



The influence of polyelectrolyte modification on nanoscale zero-valent iron (nZVI): Aggregation, sedimentation, and reactivity with Ni(II) in water



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HIGHLIGHTS

- SEM, XRD, FT-IR were used to characterize modified-nZVI.
- APAM modification made nZVI aggregate aggressively in water.
- CMC-modified nZVI had better colloidal stability.
- nZVI modified by APAM and CMC had the slow oxidation rate.
- The Ni²⁺ removal efficiency with nZVI decreased after CMC modification.

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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 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 Ni²⁺ removal efficiency than that of bare nZVI while CMC-modified nZVI had higher Ni²⁺ 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.

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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

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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. Fig. 1 illustrated the APAM and CMC structural formula. Ultra-

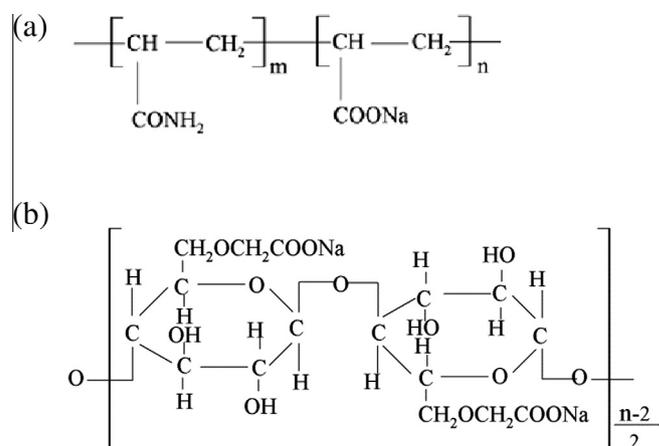


Fig. 1. Structural formula of (a) APAM and (b) CMC.

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 min 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 minutes (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.

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