



Removal of nitrate by zero-valent iron and pillared bentonite

Jianfa Li, Yimin Li*, Qingling Meng

Department of Chemistry, Shaoxing University, Huancheng West Road 508, Shaoxing, Zhejiang 312000, China

ARTICLE INFO

Article history:

Received 31 January 2009

Received in revised form 5 September 2009

Accepted 9 September 2009

Available online 16 September 2009

Keywords:

Nitrate

Zero-valent iron

Clay

Reduction

Adsorption

ABSTRACT

The pillared bentonite prepared by intercalating poly(hydroxo Al(III)) cations into bentonite interlayers was used together with Fe(0) for removing nitrate in column experiments. The obvious synergetic effect on nitrate removal was exhibited through uniformly mixing the pillared bentonite with Fe(0). In such a mixing manner, the nitrate was 100% removed, and the removal efficiency was much higher than the simple summation of adsorption by the pillared bentonite and reduction by Fe(0). The influencing factors such as bentonite type, amount of the pillared bentonite and initial pH of nitrate solutions were investigated. In this uniform mixture, the pillared bentonite could adsorb nitrate ions, and facilitated the mass transfer of nitrate onto Fe(0) surface, then accelerated the nitrate reduction. The pillared bentonite could also act as the proton-donor, and helped to keep the complete nitrate removal for at least 10 h even when the nitrate solution was fed at nearly neutral pH.

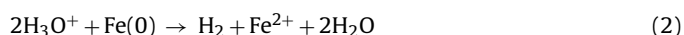
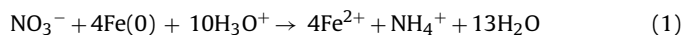
© 2009 Published by Elsevier B.V.

1. Introduction

Zero-valent iron (Fe(0)) has been demonstrated to be an efficient reductant to many pollutants, and has been extensively investigated for remediation of water contaminated by chlorinated hydrocarbons [1–3], nitro aromatics [4,5] and heavy metals such as Cr(VI) [6–8]. In recent years, Fe(0) has also been investigated on its potential to reduce nitrate (NO₃⁻) in water [9–17].

Nitrate contamination in water mainly comes from the agricultural runoff, animal wastes and industrial processes, etc., and has become a worldwide environmental problem. Nitrate will pose a serious threat to the human health when it is reduced to nitrite (NO₂⁻), and cause health effects including liver damage, cancers, and methemoglobinemia. Despite a lot of other methods have been proposed for the treatment of nitrate in water, Fe(0) treatment has received much attention due to its relatively cheap costs and easy operations [18,19].

The performance of Fe(0) treatment is strongly dependent on pH value in aqueous system [9–11]. Huang et al. [11] reported that rapid reduction of nitrate by Fe(0) only occurred at pH ≤ 4, which is probably related to the enhanced iron corrosion in acid solution [10,11]:



At pH > 4, the nitrate reduction is insignificant, because the ferrous hydroxide produced during the reaction may form a passive oxide layer, and hinder the iron corrosion [11]. In order to keep the nitrate being reduced at a satisfying rate, the methods for adjusting pH by adding acids or buffering agents have been reported [10,11,13–15]. But these methods are not convenient in view of practical applications. So other methods such as pretreatment of iron surface [17], deposition of copper as catalyst [17,20] and elevated temperature [18] were also proposed for accelerating nitrate reduction by Fe(0).

The accumulation of contaminants on iron surface is beneficial for enhancing the removal efficiency by Fe(0) [21,22]. When surfactant-modified zeolite and Fe(0) was used together, the enhanced performance on Cr(VI) removal was observed due to the combined effects of adsorption by zeolite and reduction by Fe(0) [23]. Recently, Oh et al. [24] reported that the amorphous silica provided excessive surfaces for scavenging the reduction products of Cr(VI), and significantly enhanced the reduction efficiency of Cr(VI) by Fe(0). So it is interesting to investigate the performance of adsorbents on removing nitrate by using adsorbents and Fe(0) together.

Bentonite is a kind of expandable clay composed primarily of montmorillonite, with permanent negative charges on its surface resulting from the isomorphous substitution of central atoms in the octahedral/tetrahedral by cations of lower valence. Such structure enables bentonite to be intercalated by inorganic and/or organic cations, and the resulting materials have high specific surface areas associated with their small particle size. These modified clays can be used as efficient adsorbents for many inorganic and organic contaminants in water [25–30]. Natural Fe-bearing clays demonstrated their capacity on reduction of Cr(VI) with or without addition of

* Corresponding author. Tel.: +86 575 8834 2386; fax: +86 575 8831 9253.
E-mail address: liyim@zscas.edu.cn (Y. Li).

other reductants [31–33]. But the combination of Fe(0) with modified clays for the reduction of aqueous contaminants has seldom been reported till now.

