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Original Research

Cr (VI) Removal from Aqueous Solution Using Starch and Sodium Carboxymethyl Cellulose-Coated Fe and Fe /Ni Nanoparticles

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Abstract

Starch and sodium carboxymethyl cellulose-coated Fe and Fe /Ni nanoparticles were synthesized and their Cr (VI) removal capabilities were evaluated and compared. We found that starch and sodium carboxymethyl cellulose-coated nanoscale zero-valent iron-nickel (SS-nZVI-Ni) showed the better Cr (VI) removal performance. The effect of acidic conditions on Cr(VI) removal by SS-Nzvi-Ni revealed that the Cr (VI) removal efficiency by SS-nZVI-Ni reached the maximum of 95.70% at pH = 2. The effect of different initial Cr (VI) concentrations showed that SS-nZVI-Ni performed well at a high Cr(VI) concentration. Langmuir-Hinshelwood first-order kinetic model could describe the reduction process well. SEM images revealed that SS-nZVI-Ni had a large surface area, which discarded the problem of aggregation. XRD and XPS analysis of SS-nZVI-Ni showed that SS-nZVI-Ni and Cr (III) formed an alloy on the surface of SS-nZVI-Ni after the reaction. The study provides an option for practical application of SS-nZVI-Ni in Cr (VI) removal.

Keywords: nanoscale zero-valent iron, sodium carboxymethyl cellulose, starch, Cr (VI) removal, first-order kinetic model

Introduction

Chromium (VI) is one of major industrial heavy metal contaminants that exists widely on the surface of the soil and in groundwater [1]. Moreover, chromium (VI), due to its high toxicity, could cause a series of problems for humans and animals. Chromium (VI) enters human body through skin contact or mist, which may lead to irritation in the upper respiratory tract, inflammation in the nose, injury in the nasal septum, and cancer in respiratory tract [2]. Many methods such as electrolytic reduction [3], chemical reduction [4], membrane filtration [5], and adsorption [6] have been applied to treat Cr(VI)-containing wastewater. It has been proven that adsorption and chemical reduction are more efficient for Cr(VI) removal due to their high removal rate, simple production process, and low cost.

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In the last two decades, nanoscale zero-valent iron (nZVI) has been widely used to tackle polluted water [7, 8]. Due to the larger reactive surface area and faster reaction rate, nZVI is considered more efficient than iron. Nevertheless, the large surface area can lead to agglomeration of the particles and be more easily oxidized in storage [9]. Researches have proven that nZVI, once being stabilized or supported, would decrease the phenomenon of agglomeration and oxidized in storage. Since then, some researchers have reported that nZVI was loading with extracts such as biochar [10], green tea4, and grape seed [11]. The advantage of extracts is that it improves the stability of nZVI. But its disadvantage is also prominent. In the processing procedure of extracts, HCl was used extensively, which caused secondary pollution. It remains waiting further research and improvement.

It has been reported that clay [12], starch [13], sodium carboxymethyl cellulose [14], and pectin [15] are good modifiers for nZVI. There is no denying that these modifiers can make a positive promotion to nZVI. In recent years, some researchers have reported the removal of chromium by using nZVI or modified nZVI [16]. But few people have focused on nZVI modification by two modifiers. Therefore, the combination of two analogous structures and organic properties applied to modify nZVI is worth researching.

In recent years, researchers have found a novel method of modifying nZVI by loading another metal (Ni [17] for example) on the surface of nZVI, shaping nano bimetal. The addition of another metal to nZVI can accelerate the corrosion of nZVI during the reaction [18]. On the contrary, the rate of another metal loaded on the surface of nZVI could cause positive or negative effects during reaction [18]. And there is still lack research modifying nZVI by combination of metal loading and organics such as starch or pectin.

In this paper, multiple modifiers were untied to optimize nZVI. And these multiple modifiers' performance on chromium (VI) removal in wastewater would be investigated. Modified nZVI with high removal efficiency would be made.

