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Decolorization of Dye Pollutions by Manganese Complexes with Rigid Cross-Bridged Cyclam Ligands and Its Mechanistic Investigations

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Exploring pH-insuspensible catalysts for pollutant treatments is still a challenge because of the pH-dependent catalyst stability. A recently developed manganese complex, $Mn(Me_2EBC)Cl_2$, (Me_2EBC: 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane) was investigated to decolorize dyes in the pH range of 1−13 using H_2O_2 as the oxidant, and its stability in service was examined by periodically adding fresh dye and oxidant. The results display that this manganese complex is capable of decoloring dye in both acid and base and keeping activity for a long service period. In addition, its modified analogue, $Mn(Et_2EBC)Cl_2$, can perform efficient decolorization in the whole pH range from pH 1 to 13. Combinatorial methods including stoichiometric treatments of dye with freshly synthetic manganese(IV) complex, utilization of radical scavenger, and intermediate analysis by UV−visible spectrophotometry were applied for its mechanistic studies, and a manganese(IV) hydroperoxide intermediate has been suspected to serve as the key active species in decolorization.

Introduction

With the rapid industrialization in developing countries such as China, environmental issues have received more and more attention, whereas the current pollution treatment technologies including biological and chemical technologies have been suffering serious challenges from increasing pollutant treatment requirements. Although the biological technologies, mostly based on enzyme-catalyzed oxidations, are capable of eliminating versatile pollutants, they also have limitations such as relatively long treatment time and sensitivity to the high pollutant concentration.[1] The chemical technologies including photocatalytic oxidation,[2,3] Fenton oxidation,[4,5] Ozonation,[6,7] and catalytic wet air oxidation[8] are the alternative choices to the biological technologies. Importantly, these technologies are particularly suitable for eliminating the pollutants with high toxicity. In the oxidation technologies for wastewater treatment using transition-metal ions as catalysts, the most serious challenge is that the pH of the wastewater has to be limited to a narrow range.[4,8,9] For example, the applicable pH range is limited to 2−4 for Fenton technologies;[4] otherwise, the precipitation of iron oxide would happen. The transition-metal ions having macrocyclic ligands have been widely applied in versatile selective oxidations in industry and academic chemistry, and the related active intermediates are generally proposed to be the transition-metal oxo species.[10] However, their applications in pollutant treatment are still very rare. The limited successful examples include the iron complexes with porphyrin[9] or TAML ligand.[10] In particular, Collins's Fe-TAML system has demonstrated the extremely high efficiency in the degradation of a series of pollutants from different wastewater sources.[11−13] Because the pH value of the wastewater may change randomly when the pollutant sources change, it is generally required to adjust the pH of the wastewater to the specific range prior to the treatment because of the stability limit of the oxidation catalyst. To the best of our knowledge, there has been no reported catalyst to demonstrate its efficient degradation capability over a wide pH range from acid to base.

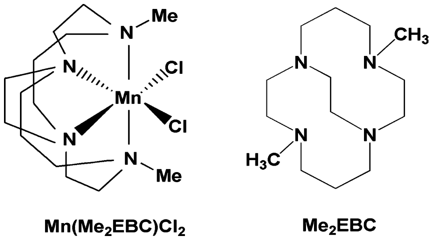

Figure 1. Structure of the manganese(II) complex having cross-bridged macrocyclic ligand.