The present work is aiming to enhance the efficiency of Fe(0) on removing nitrate by using the pillared bentonite as adsorbent. For this purpose, the pillared bentonite was prepared by intercalation of poly(hydroxo Al(III)) cations. The continuous column experiments were performed to examine the efficiency on nitrate removal by Fe(0) mixed with the pillared bentonite. For the comparison study, the nitrate reduction by Fe(0) alone and the nitrate adsorption on the pillared bentonite were also investigated.

2. Materials and methods

2.1. Materials

The bentonite was primarily of Na⁺-montmorillonite (denoted by Na-bent) from Inner Mongolia, China. Its cation exchange capacity was determined to be 115 cmol/kg. The sand was washed and dried, and the fraction with size of 0.2–0.9 mm was collected for use. Commercial iron powder was purchased from Shanghai Chemical Co., China, and the fraction of passing through a sieve of 100 mesh (size <150 μm, specific surface area ≈ 0.35 m²/g, and iron content of 91.2%) was used. Potassium nitrate of analytical grade was used to prepare aqueous nitrate solutions. NaOH and AlCl₃·6H₂O were both of analytical grade.

2.2. Preparation and characterizations of the pillared bentonite

The pillared bentonite was prepared from Na-bent by intercalating with poly(hydroxo Al(III)) cations. Firstly, NaOH solution was added dropwise to a solution of 0.2 mol L⁻¹ AlCl₃ until the molar ratio [OH⁻]/[Al³⁺]=2.0. The resulting pillaring solution was slowly added in a Na-bent suspension of 10 g in 500 mL of de-ionized water until the [Al³⁺]/bentonite ratio of 10 mmol/g was reached. The resulting mixture was heated at 70 °C for 48 h and the modified bentonite was washed, centrifuged, and dried to a constant weight. The bentonite sample (denoted by OH-Al-bent) was mechanically ground to less than 100 mesh and heated at 115 °C for 2 h before use.

The Brunauer–Emmett–Teller (BET) surface areas of Na-bent and OH-Al-bent were 31.8 and 129 m²/g, respectively, as obtained from nitrogen adsorption data at 77 K in an accelerated surface area and porosimetry system, ASAP 2020 (Micromeritics). The samples were degassed at 115 °C for 4 h under vacuum prior to adsorption. The basal spacings of bentonite samples were 1.27 nm for Na-bent and 1.79 nm for OH-Al-bent, respectively, as measured by X-ray diffraction (XRD) in a Rigaku D/MAX-2500 equipment with Cu Kα radiation and a goniometer rate of 4° min⁻¹.

2.3. Nitrate adsorption on bentonite samples

The adsorption isotherms were determined by batch equilibration of 0.050 g of each bentonite sample with 50 mL of aqueous nitrate solutions of varied initial concentrations. Experiments were carried out in a thermostatic shaker bath at 25 ± 0.1 °C for 2 h. Preliminary experiments confirmed that the adsorption equilibrium time was less than 2 h. After equilibration, the suspension was centrifuged, the supernatant was filtered, and the nitrate concentration in supernatant (C_e) was measured. The amount adsorbed (Q_e) was calculated from the difference in concentration between the initial (C₀) and the equilibrium (C_e) solution.

2.4. Nitrate removal studies

The removal studies were carried out continuously in packed columns [3,12]. The mixture of sand, iron powder and/or bentonite samples with total weight of 100 g was installed in the column of 20 cm × 2 cm i.d. Four columns using different packing manners were tested: (i) uniform mixture of 90 wt% of sand with 10 wt% of OH-Al-bent; (ii) uniform mixture of 90 wt% of sand with 10 wt% of Fe(0); (iii) the lower half of column was packed with the mixture of sand (40 wt%) and Fe(0) (10 wt%), and the upper half of column with the mixture of sand (40 wt%) and bentonite (10 wt%); (iv) uniform mixture of 80 wt% of sand, 10 wt% of Fe(0) and 10 wt% of bentonite.

The de-ionized water was flowed through the column for 5 h before the nitrate solution was pumped in. Then the nitrate solution of 100 mg/L (C₀ = 1.61 mmol/L) was fed continuously at a rate of 0.5 mL/min by a peristaltic pump, and passed slowly through the column in an upward flow mode. The nitrate concentration of effluent sample at time *t* (C_t) was determined. The removal efficiency was calculated as

$$\text{removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

The effects of pH on nitrate removal were determined by adjusting the initial pH values of influent nitrate solution with HCl and NaOH solutions.

2.5. Analytical methods

Concentrations of nitrate, nitrite and ammonium species in effluent samples were determined by using a UV–vis spectrophotometer (SP-756P, Shanghai Spectrum, China) [34–36]. The nitrate concentration was calculated by ultraviolet absorbance measurement, which was made at 220 nm and corrected by subtracting a second measurement at 275 nm. The nitrite concentration was determined by visible absorbance measurement at 540 nm, due to the diazonium complex formed by reaction involving NO₂⁻, sulfanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride. The ammonium concentration was determined by Nessler's method, in which the derivative of ammonium was measured by absorbance at 420 nm.

