The Influence of Polyelectrolyte Modification on Nanoscale Zero-Valent Iron (nZVI): Aggregation, Sedimentation, and Reactivity with Ni(II) in Water

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Abstract

Polyelectrolyte modification on the surface of nanoscale zero-valent Iron (nZVI) particles could affect colloidal stability, aggregation, mobility, oxidation as well as reactivity. In this article, two anionic polyelectrolytes with different molecular weight (MW), anionic polyacrylamide (APAM, MW=3 million) and carboxymethylcellulose sodium (CMC, MW=300-800) were modified on the surface of nZVI. Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and X-ray diffraction (XRD) were used to characterize the polyelectrolyte-modified nZVI. Results from UV-Vis spectrophotometer (UV) and sedimentation tests showed that APAM modification led to the aggregation of nZVI in suspension, CMC modification

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made nZVI disperse well. XRD results indicated that polyelectrolyte modification made the slow oxidation of nZVI under ambient conditions. APAM-modified nZVI had much lower Ni^{2+} removal efficiency than that of bare nZVI while CMC-modified nZVI had higher Ni^{2+} removal efficiency after 1.5 hours (h). The study provided the information on the modification effect of nZVI on the colloidal stability and aggregation, sedimentation, reduction and sorption of heavy metal ions in the environment.

Keyword: Nanoscale zero-valent iron, Anionic polyelectrolytes, Aggregation, Sedimentation, Reactivity

1. Introduction

As one of the popular engineered nanomaterials, nanoscale zero-valent iron (nZVI) was widely used in environmental remediation and hazardous waste treatment [1-4]. nZVI particles made from reduction with borohydride tended to associate into dendrimer or fractal aggregates due to chemical and magnetic interactions in the absence of surface stabilizing chemicals [5-7]. Aggregation for unmodified nZVI affected the transport behavior of nZVI both in in-situ groundwater remediation and in porous media to target contaminated sites [8-9], which was an obstacle for practical applications. Numerous efforts had been made to prevent aggregation, promote the mobility of nZVI particles by modifying the surface of nZVI particles with agents, such as surfactants and polyelectrolytes [10,11]. When the particles were coated with poly acrylic acid (PAA), poly methacrylic acid (PMAA) or poly methacrylic acid (PMAA), and poly styrene sulfonate (PSS), the mobility in saturated quartz sand was increased [7]. The existing of natural organic matter also enhanced the mobility

of bare nZVI [12]. In general, the polymer's modification had been prepared by mixing the as-synthesized nZVI with polymer solutions (post-synthesis method), or adding the polymer stabilizers into iron salt precursor solution prior to the nanoparticle synthesis (pre-synthesis method). Cirtiu et al. compared the stabilizing efficiency of four types of polymers, such as carboxymethylcellulose sodium (CMC), polyacrylamide (PAM), PSS, and PAA, using both pregrafting and postgrafting surface modification approaches [8]. The study demonstrated that colloidal stabilization by pregrafted CMC was more efficient than that of other pre or postgrafted polymers and attributed this to a strong chemical bond between the carboxylate groups of CMC and the iron oxide surface of nZVI. The attracting features of CMC also included to be binder in electrodes for sodium batteries [13], effective component of nanocatalysts [14] and dye solar cells [15]. Surface coating with polyelectrolytes improved nZVI stability via charge and steric stabilization [16]. Negative charge surfaces were preferred in the applications because aquifer soils generally had universal negative surface charges in the neutral pH ranges [5].

Recently, nZVI was also used in industrial wastewater treatment in the field study [17,18]. Results showed that nZVI particles settled down slowly and incompletely, which affected the removal efficiency of heavy metals in sedimentation tanks and the processing capacity in the nZVI reactor. In addition, the effluent quality could be decreased because the residual nZVI could absorb contaminants. Finding a way by which nZVI precipitated quickly and completely was significant for nZVI's application in industrial wastewater treatment [19]. Polyelectrolyte modification maybe affect the reactivity of nZVI with organic contaminants [20-22]. However, few studies had been conducted

to investigate the effect of polyelectrolytes modification on the reactivity of nZVI with heavy metal.

