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Degradation of bromamine acid by a heterogeneous Fenton-like catalyst Fe/Mn supported on sepiolite

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ABSTRACT

A heterogeneous Fenton-like catalyst, Fe/Mn supported on sepiolite, was proved to be effective in the degradation of bromamine acid aqueous solution. The catalyst was prepared with a complex sol-gel method using sepiolite as a carrier and citric acid as a complexing agent. The prepared catalyst was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM), and the results showed that the existence forms of Fe and Mn were γ-Fe_2O_3 and MnO and they were distributed evenly on the surface of sepiolite. In the degradation of bromamine acid aqueous solution, the catalyst could possess high catalytic activity when the initial pH of the solution ranged between 3 and 11. In addition, the degradation results showed that there was a synergistic effect between Fe and Mn. The inorganic ions inhibited the degradation efficiency in the early reaction period because of the scavenging effects on $^\bullet$OH, but the inhibition effect became weaker with the reaction time because of the fixation of metal ions on sepiolite.

Keywords: Fe/Mn/sepiolite; Heterogeneous Fenton-like process; Bromamine acid aqueous solution; pH scope; Inorganic anions

1. Introduction

Dyestuff wastewater is one of the serious problems in environmental field, especially in the water environment. Not only it is directly toxic to the biological world, but it also has a dark color, which blocks sun light. By these reasons, it causes many problems to the ecosystem. Numerous physical, chemical, and biological methods are presently available for the decolorization of dyestuff wastewater. However, the physical methods are not advantages as they only simply transfer the pollutants form one media to another. The biological methods are also limited because of the toxicity to the bacterium. Alternatively, chemical methods like "Advanced Oxidation Process" can mineralize the organic pollutants and can be applied over a wide range of organic. For example, Choi et al. used ozone to degrade the bromamine acid dyestuff wastewater and the results showed that the decolorization could be complete after 30 min and the COD removal rate could reach

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up to 93% [1]. But the cost for the operation of ozone generator was high because of the low efficiency of ozone production. In comparison, Fenton technology has simple reaction process and cheap materials. It also has strong oxidation capacity, wide application filed, and no pollutants selectivity because of the production of $^{\bullet}OH$, which can degrade the non-biodegradable organic pollutants effectively [2–4]. In addition, it can combine with other technologies to improve treatment efficiency, such as irradiation [5,6], microwaves [7], and ultrasound [8].

However, the homogeneous Fenton system still exist some disadvantages. For example, iron ions run off easily because of the formation of iron hydroxide that produces large amount of sludge and bring secondary pollution and which also results in a narrow pH values of the application of Fenton process and an increase in the processing cost [9]. In the past decade, researchers studied the preparation of heterogeneous Fenton-like catalyst extensively and they prepared the supported Fenton-like catalyst through the fixing metal on a certain carrier including clay [10], zeolite [11–13], montmorillonite K10 [14], and resin [15] to realize the separation and recycle of the catalyst and avoid secondary pollution. Compared with other supporting media, sepiolite is cheap, abundant and has good adsorption capability [16]. And it has been widely used as a carrier to prepare the supported catalysts which are used in the treatment of wastewater [17]. In this study, sepiolite was used as a carrier to prepare a double-metal Fe/Mn-loaded Fenton-like catalyst by a citric acid complexation method. Some research illustrated that Mn^{2+} could react with H_2O_2 to produce $^{\bullet}OH$ through a Fenton-like reaction [18]. The addition of Mn^{2+} could improve the reaction rate of the heterogeneous Fenton-like reaction. Complexation with citric acid was a method to prepare uniform ultrafine multicomponent oxide powder [19,20]. Its cardinal principle was that the polyfunctional group of citric acid would form chelate compound in the complex reaction, which made the active component distribute homogeneously on the surface of the carrier. Therefore, composited oxide powder could be prepared in a short heat treatment time at a low temperature.

The prepared Fenton-like catalyst Fe/Mn supported on sepiolite was applied to the degradation of bromamine acid aqueous solution, and the effects of Mn-loading amount, initial concentration and initial pH of bromamine acid solution, and inorganic ions on the degradation efficiency were assessed.

