



Preparation of gelatin-modified nano-iron and the effect on removing methyl orange

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ABSTRACT

In this paper, the gelatin-modified nano-iron was prepared by the liquid-reduction process. Scanning electron microscopy (SEM), infrared spectrum as well as sedimentation rate were used to characterize the prepared samples. The effect of the gelatin-modified nano-iron on removing methyl orange (MO) was investigated. The results show that the dispersion and stability of the gelatin-modified nano-iron are significantly improved; the combining mechanism between the gelatin and the nano-iron is deduced to be the coordination between the iron and the amino nitrogen of the gelatin; the removal rate of MO by the gelatin-modified nano-iron is higher than that by the non-modified one; the initial concentration of MO, the initial pH value and the content of dissolved oxygen have negative effects on the removal rate, but the amount of the modified nano-iron and temperature have positive effects; NO_3^- and CO_3^{2-} inhibit the removal of MO, and the concentration of SO_4^{2-} determines its effect on the removal is positive or negative.

Keywords: Nano-iron; Modification; Gelatin; Methyl orange (MO)

1. Introduction

Removing pollutants by zero-valent iron has received widespread attention nowadays. Compared with the normal iron particles, nano-iron has a smaller size and a larger specific surface area. Thus, the zero-valent nano-iron technology can obviously improve the reaction activity of zero-valent iron and has been successfully used to remove the pollutants like organochlorine compounds, bromate, nitro compounds, polycyclic aromatic hydrocarbons, heavy metals, dyes, etc [1–3]. But due to the magnetic force and van der Waals force among the particles, the nano-iron is very easy to agglomerate, and this leads to a decrease of the reaction activity and stability of the nano-iron. Hence, modifying the nano-iron to improve its reaction activity and stability is of great significance in the application of the technology to environmental remediation.

One of the important methods to modify nano-iron is coating. By this method, the nano-iron particles combine with coating agents, such as surfactants or macromolecular compounds, via covalent bond or other forces and the surface characteristics are improved. Coating can not only slow the oxidation of the nano-iron but also inhibit the agglomeration through electrostatic repulsion or steric hindrance. Besides, coating can avoid some adverse effects caused by the exposure of nano-iron to the environment. The common coating agents of nano-iron are starch [4–7], chitosan [6,7], carboxymethyl cellulose [8], biological glue [9], polyphenols [10], etc.

As a kind of natural polymer, gelatin has many advantages such as inexpensiveness, biocompatibility and degradability, nontoxicity and harmlessness. Therefore, using gelatin as a coating agent to combine nano particles, which is also called an easy and “green (environmentally-friendly)” method, has received increasing attentions. Gelatin has a good dispersion

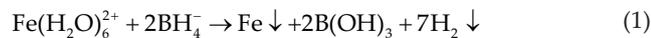
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effect and has been used on the modification of several kinds of nano particles (such as Ag [11], Au [12, 13], Fe₃O₄ [14], etc.), but there were no reports on preparing nano-iron particles by using gelatin as a coating agent. Hence, in this paper, we used gelatin as the coating agent to modify the nano-iron, and investigated the removal effect of the gelatin-modified nano-iron on methyl orange (MO) as well as the influencing factors.

2. Materials and methods

2.1. Preparation of the gelatin-modified nano-iron

All reagents used in the experiment were analytical grade and without further purification. A stock solution of gelatin (2 g/L) was prepared by dissolving 0.1 g of gelatin in 50 mL of water and then heating it to 40°C. In a typical synthesis, 0.4964 g of FeSO₄·7H₂O was dissolved in 100 mL of ethanol-water (1:1) mixed solvent in a 500 mL three-necked round-bottomed flask, and then the solution was bubbled with nitrogen for 30 min under vigorous stirring at 40°C to remove the dissolved oxygen. 50 mL of the gelatin stock solution was added into the solution in the flask. After the solution was stirred for 30 min, a total of 50 mL of KBH₄ solution (4.732 g/L) was added into the solution dropwise. Then, the solution in the flask turned from colorless to grey-green and finally to black. The resulting mixture was further stirred for 20 min. The whole process above was carried out in the nitrogen atmosphere, and lots of hydrogen was produced (Eq. (1)).



The non-modified nano-iron was synthesized by the same reaction conditions but substituting 50 mL distilled water for the gelatin solution (Fig. 1).

