



Mn²⁺-mediated homogeneous Fenton-like reaction of Fe(III)-NTA complex for efficient degradation of organic contaminants under neutral conditions



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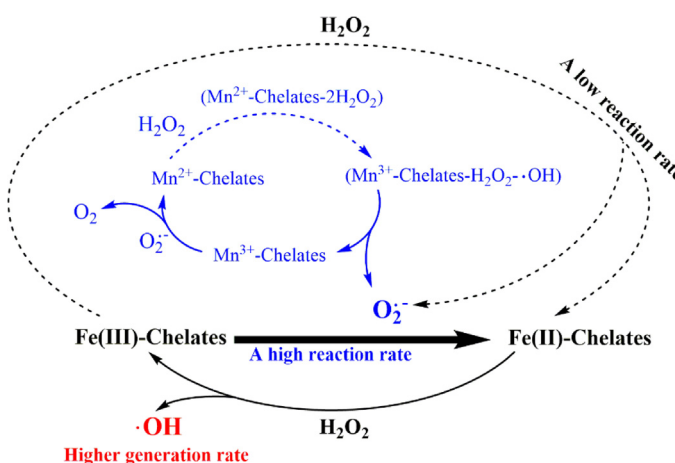
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HIGHLIGHTS

- Mn²⁺ markedly enhanced Fe(III)-NTA catalyzed Fenton-like reaction at circumneutral pH.
- Ca²⁺, Mg²⁺, Co²⁺ and Cu²⁺ had no or little inhibitory effects on such process.
- CRMT and DEET were rapidly degraded by Fe(III)-NTA-Mn²⁺ Fenton-like process.
- Generation of HO[•] and O₂^{•-} in Fe(III)-NTA-Mn²⁺ Fenton-like process were suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report a novel Mn²⁺-mediated Fenton-like process based on Fe(III)-NTA complex that is super-efficient at circumneutral pH range. Kinetics experiments showed that the presence of Mn²⁺ significantly enhanced the effectiveness of Fe(III)-NTA complex catalyzed Fenton-like reaction. The degradation rate constant of crotamiton (CRMT), a model compound, by the Fe(III)-NTA-Mn²⁺ Fenton-like process was at least 1.6 orders of magnitude larger than that in the absence of Mn²⁺. Other metal ions such as Ca²⁺, Mg²⁺, Co²⁺ and Cu²⁺ had no impacts or little inhibitory effect on the Fe(III)-NTA complex catalyzed Fenton-like reaction. The generation of hydroxyl radical (HO[•]) and superoxide radical anion (O₂^{•-}) in the Fe(III)-NTA-Mn²⁺ Fenton-like process were suggested by radicals scavenging experiments. The degradation efficiency of CRMT was inhibited significantly (approximately 92%) by the addition of HO[•] scavenger 2-propanol, while the addition of O₂^{•-} scavenger chloroform resulted in 68% inhibition. Moreover, the results showed that other chelating agents such as EDTA- and s,s-EDDS-Fe(III) catalyzed Fenton-like reactions were also enhanced significantly by the presence of Mn²⁺. The mechanism involves an enhanced

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generation of $O_2^{\bullet-}$ from the reactions of Mn^{2+} -chelates with H_2O_2 , indirectly promoting the generation of HO^{\bullet} by accelerating the reduction rate of Fe(III)-chelates to Fe(II)-chelates.

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1. Introduction

Hydroxyl radical (HO^{\bullet}) is highly aggressive and destroys most organic compounds with reaction rate constants in the range 10^8 – $10^{10} M^{-1} s^{-1}$ [1]. It has been shown HO^{\bullet} plays an important role in degrading organic pollutants in the natural environments, especially in the earth's atmosphere [2]. In natural aquatic environment, photochemical production of HO^{\bullet} at low concentration ($\sim 10^{-17}$ – $10^{-18} M$) has been detected in natural fresh waters and seawaters [3,4]. In addition, HO^{\bullet} can be generated by nonphotochemical Fenton-type chemistry in natural aquatic systems [5]. More recently, dark formation of HO^{\bullet} during oxidation of reduced aquatic dissolved organic matter (DOM) by oxygen has been reported, which may also be an important source of HO^{\bullet} production in natural aquatic systems [6].

The simplest and most efficient chemical pathway to produce HO^{\bullet} is the reaction of hydrogen peroxide (H_2O_2) with ferrous ion (Fe(II)) at acidic pH, i.e., the Fenton's reagent. Owing to high generation of HO^{\bullet} , applications of the Fenton's reagent in degrading various organic pollutants in water and soils have been intensively investigated for almost five decades [7]. The efficiency of the Fenton's reagent decreases significantly at $pH > 5.0$ due to the precipitation of Fe(II)/Fe(III), limiting its practical applications. Particular interest has increased in the modified Fenton's reaction at neutral or circumneutral pH. Natural or synthetic iron oxides catalyzed heterogeneous Fenton-like reactions have been applied for this purpose [8–11]. Although iron oxides can catalyze the production of HO^{\bullet} from H_2O_2 at neutral pH, a particular challenge is that the generation of HO^{\bullet} is inefficient and typically requires large excess of H_2O_2 to achieve a moderate level of HO^{\bullet} [8,10–13]. The problem is closely related to the non-radical producing pathways in H_2O_2 decomposition. Moreover, the rate of contaminant degradation is typically dependent on the sorption and desorption rate on the catalysts, because HO^{\bullet} is produced primarily on catalyst surface [14,15].

An alternative approach is the use of chelating agents to prevent the precipitation of Fe(III) [16–24]. Researchers have studied the possibility of using Fe(III)-chelates as homogeneous Fenton-like catalysts. The activation of H_2O_2 by Fe(III) complex of aminopolycarboxylates such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and *s,s*-ethylenediamine-*N,N'*-disuccinic acid (*s,s*-EDDS) generate reactive species capable of degrading numerous water contaminants at neutral pH [18–21,23]. Although the mechanism of Fe(III)-chelates catalyzed Fenton-like reaction has not yet been clarified, it is generally accepted that HO^{\bullet} plays a major role in the degradation of contaminants [18,19,21–24]. Furthermore, Fe(III) complex of tetraamido macrocyclic ligands (TAMLs) exhibit remarkable catalytic activity for the activation of H_2O_2 toward organic contaminant degradation in water at pH 7–11 [25,26], the mechanism however most likely involves the formation of high-valent oxoiron (Fe(IV)) species [27].