Materials and Methods

Materials and Chemicals

Ferrous sulfate heptahydrate($FeSO_4{\cdot}7H_2O$) and Potassium dichromate($K_2Cr_2O_7$) were purchased from Tianjin Fuchen Chemical Reagents Factory; sodium carboxymethyl cellulose was purchased from Sinipharm Chemical Reagent Co., Ltd.; Starch soluble and Nickel chloride hexahydrate were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

Preparation of nZVI and Modified nZVI

NZVI was prepared by liquid phase reaction. In a typical redox reaction, 0.3 M $NaBH_4$ (freshly prepared) aqueous solution was subtly added dropwise into 0.5 M $FeSO_4$ aqueous solution with magnetic stirring apparatus mixing. The whole reaction process was protected under N_2. The mixed suspension was filtered and watered by ethanol one time and ultra-pure water three times. Then nZVI was dried at 100ºC in a vacuum oven for half an hour. The reaction equation is:

$$Fe^{2+} + BH^-_4 + 2H_2O = Fe^0 + BO^-_2 + 2H^+ + 3H_2 \qquad (1)$$

Then dried nZVI was added into 0.3M $NiCl_2$ aqueous solution with a magnetic stirring apparatus mixing 20 min under N_2 protection. The reaction equation is:

$$Fe^0 + Ni^{2+} = Ni + Fe^{2+} \qquad (2)$$

Ni obtained by displacement reaction would load on Fe surface area [19]. In addition, starch-sodium citrate-nZVI (SS-nZVI) was prepared by adding starch and sodium carboxymethyl cellulose into 100 ml 0.5M $FeSO_4$ aqueous solution. Then $NaBH_4$ aqueous solution was subtly added with mixing 30 min under N_2 protection. Starch-Sodium carboxymethyl cellulose-nZVI-Ni (SS-nZVI-Ni) was prepared by adding SS-nZVI into 0.3M $NiCl_2$ aqueous solution with mixing 20 min under N_2 protection.

Characterizations

To figure out the differences between SS-nZVI-Ni and those after reaction with Cr (VI), XRD (X'Pert Pro) and XPS (ESCALAB250Xi) were used to detect the composition of SS-nZVI-Ni surface elements. Scanning electron microscope (SEM) images were obtained with / Nova 400 NanoSEM for surface feature observation.

Cr(VI) Removal Experiments

Cr(VI) removal by two multiple modified nZVIs and original nZVI (SS-nZVI, SS-nZVI-Ni and nZVI) were examined by adding the adsorbent (1 g) into 100 mL Cr(VI) solutions (1 mg/L) at room temperature (25±2ºC). After that, the capped conical flasks were shaken at 150 rpm in a constant temperature shaker. 1 mL of solution sample was withdrawn and filtered through a 0.45 μm membrane at selected time intervals for analysis of the concentration of Cr(VI) by the 1,5-diphenylcarbazide method, with an ultraviolet-visible UV-6100S double beam spectrophotometer at $\lambda = 540$ nm.

The effects of different solution pH and initial Cr(VI) concentration on Cr(VI) removal were also examined. The effect of pH was studied by adjusting initial pH from 2 to 7 using 0.05 M H_2SO_4. The effect of initial Cr(VI) concentration was studied at the Cr(VI) concentrations varying from 0.2 to 1 mg/L. Within a predetermined time, 0.05 g of modified nZVI was added into this simulated contaminated liquid.

The rate of SS-nZVI-Ni for Cr(VI) reduction was obtained by the following formula:

$$R\ (\%) = \frac{C_0 \quad C_1}{C_0} \times 100\%$$

…where R (%) is the reduction rate of SS-nZVI-Ni for Cr(VI), C_0 is the initial Cr(VI) concentration, and C_1 is the concentration of Cr(VI) at a predetermined time.

Results and Discussion

Characterization of SS-nZVI-Ni

In order to study the mechanism of Cr(VI) removal by SS-nZVI-Ni, XPS and XRD analyses were performed to measure the chemical compositions on the surface. The XPS spectra confirmed that the prepared SS-nZVI-Ni contained the elements Fe, C, O, and Ni, which indicated that both starch and sodium citrate wrapped on the surface of nZVI and Ni was loaded on the nZVI. Cr can be observed in the survey of SS-nZVI-Ni after reaction with Cr(VI) (Fig. 1a). The Cr2p spectra after the reaction have two peaks – at 586.3eV ($Cr2p_{1/2}$) and 576.2 eV($Cr2p_{3/2}$) (Fig. 1b). The binding energy at 576.2eV conforms to Cr_2O_3, and the binding energy at 586.3eV corresponds to Cr oxides, which indicates that Cr_2O_3 precipitate was formed during the adsorption and the reduction of Cr(VI) [20].

