



# Comparison of metoprolol degradation by $\text{Fe}^{\text{III}}$ -NTA modified Fenton-like reaction in the absence and presence of manganese: Efficiency and intermediates

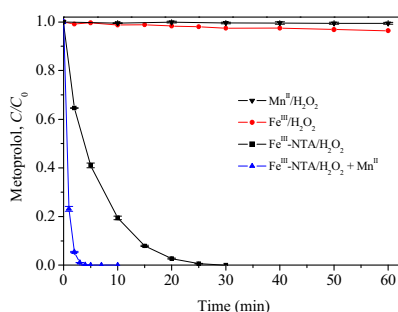
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## HIGHLIGHTS

- Metoprolol degradation by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  was enhanced in the presence of  $\text{Mn}^{\text{II}}$ .
- Rapid degradation of metoprolol was obtained by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn at pH 4.0–8.0.
- $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn led to more efficient degradation of metoprolol and intermediates.
- Degradation pathways of metoprolol were proposed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The degradation of metoprolol in aqueous solutions by traditional Fenton-like reaction ( $\text{Fe}^{\text{III}}/\text{H}_2\text{O}_2$ ), and  $\text{Fe}^{\text{III}}$ -NTA modified Fenton-like reaction ( $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ ) in the absence and presence of  $\text{Mn}^{\text{II}}$  ( $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn) have been investigated. The results show that  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  is able to degrade metoprolol at initial neutral pH. In particular, the presence of  $\text{Mn}^{\text{II}}$  greatly improved the degradation rate of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  over a wide pH range of 4.0–8.0. Under the same conditions, the degradation rate constants of metoprolol ( ) obtained in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were typically 7–9-fold larger than those obtained in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. The involved reactions in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were proposed on the basis of important parameters analysis including ferrous ion concentration, dissolved oxygen (DO) concentration, and the quenching experiments for hydroxyl radical ( $\text{HO}^\bullet$ ) and superoxide anion radical ( $\text{O}_2^{\bullet-}$ ). Several intermediates have been identified by mass spectrometry. Our results suggest that the degradation of metoprolol in both  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems were caused by  $\text{HO}^\bullet$  attack. The degradation pathways of metoprolol were proposed on the basis of the identified intermediates.  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system led to more efficient degradation of metoprolol and its intermediates.

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## 1.

Metoprolol, a selective  $\beta_1$  receptor blocking drug, is widely used in the therapy of hypertension and angina. In the past decade, metoprolol and its metabolites have been detected in sewage treatment plant effluents, surface water, groundwater, and even

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in drinking water, which pose a potential risk to human health [1,2]. The degradation rate of metoprolol in water by the direct photolysis is small, e.g., the extrapolated half-lives of metoprolol in central Europe and the U.S. were reported at 28–95 d in summer and 190–449 d in winter [3]. Thus, metoprolol is most likely to be pseudo-persistent in natural waters if do not consider the indirect photolysis effects. In addition, the efficiency of metoprolol removal is lower than 30% in traditional sewage treatment plant [4]. There is an urgent need to improve the removal efficiencies of pharmaceuticals in water.

