

Enhanced removal of soluble Cr(VI) by using zero-valent iron composite supported by surfactant-modified zeolites

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ABSTRACT

Zero-valent iron (ZVI) was immobilized onto surfactant-modified zeolites (SMZ) using calcium alginate. Scanning electron microscopy showed that ZVI powder was uniformly immobilized on the surface of the SMZ. The added ZVI powder resulted in enhanced dichromate removal efficiency and the heterogeneous surface of the composite. The adsorption of dichromate onto the ZVI–SMZ composites fitted well to a pseudo-second-order model and the Langmuir adsorption isotherm. The maximum dichromate adsorption capacity of the composite was 2.49 mg/g at the temperature of 293 K. Higher removal efficiency was obtained at pH lower than 7. X-ray photoelectron spectrometry revealed that the composites combined the strong reductive quality of ZVI and superior adsorption of SMZ.

Key words | alginate, dichromate, surfactant-modified zeolites, zero-valent iron

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INTRODUCTION

Chromium normally exists in water with two stable oxidation states: hexavalent (Cr(VI)) and trivalent (Cr(III)). Cr(VI) is carcinogenic and mutagenic to living organisms (CieslakGolonka 1996). Improper disposal of chromium wastes from industry processes leads to severe groundwater contamination (Owlad *et al.* 2009). Compared to Cr(VI), Cr(III) is essential to maintain the normal metabolism of glucose and fat in the bodies of animals and plants (Miretzky & Cirelli 2010). Therefore, the conventional treatment of chromate-rich effluent is to reduce Cr(VI) to Cr(III) (Bajda & Klapayta 2013). Zero-valent iron (ZVI) has been effectively used as permeable reactive barrier (PRB) materials to intercept and reduce Cr(VI) (Puls *et al.* 1999; Flury *et al.* 2009).

Similar to chemical reduction, the use of adsorbents is another feasible method. Natural zeolites have large surface areas as well as high cation exchange capacity. Their rigid three-dimensional structure offers superior hydraulic properties, so that they are suitable for use in PRB (Bowman 2003), but they show no affinity for anions (Du *et al.* 2012), including Cr(VI) anions. The anion exchange capacity of zeolites can be considerably improved after modification through hexadecyltrimethyl-ammonium bromide (HDTMA-Br) (Li & Bowman 1997), by forming a bilayer on the negatively charged surface of natural zeolites, the charge on zeolite will reverse from negative to positive (Chutia *et al.* 2009),

and the surfactant-modified zeolite (SMZ) has shown good potential for removing Cr(VI) from aqueous solutions (Bajda & Klapayta 2013).

Alginate bead is a common and well-known supportive material for immobilization of enzymes and living cells as alginate is inexpensive, non-toxic, and efficient (Anisha & Prema 2008). The bead is made through a sol–gel transition in the presence of multivalent cations and more specifically with calcium ions (Rocher *et al.* 2008). Recently, nano-scale ZVI was immobilized onto alginate beads, which were successfully used for the degradation of trichloroethylene (Kim *et al.* 2010). Activated carbon has been entrapped in calcium-alginate beads for the clarification of winery wastewaters (Devesa-Rey *et al.* 2011), and grape marc entrapped in calcium-alginate beads has been used to make a biopolymer for the removal of pigments from industrial effluent (Perez-Ameneiro *et al.* 2014).

In this work, HDTMA-Br and ZVI were used for modification of natural zeolites and reduction of Cr(VI), respectively. Sol–gel transition was used to prepare a composite, in which micro-scale ZVI powder was entrapped in a thin calcium-alginate film on the SMZ surface to remove soluble Cr(VI). The synthesized composite was characterized and the adsorption of dichromate ($\text{Cr}_2\text{O}_7^{2-}$), as a model for Cr(VI), was investigated.