3. Results and discussion

3.1. Comparison of various mixing manners on nitrate removal

Four columns were packed with various materials and manners as mentioned in Section 2.4, so as to investigate the performance of the pillared bentonite on nitrate removal by Fe(0). The pH of influent nitrate sample was kept at 3.0, and the changes of nitrate concentration in effluent with time for the four columns are shown in Fig. 1.

In column (i) packed with mixture of sand and OH-Al-bent, the nitrate was removed by only a very small fraction. The nitrate removal in this case could only be ascribed to the adsorption by OH-Al-bent because there was not any reductant in this column. In column (ii) packed with mixture of sand and Fe(0), the nitrate was removed by a higher efficiency and less nitrate was detected in effluent. This shows that nitrate was reduced by Fe(0) in this column, but the reduction alone is not sufficient for the complete removal of nitrate under the experimental conditions. In column (iii), the nitrate was partly adsorbed by the pillared bentonite in the upper layer, and partly reduced by Fe(0) in the lower layer. As can be seen in Fig. 2, at a certain time the removal efficiency in column (iii) is approximately equal to the sum of removal efficiencies in columns (i) and (ii). This indicates that, the nitrate removal with such a mixing manner as in column (iii) is resulted from the

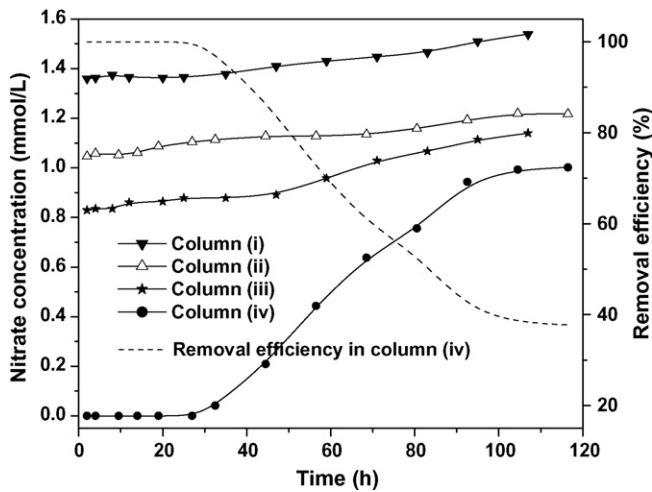


Fig. 1. Nitrate concentrations in effluents from various columns and removal efficiency in column (iv) (initial pH of influent solutions = 3).

cumulative effect of adsorption by the bentonite and reduction by Fe(0).

The column (iv) showed a surprisingly higher efficiency on removing nitrate than that in other columns (see Fig. 1). The removal efficiency in the initial 27 h was kept at 100%, which is much higher than that in column (iii). In this way, the pillared bentonite improved the efficiency of nitrate removal by Fe(0) on the below two aspects: (1) the more complete removal of nitrate and (2) the long time for the complete removal. The results indicate that, in this uniformly mixing system, the nitrate removal is not a simple summation of adsorption by the bentonite and reduction by Fe(0). There must be synergetic effect existing between the pillared bentonite and Fe(0) on removing nitrate.

3.2. Effect of different bentonites on nitrate removal

The synergetic effect of OH-Al-bent on nitrate removal by Fe(0) was further explored by using Na-bent (instead of OH-Al-bent) in column (iv). As can be seen in Fig. 3, when the Na-bent was used together with Fe(0), the removal efficiency of nitrate was kept at a level slightly higher than that by Fe(0) alone, but much lower than that treated by the mixture of OH-Al-bent and Fe(0). The results

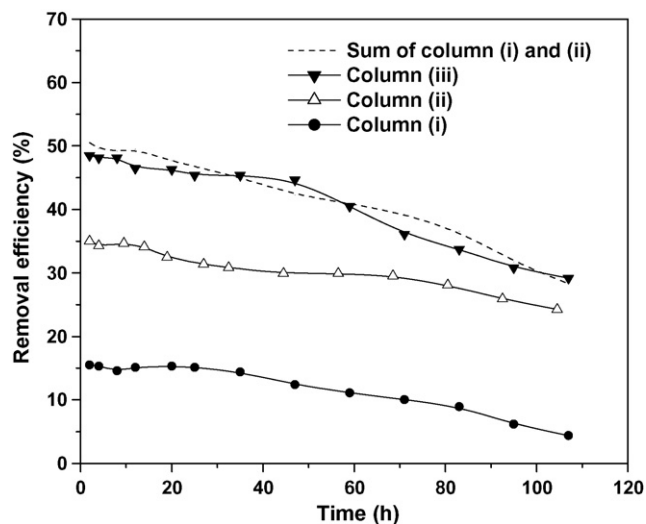


Fig. 2. Nitrate removal efficiency in columns (i), (ii) and (iii) (initial pH of influent solutions = 3).