A far more effective method is the so-called advanced oxidation processes (AOPs), involving the generation of hydroxyl radical ( $\text{HO}^\bullet$ ) [5–7], have been widely applied in water treatment for harmful organic compounds removal. Efficient degradation of metoprolol has been obtained by photocatalysis, UV/ $\text{H}_2\text{O}_2$  and Fenton-related processes [8–10]. Two decades ago, research by Sun and Pignatello [11] showed the successful degradation of 2,4-dichlorophen-oxyacetic acid at pH 6.0 by chelates modified Fenton-like reaction. Chelating agents modified Fenton-like reaction has been receiving increasing attention because it can work at neutral pH conditions, which overcomes the limitation of acidic pH (e.g., optimal pH 2.8–3.0) by using traditional Fenton and/or Fenton-like reaction. S,S-ethylenediamine-N,N'-disuccinic acid (EDDS) modified Fenton reaction (i.e.,  $\text{Fe}^{\text{II}}$ -EDDS/ $\text{H}_2\text{O}_2$ ) and Fenton-like reaction (i.e.,  $\text{Fe}^{\text{III}}$ -EDDS/ $\text{H}_2\text{O}_2$ ) are capable of degrading 4-chlorophenol, bisphenol A, naphthenic acid, and 4-tert-butylphenol at near neutral or basic pH conditions [12–15]. The use of  $\text{Fe}^{\text{III}}$ -EDDS for photo-Fenton reaction at neutral pH is also successful in degrading micro-pollutants in wastewater treatment plant effluents [16–18]. In addition, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) modified Fenton-like reactions (i.e.,  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -EDTA/ $\text{H}_2\text{O}_2$ ) have also been proved to be highly effective in degrading atrazine, carbamazepine, fenuron, naphthenic acid, parachlorobenzoic acid and sulfamethoxazole at neutral or slightly basic pH conditions [19–22]. In particular, our recent finding suggested that the presence of manganese ( $\text{Mn}^{\text{II}}$ ) could greatly enhance the Fenton-like catalytic activity of  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  [23]. The potential mechanism may involve an enhanced generation of superoxide anion radical ( $\text{O}_2^{\bullet-}$ ) by the  $\text{Mn}^{\text{II}}$ , which can accelerate the reduction of  $\text{Fe}^{\text{III}}$ -NTA to  $\text{Fe}^{\text{II}}$ -NTA and indirectly improve the generation of  $\text{HO}^\bullet$  [23]. The  $\text{Mn}^{\text{II}}$ / $\text{Fe}^{\text{III}}$ -NTA catalytic system would be very promising since  $\text{Fe}^{\text{III}}$  and  $\text{Mn}^{\text{II}}$  are quite ubiquitous in the environment and can be used as natural Fenton-like catalyst in the presence of NTA (or natural  $\text{Fe}^{\text{III}}$  complexing agents) and  $\text{H}_2\text{O}_2$ . However, little research on this system has been reported.

The purpose of this study is to demonstrate the potential effectiveness of  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn for water treatment. In the present study, we choose metoprolol as a target compound, to evaluate the efficiency and intermediates generated from metoprolol degradation by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  in the absence and presence of  $\text{Mn}^{\text{II}}$ . The degradation kinetics of metoprolol in both systems were compared under various conditions. The involved reactions in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were proposed on the basis of certain important parameters analysis such as ferrous ion concentration, dissolved oxygen (DO) concentration, and the quenching experiments for  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$ . The intermediates were identified by liquid chromatography/mass spectrometry.

## 2.

### 2.1. C

Ferric chloride hexahydrate, hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ , w/w), sodium hydroxide and sulfuric acid were purchased from Sino-

pharm Chemical Reagent Co., Ltd. Metoprolol tartrate (purity  $\geq 98\%$ ) was purchased from LKT Laboratories, Inc. NTA was purchased from Acros Organics. Formic acid and manganese nitrate tetrahydrate were purchased from Sigma-Aldrich. HPLC-grade methanol, 2-propanol and water were purchased from Fisher Scientific. Chloroform was purchased from Chinasun Specialty Products Co., Ltd. All chemicals were of reagent grade or better, and used as received without further purification. Milli-Q water was used to prepare solutions.

### 2.2. E

All experiments were performed in 125 ml glass Erlenmeyer flasks. Briefly, 100 ml of metoprolol aqueous solution and an appropriate amount of freshly prepared  $\text{Fe}^{\text{III}}$ -NTA solution were added into the flask. The flask was then placed in a water-jacketed glass vessel water bath ( $25 \pm 1^\circ\text{C}$ ) under a magnetic stirring condition. After that, an appropriate amount of  $\text{Mn}^{\text{II}}$  was added to the solution. The pH of the solution was then adjusted to the desired value using 1.0/0.1 M NaOH or 1.0/0.1 M  $\text{H}_2\text{SO}_4$ . Finally, Fenton-like reaction was started by the addition of an appropriate amount of  $\text{H}_2\text{O}_2$ . It is worth noting that the water-jacketed glass vessel was covered with aluminum foil to prevent the effect of light on the Fenton-like reaction. Samples (1 ml) were withdrawn at different time intervals and mixed with 0.1 ml of methanol immediately to quench the reaction.

### 2.3. A

The concentration of metoprolol was determined by a high performance liquid chromatography (HPLC, Agilent 1100) with fluorescence detection. An Ultra C-18 column ( $5\ \mu\text{m}$ ,  $250 \times 4.6\ \text{mm}$ ) was used for the chromatographic separation. The mobile phase consisted of methanol and 0.1% formic acid aqueous solution (35:65, v/v) at a flow rate of  $0.9\ \text{ml min}^{-1}$ . The column temperature was  $30^\circ\text{C}$ . The injection volume was  $20\ \mu\text{l}$ , and the fluorescence detection was performed at 275 nm of excitation and 298 nm of emission.