Recent advances in Fe(III)-chelates catalyzed Fenton-like reaction are particularly focusing on the use of biodegradable chelates such as NTA, *s,s*-EDDS and oxalic acid, etc., because the non-degradable chelates are persistent in the environment. Beyond the benefit of working at neutral pH, an important advantage of using chelating agents modified Fenton-like reaction is that the efficiency of H_2O_2 utilization can be improved significantly [28].

The generation of reactive species depends greatly on the properties of chelates (e.g., type and number of functional groups), the molar ratio of chelates to Fe(III), H_2O_2 and Fe(III) concentrations, and the pH [16,17,20]. However, little is known relative to the impact of competing metal ions (Mes) on these processes. The equilibrium speciation of complexes is dependent upon all the Mes and concentration of chelates and their stability constants [29]. The presence of competing Mes may directly influence the effectiveness of Fe(III)-chelates catalyzed Fenton-like reaction by a competitive complexation of Mes with chelates. Therefore, the main motivation for the present study was to evaluate the potential impact of major divalent Mes (e.g., Ca^{2+} , Mg^{2+} , Mn^{2+} , Cu^{2+} and Co^{2+}) on Fe(III)-chelates such as Fe(III)-NTA, Fe(III)-*s,s*-EDDS and Fe(III)-EDTA catalyzed Fenton-like reactions. To achieve this, a series of kinetics experiments were performed by using crotonamiton (CRMT) and *N,N*-diethyl-*meta*-toluamide (DEET) as the model compounds. Chemical structures of the model compounds and chelates used in the present study were shown in Table S1. The main reactive species were identified by radicals scavenging experiments. Moreover, the specific reaction mechanism was proposed on the basis of the experimental observations.

2. Materials and methods

2.1. Chemicals

Ferric chloride hexahydrate, hydrogen peroxide (30% H_2O_2 , w/w), calcium nitrate tetrahydrate, magnesium nitrate hexahydrate, sodium nitrate, sodium hydroxide and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. NTA was purchased from Acros Organics. EDTA disodium salt dehydrate, *s,s*-EDDS trisodium salt solution (35% in H_2O), formic acid, manganese nitrate tetrahydrate, copper nitrate trihydrate and cobalt nitrate hexahydrate were purchased from Sigma-Aldrich. CRMT (purity > 98%) and DEET (purity > 98%) were purchased from Adamas Reagent Co., Ltd. Chloroform was purchased from Chinasun Specialty Products Co., Ltd. HPLC-grade methanol, 2-propanol and water were purchased from Fisher Scientific. All chemicals were of reagent grade or better, and used as received without further purification. All solutions were prepared with MilliQ water.

2.2. Experimental procedures

The kinetics experiments were carried out in a 125 ml glass Erlenmeyer flask. The flask was placed in a water-jacketed glass vessel water bath with constant temperature (25 °C, unless otherwise indicated) and in the dark. 100 ml aqueous solution with an initial concentration of 49.2 μM CRMT (or 52.3 μM DEET) was added to the flask. An appropriate amount of freshly prepared Fe(III)-chelates was then added to achieve the desired concentration of Fe(III)-chelates. After that, an appropriate amount of Mes was added into the solution. The solution pH was adjusted to the desired value using 1.0/0.1 M NaOH or 1.0/0.1 M H_2SO_4 . The reaction was started by the addition of H_2O_2 . At regular time interval, 1 ml aqueous sample was withdrawn and mixed immediately with 0.1 ml methanol to quench the reaction. During the reaction process, the solutions were well mixed by a magnetic stirrer.

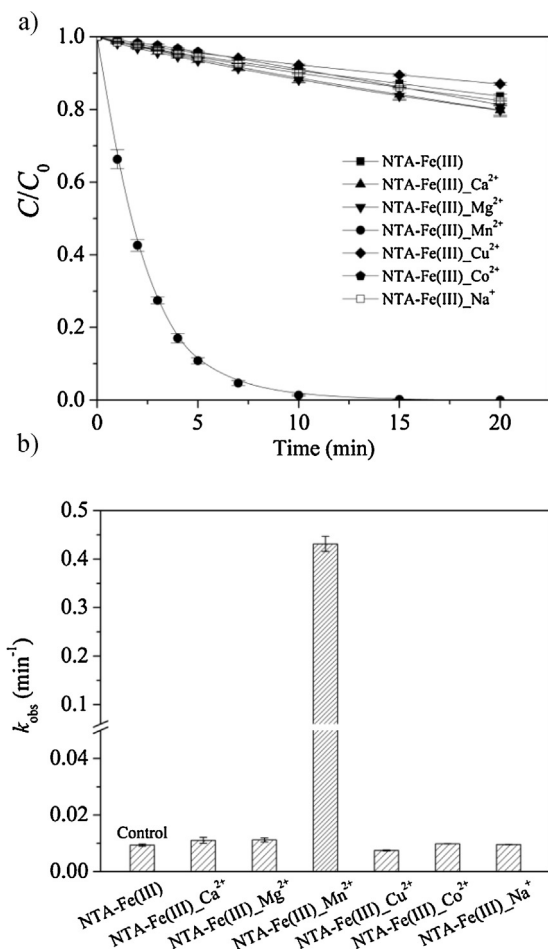


Fig. 1. Degradation kinetics of CRMT in aqueous solutions by Fe(III)-NTA complexes catalyzed Fenton-like reaction in the absence or presence of various Mes. Initial conditions: CRMT = 49.2 μ M, 0.1 mM Fe(III), NTA:Fe(III) = 2:1, H₂O₂:Fe(III) = 20:1, Me:Fe(III) = 1:1 and pH = 7.0.