2.2. Sample-characterizing

A scanning electron microscope (SEM, 4800FRigaku Corporation, Japan) was used to observe the surface morphology of the nano-iron and the gelatin-modified nano-iron. The infrared spectrum (IR) determined by a infrared spectrometer (Nicolet Impact 410 infrared spectrometer, Nicolet Company, USA) was used to characterize the interaction between the nano-iron and the gelatin. And the stability of the nano-iron and the gelatin-modified nano-iron was compared by the sedimentation rate.

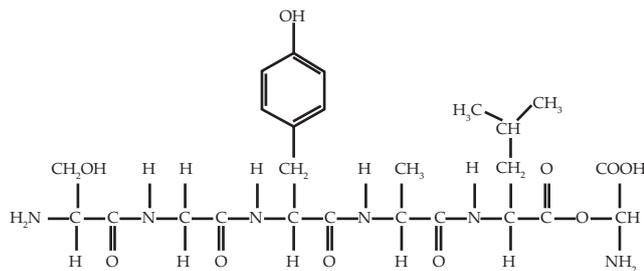


Fig. 1. The structure of gelatin.

2.3. Removal of MO by the gelatin-modified nano-iron

MO stock solution (500 mg/L) was prepared by dissolving 0.125 g of MO into 250 mL of distilled water and kept in dark place at 4°C. A certain volume of the MO stock solution and freshly prepared nano-iron solution were added into a 50 mL conical flask with a cover, and then the mixed solution was diluted to 50 mL with the distilled water. After shook for about 10 min in a constant temperature oscillator (20°C, 100 rpm), the mixed solution was centrifuged for 3 min at 10,000 rpm. The concentration of MO in the supernatant was analyzed at 464 nm using a visible spectrophotometer (WFJ 7,200 visible spectrophotometer, Unico, Shanghai, Instrument Co., LTD).

3. Results and discussions

3.1. Characterizations of the samples

3.1.1. SEM analysis

SEM was used to characterize the morphology of the nano-iron. An observable agglomeration occurs for the non-modified nano-iron particles (Fig. 2(a)) because they are linked together and grown into a block or chain structure by the van der Waals force and the magnetic force. The gelatin-modified nano-iron particles, however, show a ball-like morphology, and the agglomeration is not so serious (Fig. 2(b)). That is

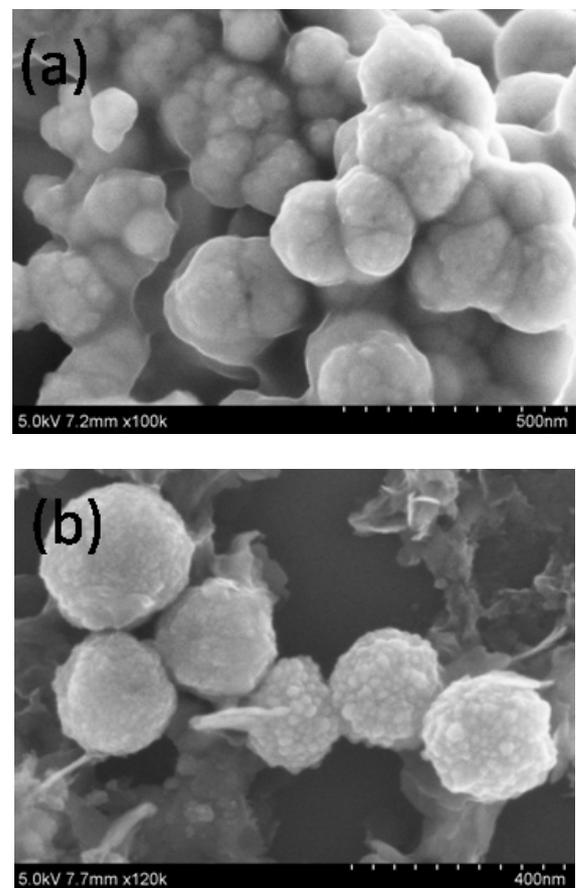


Fig. 2. SEMs of non-modified nano-iron (a) and the gelatin-modified nano-iron (b).

because the gelatin can lead to electrostatic repulsion and steric hindrance which can inhibit the agglomeration.