The high surface activity and strong reducibility of nZVI led it easy to oxidize. The iron oxides/hydroxide shell would grow thicker during oxidation, resulting significant variation in structure, composition and reactivity [23,24]. Fewer studies had been reported on minimization of the rapid oxidation of nZVI particles than studies on the surface modification to enhance the mobility of the nZVI particles during the subsurface delivery. Thus substantial efforts were required to prevent the oxidation of nZVI particles during their storage and application [25].

This study focused on the effect of polyelectrolytes on nZVI aggregation, stability, sedimentation, and reactivity with nickel ions in the aqueous solution. Two commercially available polyelectrolytes with big difference in molecular weight (MW), anionic polyacrylamide (APAM, MW=3 million), and carboxymethylcellulose sodium (CMC, MW=300-800) were used in the experiment. Results showed that APAM modification caused aggregation of nZVI, and CMC modification made nZVI disperse well. Structure and composition transformation of polyelectrolyte-modified nZVI were investigated using scanning electron microscope (SEM), X-ray diffraction (XRD), and fourier transform infrared spectroscopy (FT-IR). Colloidal stability, sedimentation, and aggregation of surface modified-nZVI were performed using UV-Vis spectrophotometer (UV), and inductively coupled plasma - absorption emission spectrum (ICP-AES). Nickel (Ni^{2+}) removal experiments were then carried out using batch experiments to test the APAM/CMC modification and oxidation effect on nZVI reactivity. The study provided the

information on the modification effect of nZVI on the colloidal stability and aggregation, sedimentation, reduction and sorption of heavy metal ions in the environment.

2. Materials and Methods

2.1 Materials and chemicals

The chemical reagents of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), NaBH_4 ($\geq 98\%$), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$), APAM (MW=3 million), CMC (MW=300-800) were analytical reagents and obtained from Sigma-Aldrich. Figure 1 illustrated the APAM and CMC structural formula. Ultra-high-purity N_2 ($\geq 99.999\%$) was used to exhaust dissolved oxygen in aqueous medium.

2.2 Synthesis and modification of nZVI

nZVI was prepared from the reduction of ferric chloride by sodium borohydride as described in previous studies [26]. Then modification on nZVI was obtained by putting 0.5 g nZVI into 100 mL APAM or CMC solution, then vigorously stirred for 15 minutes by an agitator at 300 rpm. The modified nZVI samples were collected by centrifuge.

Due to the relative molecular weight of CMC (300-800) and APAM (3 million) used in the study was notable discrepancy, the final mass ratio of APAM / nZVI and CMC / nZVI mass ratio was 1% and 20% with a nZVI dosage of $5 \text{ g} \cdot \text{L}^{-1}$.

2.3 Sedimentation and oxidation experiments of APAM- and CMC-modified nZVI

For the sedimentation experiments, APAM- and CMC- modified nZVI suspensions were prepared by putting nanoparticles ($5 \text{ g} \cdot \text{L}^{-1}$) in 1 L flask reactor, then 50 mL of nanoparticle suspensions were transferred from the

flask reactor into 50 mL glass tubes. The suspension was shaken without sonication before the experiment. The sedimentation profiles were obtained by measuring the optical density as a function of time at a wavelength of 508 nm using a UV-Vis spectrophotometer (UV-2550, Shimadzu Instrument Corporation) [8]. The samples were drawn at periodic interval, and then the iron concentration was measured.

The oxidation experiment was carried out by vigorously stirring the suspension containing the same concentration polyelectrolyte-modified nZVI ($5 \text{ g}\cdot\text{L}^{-1}$) by an agitator at 300 rpm for 2 h under dissolved oxygen concentration at $8\text{-}9 \text{ mg}\cdot\text{L}^{-1}$ at room temperature.