In the Fe2p XPS spectrum, the peak at 710.2eV binding energy correspond to $Fe2p_{3/2}$ of Fe_3O_4 or FeO, while the peak at 724.6eV binding energy correspond to $Fe2p_{1/2,}$ which confirms the existence of elemental Fe. After the reaction, the percentages of Fe and Ni atoms in SS-nZVI-Ni decreased from 19.05% to 18.89-3.19% to 2.92%. In contrast, the percentages of C and Cr atoms increased from 23.18% to 25.10-0% to 0.79%. Therefore, the C/O ratio in SS-nZVI-Ni increased from 0.425 to 0.480 after reaction with Cr(VI). And these result implied that iron oxides and Ni had participated in the adsorption and reduction of Cr (VI).

The XRD patterns of SS-nZVI-Ni before reaction with Cr(VI) showed a peak of Fe and Ni alloy (2θ = 44.76°), which decreased dramatically after the reaction. The XRD patterns of SS-nZVI-Ni after reaction with Cr(VI) indicated the appearance of $Fe_{.99}Fe_{1.97}Cr_{.03}Ni_{.01}O_4$ (2θ = 35.43°) and Fe_3O_4 (2θ = 35.44°), which were not detected before the reaction [10, 21]. After reaction, Cr (III) was found in an oxide consisting of Ni, Cr, Fe, and O, which demonstrated that SS-nZVI-Ni had participated in Cr (VI) redox reaction. Thus from the result in Fig. 2, Cr(VI) in initial solutions was reduced to an alloy containing Cr(III), which was

