Degradation of an Organic Dye by Bisulfite Catalytically Activated with Iron Manganese Oxides: The Role of Superoxide Radicals

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1. INTRODUCTION

Currently, more and more refractory organic pollutants are being released into the aquatic environment, causing serious water pollution.1,2 Various physical and biological techniques have been proposed to degrade organic matter in water, such as adsorption,3 filtration,4 and membrane bioreactors.5 However, these methods only transfer contaminants to another phase instead of destroying them. Other chemical treatment technologies, such as advanced oxidation processes (AOPs) based on sulfate radicals (SO4\(^{\cdot-}\)), have attracted increasing attention in the search for a solution. SO4\(^{\cdot-}\) has a similar redox potential (E\(^0\) = 2.5–3.1 V vs standard hydrogen electrode, SHE) similar to a hydroxyl radical (HO\(^{\cdot-}\), E\(^0\) = 2.8 V vs SHE) but is more selective.6 Typically, SO4\(^{\cdot-}\) is primarily derived from the activation of persulfates (PSs) by heating, UV irradiation, and transition metal.7 However, PSs show many disadvantages, such as high cost and strong stability leading to secondary pollution. Therefore, the search for effective, environmentally friendly, and economical oxidants has drawn considerable attention.

Further, SO4\(^{\cdot-}\) can also be produced by activating bisulfite. The activation methods of bisulfite include energy-input and transition metal-involved reactions.8,9 Currently, SO4\(^{\cdot-}\) and HO\(^{\cdot-}\) produced by activating bisulfite are thought to be the cause of organic degradation.10 However, Sun et al.11 found that in a MnO\(_2\)/bisulfite system, organic pollutants are oxidized by Mn(III)\(_{aq}\) through electrophilic attack. In addition, Dong et al.12 confirmed the formation of Cr(V) in Cr(VI)/sulfite process and proposed a new mechanism for Cr(V) degradation of organic pollutants in oxygen-containing solutions. These studies have proposed a non-radical oxidation mechanism in light of findings that methanol (MeOH) or tert-butanol (TBA) (scavengers for SO4\(^{\cdot-}\) or HO\(^{\cdot-}\), respectively) did not significantly inhibit the degradation of organic compounds caused by the transition-metal-ion activation of bisulfite.13 Sun et al.14 showed that in an established permanganate/bisulfite system, a large amount of Mn(III) species (existing in the form of hydroxo-Mn\(_3^+\), Mn(III)-sulfur complex, or other types of intermediate) with strong oxidizing power were produced in a short period of time, leading to degradation of organic compounds. In addition, Zhang et al.15 found that the Fe\(_2^+\)/Mn\(_{aq}\)/sulfite process could be rendered a more cost-effective oxidation process by promoting the production of SO4\(^{\cdot-}\) to accelerate the oxidation of Mn(II) to Mn(III). Although these processes oxidize organic contaminants at very high rates, they are homogeneous oxidation techniques that are only active in a narrow working pH range (2–3), and the oxidants cannot be recycled and reused.

Herein, we proposed a novel FeMn oxide/bisulfite system to degrade organic contaminants in aqueous solution and then evaluated the system’s performance. Effects of important factors, including bisulfite concentration, catalyst dosage, solution pH, and dissolved oxygen concentration, on the dye degradation of rhodamine B (Rhb).
degradation efficiency of the system were investigated. A new mechanism based on $O_2^{-*}$ degradation of organic pollutants was then proposed based on radical quenching tests and X-ray photoelectron spectroscopy (XPS).

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. The X-ray diffraction (XRD) technique was initially used to determine the crystallized phases of the FeO$_x$, MnO$_x$, and FeMn oxides and their crystallinity (Figure 1a). The diffraction peaks of FeO$_x$, Mn$_2$O$_3$ (PDF\#33-0664),16 The peaks in the XRD pattern of the MnO$_x$ samples can be attributed to Mn$_2$O$_3$ (PDF\#25-0508). In the case of the Fe2Mn1 sample, diffraction peaks corresponding to MnFe$_2$O$_4$ (10-0319) were observed, indicating a crystalline structure phase. As the molar ratio of Mn increases, the Fe1Mn1 and Fe1Mn2 samples not only show the original MnFe$_2$O$_4$ peak but also have additional peaks (41 and 42°), which can be attributed to MnO$_2$.13 Furthermore, the peaks of iron oxide gradually weakened, and only the diffraction peaks of Mn$_2$O$_3$ (PDF\#24-0734) were observed in Fe1Mn5.

The surface morphology of as-prepared catalysts was investigated by scanning electron microscopy (SEM) images (Figure 1b). The scanning electron micrographs clearly indicated that the synthesized Fe2Mn1 had large particles with a porous structure, and as the proportion of manganese increased, the pore size gradually decreased and Fe2Mn1 showed a loose sheet-like structure (Figure 1b).