In recent years, Busch and coworkers developed a series of transition-metal complexes with ultra rigid, cross-bridged macrocyclic ligands.[14] Those metal complexes have demonstrated extreme stability compared with other reported transition-metal complexes. For example, The half-life ($t_{1/2}$) of $Mn(Me_2EBC)Cl_2$ (Figure 1) in 1 M DCl was found to be 13.8 h at 298 K, which was nine orders of magnitude slower than that of tetra(3-*N*-methylpyridyl) porphyrin ligand ($t_{1/2} = 74\ \mu s$), whereas in base, $Mn(Me_2EBC)Cl_2$ can be oxidized by oxygen to the corresponding manganese(III) complex, which can stand in air for months.[15] Because of its extreme stability over a wide pH range, it provides a peculiar chance to explore its applications in degrading versatile pollutants without pH adjustments. In this contribution, the applications of the manganese complexes having Me_2EBC and related ligands in dye degradation were investigated using hydrogen peroxide as the terminal oxidant. It was found that the manganese complex demonstrated the remarkable degradation activity over a wide pH range from 1 to 13, and detailed investigations revealed that this manganese complex can play multiroles in pollutant elimination.

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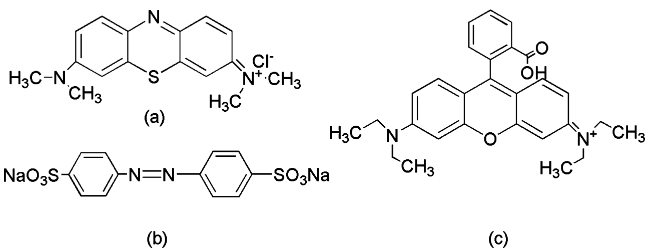

Figure 2. Structures of (a) methylene blue, (b) methyl orange, and (c) Rhodamine B.

Experimental Section

Materials and Instruments. $Mn^{II}(Me_2EBC)Cl_2$ and $Mn^{II}(Et_2EBC)Cl_2$ were generously presented by Professor Busch at the University of Kansas; the manganese(IV) complex, $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$, was conveniently synthesized according to the literature.[15] Methylene blue (MB), methyl orange (MO), and Rhodamine B (RhB) (Figure 2) were from Sinopharm Chemical Reagent. All other chemicals were analytical grade reagents and used without further purification. UV−visible spectra were recorded on a Hitachi U3100 spectrophotometer, and the total organic carbon (TOC) was determined by an Apollo 9000 TOC analyzer.

General Decolorization Procedures. The dye decolorizations were performed in aqueous solution having specific pH values at room temperature (298 K). The pH of the solution was adjusted by NaOH or HCl as needed. In a typical reaction, the pH of 25 mL of aqueous solution containing 0.40 mM $Mn^{II}(Me_2EBC)Cl_2$ catalyst and 1.34 mM MB was adjusted to pH 1.3 by HCl; then, the reaction was initialized by the addition of 0.25 mL of H_2O_2 (30%). To monitor the reaction proceeding, 1 mL of aqueous solution was withdrawn from the reaction mixtures periodically and diluted to 100 mL of aqueous solution immediately. The resulting diluted solution was analyzed by UV−visible spectrophotometry to monitor the decay of the characteristic absorbance of MB at 664 nm. We evaluated the stability of $Mn^{II}(Me_2EBC)Cl_2$ catalyst in service by adding fresh dyes and H_2O_2 in the same reaction solution periodically, and the degradation analysis was conducted as described above.

Results and Discussion

Oxidative Degradation of Organic Dyes in the Presence of $Mn^{II}(Me_2EBC)Cl_2$. Because the dye pollutants change widely from their sources such as dyestuff manufacturing, dying, printing, and textile industries, three common dye materials including MB, MO, and RhB were selected to test the catalytic decolorization capability of the manganese(II) complex, $Mn(Me_2EBC)Cl_2$, using H_2O_2 as the terminal oxidant. The decolorization of dyes was performed in aqueous solution at room temperature (298 K) and monitored by UV−visible spectrophotometry. In Figure 3, one may see that in the blank experiments hydrogen peroxide itself is incapable of degrading MB, MO, or RhB in the neutral aqueous solution. Within 300 min of treatment by H_2O_2, the absorbance of three dyes remains unchanged in the absence of the manganese(II) catalyst. Also, there was no obvious decolorization of MB observed in the case of the addition of $MnCl_2$ as the catalyst. Upon the addition of $Mn(Me_2EBC)Cl_2$ catalyst, decolorization of dyes occurs immediately. Complete decolorization of MO and RhB can be completed in 5−14 min, respectively, whereas MB decolorization proceeds by a relatively slow rate. Within 300 min of treatment, ~50% of MB can be decolorizated in the neutral aqueous solution. During the decolorization process under the neutral conditions applied here, many bubbles were released from the reaction mixtures, caused by manganese(II)-complex-catalyzed decomposition of H_2O_2. For convenient monitoring of the catalytic efficiency of the manganese(II) complex and its mechanistic studies in pollutant degradation, the relatively robust substrate MB was selected as the dye model in the following investigations.