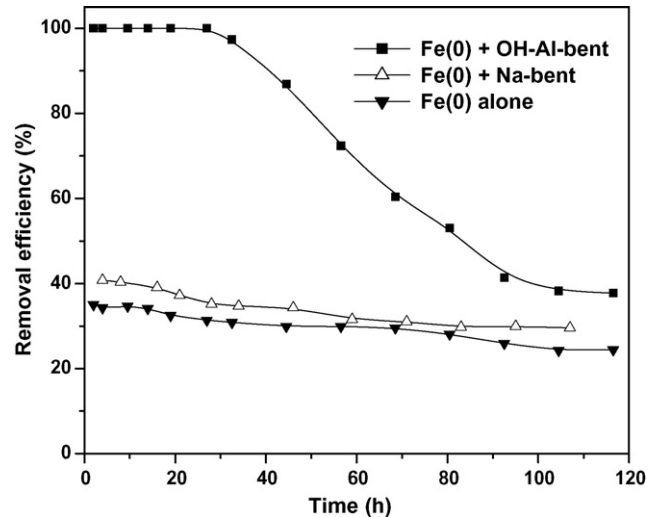


Fig. 3. Nitrate removal efficiency by Fe(0) mixed with different bentonites in column (iv) (initial pH of influent solutions = 3).

indicate that, the pillared modification with poly(hydroxo Al(III)) cations is necessary for the bentonite to achieve higher efficiency on removing nitrate.

For the multi-phase reaction system composed of both liquid and solid reactants, the adsorption or accumulation of reactants on the solid phase is very important [19]. For example, surface modification of Fe(0) with cationic surfactants improved the accumulation of perchloroethylene on reactive sites of iron, which resulted in the increased degradation of perchloroethylene [21,22]. In order to explain the synergetic effect of the pillared bentonite, the adsorption of nitrate on the bentonites was investigated (Fig. 4). The Na-bent did not show noticeable adsorption to nitrate ions, which may be due to the repulsion between anionic NO_3^- and the negatively charged bentonite surface [37]. The modification of bentonite with poly(hydroxo Al(III)) cations partly reduced the negative charge density. At the meantime, the basal spacing and specific surface area of bentonite were both enlarged. So the nitrate ions could be adsorbed by OH-Al-bent with a noticeably higher amount than that by Na-bent.

Due to the enhanced adsorption of nitrate ions on the pillared bentonite, more contaminants accumulated on the solid phase, which made them easily approach the reactive sites of iron sur-

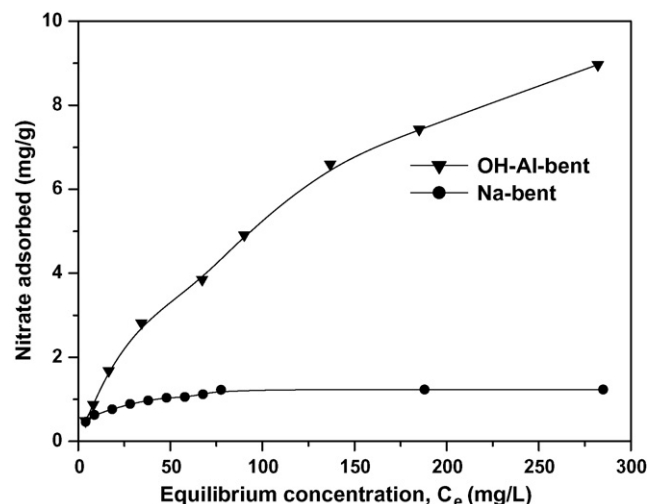


Fig. 4. Adsorption isotherms of nitrate on various bentonites at 25 °C.

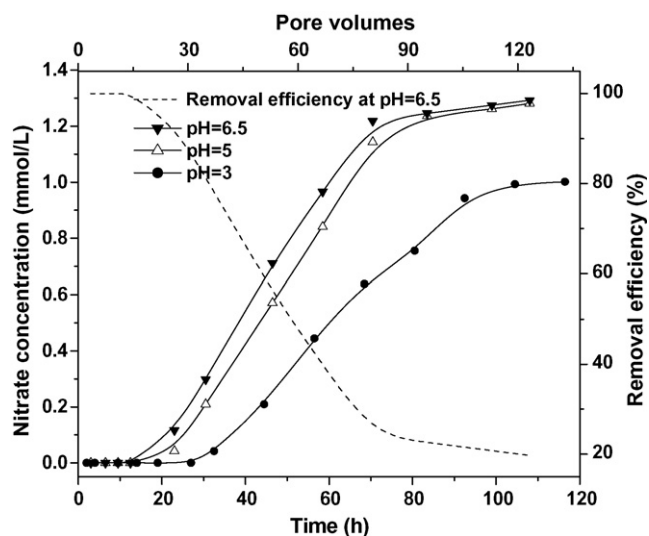


Fig. 5. Nitrate concentrations in effluents when influents of various initial pH were used in column (iv).

face. As a result, the mass transfer of nitrate from the solution to the iron surface was facilitated, and then the surface reaction was accelerated. In this regard, the pillared bentonite performed just like organic-bentonites for the Fe(0) reduction of trichloroethylene [38] and 2,4-dichlorophenol [39]. Because the direct contact of nitrate with Fe(0) is necessary for electron transfer to occur, the close contact of the pillared bentonite with Fe(0) is very important for accelerating the surface reaction. Therefore, the synergetic effect was observed only when the pillared bentonite was uniformly mixed with Fe(0).