2.3. Analytical methods

CRMT and DEET were determined by a high performance liquid chromatography (HPLC, Agilent 1260) equipped with a diode array detector. An Eclipse Plus C18 column (3.5 μ m, 4.6 \times 100 mm) was used for the separation. The mobile phase consisted of methanol/0.1% formic acid in water 65:35 (vol/vol) for CRMT and 60:40 (vol/vol) for DEET at a flow rate of 0.5 ml min⁻¹. The injection volume was 20 μ l and the column temperature was 30 °C. The detection wavelength was performed at 240 nm for CRMT (and 220 nm for DEET).

H₂O₂ concentration was detected by the iodide method [30]. The absorbance was measured at 352 nm with a detection limit of $\sim 10^{-6}$ M. The UV/Vis spectroscopy measurements were performed on a UV/Vis spectrometer (SpectraMax M5, Molecular Devices).

3. Results and discussion

3.1. Effects of mes. on Fe(III)-NTA complex catalyzed fenton-like reaction

Fig. 1 shows the degradation kinetics of CRMT in aqueous solutions by Fe(III)-NTA complex catalyzed Fenton-like reaction at initial neutral pH in the absence or presence of various Mes. Under the given conditions, the degradation efficiency of CRMT was small by Fe(III)-NTA complex catalyzed Fenton-like reaction, with 16.4%

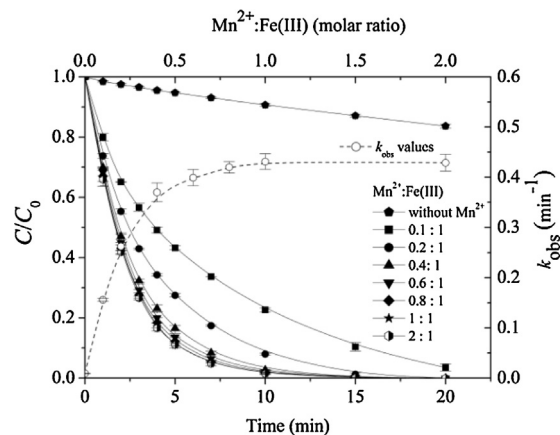


Fig. 2. Degradation kinetics of CRMT in aqueous solutions by the Fe(III)-NTA.Mn²⁺ Fenton-like process as a function of the Mn²⁺:Fe(III) molar ratios. Initial conditions: CRMT = 49.2 μ M, 0.1 mM Fe(III), NTA:Fe(III) = 2:1, H₂O₂:Fe(III) = 20:1 and pH = 7.0.

CRMT degradation after 20 min of reaction time. No statistically significant difference was observed in the degradation kinetics of CRMT in the absence or presence of Ca²⁺, Mg²⁺ and Co²⁺ ($p = 0.11$ – 0.38). In addition, the presence of Cu²⁺ had a slight inhibitory effect on CRMT degradation. In contrast to the other Mes, the presence of Mn²⁺ resulted in more than 99% CRMT degradation after 15 min of reaction time. The observed rate constant (k_{obs}) was determined to be 0.43 min⁻¹, which was far larger (~ 46 -fold) than that in the absence of Mn²⁺. Moreover, the results presented in Fig. S1 indicated that the degradation of another model compound DEET was also markedly enhanced by Fe(III)-NTA complex catalyzed Fenton-like reaction in the presence of Mn²⁺ (named Fe(III)-NTA.Mn²⁺ Fenton-like process).

Our preliminary tests showed that negligible degradation of CRMT was observed by Ca²⁺-NTA, Mg²⁺-NTA, Mn²⁺-NTA, Cu²⁺-NTA or Co²⁺-NTA complex in combination with H₂O₂ (data not shown), indicating that those complexes were inactive in catalyzing H₂O₂ to generate the highly active oxidants. The stability constants for Ca²⁺, Mg²⁺, Mn²⁺, Cu²⁺ and Co²⁺ complex of NTA ($\log K_{Ca-NTA} = 6.39$, $\log K_{Mg-NTA} = 5.47$, $\log K_{Mn-NTA} = 7.46$, $\log K_{Cu-NTA} = 12.94$ and $\log K_{Co-NTA} = 10.38$) are much smaller than that of Fe(III)-NTA ($\log K_{Fe(III)-NTA} = 15.9$) [31], thus the presence of these Mes is supposed to have minimal effect on the concentration of Fe(III)-NTA complex. It is worth to mention that a 10:1 molar ratio of Ca²⁺:Fe(III) and Mg²⁺:Fe(III) did not show any inhibitory effect on the degradation of CRMT by Fe(III)-NTA complex catalyzed Fenton-like reaction. Although the stability constant for Fe(II) complex of NTA was reported as $\log K_{Fe(II)-NTA} = 8.33$ [31], which is smaller than that of Cu²⁺-NTA and Co²⁺-NTA. No significant inhibition on the degradation of CRMT by the presence of Cu²⁺ and Co²⁺. This is probably due to that Fe(II)-NTA complex as an intermediate which could be rapidly oxidized to Fe(III)-NTA complex in this system. The slight inhibition in CRMT degradation by the presence of Cu²⁺ is most likely due to that Cu²⁺-NTA complex can compete with Fe(III)-NTA complex for reactive oxygen species (ROS) such as superoxide radical anion (O₂^{•-}), resulting in the inhibition of Fe(III)-NTA reduction.