MATERIALS AND METHODS

Materials

Natural clinoptilolite obtained from Yuanheng company (Zhengzhou, PRC) was ground. ZVI powder (98% wt. Fe) had a particle size of 0.074 mm (200 mesh) and was obtained from Chuanghui Co., Ltd (Shenzhen, PRC). All reagents were analytical grade, purchased from Tianjin Fuchen Chemical Co., Ltd (Tianjin, PRC). In addition, de-ionized water was used throughout the preparation stage.

Preparation of ZVI-SMZ composite

Modification of zeolites

The ground clinoptilolite was carefully sieved through a 1–2 mm standard sieve, washed with de-ionized water, dried at 398 K and weighed. A 500 mL HDTMA-Br solution with a concentration of 18 g/L was added to 150 g of clinoptilolite at 293 K. The mixture was sealed and shaken at 150 rpm in an air bath at a stable temperature for 24 hours, which was sufficient to enable the adsorption of HDTMA-Br to reach equilibrium (Chutia *et al.* 2009). Thereafter, the resulting mixture was filtered and washed three times with 1 L of deionized water, to remove the superficially excess HDTMA-Br. Finally, The SMZ product was dried at 398 K.

Immobilization of ZVI

ZVI powder (36 g) was added to 30 mL of 20 g/L sodium alginate solution. The suspension was stirred to fully disperse the ZVI. This dispersion was then mixed with 144 g of SMZ and stirred for 20 min to sufficiently coat the SMZ surface with ZVI powder. The ZVI/sodium alginate/SMZ pellets were dropped into 100 mL of 20 g/L CaCl₂ solution. By immersing in the CaCl₂ solution for 24 h, the gelation reaction had enough time to be carried out (Rocher *et al.* 2008), and ZVI powders could immobilize into calcium-alginate film, which was on the outside of the SMZ. Prior to use, the composites were washed with 0.5 M HCl, followed by deionized water to remove excess ZVI powder and acidic precipitation.

ZVI-SMZ composite characterization

The integrity and morphology of the composite was observed with scanning electron microscopy (SEM) on

Hitachi SU8020 (Japan). The chemical species as well as their atomic percentages on the surface of particles were analyzed using X-ray photoelectron spectrometer (XPS) ESCALAB 250 from ThermoFisher Scientific (USA), using monochromatic Al K α radiation. The immobilized ZVI content was calculated by dividing the immobilized weight of ZVI on the composite by the recorded weight of the composite.

Dichromate adsorption

The comparison of removal efficiency between the prepared composite and SMZ was taken in an air bath constant temperature shaker at 293 K. It was conducted by taking 10 g of the composite and SMZ at the same weight as its amount in the composite into 500 mL of 50 mg/L Cr(VI) solution at a pH of 7, separately. Then the solutions were stirred at 120 rpm until the Cr(VI) concentration stopped decreasing.

The Cr(VI) adsorption isotherm for the composite was carried out at the initial Cr(VI) concentration of 5, 10, 20, 30, 50, 70, 100, 150, 200, and 300 mg/L in the above conditions. A constant mass of 2 g of composite was added into 200 mL of Cr(VI) solution and at a pH of 7.

The effect of pH on the adsorption was investigated. The solution pH was periodically adjusted to 3, 5, 7, 9, 11 by using 0.1 M NaOH or 0.1 M HCl. The initial Cr(VI) concentration was 20 mg/L with 2 g of composite.

The amount of Cr(VI) adsorbed on the composite was calculated from the difference between the initial and equilibrium Cr(VI) concentrations. The Cr(VI) concentration in the solution was analyzed with a spectrophotometer at the wave length of 540 nm after coloration with diphenylcarbazide (Du *et al.* 2012).