3.1.2. Infrared spectrum analysis

To identify the interactions between the iron and the gelatin, the IR of the gelatin and the nano-iron before and after the modification are compared in Fig. 3. For the gelatin, the bands between 3000–3600 cm^{-1} are attributed to the stretching vibrations of N–H, the band at 1650 cm^{-1} is dominated by the stretching vibrations of C=O, and the band at 1535 cm^{-1} is related to the combination of in-plane bending vibrations of N–H and stretching vibrations of C=N [15]. For the non-modified nano-iron, the broad peak near 3176 cm^{-1} may be assigned to the stretching vibrations of hydrogen bonds of H_2O adsorbed on the surface, and the peak at 1340 cm^{-1} is attributed to the stretching vibrations of the B–O bond which is caused by boron(B) introduced from the preparation. The absorption at 1020 cm^{-1} is the characteristic peak of Fe_2O_3 , it shows that the nano-iron was partly oxidized. For the modified nano-iron, there appears characteristic peaks of the gelatin. But the absorption peaks become much more narrow and sharper, and the characteristic peaks of the gelatin (1650 cm^{-1} , 1535 cm^{-1}) have red shifts (1652 cm^{-1} , 1542 cm^{-1}). All these show the formation of the new chemical bonds between the iron and the chelating groups of gelatin [15].

3.1.3. Stability analysis

Nano-iron particles have small size and large specific surface area, and very easily agglomerate and precipitate via gravity. This property prevents them from contacting with pollutants and results in an unsatisfactory effect on the pollution remediation. To investigate the stability of the modified nano-iron, a sedimentation experiment was carried out. That is, the freshly prepared non-modified and gelatin-modified nano-iron samples were put into two different glass bottles and stood for some time, the results are shown in Fig. 4. The non-modified nano-iron sample had a bad stability, most of them precipitated down to the bottom after 5 min (Fig. 4(a)), while the gelatin-modified one (Fig. 4(b)) just started to precipitate after 4 d. It shows that the gelatin-modified nano-iron particles have a better stability which is attributed to the electrostatic repulsion and steric hindrance of gelatin.

3.2. Effects between the gelatin-modified nano-iron and the non-modified nano-iron on removing MO

MO, a typical pollutant, was selected as the target pollutant to investigate the effect of the gelatin-modified nano-iron on removing pollutant. The comparison of effects on MO removal by the gelatin-modified nano-iron and the non-modified one are shown in Fig. 5. The removal rate of MO by the gelatin-modified nano-iron was higher than that by the non-modified one, no matter what the concentration of MO was. This is because the electrostatic repulsion and steric hindrance caused by the gelatin on the nano-iron surface inhibit the agglomeration of the nano-iron particles, increase the specific surface area, improve the reaction activity, and finally lead to the improvement of MO removal rate.

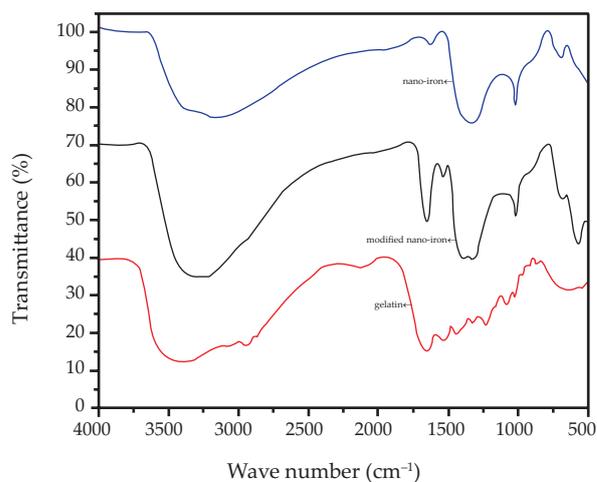


Fig. 3. The IR spectra of gelatin, nano-iron and modified nano-iron.