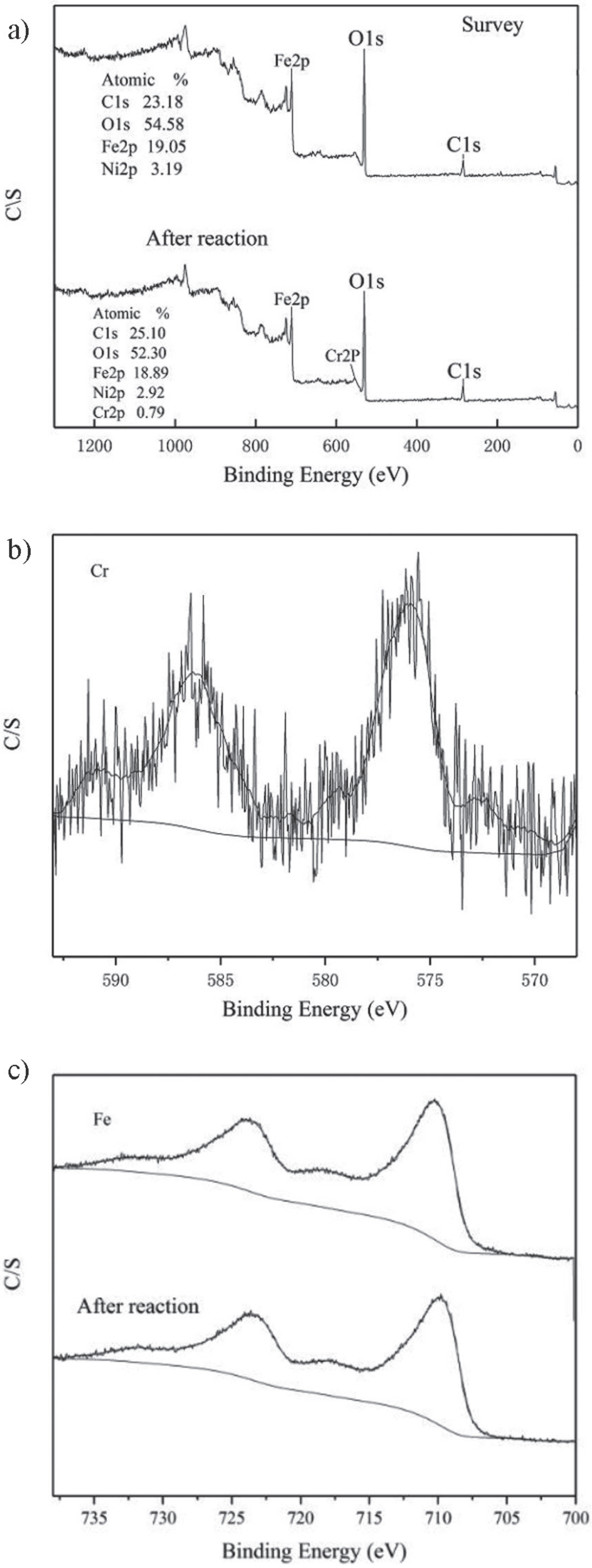

Fig. 1. XPS patterns; a) XPS spectra; b) XPS spectra for Cr 2p in SS-nZVI-Ni; c) XPS spectra for Fe 2p in SS-nZVI-Ni.

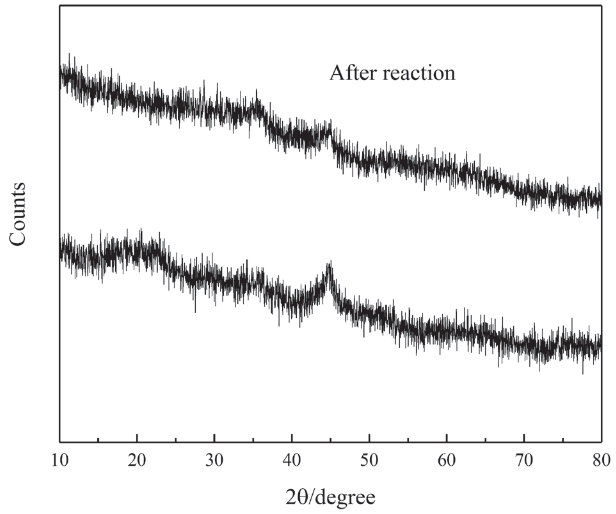

Fig. 2. XRD patterns of SS-nZVI-Ni.

immobilized on the surface of SS-nZVI-Ni. And for iron particles, nZVI was oxidized to Fe_3O_4 and an alloy containing Fe(II) and Fe(III).

To further investigate the removal mechanism, the microstructural features of SS-nZVI-Ni before and after reaction with Cr(VI) were analyzed by SEM (Figs 3a and 3c, respectively), SS-nZVI-Ni existed in the form of a sphere, with sizes ranging from 100~150 nm. NZVI-Gr coated by starch [13], nZVI supported by pumice [22], and nZVI supported by activated carbon [23] gained similar results. While after reaction, the SEM images showed that SS-nZVI-Ni particles become larger, with sizes ranging from 200~250 nm. Before the reaction, there is a relatively wide gap between the particles, which could make Cr(VI) be adsorbed on SS-nZVI-Ni surface. And after the reaction, the gap between the particles narrowed due to the adsorption and reduction of Cr(VI), an alloy containing Cr formed on the surface of SS-nZVI-Ni.

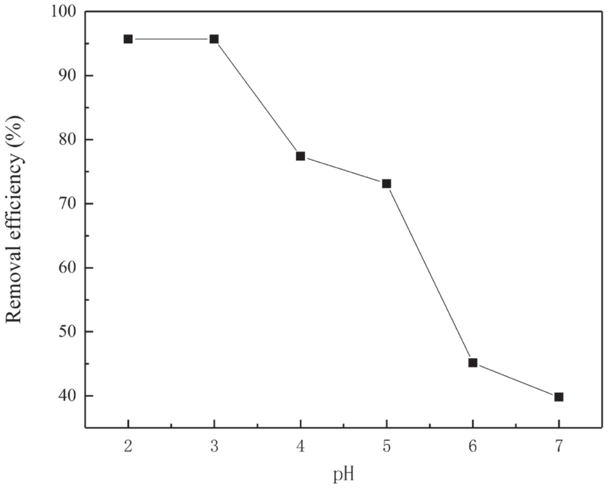

Fig. 4. Effect of pH on Cr (VI) removal of SS-nZVI-Ni.

