

A novel Fenton-like system with hydrogen peroxide , hydroxylamine and Fe (III) for the degradation of benzoic acid

CHEN Li-wei , MA Jun , LI Xu-chun , GUAN Ying-hong

(State Key Laboratory of Urban Water Resource and Environment , Harbin Institute of Technology , Harbin 150090 , China)

Abstract: A novel homogeneous Fenton like system (Fenton-like-HA system) composed of Fe (III) , hydrogen peroxide (H_2O_2) , and hydroxylamine (NH_2OH) on the benzoic acid (BA) oxidation was studied. Compared to other systems , the Fenton-like-HA system showed notable advantages in both BA conversion and practical application due to the accelerated redox cycles of Fe (II) /Fe (III) by NH_2OH and the widely used of Fe (III) . Besides , the BA conversion increased with the increase of H_2O_2 , Fe (III) and NH_2OH dosages and all well fitted pseudo-first-order kinetics during the whole process. The Fenton-like-HA system showed high H_2O_2 utilization efficiency and $HO \cdot$ generation rates. The concentrations of Fe (III) after a few seconds were kept in dynamic equilibrium (almost $5.3 \mu mol \cdot L^{-1}$) due to the role of NH_2OH , which explained the pseudo-first-order kinetics of the system. The novel Fenton-like system could increase the BA oxidation , H_2O_2 utilization efficiency and save the dosage of iron and H_2O_2 . Accordingly , it has great potential for practical application.

Key words: Fenton like; H_2O_2 ; Fe (III) ; NH_2OH

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0 Introduction

Benzoic acid (BA) constitutes the parent molecule of many phenolic compounds such as vanillic , gallic , veratric , syringic , protocatechuic and hydroxybenzoic acids that are commonly detected in agro - industrial effluents^[1] and usually characterized by low biodegradability and high ecotoxicity. Moreover , BA is often received as a model compound in advanced oxidation processes (AOPs) due to its reaction with hydroxide radical ($HO \cdot$) to form *p* - , *m* - , *o* - hydroxybenzoic acids and other products^[1-2].

Among the AOPs , Fenton system is one of the best options for its easy to handle , fast reaction and environmental benign^[3]. The Fenton's reagents employ hydrogen peroxide (H_2O_2) and Fe (II) to generate reactive species such as $HO \cdot$ ^[4] shown in equation (1) or ferryl^[5] shown in equation (8) . These reactants can be used to initiate chain reactions and degrade modal pollutants shown in equations (2) to (7) . Besides , if Fe (III) and H_2O_2 (called Fenton - like system) are originally present , Fe (II) could be slowly generated by equation (2) to initiate the chain reactions^[4]. So some studies^[6-7] focused on the lower cost Fe (III) because the oxidation in Fenton-like system also effective.

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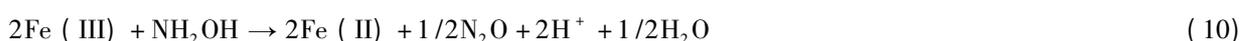
Biography: Ms CHEN Li - wei (1981 -) , Ph. D. candidate , interested in: environmental chemistry

Corresponding author: Mr. MA Jun (1962 -) , professor , Ph. D. , advisor of Ph. D. , Yangtze River Scholars

Even at optimal pH of 3.0 in homogeneous, the rate of H_2O_2 decomposition and the rate of modal pollutants oxidation are much slower in Fenton like system than that in Fenton system^[3]. Consequently, various methods have been introduced to increase the reaction rates in Fenton like system, such as the addition of UV^[6] and quinone^[8] to accelerate the redox cycles between Fe (III) and Fe (II). But they also add cost for introduce the energy or lower the efficiencies of oxidation for the competitive effect with pollutants on the reactive species.

In our previous study, we introduced hydroxylamine (NH_2OH) into Fenton system^[9] (Fenton-HA system) to accelerate the reaction efficiencies for that NH_2OH could reduce Fe (III) to Fe (II) via equation (9) or (10)^[10] and show no obvious quenching effect on $\text{HO}\cdot$ at the pH of 3.0^[11]. Since NH_2OH could reduce Fe (III) to Fe (II) in Fenton system, it also ought to be feasible in Fenton like system.