3.3. Effects of pH on nitrate removal

When the uniform mixture of OH-Al-bent with Fe(0) and sand was packed in column (iv), the nitrate removal for influent solutions of various initial pH were tested (Fig. 5). In all the treatments, the complete removal of nitrate was observed in the early period, which was shortened with the increasing pH from 3 to 6.5. According to the kinetics of nitrate reduction by Fe(0), the higher the pH in nitrate solution, the slower the reduction rate [11,14,19,40]. But in this column test, the mixture of OH-Al-bent with Fe(0) could still provide a high efficiency of 100% nitrate removal even when the nitrate solution was fed at nearly neutral pH. This is an important advancement, because most reports indicated that nitrate could be reduced by Fe(0) at a satisfying rate only in an acid medium, except that catalysts were used [17,20].

As it is known, the nitrate reduction by Fe(0) is a surface reaction driven by hydrogen protons. The protons may directly participate in the redox reaction or accelerate the reaction by dissolving away the passive layer on the iron surface [11,14]. In the pillared bentonite, there are many proton-donating hydroxyl groups derived from the intercalated poly(hydroxo Al(III)) cations, which results in the acidity of bentonite surface [41]. Due to the acidity of pillared clays, they can be used for catalyzing the reduction of nitric oxide [42]. The OH-Al-bent in this mixing system might also act as the acid catalyst for the nitrate reduction.

The high efficiency of this mixing system might be explained by another proposed reason that was related to the adsorption of by-products by OH-Al-bent. As indicated in Eqs. (1) and (2), at the meantime of nitrate reduction, Fe(0) itself was converted into the form of Fe^{2+} , which might be adsorbed by the pillared bentonite. Due to the complexity of the column system involving various iron and nitrogen species, the adsorption mechanisms

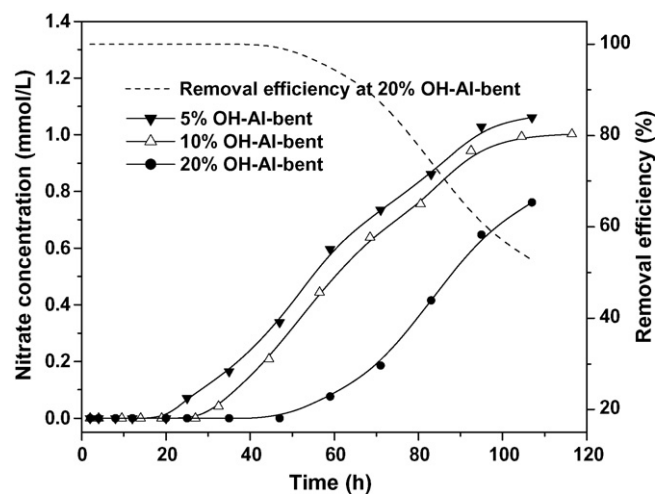


Fig. 6. Nitrate concentrations in effluents when various amounts of OH-Al-bent were used in column (iv) (initial pH of influent solutions = 3).

on bentonite are obviously complicated. If only iron metal cations were considered, the cation exchange mechanism could be used to explain their adsorption by clays [43]. In the case of bentonite pillared with poly(hydroxo Al(III)) cations, the adsorption occurred in the manner of displacement of protons from surface hydroxyls by iron cations (Fe^{2+} and Fe^{3+}), which was accompanied by the H^+ release [44,45]. The released protons could help to improve the Fe(0) activity in the following ways: (1) the nitrate reduction could continue with high reaction rate; (2) the removal efficiency could be kept at nearly 100% for a period.

3.4. Effect of amount of the pillared bentonite on nitrate removal

Fig. 6 shows the nitrate removal by the uniform mixtures of OH-Al-bent and Fe(0) with various amounts of bentonite in column (iv). When Fe(0) was used at a fixed amount, the higher amount of bentonite used in the mixtures resulted in the longer service time of Fe(0) for the complete nitrate removal. This could be explained by the above proposed mechanism. When the pillared bentonite was used with a higher amount, the cation exchange between bentonite and the by-product iron cations could last for a longer time, and more protons would be released into the column system. Therefore, the nitrate reduction could be kept at a high reaction rate for a longer period.