RESULTS AND DISCUSSION

Characteristics of the ZVI-SMZ composite

The SEM images of raw zeolite, SMZ and composite are presented in Figure 1. Compared with the well-formed crystals of raw zeolite (Figure 1(a)), the SMZ is covered with the HDTMA-Br layer (Figure 1(b)). After gelation, the ZVI containing calcium-alginate film coated onto the HDTMA-Br layer (Figure 1(c-1)). Because of the porous structure of calcium alginate, the dichromate would easily react with HDTMA-Br and ZVI. Also, the ZVI powders were dispersed in the film (Figure 1(c-2)).

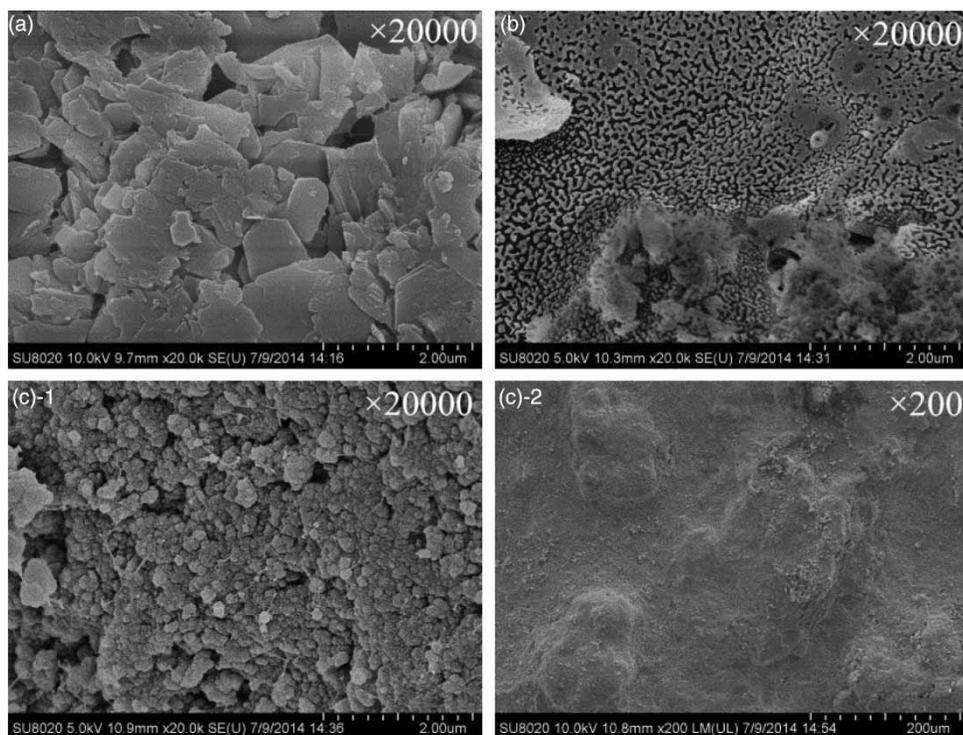


Figure 1 | SEM images of different materials: (a) raw zeolites, (b) SMZ, (c) ZVI-SMZ composites.

Dichromate adsorption onto ZVI-SMZ and SMZ

The composites used in the experiments were prepared with an initial ZVI content of 20%, of which only 8.6% was adhered onto the film. This was mainly because of the small bubble produced by the contact between the surfactant and water while stirring the SMZ with ZVI/sodium alginate, which impeded the entrapment of the ZVI powder in the sodium alginate.

The comparison of removal efficiency between the composite and SMZ was conducted by adding 10 g of

composite and 9.14 g of SMZ to the Cr(VI) solution; the specific concentration and mass of the Cr(VI) solution have been given in the 'Dichromate adsorption' section of 'Materials and methods'. Figure 2(a) shows the improved treatment efficiency of the composite when compared to that of SMZ. After 9 h the gradual increase in Cr(VI) removal efficiency by the composite resulted from the adsorption of Cr(VI) onto Cr-Fe-hydroxide and came after the reaction between ZVI and Cr(VI). The ZVI changed from Fe(0) to Fe(II), and ultimately to Fe(III) (Lee et al. 2003).

