Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/jhazmat

Cr(VI) retention and transport through Fe(III)-coated natural zeolite

Gaoxiang Du^a, Zhaohui Li^{a,b,c,*}, Libing Liao^a, Renee Hanson^b, Samantha Leick^b, Nicole Hoeppner^b, Wei-Teh Jiang^c

^a School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

^b Geosciences Department, University of Wisconsin-Parkside, Kenosha, WI 53144, USA

^c Department of Earth Sciences, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan

ARTICLE INFO

Article history: Received 19 January 2012 Received in revised form 16 March 2012 Accepted 7 April 2012 Available online 13 April 2012

Keywords: Adsorption Chromate Ferric iron Retention Transport Zeolite

ABSTRACT

Cr(VI) is a group A chemical based on the weight of evidence of carcinogenicity. Its transport and retention in soils and groundwater have been studied extensively. Zeolite is a major component in deposits originated from volcanic ash and tuff after alteration. In this study, zeolite aggregates with the particle size of 1.4–2.4 mm were preloaded with Fe(III). The influence of present Fe(III) on Cr(VI) retention by and transport through zeolite was studied under batch and column experiments. The added Fe(III) resulted in an enhanced Cr(VI) retention by the zeolite with a capacity of 82 mg/kg. The Cr(VI) adsorption on Fe(III)-zeolite followed a pseudo-second order kinetically and the Freundlich adsorption isotherm thermodynamically. Fitting the column experimental data to HYDRUS-1D resulted in a retardation factor of 3 in comparison to 5 calculated from batch tests at an initial Cr(VI) concentration of 3 mg/L. The results from this study showed that enhanced adsorption and retention of Cr(VI) may happen in soils derived from volcanic ash and tuff that contains significant amounts of zeolite with extensive Fe(III) coating. © 2012 Elsevier B.V. All rights reserved.

1. Introduction

Chromium is one of the most important heavy metals present in the environment. The valence states of natural present Cr are III and VI. Cr(VI) is the carcinogenic form of Cr prevailed under oxidized and neutral to alkaline conditions. Compared to Cr(VI), Cr(III) is less toxic and less mobile. Thus, many studies were conducted to reduce Cr(VI) to Cr(III) via in situ chemical reduction [1,2], or using zero valent iron Fe(0) as the materials for permeable reactive barriers (PRBs) to intercept and reduce Cr(VI) into Cr(III) [3]. The presence of Fe(II) or Fe(II)-bearing minerals in soils could also limit the Cr(VI) transport as demonstrated by a field study [4]. In addition, Cr(VI) could be reduced by green rust, which is made of ferrous-ferric iron oxides. The reduction rate was affected by Fe(II) concentration and the types of anions with chloride showing the fastest rate in comparison to carbonate and sulfate [5]. Furthermore, combination of Fe(0) and Fe₃O₄ resulted in a much higher Cr(VI) reduction rate in comparison to $Fe(0)/\alpha$ - Fe_2O_3 , $Fe(0)/\gamma$ - Fe_2O_3 and Fe(0)/FeOOH [6]. In municipal landfill leachate under a reducing condition (Redox potential of -310 mV in the presence of bacteria, Fe(III) and Fe(II) were the crucial components for Cr(VI) reduction via an electron shuttle process where Fe(III) was microbially reduced to Fe(II) which then chemically reduced Cr(VI) to Cr(III) [7].

Besides *in situ* reduction, sorptive removal of chromate from water was also experienced extensive studies. Ferric iron oxides and hydroxides had strong affinity for Cr(VI) and arsenic. Cr(VI) adsorption capacity was 2.3 and 2.0 mg/g on hematite and goethite, respectively [8]. The presence of high concentrations of phosphate greatly reduced Cr(VI) adsorption by Fe(III) [9]. Higher partial pressure of CO₂ shifted Cr(VI) adsorption edge on goethite drastically to the low pH side [10]. At lower partial pressure of CO₂, the innersphere Cr(VI) surface complex dominated the adsorption behavior, while the outer-sphere complex was prevalent at a CO₂ partial pressure of 40 matm [10].

In addition to iron and aluminum (oxy)hydroxides, other materials used to remove Cr(VI) include maize tassel [11] and weathered basalt andesite products [12]. Zeolite has higher cation exchange capacity (CEC), thus enabling it to be used as a substrate to remove heavy metal cations including Cr(III) under column and fixed bed tests [13,14]. Although the sorption capacity of Cr(III) on zeolite was as high as 4% [15], the unmodified zeolite showed no affinity for anions [16]. Under pH 4–12, raw zeolite could not remove more than 20% of the input Cr(VI) [17].