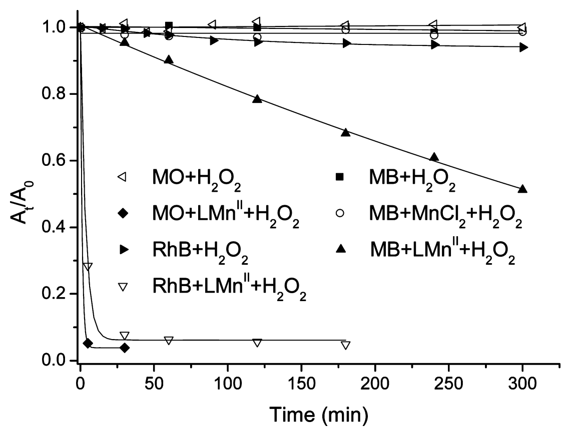

Figure 3. Decolorization of dye pollutants with $Mn^{II}(Me_2EBC)Cl_2$. Reaction conditions: [LMn^{II}] 0.40 mmol/L; [$MnCl_2$] 0.40 mmol/L; [H_2O_2] 97.9 mmol/L; [MO] 1.53 mmol/L; [RhB] 1.04 mmol/L; [MB]1.34 mmol/L; neutral solution pH; 298 K.

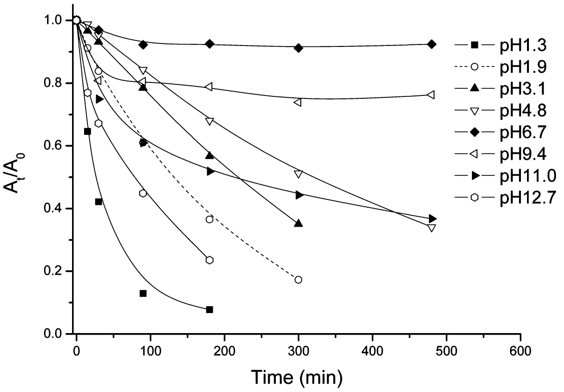

Figure 4. Effect of the initial pH on decolorization of MB with $Mn^{II}(Me_2EBC)Cl_2$. Reaction conditions: [LMn^{II}] 0.4 mmol/L; [H_2O_2] 97.9 mmol/L; [MB] 1.34 mmol/L; 298 K.

Effect of the Initial pH on Decolorization of Methylene Blue with $Mn^{II}(Me_2EBC)Cl_2$. Compared with other redox transition-metal complexes, one of the important features of this manganese(II) complex is that it displays an unusual stability over a wide pH range,[15] which provides a basis for its potential application in a pH-insusceptible pollution treatment. Figure 4 displays the influence of the initial pH of the reaction medium on MB decolorization. Obviously, the $Mn^{II}(Me_2EBC)Cl_2$ catalyst demonstrates a remarkably catalytic activity from acid to base. The highest catalytic efficiency occurs at pH as low as 1.3 in acid or as high as 12.7 in base, whereas the catalyst demonstrates a relatively low efficiency at neutral pH because of the catalytic decomposition of H_2O_2 by catalysis. During the decolorization, there was no obvious dioxygen release observed from the reaction medium at the initial pH 1.3, and only minor dioxygen release was observed at the initial pH 12.7, whereas much dioxygen release occurred at the neutral pH 6.7, resulting in the loss of catalytic efficiency. The oxygen release was also identified by GC analysis with a TCD detector. In line with these observations, a similar pH-dependent decomposition of H_2O_2 by the $Mn^{II}(Me_2EBC)Cl_2$ catalyst was also observed in