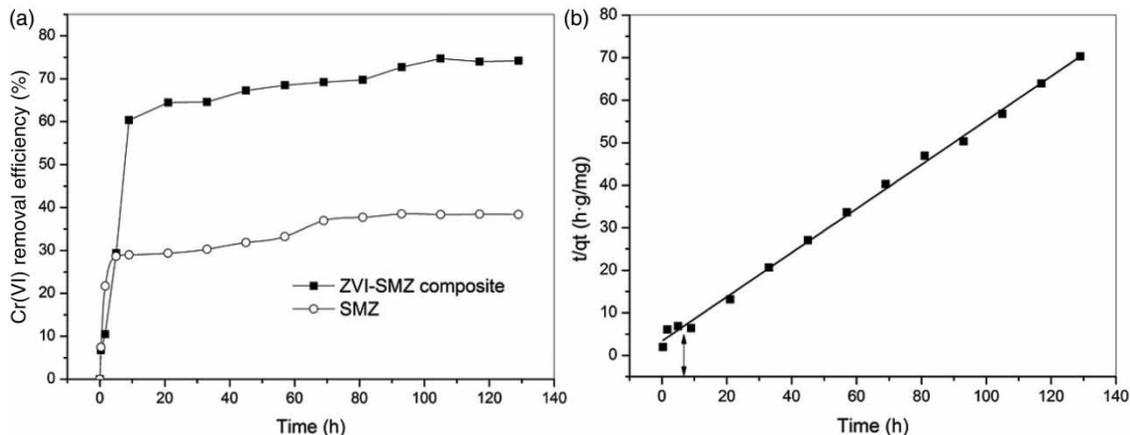


Figure 2 | (a) Cr(VI) removal efficiency of ZVI-SMZ composite and SMZ; (b) kinetics of Cr(VI) adsorption by ZVI-SMZ fitted to the pseudo-second-order kinetics.

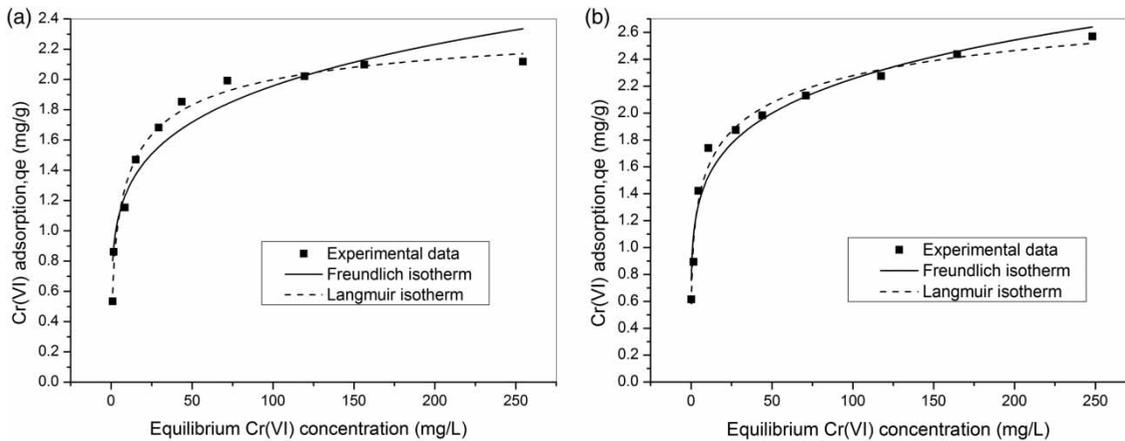


Figure 3 | Cr(VI) adsorption experimental data of composites fitting to Langmuir and Freundlich isotherms. (a) At 293 K, (b) at 323 K.

Chemisorption was described by the pseudo-second-order kinetic model which has been widely applied to the sorption of pollutants from aqueous solutions (Du *et al.* 2012):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where k (g/(mg h)) is the rate constant of adsorption, q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, and q_t (mg/g) is the amount of Cr(VI) adsorbed on composite at any time.