Effect of pH on Cr(VI) Removal by SS-nZVI-Ni

Fig. 4 shows that with the increase in pH, the removal rate of Cr(VI) in one hour decreased rapidly. Especially when the pH reached 7 did the removal rate sink to 39.78%. These results demonstrated that

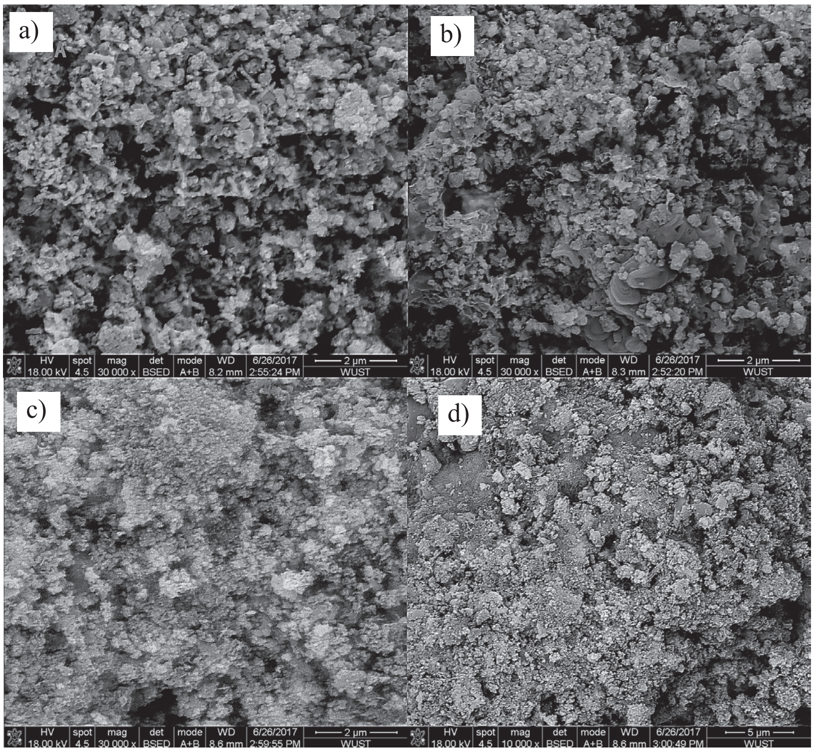

Fig. 3. SEM images of SS-nZVI-Ni; a,b) SEM images of SS-nZVI-Ni before reaction; c,d) SEM images of SS-nZVI-Ni after reaction.

the lower the pH, the more obvious the removal effect. In the range of pH from 2 to 7, Cr(VI) mainly exists in tow forms, HCrO-4 (between pH from 2 to 6) and CrO_2 - 4(above pH 6). The following redox reaction is promoted due to the strong acid environment generated by H^+ [24].

$$HCrO^{-}_{4} + 7H^{+} + Fe^{0} \rightarrow Fe^{3+} + Cr^{3+} + 4H_{2}O \tag{3}$$

$$CrO^{2-}_{4} + Fe^{0} + 8H^{+} \rightarrow Cr^{3+} + Fe^{3+} + 4H_{2}O \tag{4}$$

$$2HCrO^{-}_{4} + 14H^{+} + 3Ni \rightarrow 3Ni^{2+} + 2Cr^{3+} + 8H_{2}O \tag{5}$$

$$2CrO^{2-}_{4} + 16H^{+} + 3Ni \rightarrow 3Ni^{2+} + 2Cr^{3+} + 8H_{2}O \tag{6}$$