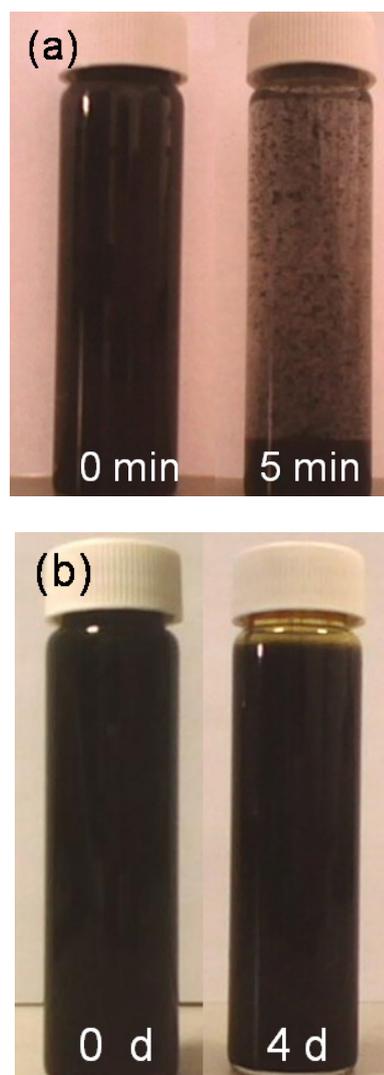


Fig. 4. Comparison of the stability between the non-modified nano-iron (a) and the gelatin-modified nano-iron (b).

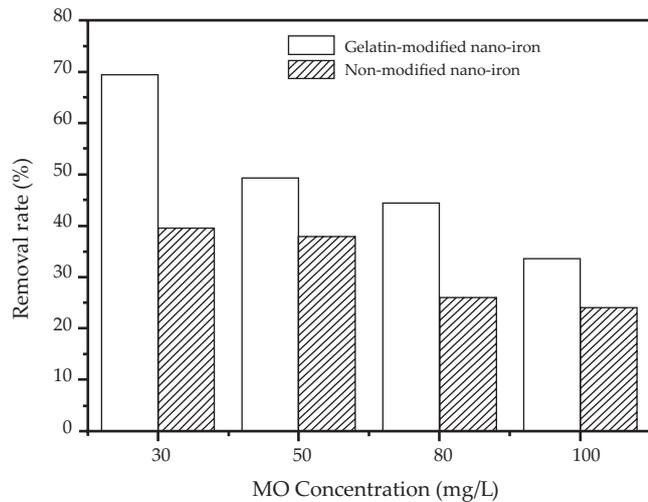


Fig. 5. Comparison of removal effects between the gelatin-modified nano-iron (white) and the non-modified one (shadow) ($C_{\text{nano-iron}} = 0.05 \text{ g/L}$, $\text{pH} = 6.25$).

3.3. Influencing factors of removing MO by the gelatin-modified nano-iron

3.3.1. The initial concentration of MO and the amount of the gelatin-modified nano-iron

The influence of the initial concentration of MO on the removal rate also can be seen in Fig. 5. The removal rate of MO decreases as the initial concentration of MO increases. When the concentration of MO increases from 30 mg/L to 100 mg/L, the removal rate decreases from 68.9% to 37.91%. Hence, the initial concentration of MO has a much more important effect on the removal rate when the amount of nano-iron is settled. The reason may be that the active sites on the nano-iron surface are excessive when the initial concentration of MO is lower, MO molecules can quickly adsorb on the active sites and react further, thus, the removal rate increases. As the concentration of MO increases, the competition of MO molecules intensifies for the active sites which number is settled, therefore, the MO molecules are uneasy to reach the active sites and the removal rate decreases. Similarly, when the amount of the nano-iron increases, the number of the active sites rises, the amount of MO molecules adsorbed and reacted increases, and thus the removal rate is promoted (Fig. 6).

3.3.2. Initial pH value

The influence of the initial pH value on the removal rate can be seen in Fig. 7. When the initial pH value increases from 4 to 10.45, the removal rate decreases from 53.74% to 27.71%. In other words, the removal rate decreases as the initial pH value increases. The following reasons may explain this result. First, the decomposition of MO consumes hydrogen ion [16], thus, the acidic condition provides more hydrogen ion and promotes the decomposition; Second, the acidic condition inhibits the formation of the surface passivation layer and promotes the dissolution of the iron oxide and hydroxide formed

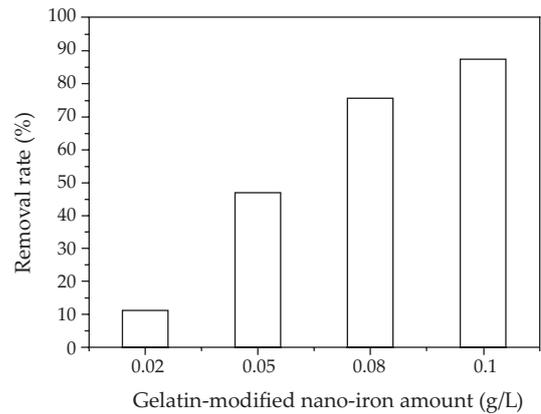


Fig. 6. Influence of the amount of the gelatin-modified nano-iron on the removal rate ($C_{\text{MO}} = 50 \text{ mg/L}$, $\text{pH} = 6.25$).