2.4 Reactivity of APAM- and CMC-modified nZVI

Batch experiments were conducted to investigate the reactivity of the APAM- and CMC-modified nZVI with Ni^{2+} . Certain concentration of nZVI ($2 \text{ g}\cdot\text{L}^{-1}$) was put into the $100 \text{ mg}\cdot\text{L}^{-1}$ Ni^{2+} aqueous solution. The water was stripped with purified N_2 for 30 min before experiment. Parallel experiments were also performed with only polyelectrolytes in water. At certain time intervals, 5 mL of sample was taken out to determine the concentration of Fe and Ni. ICP-AES (Perkin Elmer Optima 2100 DV) was used to determine the heavy metal concentration.

2.5 Characterization

The morphologies and structures of samples were examined by SEM (FEI Nova NanoSEM 450) operating at 20 kV. XRD (D8 Advance X, Bruker) analyses were conducted with $\text{Cu K}\alpha$ operated at 40 kV and 40 mA; continuous scanned from 30° to 70° , 2θ were collected with a step size of 0.01° and a count time of 0.2 s per step. The scanned area of FT-IR (Nicolet 5700)

was 400 ~ 2000 cm^{-1} with a resolution of 4 cm^{-1} .

3. Results and Discussion

3.1 Characterization of bare-, polyelectrolyte modified- nZVI before and after oxidation

The shape, size, and morphology of bare-, polyelectrolytes modified- and oxidized - nZVI particles' were characterized by SEM as shown in Fig. 2. The nanoparticles with the majority in the size range of 50–100 nm connected into chainlike structures due to magnetic dipole interactions and chemical aggregation [27]. Fig. 2a showed that bare nZVI particles with spherical shape were clear in structure. The thin film was found onto the nZVI surface for APAM- and CMC-modified samples, which was ascribed to APAM and CMC modification (Fig.2b,c). After 2 h oxidation in water, some flakes were observed onto the surface of bare-nZVI (Fig.2d). However, there was little flaky structure for polyelectrolyte-modified nZVI, as results of the protective effect of APAM and CMC coating (Fig.2e, f).

Figure 3 showed the XRD patterns of bare, polyelectrolyte-modified nZVI before and after 2 h oxidation in water. The major broad peak at 2θ of 44.7° indicated the existing of $\alpha\text{-Fe}^0$ with poorly ordered and amorphous nature. Bare and polyelectrolyte-modified nZVI that was oxidized for 2 h in aquatic conditions showed more obvious characteristic peaks at 2θ of 35.60° and 62.73° , which matched corrosion products, magnetite (Fe_3O_4), and/or maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [28]. Bare nZVI showed the larger ratio of iron oxides / Fe^0 peaks compared to polyelectrolyte-modified nZVI when both of them reacted in water for 2 h (Fig. 3b, c, d). This gave a proof that both CMC APAM

coated on the surface of nZVI could block the water and dissolve oxygen to react with nZVI.

FT-IR spectrum was used to characterize the functional groups of APAM- and CMC- modified nZVI (Fig. 4). The chemical functional groups tended to absorb infrared radiation close to a specific wavenumber range regardless of the structure of the rest of the molecule. A band wavenumber at 614 cm^{-1} belonged to Fe-O transverse vibration [29]. The weak absorption band at 1631 cm^{-1} was assigned to the bending mode of water adsorbed onto the nZVI surface. When APAM adsorbed onto nZVI, there was a band resulting from the carbonyl (C=O) stretching vibration (which is in all cases present due to the primary amide group) at 1640 cm^{-1} . The band at about 1614 cm^{-1} was ascribed to the bending vibration of the NH_2 groups, while the wavenumber at 1380 cm^{-1} generated by the bending of CH_2 group [30]. The above results showed that the polyelectrolytes were successfully bound onto the surface of nZVI. The FT-IR band wavenumber at 1560 cm^{-1} and 1417 cm^{-1} indicated the asymmetric stretching and symmetric stretching of COO^- , which proved that CMC molecular bonded onto the iron surface through a bidentate bridging [8].