From the previous analysis of the XPS spectra, Cr(VI) removed by SS-nZVI-Ni contains adsorption and reduction [20]. In the beginning of the reaction, Cr(VI) ions were adsorbed onto the SS-nZVI-Ni surface, and reduced to Cr(III) by ZVI and Ni (Eqs 1-4). Subsequently, Cr(III), Fe(II), Fe(III), and Ni(II) oxides formed an alloy. Cr (III) would precipitate out of the alloy and then from the water [25, 26]. From those equations, we can prove that H^+ plays an important role in the whole reaction. The increasing of H^+ can shift the reaction equilibrium toward the positive side and can explain that lower pH is advantageous to the removal of Cr(VI). At lower pH, the corrosion of ZVI and Ni accelerated. ZVI was corroded by H^+ into Fe^{2+}, which resulted in Fe^{2+} continuing to participate in the reaction. Therefore, an acidic environment promoted the reaction between Cr(VI) and Fe [27]. In this study, pH was also recorded when the predetermined time was reached. The result showed that the initial pH 5, 7 varied to 5.6, 7.6, respectively. The increase in pH at the initial pH5 further confirms the higher degree of ZVI corrosion under an acidic environment.

The Effect of Different Initial Cr(VI) Concentrations

To investigate the effect of different initial Cr(VI) concentrations on SS-nZVI-Ni removal efficiency, 0.2-1 mg/L Cr(VI) were prepared. It is shown in Fig. 5 that with the increase in concentration, reduction efficiency decreased. At an initial Cr(VI) concentration of 0.2, within 5 min the reduction rate reached 97%, and as time went by, the growth of reduction rate was not distinct. At an initial Cr(VI) concentration of 0.6 mg/L and 0.8 mg/L, the average reaction rate of Cr(VI) decreased from 0.1591 mg/min to 0.1326 mg/min, and the next 90 min. the removal rate grew steadily over time. In general, as the initial Cr(VI) concentration increased, the final removal rate decreased. Because Cr(VI) is a strong oxidant, when high Cr(VI) concentration contacted with nZVI and Ni, both nZVI and Ni could be oxidized and lost their power of reducing in a moment. And XRD patterns demonstrated that nZVI, Ni, and Cr(III) formed an alloy that attached to the surface of SS-nZVI-Ni. In this way, the precipitated product could slow down the further contact of nZVI and Cr(VI). Lu used MCM-41 to stabilize nZVI for Cr(VI) removal [28] illustrating that it was the formation of precipitated product that slows down the reaction. And Fu [29] gains similar results. Thus, nZVI that was modified by multiple matters plays a promoting role in keeping the reactivity of nZVI.

The Effects of Different Modifiers Coating nZVI

nZVI were modified by multiple organic materials and Ni, which were used for Cr(VI) removal. Fig. 6 shows the good performance of SS-nZVI-Ni and SS-nZVI. Obviously, in the first 5 min. of the

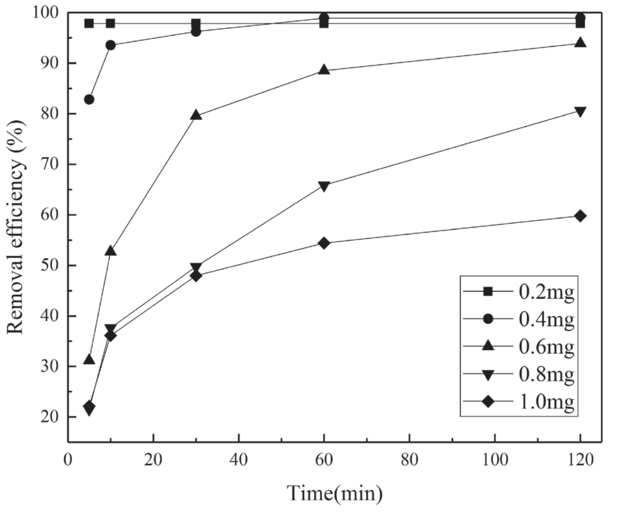

Fig. 5. Effect of different initial Cr (VI) concentration removed by SS-nZVI-Ni versus time.