3.2. Role of Mn²⁺ in Fe(III)-NTA.Mn²⁺ fenton-like process

To confirm the important role of Mn²⁺, we conducted experiments with various Mn²⁺:Fe(III) molar ratios. The results presented in Fig. 2 show that the Mn²⁺:Fe(III) molar ratio had significant effect on the degradation kinetics of CRMT. The degradation efficiency of CRMT reached 96.5% after 20 min of reaction time even at a small Mn²⁺:Fe(III) molar ratio of 0.1:1, which was much higher than that by Fe(III)-NTA complex catalyzed Fenton-like reaction in

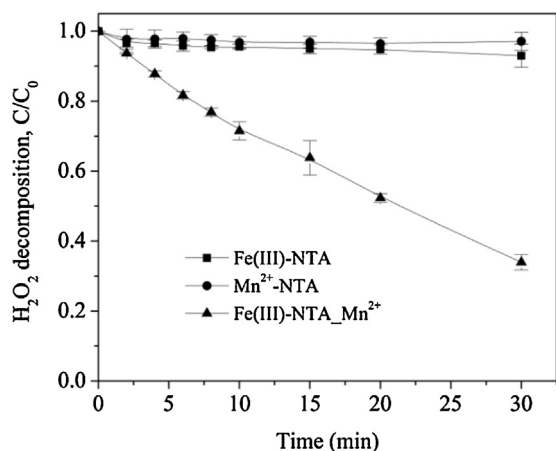


Fig. 3. Kinetics of H_2O_2 decomposition by Fe(III)-NTA complexes, Mn^{2+} -NTA complexes and their combinations. Initial conditions: CRMT = $49.2 \mu\text{M}$, 0.1 mM Fe(III), NTA:Fe(III) = 2:1, Mn^{2+} :Fe(III) = 1:1, H_2O_2 :Fe(III) = 20:1 and pH = 7.0.

the absence of Mn^{2+} . As the Mn^{2+} :Fe(III) molar ratio increased, the degradation rate of CRMT increased correspondingly. The k_{obs} value increased sharply from 0.16 to 0.43 min^{-1} and reached a plateau with increasing the Mn^{2+} :Fe(III) molar ratio from 0.1:1 to 1:1, and then no further increase of the k_{obs} value was observed at a higher Mn^{2+} :Fe(III) molar ratio of 2:1.

When the molar ratio of Mn^{2+} :Fe(III) was smaller than 1:1, most of the Mn^{2+} is presented in the solution as Mn^{2+} -NTA complex under the given conditions. At Mn^{2+} :Fe(III) molar ratio of 2:1, half of Mn^{2+} is presented as the Mn^{2+} -NTA complex and the other half would be amorphous manganese oxide. Since no statistically significant difference in the degradation kinetics of CRMT was observed at Mn^{2+} :Fe(III) molar ratios of 1:1 and 2:1. It is reasonable to infer that the Mn^{2+} -NTA complex may play an important role in enhancing the Fe(III)-NTA complex catalyzed Fenton-like reaction. The UV-vis spectra presented in Fig. S2(a) rules out the formation of new complexes from Fe(III)-NTA complex in combination with Mn^{2+} -NTA complex. In addition, no obvious changes in the UV-vis spectra of Fe(III)-NTA alone and Mn^{2+} -NTA complex alone were observed by adding 2 mM H_2O_2 (Fig. S2(b)). On the contrary, the mixture of Fe(III)-NTA complex and Mn^{2+} -NTA complex showed obvious spectral change after the addition of H_2O_2 . Its absorbance profile extended to the visible light region (e.g., starting from 380 nm versus 500 nm before and after the addition of H_2O_2), and also showed a large decrease in UV absorbance. The results suggest that new compounds are formed from the mixture of Fe(III)-NTA complex and Mn^{2+} -NTA complex in the presence of H_2O_2 . Moreover, the results presented in Fig. 3 provide strong evidence for significant synergistic action of Fe(III)-NTA and Mn^{2+} -NTA complex in catalyzing the decomposition of H_2O_2 . It can be seen that the decomposition rate of H_2O_2 was significantly enhanced by the combination of Fe(III)-NTA complex and Mn^{2+} -NTA complex. The results are consistent with the degradation of CRMT. The mechanism for the cooperative catalysis of Fe(III)-NTA complex and Mn^{2+} -NTA complex in accelerating H_2O_2 decomposition is discussed in a later section.

3.3. The main active species in Fe(III)-NTA- Mn^{2+} fenton-like process

In order to identify the reactive species formed in the Fe(III)-NTA- Mn^{2+} Fenton-like process, 2-propanol and chloroform were used as a HO^\bullet scavenger and a $\text{O}_2^{\bullet-}$ scavenger [32], respectively. Fig. 4 shows the degradation kinetics of CRMT by the Fe(III)-NTA- Mn^{2+} Fenton-like process in the presence of 2-propanol

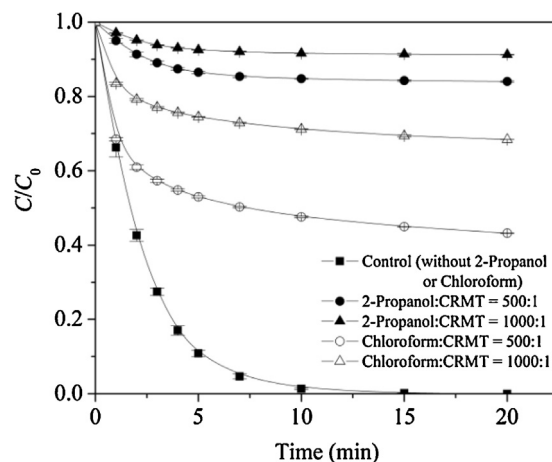


Fig. 4. Effect of 2-propanol and chloroform on the degradation kinetics of CRMT in aqueous solutions by the Fe(III)-NTA- Mn^{2+} Fenton-like process. Initial conditions: CRMT = $49.2 \mu\text{M}$, 0.1 mM Fe(III), H_2O_2 :Fe(III) = 20:1, NTA:Fe(III) = 2:1, Mn^{2+} :Fe(III) = 1:1 and pH = 7.0.

or chloroform. It can be seen that the degradation of CRMT was inhibited significantly in the presence of 2-propanol. When 2-propanol:CRMT molar ratio were 500:1 and 1000:1, the degradation efficiency of CRMT at 20 min of reaction time achieved 15.8% and 8.7%, respectively. The results suggest that the degradation of CRMT can be attributed to the generation of HO^\bullet . In addition, the presence of chloroform slowed the degradation of CRMT, the degradation efficiency decreased to 56.8% and 31.6% when chloroform:CRMT molar ratio was 500:1 and 1000:1, respectively. It is important to mention that the degradation of chloroform was clearly observed in $\text{O}_2^{\bullet-}$ scavenging experiments. This strongly suggests that $\text{O}_2^{\bullet-}$ was produced in the Fe(III)-NTA- Mn^{2+} Fenton-like process.