and

3.2 Sedimentation and stability experiments of APAM and CMC modified nZVI

The colloidal stability of polyelectrolyte-modified nZVI was qualitatively characterized by sedimentation tests (Fig. 5). The transmittance of nanoparticles suspension as function of time at 508 nm was shown in Fig. 5a. It was observed that the transmittance value of supernatant increased abruptly at the initial 5 minutes for APAM-modified nZVI. However, the value decreased

after 5 minutes to APAM-modified nZVI. The results was due to the reaction between iron and water, as well as the generating H_2 leaded to the particles' flotation [6]. Then the transmittance value of APAM- modified nZVI suspension kept stable after 15 minutes. For CMC-modified nZVI suspension, the transmission values increased slowly, then reached stable after 30 minutes. The maximum value was much smaller than that of bare- and APAM-modified nZVI. The results showed that the CMC- modified nZVI had better dispersity.

The concentration of total Fe in suspension versus time was shown in Fig. 5b. Results showed the opposite tendency compared to the absorbance data at 508 nm. The Fe concentration from CMC-modified nZVI suspension decreased slowly, which demonstrated its better colloidal stability than that of bare nZVI. The settlement equilibrium could be reached in 30 minutes, as well as the supernatant became clear. APAM- modified nZVI settled out of suspension rapidly, which could completely precipitate from solution in 1 minute. The efficient flocculation and stabilization of nZVI with APAM and CMC were also demonstrated through settling experiments as shown in Fig. 6. The bare nZVI settled to the bottom section in 10 minutes while no visible black iron can be seen in the tube in 1 minute to APAM -modified nZVI (Fig. 6a, b), and CMC-modified nZVI remained in suspension over an extended period of time (>30 minutes) (Fig. 6c).

3.3 The effect on the reactivity with Ni^{2+} of nZVI due to APAM / CMC modification in water

Figure 7 showed the removal of Ni^{2+} with different kinds of nZVI, such as bare- and polyelectrolyte-modified nZVI. Results indicated all kinds of nZVI could remove over 80% Ni^{2+} within 2 h. From the perspective of a

surface-mediated reaction, reactivity was proportional to the available surface area [2]. APAM had a good flocculation effect on nZVI, which could make the nanoparticles agglomerate, decrease the surface area, and reduce the active site of nZVI contact with Ni^{2+} . Therefore, APAM-modified nZVI decreased reactivity and had lower Ni^{2+} removal efficiency than that of bare nZVI (Fig. 7). For CMC-modified nZVI, the Ni^{2+} removal efficiency was lower than that of bare nZVI within 1 h and higher after 1.5 h (Fig. 7). Thus, it was possible that a large fraction of reactive surface was occupied by the adsorbed CMC molecules and unavailable for direct reaction with Ni^{2+} within 1 h. CMC-modified nZVI particles were much smaller and consequently had a much larger total surface area per unit mass. CMC-modified nZVI was more effective for removing Ni^{2+} after 1.5 h, since the modification of CMC on the surface could prevent nZVI oxidation by water and dissolved oxygen.