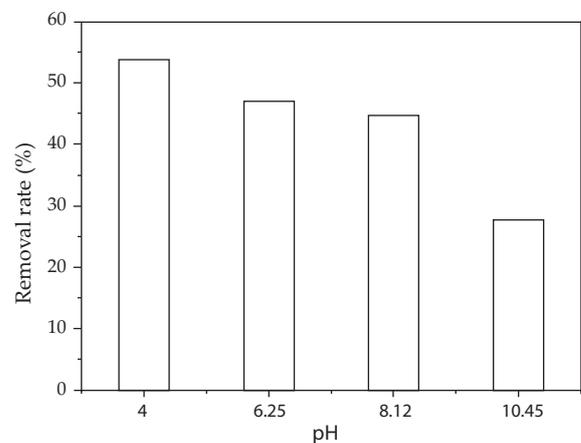


Fig. 7. The influence of the initial pH value on the removal rate ($C_{\text{nano-iron}} = 0.05 \text{ g/L}$, $C_{\text{MO}} = 50 \text{ mg/L}$).

on the surface of the nano-iron; therefore, more active sites are provided for the MO molecules and the removal rate was increased [7, 17].

3.3.3. Temperature

The temperature has an evident impact on the removal rate (Fig. 8). The rate increases as the temperature rises. When the temperature rises from 10 °C to 40 °C, the removal rate increases from 32.48% to 89.53%. The reason may be that the diffusion or migration of MO to the surface of the nano-iron is promoted at the higher temperature, and thus, the rate of the removal reaction is enhanced [18].

3.3.4. Dissolved oxygen

There are different amounts of dissolved oxygen in various waters. For example, the content of dissolved oxygen in the surface water is more than that in the groundwater. Hence, it is of importance to understand the influence of dissolved oxygen content on removal rate in view of the practical use of the nano-iron.

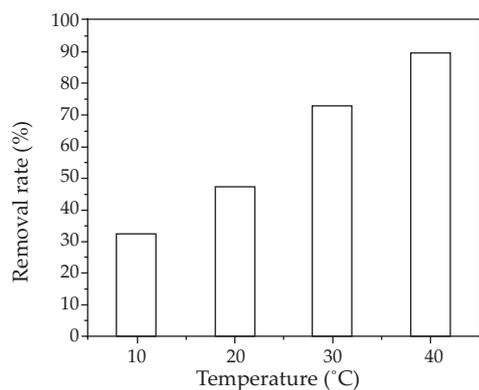


Fig. 8. Influence of the temperature on the removal rate ($C_{\text{nano-iron}} = 0.05 \text{ g/L}$, $C_{\text{MO}} = 50 \text{ mg/L}$).

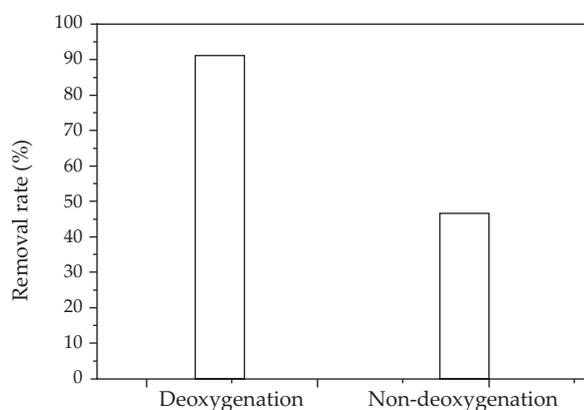


Fig. 9. Influence of the dissolved oxygen on gelatin-modified nano-iron removing MO ($C_{\text{nano-iron}} = 0.05 \text{ g/L}$, $C_{\text{MO}} = 50 \text{ mg/L}$, $\text{pH} = 6.25$).