3.4. Reaction mechanism of Fe(III)-NTA- Mn^{2+} fenton-like process

The reaction of Mn^{2+} with H_2O_2 is very complex and might involve Mn^{4+} , Mn^{3+} , HO^\bullet and $\text{O}_2^{\bullet-}$. Watts et al. showed that the soluble Mn^{2+} catalyzed decomposition of H_2O_2 to generate HO^\bullet at acidic pH [33]. However, the present study showed that the Mn^{2+} -NTA complex were not capable of catalyzing H_2O_2 to generate HO^\bullet at neutral pH. In the absence of the complexing ligands, the reaction of Mn^{2+} with H_2O_2 results in the formation of Mn^{4+} (MnO_2) and hydroxyl ion (OH^-) under neutral and/or alkaline conditions [34]. Mn^{3+} has been considered to be the initial products of Mn^{2+} oxidation, which would rapidly disproportionate into Mn^{2+} and Mn^{4+} [35]. On the contrary, the reduction of Mn^{4+} (MnO_2) by H_2O_2 was suggested to form Mn^{2+} , H_2O and O_2 at acidic pH [36,37], and to form Mn^{3+} , Mn^{2+} and $\text{O}_2^{\bullet-}$ under neutral and/or alkaline conditions [34]. In the presence of the complexing ligands such as pyrophosphate, bicarbonate and EDTA, the reaction of Mn^{2+} -ligand complex with H_2O_2 is more likely to generate $\text{O}_2^{\bullet-}$. Stadtman's group showed that $\text{O}_2^{\bullet-}$ was the major product of the reaction of Mn^{2+} -bicarbonate complex with H_2O_2 (at pH 7.5) [38,39]. They proposed that a transient "caged" HO^\bullet was formatted in the inner coordination sphere of $\text{Mn}^{2+}/\text{Mn}^{3+}$, which was then likely to undergo an intramolecular H-atom abstraction from the Mn-bound H_2O_2 to form $\text{O}_2^{\bullet-}$ [38]. Therefore, it is reasonable to infer that the Mn^{2+} -NTA complex enhanced the production of $\text{O}_2^{\bullet-}$ in the Fe(III)-NTA- Mn^{2+} Fenton-like process. Table 1 presents main reactions for the Fe(III)-chelates catalyzed decomposition of H_2O_2 (R1-R10). Particularly noteworthy is the R4. An important role of $\text{O}_2^{\bullet-}$ is to reduce Fe(III)-chelates to Fe(II)-chelates with rate constants of $\sim 10^7$ – $10^8 \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, H_2O_2 itself is

Table 1
Reactions in Fe(III)-NTA-Mn²⁺ Fenton-like process.

No.	Reaction	Rate constant (M ⁻¹ s ⁻¹)	Ref.
R1	Fe(III)-chelates + H ₂ O ₂ ↔ Fe(III)-chelates-H ₂ O ₂	–	[17]
R2	Fe(III)-chelates-H ₂ O ₂ → Fe(II)-chelates + 2H ⁺ + O ₂ ^{•-}	0.01–0.02	[17,42]
R3	Fe(II)-chelates + H ₂ O ₂ → Fe(III)-chelates + •OH + OH ⁻	~10 ³ –10 ⁴	[17,22]
R4	Fe(III)-chelates + O ₂ ^{•-} → Fe(II)-chelates + O ₂	~10 ⁷ –10 ⁸	[22,42]
R5	Fe(II)-chelates + •OH → Fe(III)-chelates + OH ⁻	~10 ⁸ –10 ⁹	[5,17]
R6	H ₂ O ₂ + •OH → O ₂ ^{•-} + H ₂ O + H ⁺	(1.2–4.5) × 10 ⁷	[5]
R7	H ₂ O ₂ + O ₂ ^{•-} → O ₂ + •OH + OH ⁻	0.13	[34]
R8	•OH + O ₂ ^{•-} → H ₂ O + O ₂	8.9 × 10 ⁹	[43]
R9	•OH + •OH → H ₂ O ₂	5.3 × 10 ⁹	[5]
R10	Chelates (complexed/uncomplexed) + •OH → Degradation products	~10 ⁸	[17,22]
R11	Mn ²⁺ -chelates + 2H ₂ O ₂ ↔ Mn ²⁺ -chelates-2H ₂ O ₂	–	[38]
R12	Mn ²⁺ -chelates-2H ₂ O ₂ → Mn ³⁺ -chelates-H ₂ O ₂ -•OH + OH ⁻	–	[38]
R13	Mn ³⁺ -chelates-H ₂ O ₂ -•OH → Mn ³⁺ -chelates + O ₂ ^{•-} + H ₂ O + H ⁺	–	[38]
R14	Mn ³⁺ -chelates + O ₂ ^{•-} → Mn ²⁺ -chelates + O ₂	(0.5–1) × 10 ⁵	[33,38,40]
R15	2Mn ³⁺ -chelates + H ₂ O ₂ → 2Mn ²⁺ -chelates + 2H ⁺ + O ₂	very slow	[40]
R16	Mn ²⁺ -chelates + O ₂ ^{•-} + 2H ⁺ → Mn ³⁺ -chelates + H ₂ O ₂	–	[39,41]

capable of reducing Fe(III)-chelates to Fe(II)-chelates with rate constants of only ~0.01–0.02 M⁻¹ s⁻¹, which is far smaller than that by O₂^{•-}.