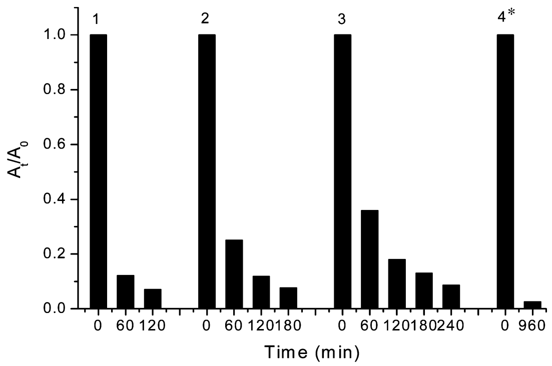

Figure 5. Endurance of the $Mn^{II}(Me_2EBC)Cl_2$ at pH 1.5 during service. Reaction conditions: $[LMn^{II}]$ 0.4 mmol/L; $[H_2O_2]$ 99.7 mmol/L; [MB] 1.34 mmol/L in runs 1, 2, and 3 and 6 mmol/L in run 4; pH 1.5; 298 K.

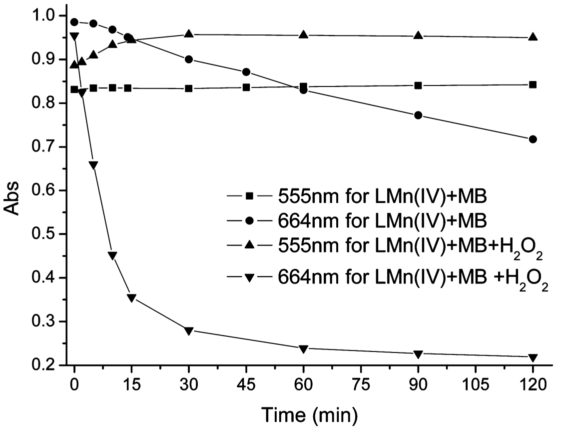

Figure 6. Decolorization of MB by $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ in the presence or absence of H_2O_2. Reaction conditions: $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ 1 mmol/L; $[H_2O_2]$ 99.7 μmol/L; [MB] 13.4 μmol/L; pH 1.5; 298 K.

the absence of dye substrates. By treatment of H_2O_2 with the manganese(II) complex in strong base (pH 12.7) or acid (pH 1.3), only minor or less-visible oxygen bubble release occurred, whereas in the neutral solution (pH 6.7), dramatic release of oxygen was observed. In addition, a similar pH-dependent decomposition of H_2O_2 through catalysis has been documented for other catalase models in the literature.[16,17] In the TOC removal test of the resulting solution, ~59% of TOC removal can be achieved in catalytic degradation of the MB process at pH 1.5. One of the most important limitations for using a redox metal complex in pollutant treatments is that the stability of a certain transition-metal complex is generally limited in a relatively narrow pH range, otherwise, dissociation of ligand may occur, causing the loss of catalytic activity and the formation of metal oxide sludge. For example, the utilization of the Fenton reagent in pollutant degradation is limited to pH 2−4. To the best of our knowledge, this manganese(II) catalyst is the first example to demonstrate its catalytic efficiency for dye decolorization under both of acidic and basic conditions.