Due to its advanced hydraulic properties, zeolite was subject to extensive studies on its modification. The advantage of using zeolite as the substrate for surface modification lies on the following two aspects: its large surface area and high CEC to facilitate contaminant removal and its good hydraulic conductivities to serve as packing

^{*} Corresponding author at: Geosciences Department, University of Wisconsin – Parkside, 900 Wood Road, Box 2000, Kenosha, WI 53144-2000, USA.

Tel.: +1 262 595 2487; fax: +1 262 595 2056.

E-mail address: li@uwp.edu (Z. Li).

^{0304-3894/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jhazmat.2012.04.016

materials for fluid bed or PRB application [18]. Fe(II)-modified zeolite showed good removal potential for both Pb and Cr(VI) [19]. The kinetics of Cr(VI) adsorption on a zeolite NaX followed the firstorder reversible reaction with an optimal solution pH of 4 [20]. In addition to modification by ferrous iron, zeolite can also be modified by aluminum to enhance the adsorption of arsenate from water [21]. Modification of zeolite by cationic surfactants resulted in significant Cr(VI) retardation [18,22,23]. Modification with even heavy metals such as Ag⁺, Hg²⁺, and Pb²⁺ could also increase the Cr(VI) uptake by zeolite dramatically [16].

This study was of two folds: (1) to assess the influence of Fe(III) present on zeolite surfaces on the adsorption and retention of Cr(VI) onto and the transport of Cr(VI) through the zeolite and (2) to explore the possibilities of using Fe(III)-coated zeolite as substrates for Cr(VI) removal from water.

2. Experimental

2.1. Materials

The zeolite was obtained from St. Cloud Mine in Winston, NM. The aggregated particle size was 1.4-2.4 mm while the size of individual crystals in the aggregates was in the micrometer range. It has an external CEC of 100 meq/kg [23] and a total CEC of 900 meq/kg [18]. The Fe(III) used was FeCl₃·6H₂O from Katayama Chemical (Osaka, Japan) and the Cr(VI) used was K₂CrO₄ from Fisher Scientific (Pittsburg, PA).

2.2. Methods of Fe(III)-zeolite characterization

The integrity and morphology of the zeolite after Fe(III) modification was observed under scanning electron microscope (SEM) on JEOL JSM-840A (Japan) at a voltage of 15 kV and a current of 0.4 nA. The element analyses with energy dispersion spectrum (EDS) were made with an XFlash detector 5010 (Bruker). Samples were coated with Au for SEM image observation and C for EDS analyses. The ⁵⁷Fe Mössbauer spectrum of Fe(III)-zeolite was acquired at room temperature using a constant acceleration spectrometer, which utilized a ⁵⁷Co (Rh) source and was calibrated with α -iron.

2.3. Preparations of Fe(III)-zeolite

To each 500 mL centrifuge bottle, 120 g of zeolite and 360 mL of 20 mmol/L Fe(III) solution were added. The mixture was shaken at room temperature for 20 h at 150 rpm. After pH was adjusted to 9 using 2 M NaOH, the mixture was allowed to settle and the supernatant removed, followed by washing the zeolite with 6 portions of de-ionized (DI) water until no chloride was detected in the supernatant using AgNO₃. The Fe(III)-zeolite was dried naturally. The Fe in the supernatant was 0.15 mg/L less than 0.3 mg/L for the secondary water standard.

2.4. Cr(VI) retention in batch system

A mass of 2.0 g Fe(III)-zeolite and a volume of 10 mL Cr(VI) solution were used in all batch experiments. They were combined in 50-mL centrifuge tubes in duplicates for each initial conditions, such as initial Cr(VI) concentration, equilibrium time, and solution pH. The amount of Cr(VI) adsorbed was calculated from the difference between the initial and the equilibrium Cr(VI) concentrations.

2.4.1. Cr(VI) adsorption isotherm

The initial Cr(VI) concentrations were 2.5, 5, 7.5, 10, 17.5, 25, 37.5, and 50 mg/L. The mixture was shaken on a reciprocal shaker table at 150 rpm for 24 h. After being centrifuged for 20 min at

4000 rpm, the supernatant was then analyzed for equilibrium Cr(V) concentration using a modification of EPA method 7196A [24].

2.4.2. Cr(VI) adsorption kinetics

With an initial Cr(VI) concentration of 5 mg/L, the mixture was shaken on a reciprocal shaker table at 150 rpm for 0.25, 0.5, 1, 2, 4, 8, and 24 h. The supernatant was then analyzed for equilibrium Cr(V) concentrations at these specific times. The samples were sacrificed after analyses.