On the basis of the present experimental results, and together with previous studies on the reactions of Mn^(2+/3+)-chelates with H₂O₂ and O₂^{•-} [38–40], the mechanism for O₂^{•-} generation from the reaction of Mn²⁺-NTA complex with H₂O₂ could be explained by R11–R15 (Table 1). Negligible CRMT degradation was observed by Mn²⁺-NTA complex with H₂O₂, which indicated that there was few if any “free” HO• produced in the aqueous solution. The results suggested that O₂^{•-} was more likely produced by an inner sphere mechanism. The reaction of Mn²⁺-NTA complex with H₂O₂ initially forms Mn²⁺-NTA-2H₂O₂ complex, which undergo one electron transfer from Mn²⁺ to the Mn-bound H₂O₂ to generate the so-called “caged” HO•, i.e., Mn³⁺-NTA-H₂O₂-HO• complex. O₂^{•-} and Mn³⁺-NTA complex are formed by an intramolecular H-atom abstraction from H₂O₂ in the Mn³⁺-NTA-H₂O₂-HO• complex. The generated O₂^{•-} would accelerate the reduction of Fe(III)-NTA complex to Fe(II)-NTA complex, and then correspondingly increase the generation rate of HO• from the reaction of Fe(II)-NTA complex with H₂O₂. This also explains the cooperative catalysis of Fe(III)-NTA complex and Mn²⁺-NTA complex in accelerating H₂O₂ decomposition. Furthermore, the formed Mn³⁺-NTA complex can be reduced to Mn²⁺-NTA complex by either O₂^{•-} (fast) or H₂O₂ (slow) [40]. The reaction of Mn²⁺-chelates with O₂^{•-} (e.g., R16, if any) would be minimal, because Mn²⁺-NTA complex oxidation by O₂^{•-} only occurred at acidic pH [40,41].

In a similar manner, our findings confirmed that the presence of Mn²⁺ can also enhance the effectiveness of other chelating agents such as EDTA and s,s-EDDS modified Fenton-like reactions (Fig. 5). Fe(III)-NTA-Mn²⁺ catalyzes Fenton-like reaction more effectively than Fe(III)-EDTA-Mn²⁺ and Fe(III)-s,s-EDDS-Mn²⁺. The reason is due to the lower HO• scavenging activity of NTA compared with EDTA and s,s-EDDS.

3.5. Important parameters in Fe(III)-NTA-Mn²⁺ fenton-like process

The effects of NTA:Fe(III) molar ratios on the degradation kinetics of CRMT are shown in Fig. 6(a). It was observed that the degradation of CRMT was strongly limited when the NTA:Fe(III) molar ratio was smaller than 1:1. For instance, only 65.1% CRMT degradation was obtained at NTA:Fe(III) molar ratio of 0.5:1 after 20 min of reaction time. Generally, one Fe(III) cation binds to one NTA molecule through three carboxylates and the amine group. The limited efficiency in terms of CRMT degradation when NTA:Fe(III) molar ratio was smaller than 1:1, it might be due to the iron

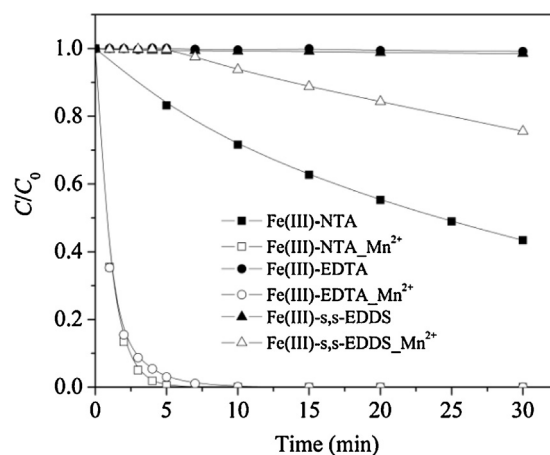


Fig. 5. Degradation kinetics of CRMT in aqueous solutions by Fe(III)-NTA, Fe(III)-EDTA and Fe(III)-s,s-EDDS catalyzed Fenton-like reactions in the absence or presence of Mn²⁺. Initial conditions: CRMT = 49.2 μM, 0.1 mM Fe(III), H₂O₂:Fe(III) = 100:1, chelates:Fe(III) = 2:1, Mn²⁺:Fe(III) = 1:1 and pH = 7.0.

available to catalyze the reaction would probably be reduced by precipitation. The fastest degradation of CRMT was observed at NTA:Fe(III) molar ratio of 1.5:1. As the NTA:Fe(III) molar ratio increased from 0.5:1 to 1.5:1, the *k*_{obs} value increased linearly from 0.057 to 0.45 min⁻¹. After that, further increasing NTA:Fe(III) molar ratio to 10:1 had negative effect on CRMT degradation, resulting in ~30% decrease in the *k*_{obs} value. Since HO• can also react with NTA (Table 1), either complexed or uncomplexed species, the excess NTA species inhibit the degradation of CRMT by scavenging HO•. This explains the slight decrease in the degradation rate of CRMT at high concentration of NTA, e.g., NTA:Fe(III) > 2:1.

The effects of H₂O₂:Fe(III) molar ratios and Fe(III) concentrations on the degradation kinetics of CRMT were clearly evident in Fig. 6(b) and (c). It can be seen that an increase in H₂O₂:Fe(III) molar ratio from 5:1 to 200:1 had positive effect on the degradation of CRMT. The *k*_{obs} value increased from 0.096 to 1.34 min⁻¹ as the molar ratio of H₂O₂:Fe(III) increased from 5:1 to 200:1. In addition, the degradation of CRMT was strongly dependent on the Fe(III) concentrations. At a small concentration of 0.01 mM Fe(III), the degradation of CRMT was inefficient. However, complete degradation of CRMT was obtained after 20 min of reaction when the Fe(III) concentration was larger than 0.1 mM Fe(III). The *k*_{obs} value increased almost linearly from 0.021 to 0.62 min⁻¹ as the Fe(III) concentration increased from 0.01 to 0.15 mM. After that, only a small increase in the *k*_{obs} value was observed by further increasing the Fe(III) concentration to 0.2 mM (~0.69 min⁻¹). With increasing