The influence of the dissolved oxygen on the removal rate can be seen in Fig. 9. One of MO solutions was deoxygenated by nitrogen blowing method (100 mL/min, 15 min). As shown in Fig. 9, the nano-iron has an obviously better removal effect under the deoxygenation condition. This is because there is a competition between the oxygen (as a strong oxidant) and MO molecules on the surface of nano-iron particles, meanwhile, the oxygen can oxidize the nano-iron. Both of the two processes make fewer active sites of the nano-iron provided for the MO molecules and lead to the lower removal rate. Thus, the nano-iron method here will have a better effect if it is applied to anaerobic water such as the groundwater.

3.3.5. Co-existing ions

There exist varieties of ions in the natural water. Some of the ions have a serious influence on the activity of the nano-iron [19]. Here, the effect of NO_3^- , CO_3^{2-} and SO_4^{2-} , which are common in the natural water, was investigated on the removal of MO by the gelatin-modified nano-iron. As shown in Fig. 10(a) and (b), NO_3^- and CO_3^{2-} both have an inhibitory effect on the removal of MO, and the effect increases with their concentration increasing. For NO_3^- , due to its

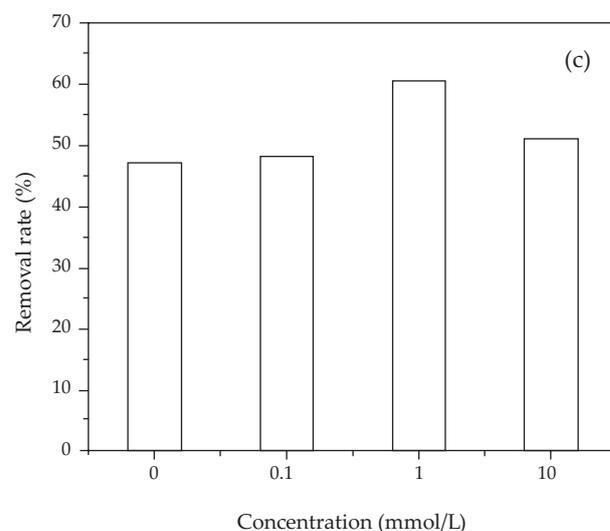
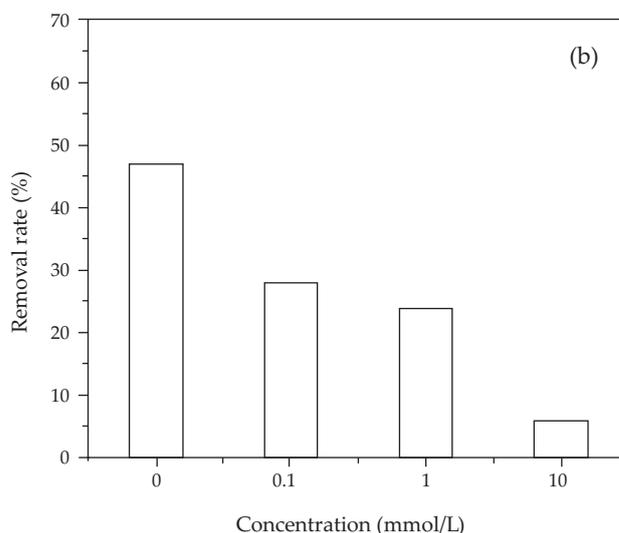
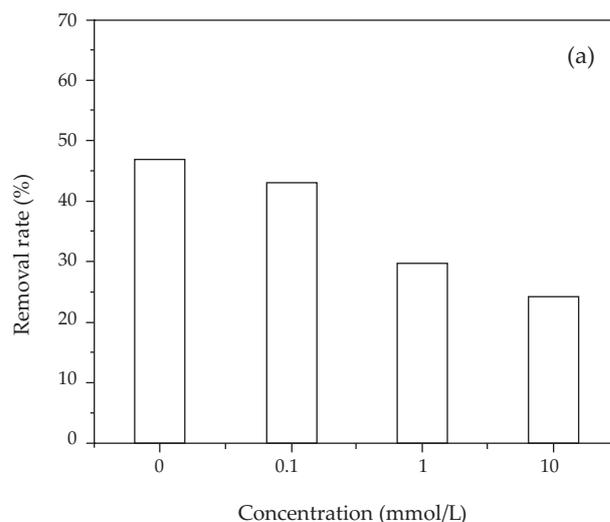
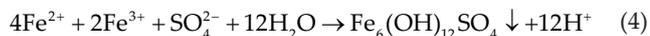