The degradation intermediates were identified by an Agilent 1200 HPLC system coupled to a 6130 quadrupole mass spectrometer. The MS detector was performed for a full scan range of 30–600 under an ESI + APCI positive mode. The MS operating conditions were as follows: Fragmentor 90, drying gas flow rate  $6\ \text{L min}^{-1}$ , nebulizer pressure 45 psi, dry gas temperature  $300^\circ\text{C}$ , vaporizer temperature  $250^\circ\text{C}$ , capillary voltage 3500 V, corona current  $4.0\ \mu\text{A}$  and charging voltage 2000 V.

The concentration of ferrous ion in the aqueous solutions was determined by using the 1,10-phenanthroline method. The concentration of  $\text{H}_2\text{O}_2$  was determined by the iodide method [24]. The dissolved oxygen (DO) concentration in the aqueous solutions during the reaction time was monitored by a  $\text{dO}_2$  sensor (Model Z010023525, AppliSens).

## 3.

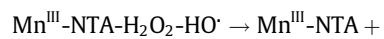
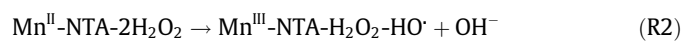
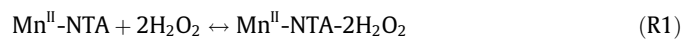
3.1. C  $\text{Fe}^{\text{III}}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{\text{III}}\text{-N A/}$   
 $\text{H}_2\text{O}_2$   $\text{Fe}^{\text{III}}\text{-N A/H}_2\text{O}_2\text{-M}$

Fig. 1 shows a comparison of metoprolol degradation by  $\text{Fe}^{\text{III}}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems at initial neutral pH. A minimum degradation of metoprolol was observed in  $\text{Fe}^{\text{III}}/\text{H}_2\text{O}_2$  system, with 3.61% degradation efficiency of metoprolol after 60 min of the reaction time. This result was expected because of the precipitation of ferric ion at pH 7.0 in the absence of chelator. In contrast,  $\text{Fe}^{\text{III}}$ -NTA complex is able to catalyze

Fenton-like reaction at pH 7.0, resulted in 100% degradation efficiency of metoprolol after 30 min of the reaction time in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. In particular,  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system led to a very fast degradation of metoprolol, with 100% degradation efficiency of metoprolol after 7 min of the reaction time. The result is consistent with our recent finding that the presence of  $\text{Mn}^{\text{II}}$  could enhance  $\text{Fe}^{\text{III}}$ -NTA-catalyzed Fenton-like reaction [23].

The effects of  $\text{Mn}^{\text{II}}$  concentration on the degradation kinetics of metoprolol in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were shown in Fig. 2. An increase in  $\text{Mn}^{\text{II}}$  concentration from 0.01 to 0.1 mM, corresponding to Mn:Fe molar ratios of 0.1:1 to 1:1, had a positive effect on metoprolol degradation. The apparent degradation rate constant of metoprolol ( $k_{\text{app}}$ ) increased from 0.7547 to 1.6048  $\text{min}^{-1}$ . However, further increasing  $\text{Mn}^{\text{II}}$  concentration from 0.2 to 1.0 mM led to a slight inhibitory effect on the degradation rate of metoprolol, e.g., the  $k_{\text{app}}$  value of metoprolol decreased from 1.6289 to 1.1103  $\text{min}^{-1}$ . This is because when  $\text{Mn}^{\text{II}}$  concentration was larger than 0.2 mM, hydrous manganese dioxide could form from free  $\text{Mn}^{\text{II}}$  in excess

from the reaction of  $\text{Fe}^{\text{III}}\text{-NTA}$  with  $\text{H}_2\text{O}_2$  in  $\text{Fe}^{\text{III}}\text{-NTA}/\text{H}_2\text{O}_2$  system (i.e., R7), thus the generation rate of  $\text{Fe}^{\text{II}}\text{-NTA}$  in  $\text{Fe}^{\text{III}}\text{-NTA}/\text{H}_2\text{O}_2$  system is much slower than that in  $\text{Fe}^{\text{III}}\text{-NTA}/\text{H}_2\text{O}_2\text{-Mn}$  system.