So the objective of the present study was to evaluate the potential of NH_2OH in Fenton like system (Fenton like-HA system) to avoid the disadvantage afore-mentioned. The comparative study among these Fenton, Fenton like, Fenton-HA and Fenton like-HA systems was considered. And the effect of Fe (III), H_2O_2 and NH_2OH dosages, the according kinetics and the mechanism were investigated.



1 Materials and methods

1.1 Materials

The following chemicals are reagent grade. Benzoic acid, hydroxylamine hydrochloride (99.999%), monosodium phosphate, sodium hydrogen phosphate, hydrogen-peroxide oxidoreductase (POD), and N,N-diethyl-p-phenylenediamine (DPD) were supplied by Sigma-Aldrich. Hydrogen peroxide (H_2O_2 , 35% v/v, stab.) was from Alfa Aesar. Sodium nitrite, ferric sulphate, perchloric acid and ascorbic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Methanol (Tedia), acetone (Tedia), methyl tert-butyl ether (MTBE from Fisher) and phosphoric acid (Dikma) were of HPLC grade.

1.2 Procedures

All experiments were carried out at 20 °C at pH of 3.0 with 250 mL triangular flasks under constant stirring with a PTFE-coated magnetic stirrer in Milli-Q water. BA, NH_2OH and Fe (III) with desired concentrations were spiked in 100 mL perchloric acid buffer. Each run was switched on by adding the desired dosage of H_2O_2 . The pH changed less than 0.2 units during the process. Samples were withdrawn at time intervals and quenched by ascorbic acid before analysis.

1.3 Sample analysis

The concentrations of BA and PHBA were analyzed on HPLC (Waters). The pH was measured by a pH Meter (Ultrabasic 7 from Denver Instrument). The Fe (III) concentrations were measured on UV-vis spectrometer (Varian Cary 300 UV-vis spectrometer) at 300 nm^[12] using 10 cm quartz sampling cells. The H_2O_2 concentrations were measured by colorimetric method using DPD^[13] on Varian Cary 300 UV-vis spectrometer.

2 Results and discussion

2.1 Comparative study with Fenton-HA and Fenton like systems

The degradation of BA in Fenton, Fenton like, Fenton-HA, and Fenton like-HA systems under the same dosage of H_2O_2 , iron and NH_2OH are shown in Fig. 1. As can be seen, Fenton like system shown no visible BA conversion. Besides, the conversion of BA was only 49.6% after 10 minutes in Fenton system, and increased to 83.5% and 92.5% in Fenton like-HA and Fenton-HA systems.

The inset shows the according regression lines for a pseudo-first-order rate model with R^2 values of 0.851, 0.994, 0.996 and rates values of 0.057, 0.183, 0.254 min^{-1} in Fenton, Fenton like-HA and Fenton-HA systems, respectively. The linearity of Fenton system was lower than Fenton-HA and Fenton like-HA systems. It means that the addition of NH_2OH to Fenton and Fenton related systems might enhance their performance.

The minimal BA conversion in Fenton like system was due to the low iron dosage ($20.0 \mu\text{mol} \cdot \text{L}^{-1}$), the slow transformation rate of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ via equation (2) and the short reaction time for only 10.0 minutes. The degradation efficiency in Fenton system was better, for the initial iron was $\text{Fe}(\text{II})$, which could directly react with H_2O_2 via equation (1) or (8) to produce reactive species to oxidize BA. After 2.0 minutes, the slow stage result from the $\text{Fe}(\text{III})$ accumulation and bad recovery of $\text{Fe}(\text{II})$ via equation (2) was dominant in Fenton system.