2. Methodology

2.1. Preparation of the catalyst

Sepiolite, an ore brought from Tianjin Zhongfa, was added into distilled water and hydrochloric acid solution with a concentration of 20% (w/w) was added until bubbling ceased, and then, the mixture was stirred for 24 h at 90℃. The mixture was filtered to obtain activated sepiolite and then washed them to neutral, dried, ground up, and sieved through a 400-mesh sieve. The powder was used as a carrier of the catalyst. The catalyst was prepared with a sol-gel method, in which iron sulfate was used as the Fe source and manganese nitrate was used as the Mn source. About 1.0 g activated sepiolite was added into a 30 mL mixed solution of $Fe_2(SO_4)_3$, $Mn(NO_3)_2$, and citric acid with a molar ration of Fe^{3+}/Mn^{2+}/citric acid = 2:1:3, and the total concentration of metal ions was 0.075 M. The mixture was strongly stirred for 15 min, and ammonia spirit was added to adjust the preparation pH to 8.0. The mixture was continuously stirred at 60℃ for 2 h until a viscous fluid was obtained. The viscous fluid was dried at 110℃ for 12 h and calcined at 450℃ in a muffle furnace for 2 h to obtain the catalyst Fe/Mn supported on sepiolite. All the chemicals used in the preparation were analytically reagent.

The prepared catalyst was characterized and analyzed by XRD (BDX330, Peking University Instrument Factory, China) and SEM (JSM-6700F, JEOL Corporation, Japan). The existing forms of Fe and Mn were determined by the comparing the XRD results with JCPDS cards and the morphology of catalyst was observed by the SEM results.

2.2. Degradation experiments

The catalytic activity of the catalyst was tested by the degradation of bromamine acid which was a typical intermediate of anthraquinone dye. The catalyst dosage and the H_2O_2 dosage were fixed at 2 g/L and 0.33 mg/L, respectively.

The different initial pH of bromamine acid aqueous solution was adjusted by the 1.0 M HNO_3 solution and 1.0 M NaOH solution. All the experiments were carried out under continuously stirring to make the catalyst disperse well. Samples were taken from the suspension at regular time intervals and immediately filtered through 0.22 μm membrane filters. And the filtrate was analyzed to determine degradation efficiency. The decrease in the absorbance of the solution was observed by a UV–vis Spectrophotometer (Shimadzu, Model No. 2550). The degree of decolorization, the removal degree of color at $\lambda_{\max}$ (485 nm) of the sample was calculated using the relation

$$\text{Degree of decolonization } (\%) = \frac{A_0 - A_t}{A_0}$$

Where A_0 was the initial absorbance of the sample and A_t was the absorbance at time t.

The reaction intermediates formed during the decolorization of bromamine acid would be long-lived and even more toxic. Therefore, it was necessary to determine the degree of mineralization of bromamine acid during the degradation. The mineralization was evaluated by the total organic carbon (TOC) removal rate which was determined by a VCPH type TOC analyzer (Shimadzu, Japan). The percentage of TOC removal was defined as

$$\text{TOC removal rate } (\%) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0}$$

TOC_0 and TOC_t represented the TOC of the solution before and after degradation for t time respectively, in the presence of H_2O_2 and the catalyst.

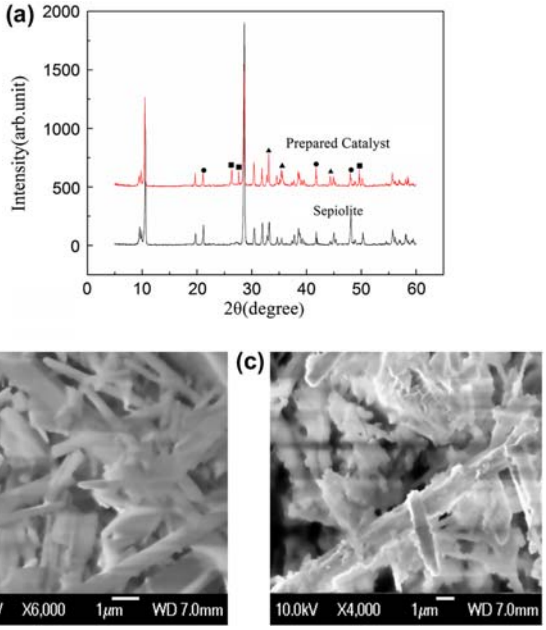

Fig. 1. Characterization pattern of the catalyst. (a) XRD pattern of the catalyst and sepiolite; (b) SEM pattern of sepiolite and (c) SEM pattern of the catalyst.

3. Results and discussion

3.1. Characterization of the catalyst

The wide angles X-ray diffraction (XRD) pattern and the scanning electron microscope (SEM) pattern of the catalyst were shown in Fig. 1.