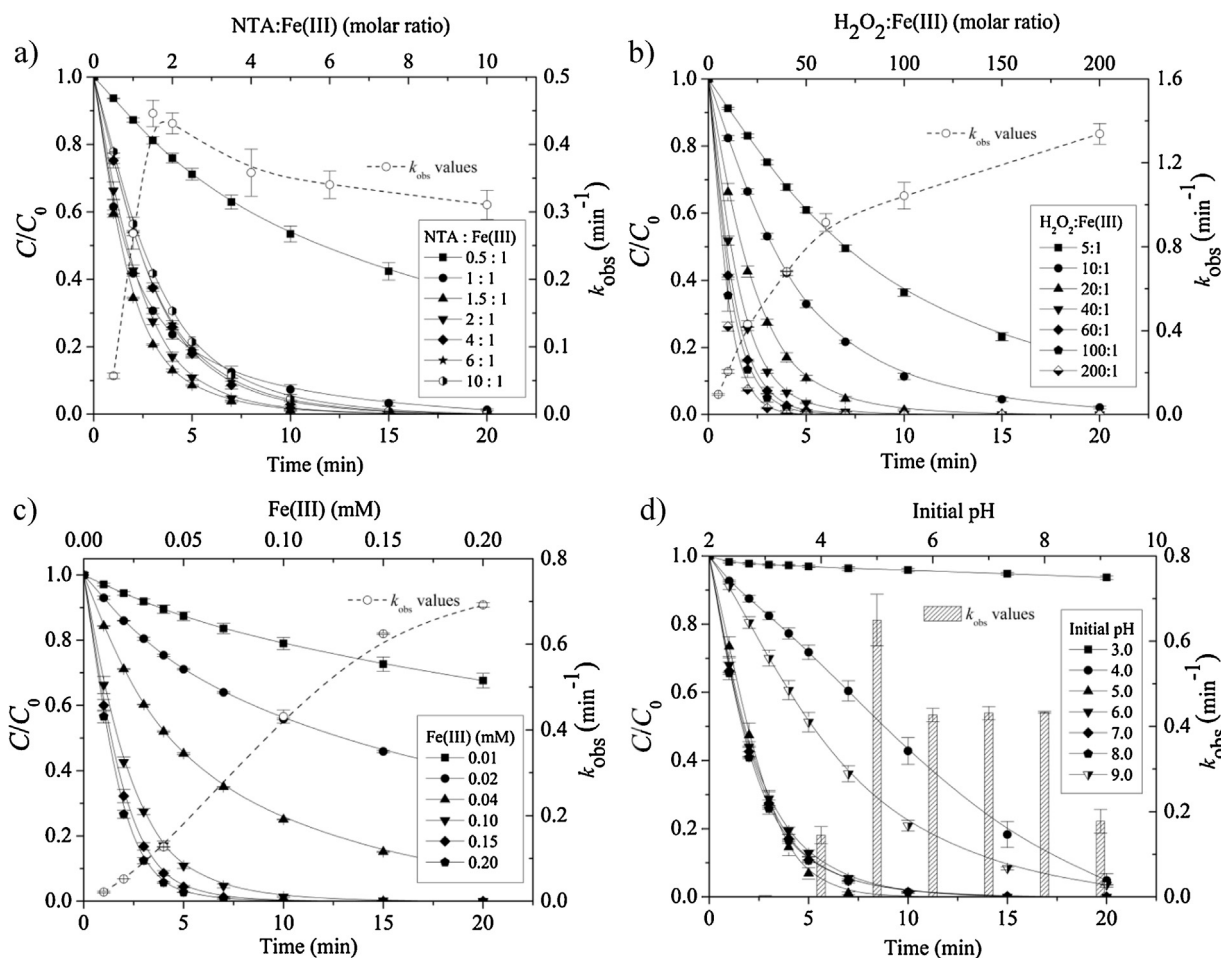


Fig. 6. Degradation kinetics of CRMT in aqueous solutions by the Fe(III)-NTA-Mn²⁺ Fenton-like process as a function of: a) the NTA:Fe(III) molar ratio (CRMT = 49.2 μM, 0.1 mM Fe(III), H₂O₂:Fe(III) = 20:1, Mn²⁺:Fe(III) = 1:1 and initial pH = 7.0); b) the H₂O₂:Fe(III) molar ratio (CRMT = 49.2 μM, 0.1 mM Fe(III), NTA:Fe(III) = 2:1, Mn²⁺:Fe(III) = 1:1 and initial pH = 7.0); c) the Fe(III) concentration (CRMT = 49.2 μM, NTA:Fe(III) = 2:1, Mn²⁺:Fe(III) = 1:1, 2 mM H₂O₂ and initial pH = 7.0), and d) the initial pH (CRMT = 49.2 μM, 0.1 mM Fe(III), H₂O₂:Fe(III) = 20:1, NTA:Fe(III) = 2:1 and Mn²⁺:Fe(III) = 1:1).

H₂O₂:Fe(III) molar ratios and Fe(III)-NTA complex concentration had positive effects on the degradation of CRMT. This is due to higher rate of HO• production at higher concentrations of H₂O₂ and Fe(III)-NTA complex. Although previous studies have suggested that H₂O₂ could react with HO• (i.e., R6), no limiting effects by H₂O₂ (the concentration was up to 20 mM) was observed in the present study.