the range of NTA:Fe molar ratios tested, the values of metoprolol in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were 7–17-fold larger than those in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. An increase in NTA/Fe molar ratio from 0.5:1 to 2:1 had positive effects on the degradation rates of metoprolol in both  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems. The values of metoprolol increased from 0.0311 to 0.1754  $\text{min}^{-1}$  in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system and increased from 0.3450 to 1.6048  $\text{min}^{-1}$  in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system, respectively. When NTA/Fe molar ratio was larger than 2:1, however, a slight decrease in the values of metoprolol was observed in either  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  or  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system. This can be explained by the fact that the free NTA in excess scavenges  $\text{HO}^\cdot$ . Although the reaction rate constant of metoprolol with  $\text{HO}^\cdot$  ( $5.2\text{--}8.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [32,33] is larger than that of  $\text{Fe}^{\text{III}}$ -NTA/free NTA with  $\text{HO}^\cdot$ , it is believed that the competitive consumption of  $\text{HO}^\cdot$  by the free NTA in excess can slightly limit the degradation of metoprolol.

### 3.4. E $\text{H}_2\text{O}_2$ : $\text{Fe}^{\text{III}}$

Fig. 6 shows the effects of  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratios on the degradation kinetics of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems at initial neutral pH. Without the addition of  $\text{H}_2\text{O}_2$ , no degradation of metoprolol was observed in both systems. Over the range of  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratios tested, the values of metoprolol in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were 5–9-fold larger than those in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. With increasing  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio from 10:1 to 200:1, the values of metoprolol continuously increased from 0.0598 to 0.2276  $\text{min}^{-1}$  in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. In  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system, the values of metoprolol increased greatly from 0.3384 to 1.6048  $\text{min}^{-1}$  and reached a plateau with increasing  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio from 100:1 to 200:1. It is expected that the use of higher molar ratio of  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  led to higher rate of  $\text{HO}^\cdot$  generation, by which faster degradation of metoprolol could be obtained. No inhibitory effect of  $\text{H}_2\text{O}_2$  on the degradation kinetics of metoprolol was observed even at  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio of 200:1. This is because the reaction rate constant of  $\text{H}_2\text{O}_2$  with  $\text{HO}^\cdot$  ( $(1.2\text{--}4.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) [34] is much smaller than those of metoprolol,  $\text{Fe}^{\text{III}}$ -NTA and free NTA with  $\text{HO}^\cdot$ .

### 3.5. E $\text{F}^{\text{III}}$

$\text{Fe}^{\text{III}}$  acts as the catalyst to initiate Fenton-like reaction, a high rate of  $\text{HO}^\cdot$  generation might be obtained at high concentration of  $\text{Fe}^{\text{III}}$ -NTA. The effects of  $\text{Fe}^{\text{III}}$  dosages on the degradation kinetics of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems at

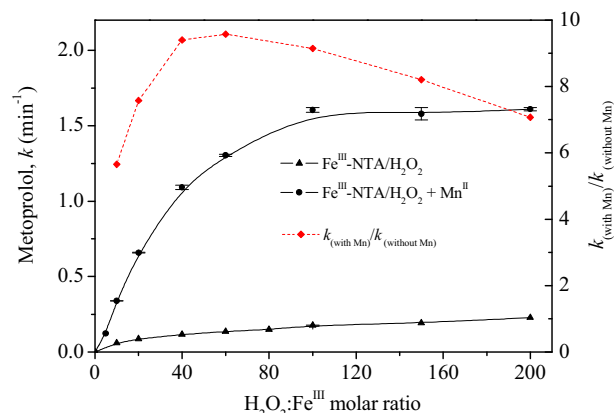


Fig. 6. Effects of  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratios on the degradation kinetics of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems. Experimental conditions: 29.2  $\mu\text{M}$  of metoprolol, 0.1 mM of  $\text{Fe}^{\text{III}}$ , NTA/ $\text{Fe}^{\text{III}}$  molar ratio of 2:1,  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio of 5:1–200:1,  $\text{Mn}^{\text{II}}$ / $\text{Fe}^{\text{III}}$  molar ratio of 1:1, and initial pH of 7.0.