Compared with the XRD pattern of sepiolite, there were several new small and broad diffraction peaks appeared in the XRD pattern of the prepared catalyst at $2\theta = 26.34$, 27.58, and 49.58°. And there were some enhanced diffraction peaks at $2\theta = 33.14$, 35.42, and 44.38° and some impaired diffraction peaks at $2\theta = 21.08$, 41.76, and 47.98°. The reason for the change in the XRD pattern of the prepared catalyst was the formation of Fe and Mn oxide on the surface of sepiolite as shown in Fig. 1(c). Compared with the JCPDS files 100319, it could be determined that the existence form for Fe and Mn oxides were γ-Fe_2O_3 and MnO. From the SEM pattern of sepiolite and prepared catalyst, it could be seen that the original of sepiolite processed a flat surface, but after being supported, there was a layer of fine metal oxide particles on the surface and they were distributed evenly.

3.2. Catalytic activity of the catalyst

3.2.1. Effect of the loading of Mn on the degradation

In order to verify the effect of the loading of Mn on the degradation efficiency, three different catalysts Fe/sepiolite, Mn/sepiolite, and Fe/Mn/sepiolite with a dosage of 2.0 g/L were adopted with 0.33 mg/L H_2O_2 for the degradation of bromamine acid aqueous

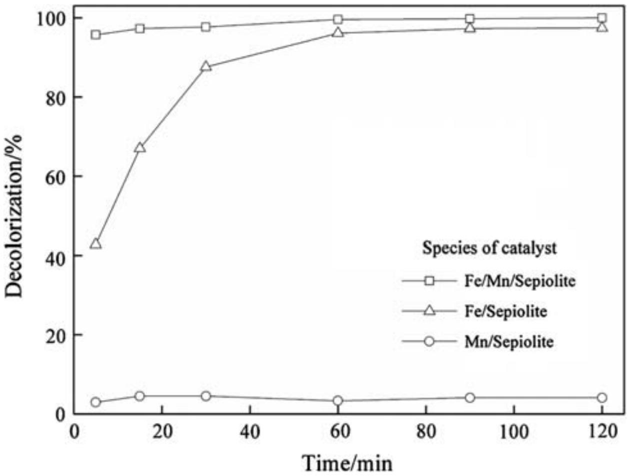

Fig. 2. Effect of the addition of Mn on the degradation. (Initial concentration: 30 mg/L, initial pH: 6.52, dosage of catalyst: 2 g/L, dosage of H_2O_2: 0.33 mg/L.)

solution with a concentration of 30 mg/L at pH=6.52. The results were shown in Fig. 2.

The results showed that the decolorization of the solution were 97.6, 87.57, and 4.47%, respectively, with the catalyst Fe/Mn, single Fe, and single Mn supported on sepiolite. It could be calculated that the decolorization of the solution with the catalyst Fe/Mn/sepiolite was higher than the plus of that with the catalyst Fe/sepiolite and Mn/sepiolite. It was indicated that the loading of Mn promoted the degradation efficiency, and there was a synergistic effect between Fe and Mn in the degradation. As the research findings reported by Costa et al. [21,22] that in the $Fe_{3-X}M_XO_4$ (M = Mn, Fe, Co, Ni) Fenton-like reaction, the reduction of Mn^{3+} species by Fe^{2+} was thermodynamically favorable as shown as follows:

$$Fe^{3+} + e^- \rightarrow Fe^{2+}\ E^0 = 0.77\ \text{V} \tag{1}$$

$$Mn^{3+} + e^- \rightarrow Mn^{2+}\ E^0 = 1.51\ \text{V} \tag{2}$$

$$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}\ E^0 = 0.73\ \text{V} \tag{3}$$

This reduction could take place by an electron transfer process within the semiconductor oxide structure. Besides, the narrow band gap of magnetite would improve the electron transport. Therefore, the regeneration of Mn^{2+} species by the process would be responsible for the promotion of degradation efficiency and the synergistic effect between Fe and Mn.

3.2.2. Effect of H_2O_2 dosage on the degradation

With an initial concentration of 30 mg/L (pH=6.52), the bromamine acid aqueous solution was degraded by the catalyst adopt with different H_2O_2 dosage ranged from 0.17 to 0.50 mg/L. Effect of H_2O_2 dosage on the degradation was investigated and the results were shown in Fig. 3.