Figure 1. Characterization of catalysts: (a) X-ray diffraction (XRD) pattern and (b) scanning electron micrographs (SEM).

2.2. Degradation Performance of the Iron Manganese Oxide/Bisulfite System. Degradation of rhodamine B under various conditions is shown in Figure 2a. The degradation of rhodamine B was negligible over the course of the reaction in the presence of bisulfite or the catalyst (Fe1Mn5) alone. This indicates that bisulfite itself did not react with rhodamine B and Fe1Mn5 exhibited a weak adsorption capacity toward rhodamine B. Other catalysts also exhibited a similar phenomenon (data not shown), which can be interpreted as the amount of added catalyst was very small. When the combination of Fe1Mn5 with bisulfite was without air bubbling, no degradation occurred. However, for the Fe1Mn5/bisulfite–air bubbling system enhanced rhodamine B degradation was observed with an efficiency of 91%. This indicates that dissolved oxygen in aerated solution (or 0.24 mM O$_2$) played an important role in degrading the target contaminant, possibly due to the generation of reactive oxygen species (ROS).6,12 Furthermore, different catalysts exhibited different degradation performances under the same experimental conditions. The degradation efficiency of Fe$_2$O$_3$ was the lowest among all of the catalysts. When the ratio of Fe/Mn was decreased from 2:1 to 1:5, the degradation efficiency increased sharply from 27 to 91% within the examined reaction time. This shows that Mn content plays a major role in the activation of sulfate. However, the degradation efficiency decreased from 91 to 60% in the Fe-free system (Mn$_2$O$_3$). Combined with XPS results (see Section 2.4 for details), it can be shown that the addition of trace Fe will promote the Mn(II)/Mn(III) cycle to enhance the degradation of rhodamine B.

To comprehensively evaluate the catalytic performance of the Fe1Mn5/bisulfite/bubbling system, the influence of the initial pH value, catalytic dosage, bisulfite concentration, and bisulfite addition modes was systematically investigated.

As shown in Figure 2b, the catalytic ability of Fe1Mn5 was significantly influenced by the solution pH. The maximum degradation was ~90% in the pH range between 4.0 and 5.0. However, when pH was decreased to 3.0, the degradation rate reduced from ~90 to 78%. This decline in degradation rate can be attributed to a reduced conversion efficiency between Fe(II) and Fe(III) due to the formation of Fe(H$_2$O)$_6^{3+}$ and Fe(H$_2$O)$_6^{2+}$.17 At pH 8 and 10, the degradation of rhodamine B was completely inhibited. These results indicate that the system was efficient at acidic and near-neutral pH.

Figure 2c indicates that catalyst dosage exerted a great influence on the rhodamine B degradation rate. We observed that when the catalyst dosage was only 109 μM, the removal rate attained was over 90%, suggesting that Fe1Mn5 has a satisfactory ability to activate bisulfite. However, when the catalyst was continuously increased to ≥109 μM, the final degradation decreased to less than 80%. The reaction rate showed a similar decreasing pattern with varying catalyst dosage. This can be attributed to the competitive consumption between metal ions and ROS on the catalyst surface.18,19 The optimal catalyst dosage was therefore 109 μM.

The degradation of rhodamine B over Fe1Mn5 was further studied at varying concentrations of bisulfite (Figure 2d). Obviously, as the bisulfite concentration increased from 1 to 10 mM, the degradation efficiency of rhodamine B increased from 68 to 90%. However, the degradation efficiency decreased somewhat when the bisulfite increased from 10 to 20 mM, from which we can infer that the reactive species provided by Fe1Mn5 was insufficient to activate bisulfite. Interestingly, the
degradation of rhodamine B presented a different trend. The maximum reaction rate was observed at a bisulfite concentration of 3 mM, and the degradation rate gradually decreased as the concentration increased. To further elucidate this phenomenon, the effect of different methods of bisulfite addition during the reaction process was investigated, the results of which are shown in Figure 2e. The rhodamine B was almost completely removed within 10 min at a bisulfite concentration of 8 mM, achieved by the addition of bisulfite to the reaction in four aliquots of 2 mM. The four aliquots of 2 mM performed better than the one-time addition of 10 mM bisulfite. This phenomenon is consistent with the results of Zhang et al., and we attributed this to the fact that excess bisulfite will react with ROS generated from the activation reaction during the initial stage, resulting in a decrease in the reaction rate. This indicates that a low bisulfite concentration or multiple low-concentration aliquots may be a preferable strategy and can reduce the reaction cost.