However, the Fenton-HA and Fenton like-HA systems show no obvious slow oxidation stage and much higher BA conversion attribute to the fast recycles from $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ by NH_2OH via equation (9)^[9]. The curve trends in the two systems were similar throughout the process, and the BA conversion discrepancies between them were nearly 10.0% since 30.0 seconds. The lag between the two systems was due to the valent of iron to initiate the chain reactions. In Fenton like-HA system, $\text{Fe}(\text{III})$ should react with NH_2OH via equation (9) (Equation (10) would not happen for the NH_2OH dosage is much higher than that of iron in our study)^[10] to produce $\text{Fe}(\text{II})$ before the generation of reactive species and the oxidation of BA. The BA conversion in Fenton and Fenton-HA systems were similar at 30.0 seconds, both of them were better than that in Fenton like-HA system, which further verified that the better oxidation efficiency in Fenton-HA system and the reason of the lag phase was attribute to the direct reaction of $\text{Fe}(\text{II})$ and H_2O_2 in the early stage of Fenton-based reactions. BA conversion in Fenton system was higher than Fenton like-HA system before 1.5 minutes, for $\text{Fe}(\text{II})$ concentration in the Fenton system at that time was still adequate to sustain the fast oxidation stage. The phenomenon of lag phase between the two systems was identical with the analysis: the role of NH_2OH in the Fenton and Fenton related systems were to accelerate the redox cycles of $\text{Fe}(\text{III})/\text{Fe}(\text{II})$.

Regardless the lag phase between the Fenton-HA and Fenton like-HA systems, the curve trends of them were coincident, that means their mechanism ought to be similar. Whether $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$ is used to initiate the chain reactions, both of them were present simultaneously and circulated well in the two systems due to the addition of NH_2OH , the reactive species formed in both systems should also be alike. Consequently, the $\text{HO} \cdot$ was recognized as the dominant reactive species not only in Fenton-HA system^[9], but also in Fenton like-HA system.

Although there was a lag phase in Fenton like-HA system compared to Fenton-HA system, the oxidation efficiency in Fenton-HA was much more superior to that in Fenton and Fenton like systems. Besides, from the econom-

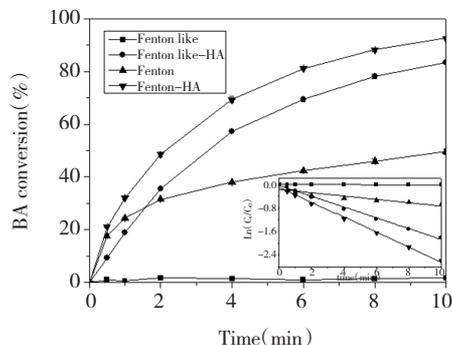


Fig. 1 The comparison study of the Fenton, Fenton like, Fenton-HA and Fenton-like-HA systems at $[\text{BA}]_0=40.0 \mu\text{mol} \cdot \text{L}^{-1}$, $[\text{H}_2\text{O}_2]_0=0.4 \text{mmol} \cdot \text{L}^{-1}$, $[\text{Fe}(\text{III})]_0=20.0 \mu\text{mol} \cdot \text{L}^{-1}$, $[\text{NH}_2\text{OH}]_0=0.4 \text{mmol} \cdot \text{L}^{-1}$

ic standpoint, Fenton like-HA system was better than the Fenton-HA systems for the practical application. So its operational parameters should be explored explicitly.

2.2 Effect of operational parameters on BA conversion

Fig. 2a shows the relationship between BA conversions as a function of time at different H_2O_2 concentrations. The increase in the BA conversion efficiency was due to the increase in $\text{HO}\cdot$ concentration via equation (1) by the increase of initial H_2O_2 dosage. It should be noted that, the Fenton and Fenton like systems usually exhibit a high H_2O_2 demand, the molar ratios between H_2O_2 to iron employed in water treatment were usually in the range of 100 to 1 000. But the dosage in our study was low, when the H_2O_2 was $0.4 \text{ mmol}\cdot\text{L}^{-1}$, 20 times higher than initial concentration of Fe (III) and 10 times higher than that of BA, the BA conversion efficiency was as good as 83.5% in 10.0 minutes. It means that the addition of NH_2OH to Fenton like system could effectively increase the H_2O_2 utilization efficiency.