3.5. Analytical results on the reduction products

Most of the reports have indicated NH_4^+ as the end product of nitrate reduction by Fe(0), although different end product such as N_2 gas has also been reported [15,46]. When the pillared bentonite was used together with Fe(0) in a uniform mixture for removing nitrate, the compositions of the effluent were analyzed (Fig. 7). In the early 27 h (30 pore volumes), the nitrogen in the effluent existed in the form of NH_4^+ , indicating the complete reduction of nitrate. After 27 h, the gradual increase of NO_3^- concentration in the effluent was observed, at the mean time the decrease of NH_4^+ concentration was measured. This might be related to the gradual saturation of adsorption on the pillared bentonite, which resulted in the declined mass transfer rate of nitrate and reduced release of hydrogen protons. So the nitrate reduction rate was slowed down, which led to more reactant (NO_3^-) and less product (NH_4^+) in the effluent. In the latter period (after 27 h in Fig. 7) of declining removal efficiency, the presence of a little NO_2^- in the effluent indicated that the nitrate was reduced through a pathway including nitrite as an

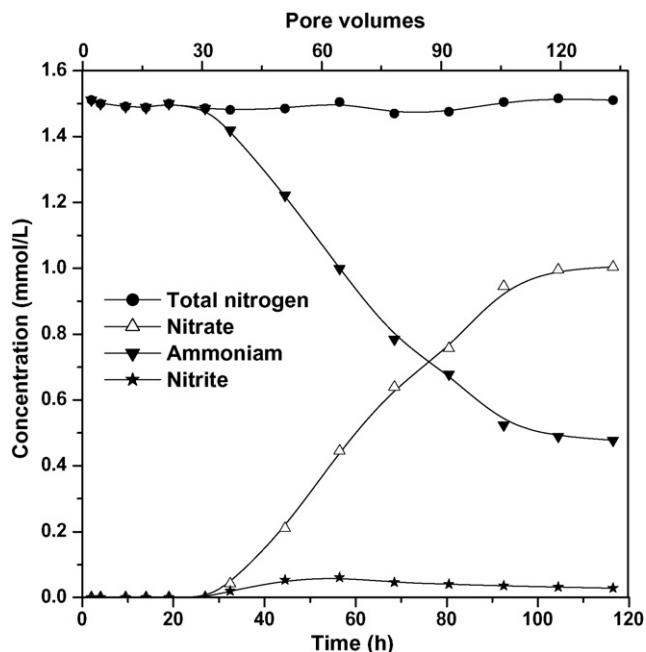


Fig. 7. Concentration changes of nitrogen species in the effluent with time (column iv), initial pH of influent solution = 3).

intermediate [11]:

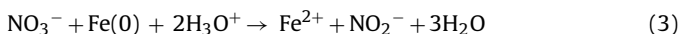


Fig. 7 also indicates that the concentration of total nitrogen in the effluent samples changed little during the whole process of nitrate removal. The amount of total nitrogen in the effluent maintained at a level of 1.49 ± 0.02 mmol/L, which is a little lower than the initial concentration of influent nitrate solution (1.61 mmol/L). This indicates that a little part of nitrate was converted into N_2 gas and escaped from the solution in the column experiments.

4. Conclusions

The pillared bentonite (OH-Al-bent) was used by mixing with Fe(0) together for nitrate removal, and the distinctly enhanced efficiency was obtained when the uniform mixture was used in the continuous column experiments. The nitrate removal efficiency was kept at 100% for 10–40 h depending on the initial pH of influent nitrate solution and the amount of OH-Al-bent used. The pillared bentonite played multiple roles in the mixture including:

- (1) adsorption to nitrate ions, which facilitated the mass transfer of nitrate from solution onto solid surface;
- (2) acid catalyst for the nitrate reduction due to its surface acidity;
- (3) the sustained release of hydrogen protons through cation exchange with iron cations (by-products in nitrate reduction), which could explain the high efficiency on nitrate removal even when the solution was fed at nearly neutral pH.

Acknowledgement

This work was supported by the National Science Foundation of China (Grant No. 20977063) and by Natural Science Foundation of Zhejiang Province, China (Grant No. Y506288).

References

- [1] R.W. Gillham, S.F. O'Hannesin, Enhanced degradation of halogenated aliphatics by zero-valent iron, *Ground Water* 32 (1994) 958–967.