3.4 Mechanism of APAM and CMC bounded with nZVI in water

The aggressive aggregation of APAM-modified nZVI, and the good dispersity of CMC-modified nZVI were ascribed to the interaction between the polyelectrolytes and nZVI. When the concentration of APAM was 0.05 g.L^{-1} (1% mass ratio of APAM / nZVI) in water, the measured pH was about 6.4. Because the iso-electric point of nZVI was near 8.3 [19][22], the nZVI had positive charges in solution containing APAM. That is, the APAM molecular with the anion groups of carboxyl (COO^-) attached to the surface of nZVI with positive charges at pH lower than 8.3 by electrostatic attraction (Fig. 8a (1)). The unique core-shell structure bestowed nZVI particles the fascinating function. The iron oxides shell bounded the appropriate number of hydroxyl groups, which could coordinate with the primary amide and carbonyl groups in

APAM molecular (Fig. 8a (2)). The nZVI particles could be bridged by the APAM long molecular chain, and made the nZVI suspension easy flocculation (Fig. 8a). So APAM modification of nZVI enhanced the settlement, decreased the contact surface area, and lowered the nZVI reactivity with Ni^{2+} .

For CMC-modified nZVI, the modification made the suspension dispersed better than bare nZVI. The pH of the CMC solution (1 g.L^{-1} , 20% mass ration of CMC / nZVI) was measured to be 7.1, similarly to APAM, as an anion polymer, CMC mostly interacted with nZVI through electrostatic adsorption by carboxylate groups. The carboxylate groups of CMC were expected to bind with the nZVI surface as three possible complexation models: (i) monodentate chelating, (ii) bidentate chelating, and (iii) bidentate bridging [8] as shown in Fig. 8b. Otherwise, the adsorption process resulted in the encapsulation of the nanoparticles with a thin layer of negatively charged CMC which was also observed in SEM. This protective CMC layer not only stabilized nanoparticles but also prevented the particles from agglomeration through the electrostatic repulsion and steric hindrance between the CMC-modified nanoparticles.

4. Conclusions

Aggregation, stability, sedimentation, and reactivity of modified-nZVI were systematically studied. It was observed that although they were both anionic polyelectrolytes, APAM modification led to nZVI aggregation, and the CMC modification made nZVI dispersal effective in water. Bare nZVI needed 10 minutes to reach sedimentation equilibrium. CMC-modified nZVI had better colloidal stability at 30 min. APAM was an efficient flocculant, and APAM-modified nZVI could settle down completely in 1 minute. Bare, polyelectrolyte-modified nZVI could remove over 80%r Ni^{2+} approximately in 2

h. APAM modification decreased nZVI reactivity and had lower Ni^{2+} removal efficiency than that of bare nZVI while CMC-modified nZVI had higher removal efficiency after 1.5 h. This study provides useful information on the real application of nZVI.

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References

- [1] D. W. Elliott, W. X. Zhang, Field assessment of nanoscale bimetallic particles for groundwater treatment, *Environ. Sci. Technol.* 35 (2001) 4922-4926.
- [2] S. Choe, S. H. Lee, Y. Y. Chang, K. Y. Hwang, J. Khim, Rapid reductive destruction of hazardous organic compounds by nanoscale Fe^0 , *Chemosphere* 42 (2001) 367-372.
- [3] S. R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic(III) from groundwater by nanoscale zero-valent iron, *Environ. Sci. Technol.* 39 (2005) 1291-1298.
- [4] X. Q. Li, W. X. Zhang, Sequestration of metal cations with zerovalent iron nanoparticles: A study with high resolution X-ray photoelectron spectroscopy (HR-XPS), *J. Phys. Chem. C* 111 (2007) 6939-6946.
- [5] P. Jiemvarangkul, W. X. Zhang, H. L. Lien, Enhanced transport of polyelectrolyte stabilized nanoscale zero-valent iron (nZVI) in porous media, *Chem. Eng. J.* 170 (2011) 482-491.
- [6] Y. Liu, T. Phenrat, G. V. Lowry, Effect of TCE concentration and dissolved