Stability of $Mn^{II}(Me_2EBC)Cl_2$ on Degradation of Methylene Blue. The extra stability of the manganese(II) catalyst in pollutant treatments is further supported by its reuse tests (shown in Figure 5). The tests were carried out by the addition of MB substrate and oxidant periodically, and the reaction was performed under harsh pH conditions, that is, pH 1.5, in which the dissociation of the coordinated ligand may happen for most of the metal complexes at a rapid rate. Although slight loss of catalytic activity still exists with each addition of substrate/H_2O_2 because of the minor dissociation of ligand in strong acid, the catalyst apparently retains its catalytic efficiency for a long service period (the half-life of catalyst is 13.8 h in 1 M DCl[14]). After 23 h of continuous treatment, the catalyst suffers no remarkable loss of catalytic efficiency. The extra stability of the catalyst in service under harsh conditions originates from its rigid, cross-bridged cyclam ligand, which inhibits the ligand dissociation, and from the methyl substitution on the unbridged nitrogen coordination atoms in the ligand that inhibits its self-degradation.[14]

Reaction Mechanism of Methylene Blue Degradation by $Mn^{II}(Me_2EBC)Cl_2$. In the literature, degradation of pollutants generally proceeds by an oxidation process, and a catalyst is commonly applied to activate the oxidant to generate the active oxygen for eliminating the pollutants.[18−20] In photocatalytic oxidation, Fenton oxidation, and ozonation, an HO• radical has been recognized to serve as the key active species in degradation,[19,20] whereas a high-oxidation-state transition-metal oxo, $M^{n+}{=}O$, plays the key role in the transition-metal-complex-catalyzed degradation and degradation by some biological technologies.[21,22] For example, in Fe(Porphyrin) and Fe-TAML catalysts, a $Fe^{IV}{=}O$ or $Fe^{V}{=}O$ species has been proposed to be the key active intermediate in pollutant degradations from versatile sources.[9,10] In the previous publications, Busch and coworkers found that this manganese(II) complex can demonstrate multifunctional redox activities. In olefin epoxidations, a manganese(IV) hydroperoxide rather than the traditional manganese(V) oxo has been proposed to be the active intermediate when using H_2O_2 as the terminal oxidant, and such an active species, $LMn^{IV}(O)(OOH)^+$, has been identified by the accurate mass measurements,[23,24] whereas in hydrogen abstraction, both manganese(IV) oxo and hydroxo are capable of abstracting hydrogen from substrate.[25]

After the realization that the manganese(IV) complex can play several roles in oxidation reactions, the freshly synthesized manganese(IV) complex, $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$, was first quantitatively treated with MB at pH 1.5 to test its decolorization capability (Figure 6). Over a long period of treatment at room temperature, the characteristic absorbance of the manganese(IV) species at 555 nm remains unchanged, whereas the characteristic absorbance of MB at 664 nm gradually decays (in the absence of the manganese(IV) complex, MB is stable at pH 1.5), indicating that a manganese(IV)-species-assisted decolorization of MB substrate occurs in the absence of H_2O_2. Upon the addition of H_2O_2, rapid decolorization of MB occurs immediately; meanwhile, the characteristic absorbance of the manganese(IV) species at 555 nm increases slightly in 15 min and then remains steady. In the presence of H_2O_2, the manganese(IV) ion is the dominant manganese ion in neutral to acidic solution, and the manganese(V) species may not exist because of the poor electron donation ability of the four tertiary nitrogen donors in the ligand.[23] Therefore, these data reveal a bifunctional decolorization of MB catalyzed by manganese(IV) complex. In the absence of oxidant, the manganese(IV) ion itself can catalyze the decolorization of dyes at a relatively slow rate by a nonoxidative style because the manganese(IV) ion remains unchanged; upon the addition of oxidant, the manganese(IV) ion can catalyze an immediate oxidative decolorization of dyes.