- [2] Y.-H. Kim, E. Carraway, Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons, *Environ. Sci. Technol.* 34 (2000) 2014–2017.
- [3] P. Zhang, X. Tao, Z. Li, R.S. Bowman, Enhanced perchloroethylene reduction in column systems using surfactant-modified zeolite/zero-valent iron pellets, *Environ. Sci. Technol.* 36 (2002) 3597–3603.
- [4] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-valent iron metal, *Environ. Sci. Technol.* 30 (1996) 153–160.
- [5] J. Klausen, P.J. Vikesland, T. Kohn, D.R. Burris, W.P. Ball, A.L. Roberts, Longevity of granular iron in groundwater treatment processes: solution composition effects on reduction of organohalides and nitroaromatic compounds, *Environ. Sci. Technol.* 37 (2003) 1208–1218.
- [6] R.M. Powell, W.P. Puls, S.K. Hightower, D.A. Sabatini, Coupled iron corrosion and chromate reduction: mechanisms for subsurface remediation, *Environ. Sci. Technol.* 29 (1995) 1913–1922.
- [7] H. Zhou, Y. He, Y. Lan, J. Mao, S. Chen, Influence of complex reagents on removal of chromium(VI) by zero-valent iron, *Chemosphere* 72 (2008) 870–874.
- [8] J. Liu, C. Wang, J. Shi, H. Liu, Y. Tong, Aqueous Cr(VI) reduction by electrodeposited zero-valent iron at neutral pH: acceleration by organic matters, *J. Hazard. Mater.* 163 (2009) 370–375.
- [9] D.P. Siantar, C.G. Schreier, C.-S. Chou, M. Reinhard, Treatment of 1,2-dibromo-3-chloropropane and nitrate-contaminated water with zero-valent iron or hydrogen/palladium catalysts, *Water Res.* 30 (1996) 2315–2322.
- [10] F. Cheng, R. Muftikian, Q. Fernando, N. Korte, Reduction of nitrate to ammonia by zero-valent iron, *Chemosphere* 35 (1997) 2689–2695.
- [11] C.-P. Huang, H.-W. Wang, P.-C. Chiu, Nitrate reduction by metallic iron, *Water Res.* 32 (1998) 2257–2264.
- [12] P. Westerhoff, J. James, Nitrate removal in zero-valent iron packed columns, *Water Res.* 37 (2003) 1818–1830.
- [13] C. Su, R.W. Puls, Nitrate reduction by zero valent iron: effects of formate, oxalate, citrate, chloride, sulfate, borate, and phosphate, *Environ. Sci. Technol.* 38 (2004) 2715–2720.
- [14] Y.H. Huang, T.C. Zhang, Effects of low pH on nitrate reduction by iron powder, *Water Res.* 38 (2004) 2631–2642.
- [15] G.C. Yang, H.L. Lee, Chemical reduction of nitrate by nanosized iron: kinetics and pathways, *Water Res.* 39 (2005) 884–894.
- [16] D. Mishra, J. Farrell, Understanding nitrate reactions with zero-valent iron using tafel analysis and electrochemical impedance spectroscopy, *Environ. Sci. Technol.* 39 (2005) 645–650.
- [17] Y.H. Liou, S.L. Lo, C.J. Lin, C.Y. Hu, W.H. Kuan, S.C. Weng, Methods for accelerating nitrate reduction using zerovalent iron at near-neutral pH: effects of H_2 -reducing pretreatment and copper deposition, *Environ. Sci. Technol.* 39 (2005) 9643–9648.
- [18] S.C. Ahn, S.-Y. Oh, D.K. Cha, Enhanced reduction of nitrate by zero-valent iron at elevated temperatures, *J. Hazard. Mater.* 156 (2008) 17–22.
- [19] J.M. Rodríguez-Maroto, F. García-Herruzo, A. García-Rubio, C. Gómez-Lahoz, C. Vereda-Alosa, Kinetics of the chemical reduction of nitrate by zero-valent iron, *Chemosphere* 74 (2008) 804–809.
- [20] Y.H. Liou, S.L. Lo, C.J. Lin, W.H. Kuan, S.C. Weng, Chemical reduction of an unbuffered nitrate solution using catalyzed and uncatalyzed nanoscale iron particles, *J. Hazard. Mater.* B127 (2008) 102–110.
- [21] Z. Li, Degradation of perchloroethylene by zero valent iron modified with cationic surfactant, *Adv. Environ. Res.* 2 (1998) 244–250.
- [22] D.S. Alessi, Z. Li, Synergistic effect of cationic surfactants on perchloroethylene degradation by zero valent iron, *Environ. Sci. Technol.* 35 (2001) 3713–3717.
- [23] Z. Li, H.K. Jones, R.S. Bowman, R. Helferich, Enhanced reduction of chromate and PCE by palletized surfactant-modified zeolite/zero-valent iron, *Environ. Sci. Technol.* 33 (1999) 4326–4330.
- [24] Y.J. Oh, H. Song, W.S. Shin, S.J. Choi, Y.H. Kim, Effect of amorphous silica and silica sand on removal of chromium(VI) by zero-valent iron, *Chemosphere* 66 (2007) 858–865.
- [25] Z. Li, R.S. Bowman, Sorption of chromate and PCE by surfactant-modified clay minerals, *Environ. Eng. Sci.* 15 (1998) 237–245.
- [26] L. Zhu, Y. Li, J. Zhang, Sorption of organobentonites to near-organic pollutants in water, *Environ. Sci. Technol.* 31 (1997) 1407–1410.
- [27] B.S. Krishna, D.S.R. Murty, B.S. Jai Prakash, Thermodynamics of chromium(VI) anionic species sorption onto surfactant-modified montmorillonite, *J. Colloid Interf. Sci.* 229 (2000) 230–236. <http://www.sciencedirect.com/hit/clay>.
- [28] O. Maryuk, S. Pikus, E. Olszewska, M. Majdan, H. Skrzypek, E. Zięba, Benzyltrimethylammonium bentonite in chromates adsorption, *Mater. Lett.* 59 (2005) 2015–2017.
- [29] C.-H. Weng, Y.C. Sharma, S.-H. Chu, Adsorption of Cr(VI) from aqueous solutions by spent activated clay, *J. Hazard. Mater.* 155 (2008) 65–75.
- [30] L. Zhu, X. Ruan, B. Chen, R. Zhu, Efficient removal and mechanisms of water soluble aromatic contaminants by a reduced-charge bentonite modified with benzyltrimethyl-ammonium cation, *Chemosphere* 70 (2008) 1987–1994.
- [31] J.D. Istok, J.E. Amonette, C.R. Cole, J.S. Fruchter, M.D. Humphrey, J.E. Szecsody, S.S. Teel, V.R. Vermeul, M.D. Williams, S.B. Yabusaki, In situ redox manipulation by dithionite injection: intermediate-scale laboratory experiments, *Ground Water* 37 (1999) 884–889.
- [32] M.F. Brigatti, G. Giuli, E. Paris, A. Mottana, Z. Wu, C. Lugli, G. Cibin, A. Marcelli, Reduction and sorption of chromium by Fe(II)-bearing phyllosilicates: chemical treatments and X-ray absorption spectroscopy (XAS) studies, *Clays Clay Miner.* 48 (2000) 272–281.
- [33] J.S. Fruchter, C.R. Cole, M.D. Williams, V.R. Vermeul, J.E. Amonette, J.E. Szecsody, J.D. Istok, M.D. Humphrey, Creation of a subsurface permeable treatment zone