Fig. 10. The influence of coexisting ions ($C_{\text{nano-iron}} = 0.05 \text{ g/L}$, $C_{\text{MO}} = 50 \text{ mg/L}$, $\text{pH} = 6.25$, a: NO_3^- , b: CO_3^{2-} , c: SO_4^{2-})

oxidability, it can compete with MO for the electrons that the nano-iron provides, and therefore this competition results in the decrease of the removal rate of MO. The inhibitory effect on MO removal caused by CO_3^{2-} results from the reaction between CO_3^{2-} and iron ion (Eqs. (2) and (3)) [7]:



If FeCO_3 and $\text{Fe}_2(\text{OH})_2\text{CO}_3$, insoluble salts, are formed, they would deposit on the surface of the nano-iron, restrain the outward migration of electrons on the nano-iron surface, then, decrease the removal rate of MO. Besides, CO_3^{2-} can result in the increase of pH value of the system, and this also makes against the MO removal. The effect of SO_4^{2-} is different from that of NO_3^- and CO_3^{2-} (Fig. 10(c)). When the concentration of SO_4^{2-} increases from 0.1 mmol/L to 1 mmol/L, the removal rate of MO increases evidently. That is because SO_4^{2-} has a corrosive effect on the passivation layer on the nano-iron surface. The mechanism is named “pitting attack” which means that part of the nano-iron surface is corroded by SO_4^{2-} and point-apertures are formed. These point-apertures are small usually, but SO_4^{2-} can concentrate at the bottom of them, make them deeper and deeper, and finally the passivation layer is penetrated and then abscised, the active sites are revealed. Therefore, the activity of the nano-iron is improved [20]. While increasing the concentration of SO_4^{2-} to 10 mmol/L, the promoting effect is inhibited. This is mainly because the concentration of SO_4^{2-} is so high that it reacts with iron ion (Eq. (4)):



Like FeCO_3 and $\text{Fe}_2(\text{OH})_2\text{CO}_3$, $\text{Fe}_6(\text{OH})_{12}\text{SO}_4$ formed as Eq. (4) can precipitate on the nano-iron surface, restrain MO to contact the active sites on the nano-iron surface and lead to the decline of the removal rate of MO.

4. Conclusions

(a) The gelatin-modified nano-iron was prepared by the liquid-reduction process. It has better dispersion and stability than that of the non-modified one. The combining mechanism between the gelatin and the nano-iron was deduced to be the coordination between the iron and the amino nitrogen of the gelatin molecule.

(b) The removal rate of MO by the gelatin-modified nano-iron decreases with the increasing of the initial concentration of MO, the initial pH value and the content of dissolved oxygen, but increases with the increasing of the amount of the modified nano-iron and temperature. NO_3^- and CO_3^{2-} both have an inhibitory effect on MO removal. SO_4^{2-} can have inhibitory or promotive effect, and which effect plays the leading role depends on the concentration of SO_4^{2-} .