2.3. Identification of ROS. A previous study reported that SO₄⁻ and HO• can be generated in the presence of bisulfite. Thus, a radical-scavenging experiment was conducted to identify ROS in the current system with three catalysts (Figure 3a). tert-Butanol was used as an effective quencher for HO• (k = 6.0 × 10⁸ M⁻¹ s⁻¹), and methanol was used as an effective quencher for both HO• (k = 9.7 × 10⁸ M⁻¹ s⁻¹) and SO₄⁻ (k = 2.5 × 10⁷ M⁻¹ s⁻¹). Compared with the blank experiment, the degradation efficiency of rhodamine B in the systems with Fe₂O₃ as the catalyst decreased by 0.59 and 18.89% with tert-butanol and methanol as scavengers, respectively. This indicates that SO₄⁻ plays a major role, and the result is
similar to the previously reported results. However, neither tert-butanol nor methanol affected degradation of rhodamine B in the systems with Fe1Mn5 and Mn2O3 as the catalyst, indicating that HO• and SO4•− were not the dominant ROS in the solution or bound on the surface of the catalyst in those systems. It has been reported that Mn(III) may dominate in the homogeneous and heterogeneous reaction of manganese to activate bisulfite. Nevertheless, an unusual phenomenon was discovered: Mn(III) was not captured throughout the degradation process (Figure 3b). Therefore, other ROS might be involved in the activated bisulfite system using manganese.

As shown in Figure 3a, the degradation efficiency of rhodamine B was almost completely quenched in the presence of benzoquinone, which is a superoxide radical (O2•−) scavenger. In contrast, the degradation efficiency of rhodamine B changed less with the addition of L-histidine, which is a scavenger of singlet oxygen (1O2). These results demonstrate that O2•− instead of HO• and SO4•− was the important ROS in the iron manganese oxide-activated bisulfite system.

2.4. Mechanism and Stability. To explore the activation mechanisms of bisulfite by Fe1Mn5, Mn and Fe before and after degradation of rhodamine B were characterized via XPS analysis (Figure 4).

As shown in Figure 4a, the Fe 2p3/2 peak at 710.6 eV is assigned to Fe(II), whereas the Fe 2p3/2 signal at 712.4 eV together with the vibrating satellite at 718.7 eV indicates the presence of surface Fe(III). The Mn 2p peaks were composed of two main spin–orbital lines, as shown in Figure 4b. The Mn 2p3/2 signal at 641.2 eV indicated the presence of surface Mn(II), whereas the Mn 2p3/2 signal at 642.8 eV indicated the presence of surface Mn(III). After three times of reuse, the Fe(II)/Fe(III) ratio decreased from 1.15 to 0.63 and the Mn(II)/Mn(III) ratio increased from 0.25 to 0.64, indicating that part of Fe(II) changed to Fe(III) and Mn(III) changed to Mn(II) during the bisulfite activation catalytic process, respectively. However, the difference in XRD patterns before and after the reaction was relatively small (Figure 4c), which can be attributed to the fact that the reaction only occurs on the surface of the catalyst. In addition, we investigated the dissolution of ions during the reaction. The results showed that only 6.82% of Fe ions and 0.52% of Mn ions were eluted in the catalyst, and the amount of elution was very small.
According to the above experimental results, we proposed a plausible mechanism of the Fe1Mn5/bisulfite system as follows (eqs 1–6).\textsuperscript{29,30}

\begin{align*}
\text{Mn(III)} + \text{HSO}_3^- & \leftrightarrow \text{Mn(II)} + \text{HSO}_4^- \quad (1) \\
\text{HSO}_3^- + \text{O}_2 & \rightarrow \text{SO}_4^- + \text{H}^+ \quad (2) \\
\text{HSO}_3^- + \text{O}_2 & \rightarrow \text{O}_2^- + \text{SO}_3^- + \text{H}^+ \quad (3) \\
\text{SO}_3^- + \text{H}_2\text{O} & \rightarrow 2\text{H}^+ + \text{SO}_4^- \quad (4) \\
\text{Mn(II)} + \text{SO}_4^- & \leftrightarrow \text{Mn(III)} + \text{SO}_3^- \quad (5) \\
\text{Fe(II)} + \text{Mn(III)} & \leftrightarrow \text{Fe(II)} + \text{Mn(II)} \quad (6)
\end{align*}