To examine whether the HO• radical occurs by Fenton-like chemistry and serves as the dominant active oxygen species for this manganese-complex-catalyzed decolorization at pH 1.5, a frequently used HO• radical scavenger, *tert*-butyl alcohol,[26] was added to this manganese(II)-complex-catalyzed MB decolorization. As shown in Figure 7, the

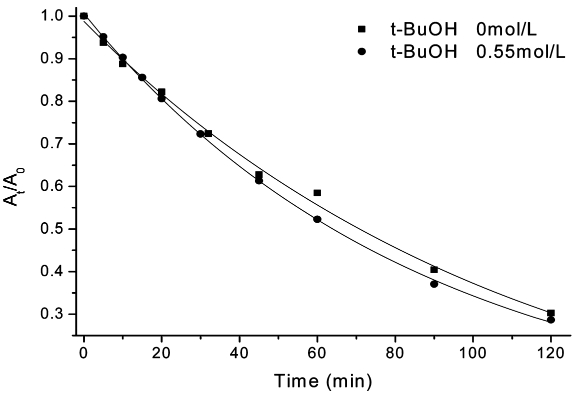

Figure 7. Effect of *tert*-butyl alcohol on the decolorization of MB. Reaction conditions: [LMn^{II}] 0.4 mmol/L; [H_2O_2] 99.7 mmol/L; [MB] 1.34 mmol/L; pH 1.5; 298 K.

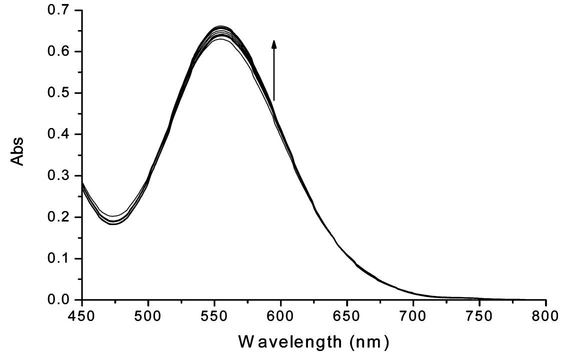

Figure 8. UV−visible spectra change of the manganese(IV) species upon the addition of H_2O_2 in aqueous solution at 278 K.

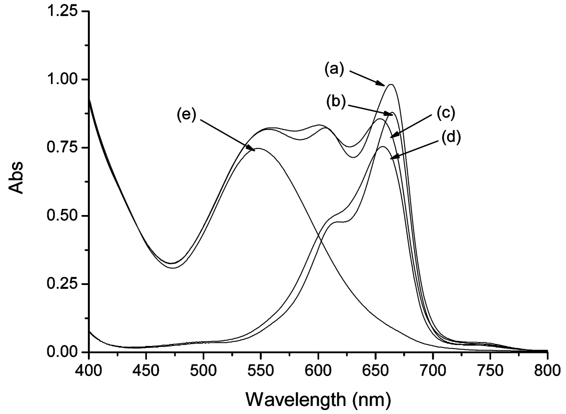

Figure 9. UV−visible spectrum of the manganese(IV) species in the presence of MB and $FeSO_4$. Reaction conditions: [LMn^{IV}] 1 mmol/L; [MB] 13.4 μmol/L; [$FeSO_4$] 5 mmol/L; pH 1.5; 298 K. (a) LMn^{IV} + MB (0 min); (b) MB; (c) LMn^{IV} + MB (60 min); (d) LMn^{IV} + MB (60 min) + Fe^{II}; (e) LMn^{IV}.