References

- [1] F.L. Fu, D.D. Dionysiou, H. Liu, The use of zero-valent iron for groundwater remediation and wastewater treatment: A review, *J. Hazard. Mater.*, 267 (2014) 194–205.
- [2] C. L. Xu, X.H. Wang, S. Lin, L.J. Zhu, Y. Chen, Enhanced removal efficiency of bromate from aqueous solutions by nanoscale zero-valent iron immobilized on activated carbon, *Desal. Water Treat.*, 54 (2015) 2480–2489.
- [3] Z.J. Xiao, Q.L. Zhou, H.J. Qin, J.L. Qiao, X.H. Guan, The enhancing effect of weak magnetic field on degradation of Orange II by zero-valent iron, *Desal. Water Treat.*, 57 (2016) 1659–1670.
- [4] L. Alidokht, A.R. Khataee, A. Reyhanitabar, S. Oustan, Reductive removal of Cr(VI) by starch-stabilized Fe^0 nanoparticles in aqueous solution, *Desalination*, 270 (2011) 105–110.
- [5] F. He, D.Y. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbon in water, *Environ. Sci. Technol.*, 39 (2005) 3314–3320.
- [6] A. Gupta, M. Yunus, N. Sankaramakrishnan, Zerovalent iron encapsulated chitosan nanospheres – A novel adsorbent for the removal of total inorganic Arsenic from aqueous systems, *Chemosphere*, 86 (2012) 150–155.
- [7] B. Geng, T.L. Li, H.J. Zhao, X.H. Qi, Synthesis of Chitosan stabilized Nanoscale Zero valent Iron for Removal of Hexavalent Chromium from Surface Water, *Chem. J. Chinese. U.*, 30 (2009) 796–799.
- [8] F. He, D.Y. Zhao, J.C. Liu, C.B. Roberts, Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater, *Ind. Eng. Chem. Res.*, 46 (2007) 29–34.
- [9] A. Tiraferri, K.L. Chen, R. Sethi, M. Elimelech, Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum, *J. Colloid. Interf. Sci.*, 324 (2008) 71–79.
- [10] C. Mystrioti, A. Xenidis, N. Papassiopi, Reduction of hexavalent chromium with polyphenol-coated nano zero-valent iron: column studies, *Desal. Water Treat.*, 56 (2015) 1162–1170.
- [11] M.B. Ahmad, J.J. Lim, K. Shameli, N.A. Ibrahim, M.Y. Tay, Synthesis of Silver Nanoparticles in Chitosan, Gelatin and Chitosan/Gelatin Bionanocomposites by a Chemical Reducing Agent and Their Characterization, *Molecules*, 16 (2011) 7237–7248.
- [12] M.P. Neupane, S.J. Lee, I.S. Park, M.H. Lee, T.S. Bae, Y. Kuboki, M. Uo, F. Watari, Synthesis of gelatin-capped gold nanoparticles with variable gelatin concentration gelatin concentration, *J. Nanopart. Res.*, 13 (2011) 491–498.
- [13] R. Brayner, T. Coradin, M.J. Vaulay, C. Mangeney, J. Livage, FernandFievet. Preparation and characterization of metal (Au)– and bimetallic alloys (AuNi)–gelatin nanocomposites, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 256 (2005) 191–197.
- [14] S.H. Wang, Z.Y. Sun, E.Y. Yan, J.H. Yuan, Y. Gao, Y.H. Bai, Y. Chen, C. Wang, Y.J. Zheng, T. Jing, Magnetic composite nanofibers fabricated by electro spinning of Fe_3O_4 /gelatin aqueous solutions, *Mater. Sci. Eng. B.*, 190 (2014) 126–132.
- [15] A. Pourjavadi, R. Soleyman, Silver nanoparticles with gelatin nanoshells: photochemical facile green synthesis and their antimicrobial activity, *J. Nanopart. Res.*, 13 (2011) 4647–4658.
- [16] J.S. Cao, L.P. Wei, Q.G. Huang, L.S. Wang, S.K. Han, Reducing degradation of azo dyes by zero-valent iron in aqueous solution, *Chemosphere*, 38 (1999) 565–571.
- [17] Y. He, J.F. Gao, F. Q. Feng, C. Liu, Y.Z. Peng, S.Y. Wang, The comparative study on the rapid decolorization of azo, anthraquinone and triphenylmethane dyes by zero-valent iron, *Chem. Eng. J.*, 179 (2012) 8–18.
- [18] J.C. Yang, X.Y. Wang, M.P. Zhu, H.L. Liu, J. Ma, Investigation of PAA/PVDF–NZVI hybrids for metronidazole removal: Synthesis, characterization, and reactivity characteristics, *J. Hazard. Mater.*, 264 (2014) 269–277.
- [19] J.H. Xu, N.Y. Gao, D.Y. Zhao, W. X. Zhang, Q.K. Xu, A.H. Xiao, Efficient reduction of bromate in water by nano-iron hydroxide impregnated granular activated carbon (Fe-GAC), *Chem. Eng. J.*, 275 (2015) 189–197.
- [20] J.F. Devlin, K.O. Allin, Major Anion Effects on the Kinetics and Reactivity of Granular Iron in Glass-Encased Magnet Batch Reactor Experiments, *Environ. Sci. Technol.*, 39 (2005) 1868–1874.