Fitting the adsorption data of the composite to the pseudo-second-order kinetic model resulted in an R^2 of 0.99 and a k value of 0.077 g/(mg h), and a q_e of 1.96 mg/g. The plot of t/q_t vs. t fell into two segments at the time of 9 h as the surface was heterogeneous (Azizian 2006): HDTMA-Br layer and ZVI, for which there was an anion exchange between HDTMA-Br and Cr(VI) and a Cr(VI) reduction by ZVI. The slope in Figure 2(b) is likely due to the added ZVI powder. The ZVI surface could reduce Cr(VI), and its reaction rate on the composite was faster than that of SMZ.

Cr(VI) adsorption isotherm

The adsorption of a solute on a solid surface was described using the Freundlich isotherm and Langmuir isotherm models to correlate the experiment data. Freundlich and Langmuir sorption equations were expressed as

$$\text{Freundlich: } q_e = K \times C_e^{1/n}$$

$$\text{Langmuir: } q_e = \frac{b \times q_m \times C_e}{1 + bC_e}$$

where C_e (mg/L) is the equilibrium Cr(VI) concentration. q_m (mg/g) is the theoretical maximum Cr(VI) uptake, and n , K , b are isotherm constants.

Fitting of the non-linear isotherms of Langmuir and Freundlich at 293 and 323 K are depicted in Figure 3 and parameters are presented in Table 1, which suggests that the Langmuir model is the best fit. This indicated a complete monolayer adsorption process. Cr(VI) removed by SMZ was attributed to surface anion exchange, with the ratio of Cr(VI) adsorbed to that of counterion bromide desorbed being close to one (Li & Bowman 1997). Also, the removal of Cr(VI) was likely due to reductive precipitation of Cr(VI) to Cr-Fe-hydroxide on the ZVI surface (Lee *et al.* 2003), which the isotherm suggested was also a monolayer process. When the temperature increased, the data also fitted the Freundlich model well since a higher temperature was helpful for the reduction of Cr(VI) and anion exchange, which resulted in a gradually increasing trend of q_e .

Effect of pH on Cr(VI) adsorption

Figure 4 clearly indicates that the adsorption capacity decreases with the increase of solution pH. For $\text{pH} > 3$ there was a distinct decrease in Cr(VI) removal, which demonstrated that the process was favored at lower pH. The corrosion of ZVI was accelerated in acidic conditions

Table 1 | Isotherm parameters at 293 and 323 K

Temperature	Langmuir isotherm			Freundlich isotherm		
	b (l/mg)	q_m (mg/g)	R^2	$1/n$	K	R^2
293 K	0.33	2.49	0.9791	0.189	0.82	0.9168
323 K	0.36	3.48	0.9793	0.174	1.01	0.9614

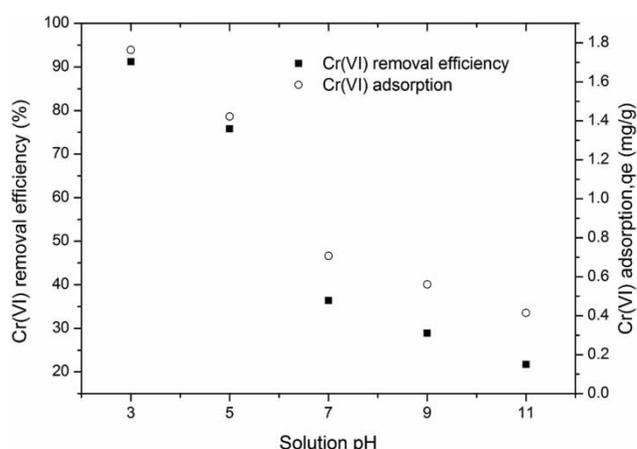


Figure 4 | Effect of the pH on Cr(VI) adsorption by ZVI-SMZ composites.

and decreased the precipitation of Cr(III) and Fe(III) hydroxides on the ZVI surface (Lee et al. 2003). Furthermore, bonding of chromates to zeolites modified with HDTMA has been described as the formation of a positively charged

bilayer of these cations on the zeolites' surface, which attracted counterions from the aqueous solution (Haggerty & Bowman 1994). So similarly, an increase of hydrogen ions (H^+) on the HDTMA bilayer at lower pH also resulted in stronger electrostatic attraction between dichromate anions and positively charged composite surfaces.