decolorization of MB could not be inhibited by the radical scavenger, even in the presence of a large amount of *tert*-butyl alcohol, supporting the conclusion that the dominant, rapid degradation process catalyzed by this manganese complex may not proceed by Fenton-like chemistry. In the previous studies,[23,24] it was demonstrated that the highly active manganese(V) oxo does not occur in this manganese complex system, and thus an alternative manganese(IV) species should be responsible for the rapid decolorization demonstrated here. In Figure 6, the increase in the characteristic absorbance of the manganese(IV) species upon the addition of H_2O_2 implicates a new manganese(IV) species generated by the addition of H_2O_2. The formation of a new manganese(IV) species was further supported by the addition of H_2O_2 to the solution containing fresh synthesized manganese(IV) complexes; a similar increase in the characteristic absorbance of the manganese(IV) species occurs immediately upon the addition of H_2O_2 (Figure 8). In the studies of olefin epoxidations in neutral aqueous solution, the formation of the active intermediate, $LMn^{IV}(O)(OOH)^+$, by ligand exchange between $LMn^{IV}(O)(OH)^+$ and H_2O_2 has been suggested, and such an intermediate is responsible for oxygen transfer to olefins.[23,24] Meanwhile, one approximate pK_a value for $[Mn^{IV}(Me_2EBC)(OH)_2](PF_6)_2$ was reported to be ∼2.[28] For this pK_a value, it represents the addition of one proton to $Mn^{IV}(Me_2EBC)(OH)_2{}^{2+}$ to generate $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$. Therefore, in the aqueous solution at pH 1.5, the dominant manganese(IV) species would be $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$. Upon the addition of H_2O_2 at pH 1.5, through ligand exchange between $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$ and hydrogen peroxide, the formation of a new manganese(IV) species, $LMn^{IV}(OOH)(OH_2)^{3+}$, is highly possible because a characteristic absorbance increase at 555 nm for manganese(IV) species was observed. The generated manganese(IV) hydroperoxide intermediate could play the key role in the rapid decolorization of substrate through oxygen transfer process as well as serving olefin epoxidation. Because there was only a slight increase in the characteristic absorbance at 555 nm, the ligand exchange equilibrium would mainly tend to form $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$; otherwise, the absorptivity of two manganese(IV) species would be highly similar (eq 1). In Busch's work about identifying the $LMn^{IV}(O)(OOH)^+$ intermediate by ESI-MS,[23] it was observed that the signal of $LMn^{IV}(O)(OH)^+$ was much stronger than that of $LMn^{IV}(O)(OOH)^+$, implicating that the equilibrium would substantially tend to $LMn^{IV}(OH)(OH_2)^{3+}$ here.

$$LMn^{IV}(OH)(OH_2)^{3+} + H_2O_2 \rightleftharpoons LMn^{IV}(OOH)(OH_2)^{3+} + H_2O \quad (1)$$

In the absence of the oxidant, the manganese(IV) species is also capable of catalyzing decolorization independently with no change of the manganese(IV) itself (Figure 6). Figure 9 displays the interaction between the manganese(IV) species and MB in the absence of oxidant. Upon the addition of the manganese(IV) complex, the characteristic absorbance of MB shifts slightly from 664 to 663 nm, and it continues shifting to 653 nm in 60 min, implicating interaction between manganese(IV) species and MB. However, the interaction between manganese(II) species and MB was not observed by treating MB with the manganese(II) complex at pH 1.5. Because the manganese(IV) ion can be easily quenched by iron(II) ion to generate colorless manganese(II) ion, an experiment was conducted to address whether the manganese(IV)-assisted degradation occurred during treatment of MB with manganese(IV) complexes. After quenching the manganese(IV) species by iron(II) ion in the solution containing MB and manganese(IV) species after 60 min treatments, the resulting visible spectrum between 500 and 750 nm is similar to that of MB, except that the characteristic absorbance of MB shifts from 664 to 656 nm with the maximum absorbance dropping from 0.876 to 0.756, implicating the degradation of MB catalyzed by the manganese(IV) complex. In addition, the similarly characteristic absorbance shift of dyes to indicate the decolorization has also been