As shown in Fig. 3(a), when H_2O_2 dosage was below 0.33 mg/L the maximum solution decolorizations were obtained at 60 min. But for the H_2O_2 dosage above 0.33 mg/L, the maximum solution decolorizations were obtained at 30 min. In addition, the solution decolorization rate for the H_2O_2 dosage of 0.33 mg/L was most quick and the solution decolorization at 15 min was 99.58%. It could see that the TOC removal rate at 30 min for the H_2O_2 dosage of 0.33 mg/L was 67.71%, which was higher than that for the other four H_2O_2 dosages. When H_2O_2 dosage increased from 0.17 to 0.33 mg/L, more $^\bullet OH$ would be produced by the reaction between H_2O_2 and the catalyst, and the solution decolorization and TOC removal rate were promoted. But when H_2O_2 dosage was above 0.33 mg/L, there would be excess H_2O_2 for the catalyst with a dosage of 2 g/L. The excess H_2O_2 was a scavenger of $^\bullet OH$, and the scavenging effect would suppress degradation efficiency [23]. In conclusion, the optimal H_2O_2 dosage for this Fenton-like process was 0.33 mg/L.

3.2.3. Effect of initial concentration of bromamine acid on the degradation

The decolorization experiment was performed at different bromamine acid concentration ranging from 30 to 150 mg/L at pH of 6.52 (pH of stock solution), and the dosage of the catalyst and H_2O_2 were 2 g/L and 0.33 mg/L, respectively. Effect of initial concentration of bromamine acid aqueous solution on the degradation was shown in Fig. 4.

It could be seen that solution decolorization was about 100% after a period of 120 min at an initial

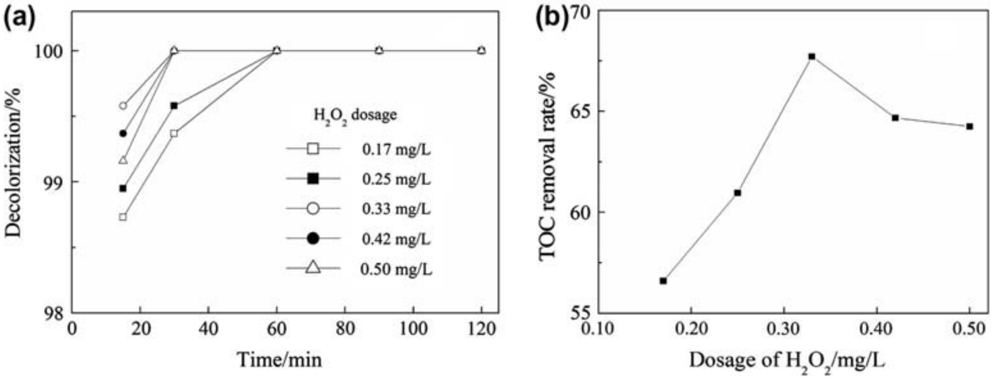

Fig. 3. Effect of H_2O_2 dosage on the degradation. (Initial pH: 6.52, initial concentration 30 mg/L, dosage of catalyst: 2 g/L.)

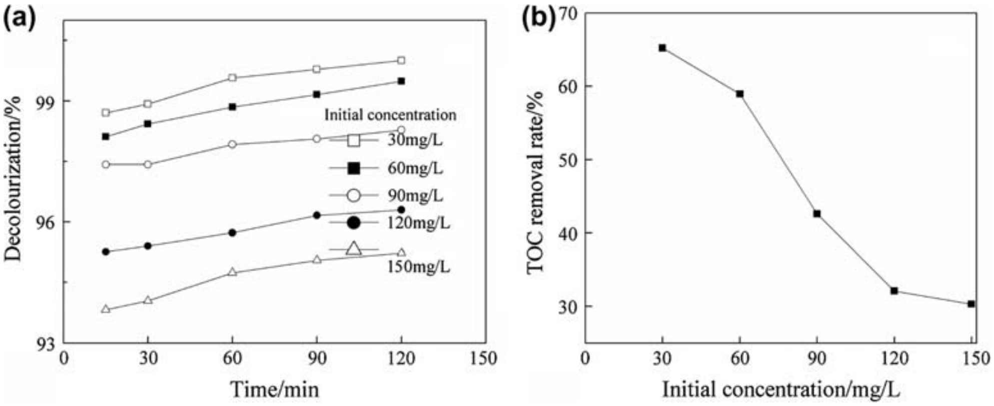

Fig. 4. Effect of initial concentration on the degradation. (Initial pH: 6.52, dosage of catalyst: 2 g/L, dosage of H_2O_2: 0.33 mg/L.)

concentration of 30 mg/L. The degree of solution decolorization for the initial concentration of 120 and 150 mg/L were 96.30 and 95.22%, respectively. According to the reported results [24], the lack of availability of active site was responsible for the decrease of the decolorization with the increase in the initial concentration. With the increase in the initial concentration of bromamine acid aqueous solution, the percentage of bromamine acid molecules which could be absorbed on the surface of the catalyst decreased, and the percentage of bromamine acid degraded by $^{\bullet}$OH decreased.