The effects of the initial pH on the degradation kinetics of CRMT were investigated in the range of pH 3.0–9.0. It was observed from Fig. 6(d) that the degradation of CRMT was very slow and inefficient at acidic pH, e.g., pH 3.0, with only 6.3% CRMT degradation after 20 min of reaction time. However, almost complete degradation of CRMT was achieved after 20 min of reaction time at initial pH range of 5.0–8.0. The highest degradation rate of CRMT was observed at initial pH 5.0, with a maximum k_{obs} value of 0.65 min⁻¹. In addition, no statistically significant difference in the k_{obs} values was observed at initial pH range of 6.0–8.0 ($p = 0.76$ – 0.88). However, it was observed that the degradation rate of CRMT decreased significantly at initial pH 9.0, with a k_{obs} value of 0.18 min⁻¹. The final pH was determined to be 4.3, 5.3, 6.5, 6.8 and 7.2 after 20 min of reaction time when the initial pH was 5.0, 6.0, 7.0, 8.0 and 9.0, respectively (Fig. S3). The decrease in the solution pH during the reaction is due to the formation of carboxylic acids from the degradation of CRMT and NTA species by HO• attack. It is noteworthy

that most of CRMT (>85%) degraded in five minutes with initial pH 5.0–8.0, the changes in the solution pH was small during that period, e.g., 0.1–0.2 pH units for pH 5.0–7.0 and ~0.5 pH units for pH 8.0. The changes in the solution pH should have a small effect on the degradation kinetics of CRMT. The smaller degradation of CRMT at pH < 5.0 can be attributed to the formation of perhydroxyl radical (•OOH). It is known that O₂^{•-} is in a dynamic equilibrium with •OOH in aqueous solution depending on the solution pH ($pK_a = 4.8$) [42]. The rate constant for Fe(III)-NTA complex reduction to Fe(II)-NTA complex by •OOH is ~3–4-order of magnitude smaller than that by O₂^{•-} [43]. As a result, it is reasonable to infer that low pH can strongly limit the regeneration of Fe(II)-chelates. Fig. 7 provides direct evidence for the inhibition of H₂O₂ decomposition at acidic pH. The decomposition rates of H₂O₂ at pH 3.0–4.0 were much smaller than those at pH 5.0–9.0. Furthermore, the inhibited degradation of CRMT at pH 9.0 can be attributed mainly to HO• scavenging by excess O₂^{•-}. Our previous study shows that Fe(III)-NTA complex catalyzed Fenton-like reaction is more effective under alkaline conditions (especially at pH 9.0) than that under acidic and/or neutral conditions [19], suggesting that more O₂^{•-} could be generated from the reaction of Fe(III)-NTA complex with H₂O₂ at pH 9.0. Although the generation rate of HO• is expected to be improved by more O₂^{•-}, excess O₂^{•-} can scavenge HO• and result in inhibiting the degradation of contaminants.

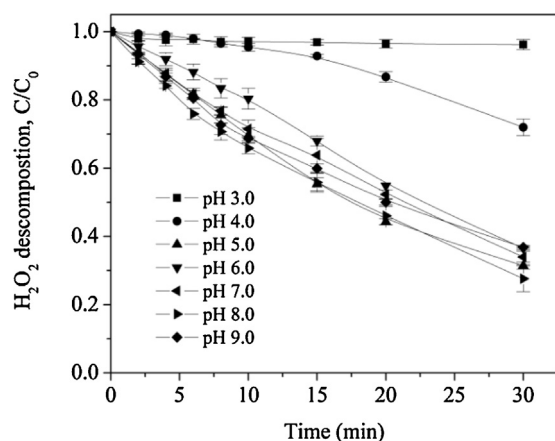


Fig. 7. Kinetics of H_2O_2 decomposition in the $\text{Fe(III)-NTA-Mn}^{2+}$ Fenton-like process under various initial pH. Initial conditions: CRMT=49.2 μM , 0.1 mM Fe(III) , $\text{H}_2\text{O}_2:\text{Fe(III)}=20:1$, $\text{NTA}:\text{Fe(III)}=2:1$ and $\text{Mn}^{2+}:\text{Fe(III)}=1:1$.

4. Conclusions

The present work has provided insight into the impact of Me on Fe(III)-NTA complex catalyzed Fenton-like reaction. The results demonstrate for the first time that the presence of Mn^{2+} can markedly enhance the effectiveness of Fe(III)-NTA complex catalyzed Fenton-like reaction at neutral pH. It is worth noting that even at a small concentration of Mn^{2+} -NTA complex (e.g., 0.01 mM Mn^{2+}), the degradation of CRMT was enhanced dramatically. In addition, 1–2 mM H_2O_2 was sufficient for the degradation of organic contaminants by the $\text{Fe(III)-NTA-Mn}^{2+}$ Fenton-like process. The concentration of H_2O_2 was much smaller than that used in the heterogeneous Fenton-like system which typically required hundreds mM H_2O_2 to achieve desirable degradation rate and efficiency, and also ten times smaller than that in Fe(III)-chelates catalyzed homogeneous Fenton-like reaction. The potential mechanism involves an enhanced generation of $\text{O}_2^{\cdot-}$ from the reaction of Mn^{2+} -chelates with H_2O_2 , thereby indirectly promoting the generation of HO^\bullet by accelerating the reduction rate of Fe(III)-NTA complex to Fe(II)-NTA complex. Unfortunately, the quantitative measurement of metal (Fe(II)- , Fe(III)- , Mn^{2+} - and Mn^{3+} -) and chelates speciation and their transformation could not be done in the present work, which would be helpful in understanding the specific mechanism of the Mn^{2+} -mediated homogeneous Fenton-like reaction of Fe(III)-NTA complex.

The system is more practical and sustainable, the high rates of both HO^\bullet and $\text{O}_2^{\cdot-}$ production at neutral pH make the $\text{Fe(III)-NTA-Mn}^{2+}$ Fenton-like process a promising technique for the treatment of a broader range of contaminants in water. Moreover, low levels of Fe(III) , Mn^{2+} , chelating agents (natural and/or synthetic) and H_2O_2 are generally ubiquitous in aquatic systems. The findings of the present study suggest that $\text{Fe(III)-chelates-Mn}^{2+}$ catalyzed Fenton-like reaction may play a crucial role in degrading organic contaminants in the aquatic environment. Addressing this issue is our current interest, and further research is required to evaluate Mn^{2+} -mediated Fenton-like reactions with natural occurring chelating agents.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.04.003>.

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