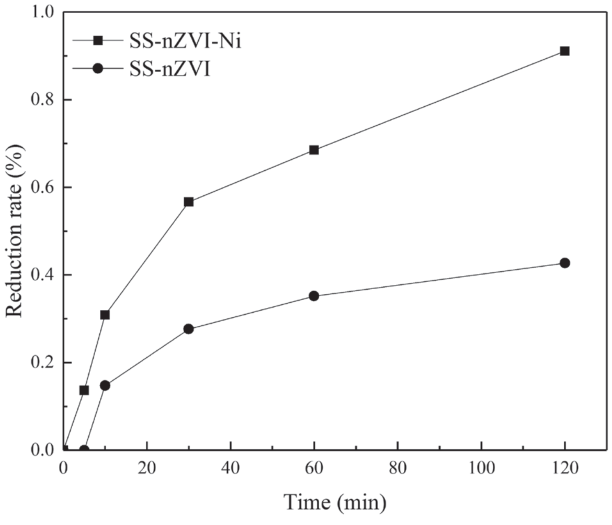

Fig. 6. Effect of different modifier coating nZVI.

experiment, SS-nZVI-Ni removes faster than SS-nZVI in the rate of removal of Cr(VI), it achieves 13.66%. After 60 min, the removal rate of SS-nZVI increases slowly over time, and meanwhile the removal rate of SS-nZVI-Ni can barely see the trend of slowing down. In 120 min., the removal rate of SS-nZVI-Ni reaches 91.08%, which is twice the rate of SS-nZVI. The SEM image indicates that SS-nZVI-Ni has a large surface area. And the XRD patterns show Ni loaded in nZVI participated in reaction. Ni also was used as a reducing agent to reduce Cr(VI) to Cr(III). Moreover, Ni also formed an alloy with Cr(III) on the surface of nZVI. All these Ni features make SS-nZVI-Ni more efficient than SS-nZVI. Kumarathilaka [13] proved that nZVI-Gn coated by starch would provide more efficient removal effect than nZVI modified by graphene composite. Chen [30] proved that nZVI modified by different and single material such as starch and sodium carboxymethyl cellulose gained a better removal rate than nZVI. And at the same time and interval and environmental impact factors, SS-nZVI-Ni the final removal rate is better than these single or double modified nZVI. This would mean that multiple modifiers of nZVI could result in higher Cr(VI) removal efficiency.

The Study of Kinetics

The reaction between SS-nZVI-Ni and Cr (VI) is associated with the multiphase surface reaction. To investigate the reduction mechanism, Zhu [27] used the Langmuir-Hinshelwood first-order kinetic model to evaluate the reaction kinetics:

$$\nu = -\frac{\mathrm{d}C}{dt} = \frac{KbC}{1+bC} \tag{7}$$

…where K represents the reaction rate constant of a solid surface and b is a constant associated with adsorption heat and temperature. When the reaction substrate concentration is very low, $bC \ll 1$ and formula (7) can be written as:

$$\nu = -\frac{\mathrm{dC}}{dt} = KbC = k_{obs}C \tag{8}$$

When k_{obs} is equal to Kb in Equation (8), the reaction can be simplified as a first-order reaction model being integrated into Equation (9):

$$\ln(C_t / C_0) = -k_{obs}t + c \tag{9}$$

…where C_t is the concentration of Cr(VI) at t min., C_0 is the initial Cr(Vi) concentration, c represents a constant, and k_{obs} is the apparent rate constant (min^{-1}), calculated from the line plot slope between $\ln(C_t/C_0)$ versus t.

The half-life $t_{1/2}$ is defined as the time at which half of the initial hexavalent chromium pollutants are degraded completely, which is calculated using the following equation:

$$t_{1/2} = \ln(2)/k_{obs} \tag{10}$$

As shown in Fig. 7a), $\ln(C_t/C_0)$ had a good linear correlation with reaction time t, suggesting that the reduction process of Cr(VI) followed the Langmuir-Hinshelwood first-order kinetic in different multiple modifier. SS-nZVI-Ni and SS-nZVI k_{obs} were 0.0188 and 0.0043 min^{-1}, respectively. Two nZVI were evidently different. SS-nZVI-Ni was obviously better than SS-nZVI in Cr(VI) removal. This meant multiple modifiers were helpful for nZVI in Cr(VI) removal. The half-life periods were 36.87 and 161.2 h between SS-nZVI-Ni and SS-nZVI, respectively. NZVI modified by more modifiers led to larger surface area, which increased the rate of Cr(VI) removal.