It should be noted that the TOC removal rate decreased when the initial concentration of bromamine acid increase from 30 to 150 mg/L. When the initial concentration was 30 mg/L, the TOC removal rate at 30 min was 59.20%, but it was only 30.31% when the initial concentration was 150 mg/L. Combined with the trend of the solution decolorization changed with the initial concentration, it could summarize that the decolorization and the TOC removal was not the same process. The decolorization of solution was the result of the breaking of anthraquinone bond of bromamine acid. But the TOC removal needed further mineralization of reaction intermediates into CO_2 and H_2O, it need more active substance (such as $^{\bullet}$OH) and longer reaction time.

3.2.4. Effect of initial pH on the degradation

The effect of initial pH value on the degradation of bromamine acid aqueous solution was investigated in the range of 3–11 under the dosage of the catalyst of 2.0 g/L, H_2O_2 of 0.33 mg/L, and the results were shown in Fig. 5.

It could see that the solution decolorization decrease when the initial pH value increased from 5 to 11, a higher initial pH resulted in more time to reach up to the maximal degree of decolorization. The reason for this was that the catalyst surface would

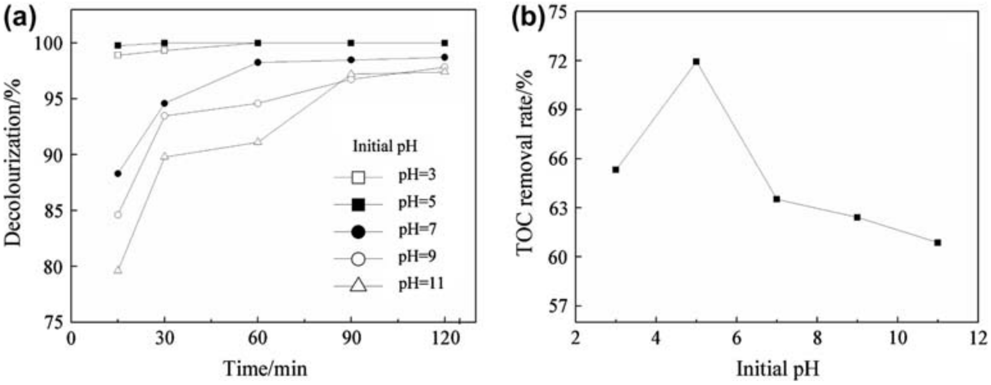

Fig. 5. Effect of initial pH of the solution on the degradation. (Initial concentration: 30 mg/L, dosage of catalyst: 2 g/L, dosage of H_2O_2: 0.33 mg/L.)

become negatively charge and the adsorption of bromamine acid (having HSO_3^-) would be inhibited [24], which resulted in the decrease in solution decolorization. But still the solution decolorization was 97.40% when the initial pH value was 11. Besides, at wide pH scope from 3 to 11, the TOC removal rates at 30 min of the solution were all above 60%. Obviously, Fe/Mn/sepiolite could possess high catalytic activity in a wide pH scope, which was different from the traditional Fenton system. In traditional Fenton system, the oxidation could only proceed efficiently at a narrow pH range ($pH < 4$), because iron would precipitate as hydroxides when the pH was above 4 [25]. In this Fenton-like process, the good adsorption capacity of sepiolite [26,27] and the fixation of Fe and Mn were responsible for the good adaptability to the solution initial pH value.

3.2.5. Leaching of metal ion in the degradation

To study the potential leaching of metal irons from the carrier sepiolite, the catalyst was filtered in hot condition to minimize re-adsorption. The solution was tested for iron content by Atomic Adsorption Spectrometry. The amount of Fe ions and Mn ions were found to be $<6.7 \times 10^{-4}$ M and $<2.0 \times 10^{-3}$ M, respectively. It was indicated that this heterogeneous Fenton-like catalysis was mainly due to metal oxide on sepiolite surface rather than the trace amount of leached metal ions in the solution. Similar observations were reported in the decolorization of Acid Blue 74 using Fe-ZSM5 and the decolorization of Methyl Orange using Fe_2O_2–SiO_2 composite [28,29]. In Fe/Mn/Sepiolite catalytic system, Fe and Mn irons were fixed well on the surface of sepiolite.

