



# Mn<sup>2+</sup>-mediated homogeneous Fenton-like reaction of Fe(III)-NTA complex for efficient degradation of organic contaminants under neutral conditions



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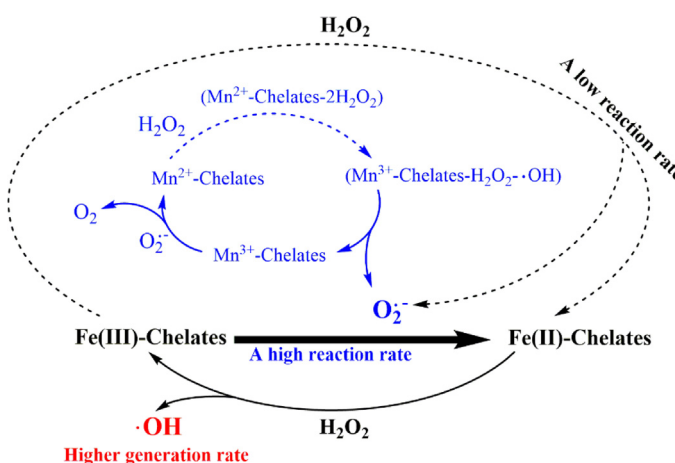
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## HIGHLIGHTS

- Mn<sup>2+</sup> markedly enhanced Fe(III)-NTA catalyzed Fenton-like reaction at circumneutral pH.
- Ca<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> had no or little inhibitory effects on such process.
- CRMT and DEET were rapidly degraded by Fe(III)-NTA-Mn<sup>2+</sup> Fenton-like process.
- Generation of HO<sup>•</sup> and O<sub>2</sub><sup>•-</sup> in Fe(III)-NTA-Mn<sup>2+</sup> Fenton-like process were suggested.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 8 February 2016  
 Received in revised form 1 April 2016  
 Accepted 3 April 2016  
 Available online 4 April 2016

### Keywords:

Mn<sup>2+</sup>  
 Fe(III)-NTA complex  
 Fenton-like reaction  
 Hydroxyl radical  
 Superoxide radical anion

## ABSTRACT

In this work, we report a novel Mn<sup>2+</sup>-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 Mn<sup>2+</sup> 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-Mn<sup>2+</sup> Fenton-like process was at least 1.6 orders of magnitude larger than that in the absence of Mn<sup>2+</sup>. Other metal ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> had no impacts or little inhibitory effect on the Fe(III)-NTA complex catalyzed Fenton-like reaction. The generation of hydroxyl radical (HO<sup>•</sup>) and superoxide radical anion (O<sub>2</sub><sup>•-</sup>) in the Fe(III)-NTA-Mn<sup>2+</sup> Fenton-like process were suggested by radicals scavenging experiments. The degradation efficiency of CRMT was inhibited significantly (approximately 92%) by the addition of HO<sup>•</sup> scavenger 2-propanol, while the addition of O<sub>2</sub><sup>•-</sup> 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 Mn<sup>2+</sup>. 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  $\mu M$  CRMT (or 52.3  $\mu M$  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.

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