3. CONCLUSIONS

In this study, a novel iron manganese oxide/bisulfite system was proposed to effectively degrade dye pollutants within a wide range of pH. Moreover, the dissolved oxygen played a crucial role in the Fe1Mn5/bisulfite system with only 8% of rhodamine B degraded under no bubbling. At a catalyst loading of 109 \(\mu\text{M}\) and a bisulfite concentration of 10 mM, 90% of rhodamine with an initial concentration of 20.9 \(\mu\text{M}\) could be degraded in 30 min. The radical-scavenging test confirmed that \(\text{O}_2^\cdot\), not \(\text{HO}^+\) or \(\text{SO}_4^\cdot\), was the important ROS in the iron manganese oxide-activated bisulfite system. Therefore, the present research indicates that the proposed system is a promising candidate for the decomposition of organic pollutants.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Commercially available dye rhodamine B obtained from Aladdin Inc. was used as the probe without further purification. All other chemicals used in this study, including ferric nitrate, manganese(II) nitrate aqueous solution (50%), citric acid, ethanediol, sodium bisulfite, sodium pyrophosphate, methanol, tert-butanol, p-benzoquinone, l-histidine, and 5,5′-dithiobis-(2-nitrobenzoic acid), were of analytical grade and were purchased from Aladdin Inc. \(\text{NaOH}\) and \(\text{H}_2\text{SO}_4\), which were used to adjust the pH of solutions, were obtained from Sinopharm Chemical Reagent Co., Ltd. Milli-Q water was used in all experiments.

4.2. Synthesis of Iron Manganese Oxides (FexMny).

The iron manganese oxide catalysts were prepared via a sol–gel process with citric acid and ethanediol as the complexing agent and dispersant according to the procedure detailed below. An appropriate amount of the ethanediol solution was added to the precursor solution of \(\text{Fe(NO}_3)_3\cdot9\text{H}_2\text{O}, \text{Mn(NO}_3)_2\), and citric acid (the molar ratio of total metal ion and citric acid was 1:1) at 80 °C under vigorous stirring to form a black or olive green gel. Thereafter, the gel was moved to a crucible and washed three times with deionized water and then dried in an oven at 75 °C. The obtained catalyst was used for the next reuse test and the reaction solution was discarded. After three replicate experiments, the catalyst was collected and washed three times with deionized water and then dried in an oven at 75 °C. The obtained catalyst was used for the next reuse test and the reaction solution was discarded. After three replicate experiments, the catalyst was analyzed via XPS and XRD.

4.3. Characterization of Catalysts.

The crystalline phases of the as-prepared FexMny were identified using a Rigaku SMARTLAB9 X-ray diffractometer (XRD) with Cu Kα radiation at a detector angle 2Φ from 10 to 80°. Morphologies of the samples were examined via a scanning electron microscope (SEM, FEI Inspet F50). X-ray photoelectron spectrometry (XPS) was used to analyze the elemental compositions of the catalyst before and after the reaction using an Escalab 250Xispectrometer (Thermo Scientific).

4.4. Experimental Procedures. All experiments were performed in 250 mL open beakers with a tubing to allow the bubbling of gas at air-conditioned room temperature (25 ± 1 °C). The reactor was operated in batch mode with rapid mixing from the bottom of the reactor. In a typical test, the desired amounts of rhodamine B and bisulfite were added to the solution, and then a quantity of FexMny was added to initiate the reaction under a certain amount of air bubbling. The amount of aeration was adjusted by a gas flow meter, and the dissolved oxygen content of the system was measured with a dissolved oxygen meter within a predetermined time interval to ensure a constant dissolved oxygen concentration in the system. The pH of the system was adjusted to the desired value using \(\text{H}_2\text{SO}_4\) or \(\text{NaOH}\) solution. The pH was not controlled for the rest of the reaction process. Samples (2 mL) were withdrawn at predetermined intervals and measured immediately after being filtered with a 0.22 \(\mu\text{m}\) filter film. Each experiment was conducted at least in duplicate and average values with standard deviations (error bars) are presented.

For the cycle experiments, the spent catalyst was collected and washed three times with deionized water and then dried in an oven at 75 °C. The obtained catalyst was used for the next reuse test and the reaction solution was discarded. After three replicate experiments, the catalyst was analyzed via XPS and XRD.

4.5. Analysis. The concentration of the rhodamine B dye \((\lambda_{\text{max}} = 554 \text{ nm})\) in the treated solution was analyzed with a UV–vis spectrophotometer (UV-2550, Shimadzu Corp., Kyoto, Japan). The bisulfite concentration was spectrophotometrically determined using the 5,5′-dithiobis-(2-nitrobenzoic acid) method,\textsuperscript{31} and Mn(III) was measured by the sodium pyrophosphate method at 258 nm.\textsuperscript{32} The Mn(II) concentration was monitored using the potassium periodate spectrophotometric method,\textsuperscript{33} and the concentrations of Fe(II) and Fe(III) were measured by the o-phenanthroline colorimetric method.\textsuperscript{34} The pH was measured with a Mettler-FE20 pH meter (Mettler-Toledo, Zürich, Greifensee, Switzerland).

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