XPS analysis and possible Cr(VI) removal mechanisms of the ZVI-SMZ composite

The ZVI-SMZ composites before and after reaction with Cr(VI) solution were analyzed by XPS and scan spectra are illustrated in Figure 5. All spectra were calibrated using the adventitious C 1s peak with a fixed binding energy of 284.5 eV. Full scan spectra of the unreacted composites are illustrated in Figure 5(a-1). Dominant elements Fe, N, and Ca were observed for ZVI powder, HDTMA-Br and calcium alginate which was loaded on the virgin composites, respectively. Figures 5(a-1) and 5(b-1) illustrate

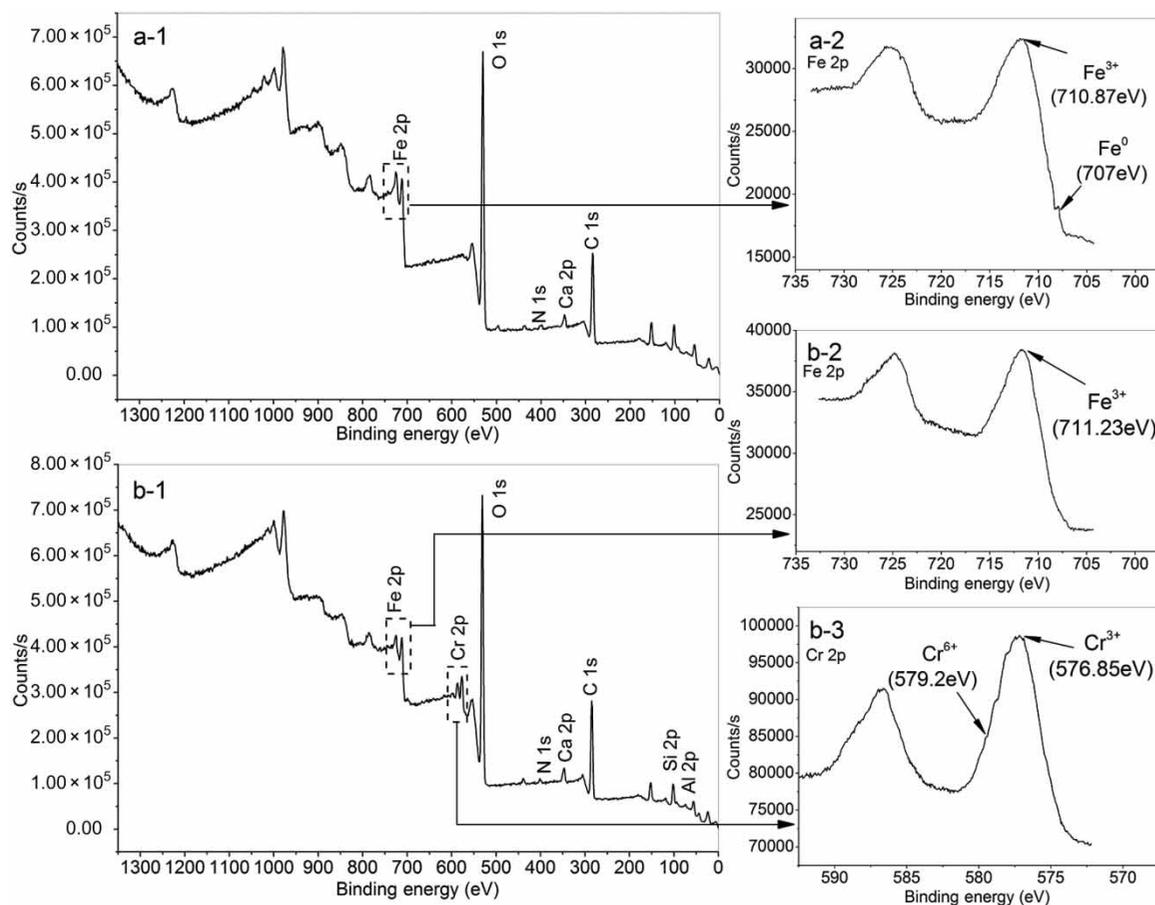


Figure 5 | XPS analysis of the ZVI-SMZ composites before and after reaction with Cr(VI) solution. (a) Full scan of the unreacted composites and high resolution scan of Fe 2p. (b) Full scan of the reacted composites, high resolution scan of Fe 2p and Cr 2p.

significant changes for the composite and SMZ after reacting with Cr(VI). At binding energy of about 580 eV was assigned the peak for Cr 2p. The appearance of the peak for Al and Si mainly came from the bear zeolite surface as a result of the colliding among the stirred composites.

High resolution spectra of the Fe 2p binding energy region are shown in Figure 5(a-2). The Fe 2p spectra indicated that the predominant surface species were ZVI oxides including hydrated ferric oxide (FeOOH), magnetite (Fe₃O₄), and hematite (Fe₂O₃) (Fiedor et al. 1998; Grosvenor et al. 2004). But the shoulder as indicated by the arrow at the binding energy of 707 eV was the peak of ZVI (Grosvenor et al. 2004). These analyses revealed that even though the sample used in the XPS analysis was dried in nitrogen, the ZVI surface oxidized rapidly through the anaerobic corrosion by water (Fiedor et al. 1998).