- groundwater solutes on NZVI-promoted TCE dechlorination and H₂ evolution, *Environ. Sci. Technol.* 41 (2007) 7881-7887.
- [7] N. Saleh, K. Sirk, Y. Liu, T. Phenrat, B. Dufour, K. Matyjaszewski, R. D. Tilton, G. V. Lowry, Surface modification enhance nanoiron transport and NAPL targeting in saturated porous media, *Environ. Eng. Sci.* 24 (2007) 45-57.
- [8] C. M. Cirtiu, T. Raychoudhury, S. Ghoshal, A. Moores, Systematic comparison of the size, surface characteristics and colloidal stability of zero valent iron nanoparticles pre- and post-grafted with common polymers, *Colloids Surf. A.* 390 (2011) 95-104.
- [9] T. Raychoudhury, N. Tufenkji, S. Ghoshal, Straining of polyelectrolyte-stabilized nanoscale zero valent iron particles during transport through granular porous media, *Water Res.* 50 (2014) 80-89.
- [10] B. Schrick, B. W. Hydutsky, J. L. Blough, T. E. Mallouk, Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater, *Chem. Mater.* 16 (2004) 2187-2193.
- [11] S. R. Kanel, D. Nepal, B. Manning, H. Choi, Transport of surface-modified iron nanoparticle in porous media and application to arsenic(III) remediation, *J. Nanopart. Res.* 9 (2007) 725-735.
- [12] R. L. Johnson, J. T. Nurmi, G. S. Johnson, D. Fan, R. L. Johnson, Z. Q. Shi, A. J. Salter-Blanc, P. G. Tratnyek, G. V. Lowry, Field scale transport and transformation of carboxymethylcellulose-stabilized nano zero-valent iron, *Environ. Sci. Technol.* 47 (2013) 1573-1580.
- [13] F. Bella, F. Col, J. R. Nair, C. Gerbaldi, Photopolymer electrolytes for sustainable, upscalable, safe, and ambient-temperature sodium-ion secondary batteries, *Chem. Sus. Chem.* 8 (2015) 3668-3676.
- [14] Y. Li, M. Kaushik, C. J. Li, A. Moores, Microwave-assisted synthesis of magnetic carboxymethyl cellulose - embedded Ag-Fe₃O₄ nanocatalysts for selective carbonyl hydrogenation, *ACS Sustain. Chem. Eng.* 4 (2016) 965-973.

- [15]F. Bella, J. R. Nair, C, Gerbaldi, Towards green, efficient and durable quasi-solid dye-sensitized solar cells integrated with a cellulose-based gel-polymer electrolyte optimized by a chemometric DoE approach, *RSC Adv.* 3 (2013) 15993-16001
- [16]X. Y. Wang, P. Wang, J. Ma, H. L. Liu, P. Ning, Synthesis, characterization, and reactivity of cellulose modified nano zero-valent iron for dye discoloration, *Appl. Surf. Sci.* 345 (2015) 57-66.
- [17]S. L. Li, W. Wang, W. L. Yan, W. X. Zhang, Nanoscale zero-valent iron (nZVI) for the treatment of concentrated Cu(II) wastewater: a field demonstration, *Environ. Sci. Proc. Impacts* 16 (2014) 524-533.
- [18]S. L. Li, W. Wang, Y. Y. Liu, W. X. Zhang, Zero-valent iron nanoparticles (nZVI) for the treatment of smelting wastewater: A pilot-scale demonstration, *Chem. Eng. J.* 254 (2014) 115-123.
- [19]W. Wang, S. L. Li, H. Lei, B. C. Pan, W. X. Zhang, Enhanced separation of nanoscale zero-valent iron (nZVI) using polyacrylamide: Performance, characterization and implication, *Chem. Eng. J.* 260 (2015) 616-622.
- [20]Y. P. Sun, X. Q. Li, W. X. Zhang, H. P. Wang, A method for the preparation of stable dispersion of zero-valent iron nanoparticles, *Colloids Surf. A.* 308 (2007) 60-66.
- [21]T. Phenrat, Y. Q. Liu, R. D. Tilton, G. V. Lowry, Adsorbed polyelectrolyte coatings decrease Fe(0) nanoparticle reactivity with TCE in water: conceptual model and mechanisms, *Environ. Sci. Technol.* 43 (2009) 1507-1514.
- [22]J. Yang, X. Wang, M. Zhu, H. Liu, J. Ma, Investigation of PAA/PVDF-NZVI hybrids for metronidazole removal: synthesis, characterization, and reactivity characteristics, *J Hazard. Mater.* 264 (2014) 269-277.
- [23]A. R. Liu, W. X. Zhang, Fine structural features of nanoscale zero-valent iron characterized by spherical aberration corrected scanning transmission electron microscopy (Cs-STEM), *Analyst* 139 (2014) 4512–4518.
- [24]A. R. Liu, J. Liu, W. X. Zhang, Transformation and composition evolution of