The effect of Fe (III) dosage on the BA conversion in the Fenton like-HA system as a function of reaction time is shown in Fig. 2b. BA conversion could be ignoring in the absence of Fe (III), it is hard to generate $\text{HO}\cdot$ in such a short time for H_2O_2 alone. The BA oxidation rate increased with an increase of the Fe (III) dosages from 10.0 to $80.0 \mu\text{mol}\cdot\text{L}^{-1}$. The increase of Fe (III) dosage could enhance the Fe (II) concentration via rapid reaction with NH_2OH , whose dosages was $0.4 \text{ mmol}\cdot\text{L}^{-1}$, sufficient to sustain equation (9). Due to the enhancement of Fe (II) concentration and excess dosage of H_2O_2 , more $\text{HO}\cdot$ could be generated via equation (1) to oxidize BA.

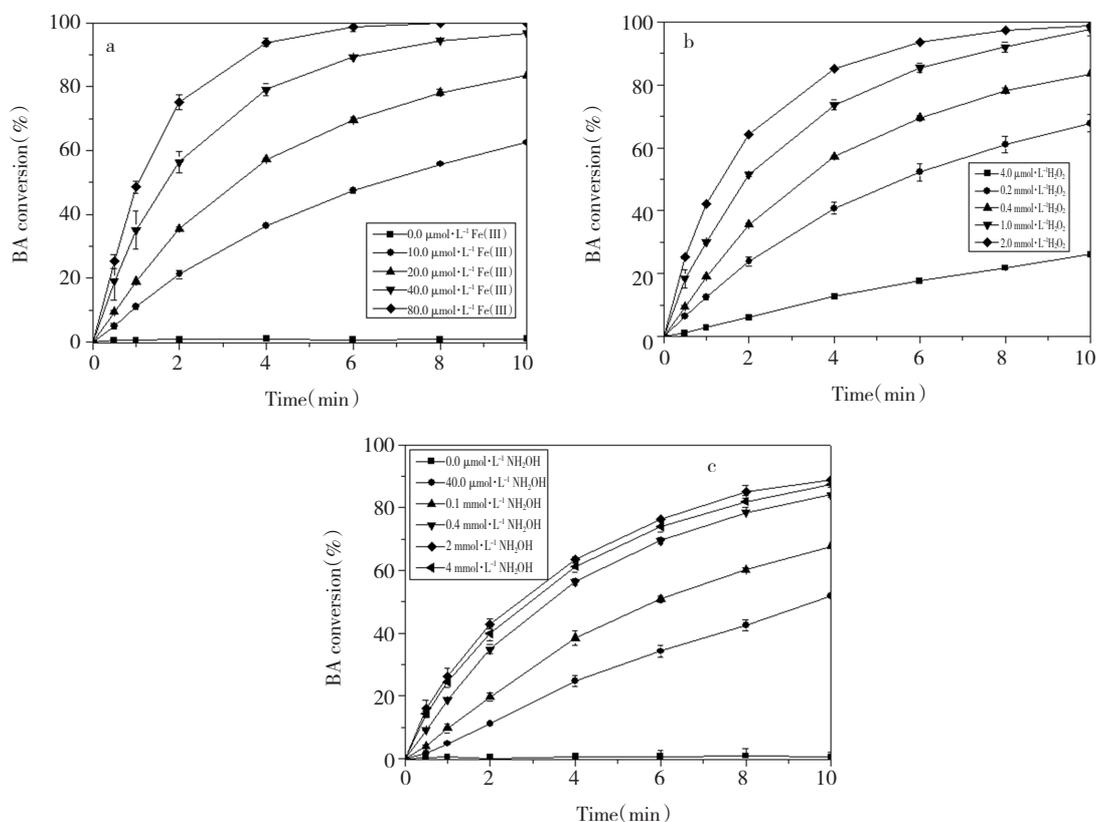


Fig. 2 The effect of Fe (III), H_2O_2 and NH_2OH dosage on Fenton-like-HA system

The legal limit of iron in solution imposed by European Union is $2.0 \text{ mg}\cdot\text{L}^{-1}$, therefore $20 \mu\text{mol}\cdot\text{L}^{-1}$ Fe (III) equals to $1.12 \text{ mg}\cdot\text{L}^{-1}$, which was employed in majority of our experiments in this study to avoid the additional steps to reduce extra iron oxides. This showed one of the advantage in the Fenton like-HA system resulted from the fine redox cycles between ferrous and ferric iron through the addition of excessive NH_2OH .

