTPA, and EDTA provided the maximum stability. The combination of stabilizers is consistent with the results from Colodette *et al.* [16], who found that the Mn^{2+} -induced peroxide decomposition decreases if DTPA, silicate, and MgSO_4 are used.

CONCLUSIONS

During the MnO_2 -induced peroxide decomposition, a small amount of MnO_2 (less than 1.5%) is converted to Mn^{2+} and

Mn^{3+} as an initiation reaction. Thereafter, a redox cycle involving Mn^{2+} and Mn^{3+} is responsible for decomposing peroxide. The initiation reaction is limited to the surface area of MnO_2 particles, and an increase in the particle surface area leads to increase in peroxide decomposition.

Experimental evidence shows that at the same manganese concentration, Mn^{2+} is more effective than MnO_2 in catalyzing peroxide decomposition, again because of the limited surface of MnO_2 . By converting Mn^{2+} to MnO_2 , we found that the Mn -induced peroxide decomposition can be reduced. Suppressing the concentration of Mn^{2+} and Mn^{3+} by using additives such as Na_2SiO_3 , DTPA, and EDTA is also effective in decreasing the MnO_2 -induced decomposition of hydrogen peroxide. **TJ**

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INSIGHTS FROM THE AUTHORS

Manganese causes hydrogen peroxide to decompose, which decreases the efficiency of the peroxide bleaching operation. Manganese dioxide (MnO_2) is one of the more stable species among various oxidation states of manganese, and many efforts have been made to understand the mechanism of hydrogen peroxide decomposition by MnO_2 .

In this study, we carried out experiments to obtain new infor-

mation regarding this reaction. We also compared the catalytic ability of Mn^{2+} with that of MnO_2 in decomposing hydrogen peroxide under the alkaline conditions of peroxide bleaching.

We were surprised to find that MnO_2 is much less catalytically active than Mn^{2+} in decomposing hydrogen peroxide when the comparison is made at the same concentration of manganese. What this conclusion means is that bleach plants mills can improve the efficiency of peroxide bleaching by converting Mn^{2+} to MnO_2 .

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