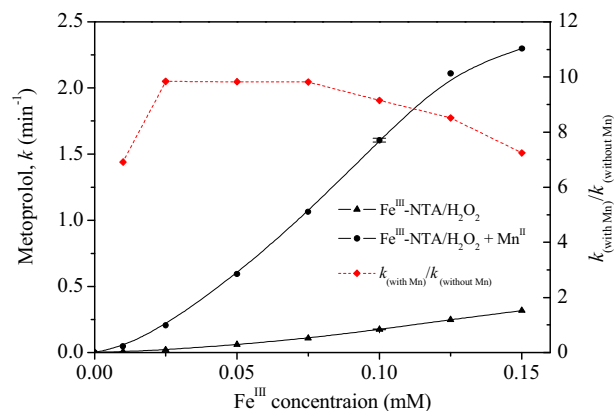


Fig. 7. Effects of  $\text{Fe}^{\text{III}}$  dosages on the degradation kinetics of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems. Experimental conditions: 29.2  $\mu\text{M}$  of metoprolol, 0.01–0.15 mM of  $\text{Fe}^{\text{III}}$ , NTA/ $\text{Fe}^{\text{III}}$  molar ratio of 2:1,  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio of 100:1,  $\text{Mn}^{\text{II}}$ / $\text{Fe}^{\text{III}}$  molar ratio of 1:1, and initial pH of 7.0.

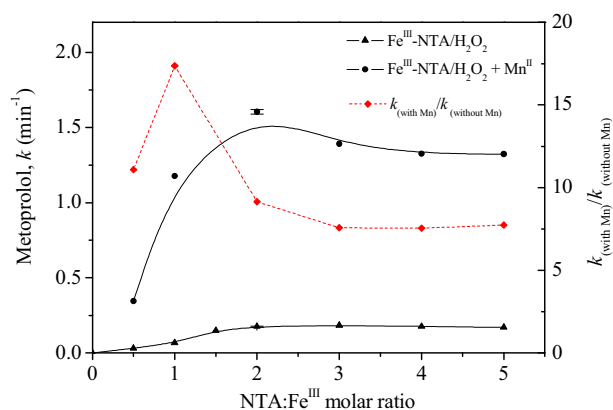
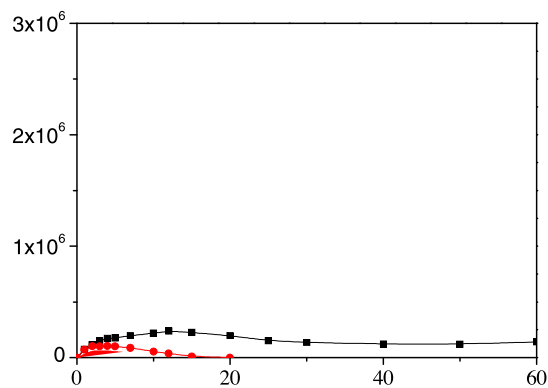


Fig. 8. Effects of NTA/ $\text{Fe}^{\text{III}}$  molar ratios on the degradation kinetics of metoprolol by  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn systems. Experimental conditions: 29.2  $\mu\text{M}$  of metoprolol, 0.1 mM of  $\text{Fe}^{\text{III}}$ , NTA/ $\text{Fe}^{\text{III}}$  molar ratio of 0.5:1–5:1,  $\text{H}_2\text{O}_2$ / $\text{Fe}^{\text{III}}$  molar ratio of 100:1,  $\text{Mn}^{\text{II}}$ / $\text{Fe}^{\text{III}}$  molar ratio of 1:1, and initial pH of 7.0.



initial neutral pH were shown in Fig. 7. No degradation of metoprolol was observed in the absence of  $\text{Fe}^{\text{III}}$ , which suggests that  $\text{HO}^\cdot$  is generated from the Fenton-like reaction of  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ . Over

the range of  $\text{Fe}^{\text{III}}$  concentrations tested, the  $k$  values of metoprolol in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system were 7–9-fold larger than that in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system. An increase in  $\text{Fe}^{\text{III}}$  concentrations from 0 to 0.15 mM has positive effects on the degradation rate of metoprolol in both systems. The  $k$  values of metoprolol increased from

0 to  $0.3174 \text{ min}^{-1}$  in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$  system and to  $2.2988 \text{ min}^{-1}$  in  $\text{Fe}^{\text{III}}$ -NTA/ $\text{H}_2\text{O}_2$ -Mn system, respectively. The results indicate that the rate of  $\text{HO}^\bullet$

$\text{Fe}^{\text{III}}$ -NTA would increase the generation rate of  $\text{Fe}^{\text{II}}$ -NTA (R5) and (R7), which in turn reacts with  $\text{H}_2\text{O}_2$

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