The effect of NH_2OH dosage on the BA conversion as a function of time is shown in Fig. 2c. The BA conversion

was in direct proportion to NH_2OH dosage when HN_2OH dosage was lower than $0.4 \text{ mmol} \cdot \text{L}^{-1}$. The NH_2OH usually regarded as a kind of effective antioxidant^[14], but it showed a little detrimental effect to BA conversion until its concentration increased to $4.0 \text{ mmol} \cdot \text{L}^{-1}$. It is no sense to raise the concentration of NH_2OH more than that of H_2O_2 .

2.3 Kinetics research

The BA conversions as a function of reaction time at different $\text{Fe}(\text{III})$, H_2O_2 and NH_2OH concentrations were all well fitted pseudo-first-order kinetics shown in Fig. 3.

The pseudo-first-order reaction rate of the influence of different H_2O_2 dosage was illustrated in Fig 3a with the R^2 values of 0.997, 0.995, 0.994, 0.962 and 0.999 and the rate values of 0.031, 0.114, 0.183, 0.372 and 0.438 for $40.0 \mu\text{mol} \cdot \text{L}^{-1}$, $0.2 \text{ mmol} \cdot \text{L}^{-1}$, $0.4 \text{ mmol} \cdot \text{L}^{-1}$, $1.0 \text{ mmol} \cdot \text{L}^{-1}$ and $2.0 \text{ mmol} \cdot \text{L}^{-1}$ H_2O_2 , respectively. The rate of BA conversion increased with a factor of about 5.9 and 3.8 when the initial concentration of H_2O_2 were increased $40.0 \mu\text{mol} \cdot \text{L}^{-1}$ to $0.4 \text{ mmol} \cdot \text{L}^{-1}$ and $0.2 \text{ mmol} \cdot \text{L}^{-1}$ to $2.0 \text{ mmol} \cdot \text{L}^{-1}$, both with a factor of ten times. Although the reaction was a pseudo-first order at fixed initial concentration of H_2O_2 , it is not proportional to the times of increased H_2O_2 overall. This phenomenon may as a result of that the untreated H_2O_2 will act as a scavenger of $\text{HO} \cdot$ via equation (2) and (3) to produce $\text{HO}_2 \cdot$, whose oxidation potential is less than $\text{HO} \cdot$.