- for aqueous chromate contamination using in situ redox manipulation, *Ground Water Monit. Rem.* 20 (2000) 66–77.
- [34] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, M.A.H. Franson (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, DC, 1992.
- [35] O. Brylev, M. Sarrazin, L. Roué, D. Bélanger, Nitrate and nitrite electrocatalytic reduction on Rh-modified pyrolytic graphite electrodes, *Electrochim. Acta* 52 (2007) 6237–6247.
- [36] J. Cai, P. Zheng, Effect of sulfide to nitrate ratios on the simultaneous anaerobic sulfide and nitrate removal, *Bioresour. Technol.* 99 (2008) 5520–5527.
- [37] M. Salman, B. El-Eswed, F. Khalili, Adsorption of humic acid on bentonite, *Appl. Clay Sci.* 38 (2007) 51–56.
- [38] H.-H. Cho, T. Lee, S.-J. Hwang, J.-W. Park, Iron and organo-bentonite for the reduction and sorption of trichloroethylene, *Chemosphere* 58 (2005) 103–108.
- [39] L. Hu, Y. Li, J. Li, Removal of 2,4-dichlorophenol by nanoscale zero-valent iron supported on organobentonite, *J. Chin. Ceram. Soc.* 36 (2008) 1220–1224.
- [40] S. Choe, H.M. Liljestrand, J. Kim, Nitrate reduction by zero-valent iron under different pH regimes, *Appl. Geochem.* 19 (2004) 335–342.
- [41] M.L. Occelli, J.E. Lester, Nature of active sites and coking reactions in a pillared clay mineral, *Ind. Eng. Chem. Prod. Res. Dev.* 24 (1985) 27–32.
- [42] R.T. Yang, J.P. Chen, E.S. Kikkides, L.S. Cheng, J.E. Cichanowicz, Pillared clays as superior catalysts for selective catalytic reduction of nitric oxide with ammonia, *Ind. Eng. Chem. Res.* 31 (1992) 1440–1445.
- [43] S.S. Tahir, R. Naseem, Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay, *Sep. Purif. Technol.* 53 (2007) 312–321.
- [44] N. Bouchenafa-Saïb, K. Khouli, O. Mohammedi, Preparation and characterization of pillared montmorillonite: application in adsorption of cadmium, *Desalination* 217 (2007) 282–290.
- [45] C. Volzone, L.B. Garrido, Use of modified hydroxy-aluminum bentonites for chromium(III) removal from solutions, *J. Environ. Manage.* 88 (2008) 1640–1648.
- [46] S. Choe, Y. Chang, K. Hwang, J. Kim, Kinetics of reductive denitrification by nanoscale zero-valent iron, *Chemosphere* 41 (2000) 1307–1311.