3.2.6. Effects of inorganic anions on the degradation

Inorganic anions (Cl^-, SO_4^{2-}, NO_3^-, etc.) always present in wastewater, and the significant effect of them on the overall reaction rates in the Fenton process were reported by researchers [30,31]. And in this article, effects of these inorganic anions with a concentration of 100 mM on the degradation were investigated and the results were shown in Table 1 and Fig. 6.

As shown in Table 1, after 15 min, the decolorization of the solution with inorganic anions was lower than that of the solution without inorganic anions. Especially when there was Cl^- in the solution, the decolorization was only 87.61% which was lower than that in the solution without inorganic anions by 11.96%. And the TOC removal rate at 30 min was lower than that in the solution without inorganic anions by 7.32%. As reported by several researchers that scavenging effects of inorganic anions on $^{\bullet}OH$ and formation of metal ion complex [32,33] were responsible for the inhibition in degradation efficiency. In conclusion, the inorganic anions restrained the degradation efficiency in early reaction period. But as shown in Fig. 6, after 30 min, the inhibition effect of inorganic anions on the decolorization became weaker, and after 120 min, the decolorizations of the solution with inorganic anions were all above 97%, which was approximate to that of the solution without any inorganic anions. As mentioned previously, the fixation of metal ions on the carrier sepiolite could account for this phenomenon because it could avoid the formation of complex compounds between metal ions and inorganic anions. The prepared catalyst Fe/Mn/Sepiolite had good adaptability to inorganic anions.

Table 1
Effect of inorganic anions on the degradation

Species of inorganic anions	Degree of decolorization (%) 15 min	TOC removal rate (%) 30 min
Cl^-	87.61	64.87
NO_3^-	96.37	70.03
SO_4^{2-}	99.14	67.56
None	99.57	72.19

Initial concentration: 30 mg/L, initial pH: 5, dosage of catalyst: 2 g/L, dosage of H_2O_2: 0.33 mg/L.

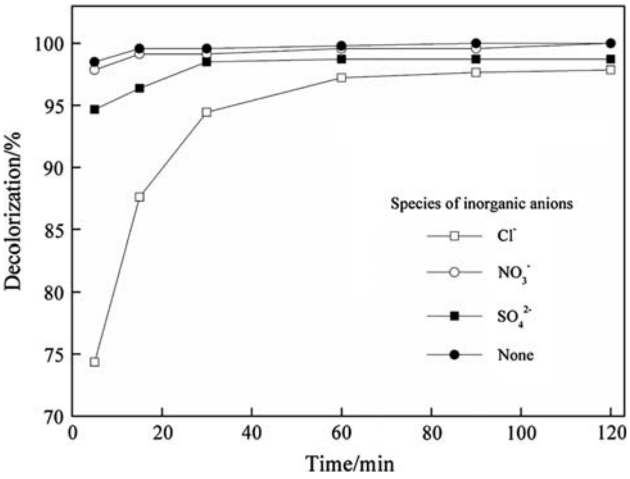

Fig. 6. Effect of inorganic anions on the degradation. (Initial concentration: 30 mg/L, initial pH: 5, dosage of catalyst: 2 g/L, dosage of H_2O_2: 0.33 mg/L.)

4. Conclusion

The Fenton-like catalyst, Fe/Mn supported on sepiolite, was prepared with a sol-gel method using citric acid as a complexing agent and sepiolite as a carrier. The catalyst was adopted with H_2O_2 for the degradation of bromamine acid aqueous solution. There was a synergistic effect between Fe and Mn during the degradation. The catalyst could proceed in a wide pH range from acidic to alkaline and the results showed that the degree of decolorization at 120 min and TOC removal rate at 30 min were all above 90 and 60%, respectively, when the initial pH of the solution ranged from 3 to 11.

The inorganic ions inhibited the degradation efficiency in the early reaction period because of the scavenging effects on $^{\bullet}OH$, but the inhibition effect became weaker as the reaction time because of the fixation of metal ions on sepiolite. The prepared catalyst Fe/Mn/sepiolite had good adaptability to inorganic anions.

Acknowledgments

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