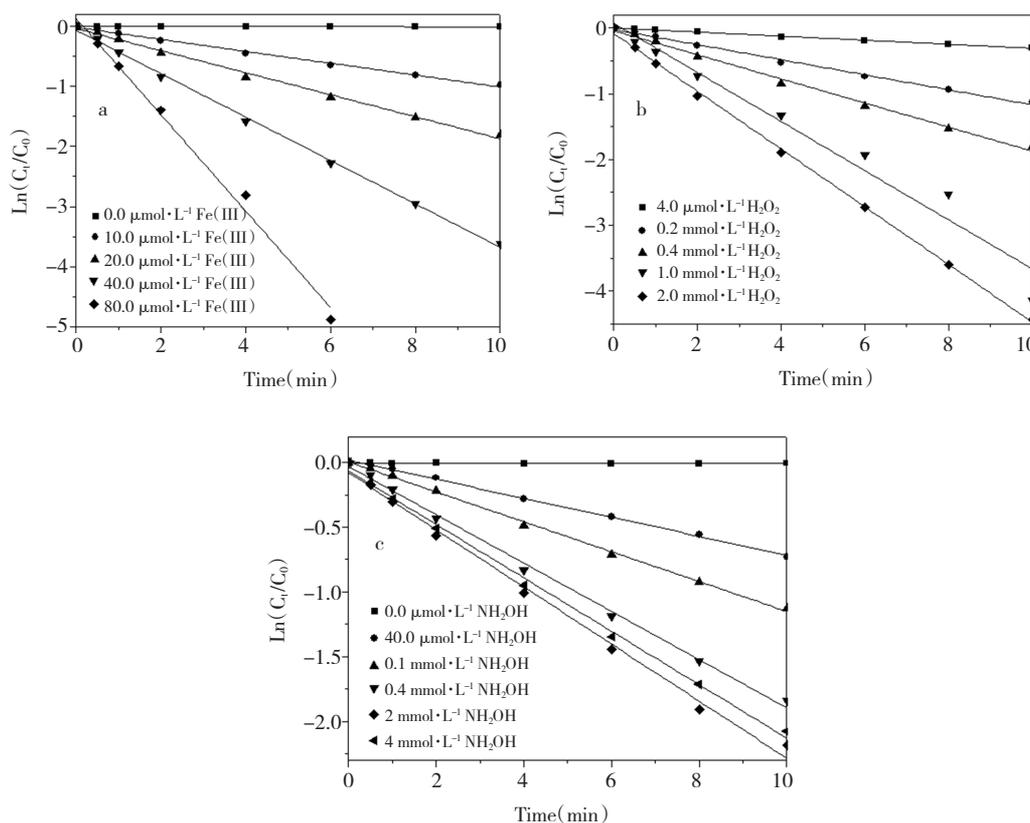


Fig. 3 The pseudo first – order rate kinetic modal with different dosage of $\text{Fe}(\text{III})$, H_2O_2 and NH_2OH in Fenton – like – HA system

Fig. 3b shows the fitted pseudo-first-order rate model of Fig. 2b during the whole runs with R^2 values of 0.995, 0.994, 0.998 and 0.991 and rates values were 0.099, 0.183, 0.361 and 0.801 min^{-1} for 10.0, 20.0, 40.0 and $80.0 \mu\text{mol} \cdot \text{L}^{-1}$ of $\text{Fe}(\text{III})$ dosages, respectively. The pseudo-first-order reaction rate of the process was proportional to the initial concentration of $\text{Fe}(\text{III})$.

The pseudo-first-order rates of Fig. 2c were shown in Fig. 3c with all the R^2 higher than 0.990. The rates were similar on condition that NH_2OH dosages were higher than $0.4 \text{ mmol} \cdot \text{L}^{-1}$. There was no regulation of multiple among the rates values, which was similar with that of H_2O_2 . While it was interesting that multiple among the rates values almost equal to that among the initial $\text{Fe}(\text{III})$ dosages in Fig. 3a. It means the factor of $\text{Fe}(\text{III})$ dosage on

BA conversion was the most important among these operational parameters. The reason might be that the H_2O_2 and NH_2OH dosages were both in excess of $\text{Fe}(\text{III})$ dosage, so the ferric concentration becomes more crucial factor for the generation of $\text{HO}\cdot$.

2.4 Mechanism discussion

Since the dominating reactive species in HA-based Fenton system was $\text{HO}\cdot$, and the generation of $\text{HO}\cdot$ was attributing to $\text{Fe}(\text{II})$ induced consumption of H_2O_2 , the H_2O_2 conversion were measured and shown in Fig. 4. More than 30% H_2O_2 was consumed in the Fenton like-HA system in 10.0 minutes, while the $\text{HO}\cdot$ concentration responsible for BA conversion was much less than H_2O_2 conversion. The extra H_2O_2 conversion might waste in the side reactions as equation (3) or to participate in the $\text{HO}\cdot$ generation to degrade intermediates of BA conversion.

As shown in Fig. 4, $\text{Fe}(\text{III})$ concentration sharply decreased within 1 minutes and kept at $5.3 \mu\text{mol}\cdot\text{L}^{-1}$ (more or less) throughout the process. Since the Ferric and ferrous iron concentration in the system was almost stable, the $\text{HO}\cdot$ production videlicet the BA conversion was merely relevant to the concentrations of H_2O_2 , which means the corresponding kinetic constant in this system should be fitted pseudo-first-order demonstrated well in Fig.3. The steady concentration of $\text{Fe}(\text{III})$ was attributing to a dynamic equilibrium of $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ in the Fenton like system: NH_2OH reduced $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ coexistent with $\text{Fe}(\text{II})$ induced H_2O_2 to produce the $\text{HO}\cdot$ and $\text{Fe}(\text{III})$.