Figure 5(b-2) shows the Fe 2p high resolution spectra of the reacted composites. The chemical shifts were obvious when compared with Figure 5(a-2). The peak for ZVI disappeared and binding energy of Fe 2p_{3/2} peak changed from 710.87 to 711.23 eV. The spectra indicate that the surface Fe species all belonged to ZVI oxide (Grosvenor et al. 2004). Cr 2p spectra in Figure 5(b-3) present the predominant surface species are Cr(III) compounds including Cr₂O₃ and Cr(OH)₃ (Chen et al. 2013), suggesting that the immobilized ZVI reduced Cr(VI) to Cr(III).

The binding energy of 579.2 eV was reported to be the Cr(VI) peak (Chen et al. 2013). The stoichiometric coefficient ratio of the reaction between Cr(VI) and ZVI was 1:1 (Lee et al. 2003), and even the Cr(VI) could be adsorbed onto Cr-Fe-hydroxide; the relative content of Cr to Fe could not surpass 2:1, and the calculated relative content of Cr to Fe on the surface of the reacted composite sample was 2.63 from the XPS data, which confirmed that Cr(VI) was also adsorbed by the bilayer of HDTMA-Br coated on the SMZ.

CONCLUSION

In this study, ZVI powder was effectively immobilized onto the SMZ surface using calcium alginate. Batch experiments indicated that the Cr(VI) adsorption on the composites was described as a pseudo-second-order kinetic model and the enhanced Cr(VI) removal efficiency resulted from the heterogeneous surface of the composite. Lower pH resulted in higher removal efficiency. XPS analysis of the composites before and after reaction with Cr(VI) solution confirmed that the composites integrated the reductive quality of ZVI

and adsorption capability of SMZ. Zeolite is a stable and low-cost mineral, and the preparation method is simple and feasible. ZVI-SMZ composites will be a promising material for the remediation of groundwater contaminated by waste containing Cr(VI) discharged from mining, tanning, and steelmaking.

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