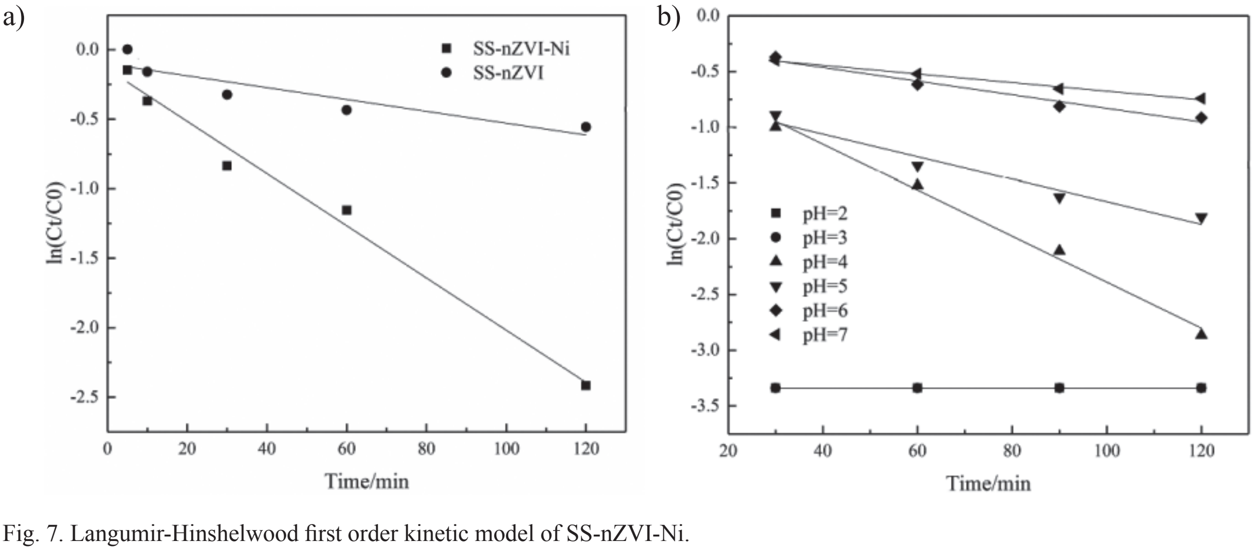

Fig. 7. Langumir-Hinshelwood first order kinetic model of SS-nZVI-Ni.

The Langmuir-Hinshelwood first-order kinetic model was applied to analyze the effect of pH on Cr(VI) reduction. Fig. 7b) showed that when pH values were 4, 5, 6, and 7, k_{obs} were 0.0206, 0.0101, 0.0061, and 0.0039 min^{-1}, respectively. The apparent rate constants k_{obs} decreased at the pH increase, which showed that acidic condition was beneficial to Cr(VI) removal by SS-nZVI-Ni. And the half-life periods were 33.65, 68.63, 113.6, and 177.7 h, respectively. This illustrated that at lower pH, SS-nZVI-Ni would reach maximum removal efficiency.

Conclusions and Implications

In this study, the feasibility of nZVI modified by multiple modifiers (starch sodium carboxymethyl cellulose and Ni) for Cr(VI) removal was investigated. The result proved that SS-nZVI-Ni was an effective and promising composite for Cr (VI) removal. The performance of SS-nZVI-Ni was highly pH dependent, and at pH = 2 the maximum Cr(VI) removal efficiency was observed. The performance of different multiples suggested that the removal efficiency of SS-nZVI-Ni on Cr(VI) removal surpassed SS-nZVI. And at higher Cr(VI) concentrations, the removal efficiency of SS-nZVI-Ni could decline less. Meanwhile SEM images revealed that SS-nZVI-Ni was capable of a larger surface area, which solved the problem of aggregation. XRD and XPS confirmed that SS-nZVI-Ni had participated in adsorption and reduction of Cr(VI). Thus, SS-nZVI-Ni proved to be an effective environmentally friendly reagent for treating Cr(VI) in groundwater.

Acknowledgements

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