Generally speaking, increase the dosage of NH_2OH and H_2O_2 ought to increase the $\text{HO}\cdot$ production and BA conversion. However, no obvious acceleration of BA conversion was observed when the dosage of NH_2OH was increased, a little regression of BA conversion was even exhibited in Fig. 2c and Fig. 3c when NH_2OH dosage was $4 \text{ mmol}\cdot\text{L}^{-1}$ – ten times higher than that of initial H_2O_2 . The enhancement of NH_2OH dosage might also increase the reaction rates between $\text{HO}\cdot$ and NH_2OH , which was frequently used as a strong reducing agent and antioxidant^[15].

The concentration of $\text{Fe}(\text{III})$ in both Fenton-HA and Fenton like-HA systems were in a dynamic equilibrium. The discrimination between the two systems was just the starting material: $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$ had no difference from the mechanistic standpoint.

3 Conclusions

The BA conversion in the Fenton-like-HA system was much higher than the Fenton and the Fenton-like systems. And the Fenton-like-HA system was also superior to Fenton-HA system from the economic and practical standpoint. The BA conversion was in direct proportion to H_2O_2 , $\text{Fe}(\text{III})$ and NH_2OH dosages, and all fitted pseudo-first-order due to the relatively steady concentration of $\text{Fe}(\text{III})$. The steady of $\text{Fe}(\text{III})$ concentration was in virtue of the well redox cycles between $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ induced by NH_2OH . So the system could be seen as a novel Fenton-like system.

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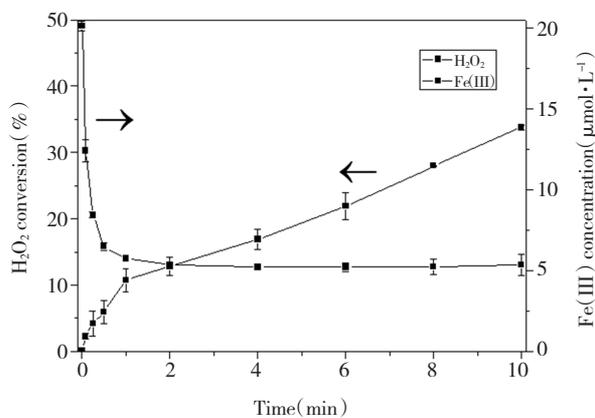


Fig. 4 The effect of reaction time on the $\text{Fe}(\text{III})$ concentration and the H_2O_2 conversion at $\text{pH}=3.0$ in Fenton-like-HA system

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一种新型的类芬顿体系对苯甲酸的降解效果研究

陈丽玮, 马军, 李旭春, 关英红

(哈尔滨工业大学 水资源与环境国家重点实验室 哈尔滨 150090)

摘要: 采用由三价铁离子、过氧化氢和羟胺组成的新型均相类芬顿对苯甲酸的去除进行了研究。与芬顿体系、类芬顿体系相比, 新型类芬顿体系由于加入了羟胺, 而羟胺能够加速三价铁和二价铁的循环, 同时不对自由基有明显的抑制。因此, 苯甲酸的去除随着过氧化氢, 三价铁离子以及羟胺投量的增加而增加, 所有反应过程均符合拟一级动力学, 拟一级速率常数超过传统芬顿体系的3~4倍。相比于传统体系, 新型的类芬顿体系显示出了很高的过氧化氢利用效率以及羟基自由基的产生速度。羟胺的加入使得三价铁离子在整个反应过程中维持一个相对稳定的浓度(5.3 μmol·L⁻¹), 从而解释了新型类芬顿体系符合拟一级动力学的原因。这种新型的类芬顿体系可以增加苯甲酸的去除, 增加过氧化氢的利用率并且节省三价铁以及过氧化氢的投加量, 具有较大的实际应用前景。

关键词: 类芬顿; 过氧化氢; 三价铁离子; 羟胺