- nanoscale zero valent iron (nZVI) synthesized by borohydride reduction in static water, *Chemosphere* 119 (2015) 1068–1074.
- [25]H. S. Kim, J. Y. Ahn, K. Y. Hwang, I. K. Kim, I. Hwang, Atmospherically stable nanoscale zero-valent iron particles formed under controlled air contact: characteristics and reactivity, *Environ. Sci. Technol.* 44 (2010) 1760-1766.
- [26]H. L. Lien, W. Zhang, Transformation of chlorinated methanes by nanoscale iron particles, *J. Environ. Eng.* 125 (1999) 1042-1047.
- [27]J. T. Nurmi, P. G. Tratnyek, V. Sarathy, D. R. Baer, J. E. Amonette, K. Pecher, C. Wang, J. C. Linehan, D. W. Matson, R. L. Penn, Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics, *Environ. Sci. Technol.* 39 (2005) 1221-1230.
- [28]Q. Wang, S. Snyder, J. Kim, H. Choi, Aqueous ethanol modified nanoscale zerovalent iron in bromate reduction: synthesis, characterization, and reactivity, *Environ. Sci. Technol.* 43 (2009) 3292-3299.
- [29]H. B. Fu, X. Quan, Complexes of fulvic acid on the surface of hematite, goethite, and akaganeite: FTIR observation, *Chemosphere* 63 (2006) 403-410.
- [30]M. J. McGuire, J. A. Mensah, K. E. Bremmell, Spectroscopic investigation of the adsorption mechanisms of polyacrylamide polymers onto iron oxide particles, *J. Colloid. Interf. Sci.* 299 (2006) 547–555.

Figure Captions

Fig. 1. Structural formula of (a) APAM and (b) CMC.

Fig. 2. SEM images. (a) nZVI, (b) APAM- modified nZVI, (c) CMC- modified nZVI, (d) nZVI oxidized for 2 h, (e) APAM- modified nZVI oxidized for 2 h, (f) CMC- modified nZVI oxidized for 2 h.

Fig.3. XRD patterns of nZVI under different conditions. (a) bare nZVI, (b) bare-nZVI reacted with water for 2 h, (c) APAM-modified reacted with water for 2 h, (d)CMC-modified nZVI reacted with water for 2 h; Peaks are referred to magnetite/maghemite ($\text{Fe}_3\text{O}_4 / \gamma\text{-Fe}_2\text{O}_3$) (M).

Fig. 4. FT-IR of bare-, APAM- , CMC- modified nZVI.

Fig.5. Colloidal stability assessed through sedimentation tests of bare and polyelectrolyte-modified nZVI. (a) UV, (b) Fe concentration in the supernatant of nZVI after reaction with APAM and CMC. The insert in figure is the enlargement of data from the sedimentation test of APAM modified nZVI.

Fig.6. Particles sedimentation images at different time. (a) bare-nZVI, (b) APAM-modified nZVI, (c) CMC- modified nZVI.

Fig. 7. Ni^{2+} removal efficiency of nZVI, APAM-modified nZVI, and CMC-modified nZVI .

Fig. 8. Conceptual model for nZVI aggregation and dispersion with (a) APAM and (b) CMC.

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