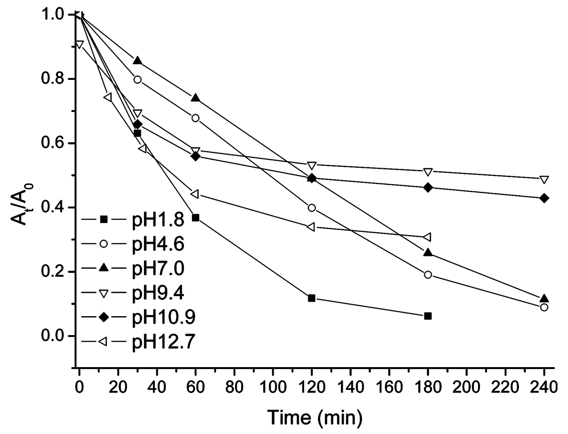

Figure 10. Effect of the initial pH on the decolorization of MB with $Mn^{II}(Et_2EBC)Cl_2$. Reaction conditions: [LMn^{II}] 0.4 mmol/L; [H_2O_2] 97.9 mmol/L; [MB] 1.34 mmol/L; 298 K.

reported in other pollutant degradation studies.[27] Because the undetermined pK_a for the addition of one proton to $Mn^{IV}(Me_2EBC)(OH)_2^{2+}$ to generate $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$ species is close to 2,[28] the dominant manganese(IV) species in aqueous solution at pH 1.5 should be $Mn^{IV}(Me_2EBC)(OH)(OH_2)^{3+}$, as previously stated. The high charge character of the manganese(IV) species at pH 1.5 may facilitate a Lewis-acid-catalyzed degradation of MB, which can be supported by the complexation formation between the manganese(IV) complex and the MB substrate, as shown in Figure 9, and the gradual degradation of MB in the presence of manganese(IV) complex, as shown in Figure 6.

Improved Decolorization of Methylene Blue with $Mn^{II}(Et_2EBC)Cl_2$. As shown in Figure 4, the $Mn(Me_2EBC)Cl_2$ complexes demonstrate the efficient decolorization of MB under both acid and basic conditions, whereas, under the neutral conditions, the decolorization efficiency is obviously low because of the rapid decomposition of H_2O_2 by catalysis. Therefore, the modifications of the ligand are essential for improving the decolorization under neutral conditions. Compared with the $Mn(Me_2EBC)Cl_2$ complex, the $Mn(Et_2EBC)Cl_2$ complex has two ethyl side arms in place of the methyl groups in the Me_2EBC ligand.[14] Figure 10 displays the preliminary decolorization efficiency of the $Mn(Et_2EBC)Cl_2$ catalyst under different pH conditions. Apparently, the $Mn(Et_2EBC)Cl_2$ catalyst displays a more active efficiency than does the $Mn(Me_2EBC)Cl_2$ catalyst under neutral conditions, whereas it still keeps the efficient decolorization under the acidic and basic conditions, indicating that the improvement of decolorization efficiency without loss of the catalyst stability through reasonable ligand modification is accessible.

Conclusions

The manganese complex, $Mn^{II}(Me_2EBC)Cl_2$, has demonstrated efficient catalytic decolorization for dyes in both acid and basic solutions. The corresponding manganese(IV) species, which is the dominant manganese species in acidic-to-neutral solution under oxidation conditions, can independently catalyze decolorization of dye at a relatively slow rate, whereas in the presence of hydrogen peroxide, the manganese complex can catalyze decolorization of dyes at a rapid rate. A manganese(IV) hydroperoxide intermediate, $LMn^{IV}-OOH$, rather than the HO• radical or manganese(V) oxo species, has been suggested to be the key active species for decolorization. The related $Mn^{II}(Et_2EBC)Cl_2$ analogue has demonstrated an improved decolorization in the pH range from pH 1 to 13, typically in the neutral aqueous solution. The results demonstrated here provide a new light to explore a practical catalyst that can degrade pollutants without preadjusting the pH of the wastewater.

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Supporting Information Available: Kinetic formation of the new manganese(IV) species upon the addition of H_2O_2 to the solution containing synthetic manganese(IV) complex as a function of time; UV−visible spectrum of MB in the presence of the manganese(II) species; UV−visible spectrum change through quenching the manganese(IV) species by iron(II); and decolorization kinetics of MB under different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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