2.4.3. Cr(VI) adsorption under different solution pH and ionic strength conditions

The initial Cr(VI) concentration was 5 mg/L. The solution pH was periodically adjusted to 3, 5, 7, 9, and 11 for the pH-dependent study using NaOH or HCl. The volume of acid or based added was recorded to correct for the final Cr(VI) concentration due to total volume change. For ionic strength study, the background electrolyte was adjusted to 0.001, 0.01, and 0.1 mmol/L of NaCl before the 5 mg/L Cr(VI) solution was made. The mixtures were shaken for 24 h at 150 rpm. After being centrifuged for 20 min at 4000 rpm, the supernatant was then analyzed for equilibrium Cr(V) concentration.

2.4.4. Cr(VI) adsorption under different temperatures

For the temperature-dependent study, the centrifuge tubes were placed in a Hybaid Micro-4 hybridization oven (Hybaid, Franklin, MA) and shaken at 23, 40, and 55 °C for 24 h. The above mentioned procedures were followed to separate the supernatant from the solid and to analyze the equilibrium Cr(VI) concentrations in the supernatant.

2.5. Cr(VI) analyses

Cr(VI) was analyzed using the EPA method 7196A with a slight modification [24]. In this study, phosphoric acid was used instead of sulfuric acid. 5 mL of supernatant was added to a 10-mL volumetric flask followed by addition of 0.2 mL of 0.5 M H_3PO_4 - KH_2PO_4 (from Aldrich) buffer (pH 2.1), and 0.3 mL of diphenylcarbazide (from Aldrich) solution (1.00 g dissolved in 100 mL of acetone). The flask was diluted to mark. The mixture was allowed to react for a minimum of 30 min for full color development. Then, the mixture was measured by an UV-vis spectrophotometer (Spectronic 20[®] Genesys, Spectronic Instrumental Inc., Rochester, NY) at the wavelength of 540 nm.

2.6. Transport of Cr(VI) through Fe(III)-zeolite column

The raw zeolite and Fe(III)-zeolite were packed in plastic columns to a higher of 11.6 cm and a diameter of 2.60 cm. The Cr(VI) solution was delivered via a 4-head peristaltic pump in an upward direction at a flow rate about 32 mL/h, resulting in a Darcy flux of 6.2 cm/h. The columns were fed with DI water until full saturation as determined by no change in weight differences between two continuous measurements. The porosity, determined by the ratio of the volume of water, *i.e.* the pore volume (PV), in saturated condition to the volume of the zeolite or Fe(III)-zeolite, was 0.6. And the bulk density was 0.95 g/cm³. Then, Cr(VI) solution at a concentration of 3 mg/L was fed into the columns until full break-through before the feeding solution was switched to DI water to determined the desorption. For the raw zeolite, the experiment lasted for 8 PVs, while it lasted about 70 PVs for Cr(VI) transport through Fe(III)-zeolite columns.

2.7. Simulation of Cr(VI) transport

Results of the column experiments were simulated using HYDRUS-1D version 2.01 [25]. The model uses the following partial

Parameter values obtained from HYDRUS-1D for Cr(VI) transport through columns packed with raw or Fe(III)-natural zeolit

Column	$\alpha_{\rm L}$ (cm)	K(L/kg)	η (L/mg)	$S_{\rm m}~({\rm mg/kg})$	β	$\mu_{ m L}$ (h ⁻¹)	r^2
Raw zeolite Fe(III)-zeolite Batch	0.5 150	N/A 2.7 4.1	N/A 0.1 0.05	N/A 27 82	0.83	0.09	0.98 0.97 0.71

differential equation to describe the one-dimensional transport of solutes undergoing equilibrium sorption in porous media [25]:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \nu\frac{\partial C}{\partial x}$$
(1)

where R is the retardation factor of the contaminant, C is the volume-averaged aqueous Cr(VI) concentration, t is the time, D is the hydrodynamic dispersion coefficient, x is the distance, and v is the mean pore velocity.

3. Results and discussion

3.1. Characterization of Fe(III)-zeolite

The integrity of the zeolite was maintained after modification. The SEM image showed euhedral crystals of clinoptilolite with individual crystals up to 10 μ m (Fig. 1a). The EDS spectrum showed major chemical composition of Si, Al, and O with minor amounts of Na, K, Ca, and Mg as exchangeable cations. A small peak of Fe was visible after Fe(III) modification (Fig. 1b). The Mössbauer spectrum of Fe(III)-zeolite at 298 K showed no band at all, confirming that the Fe(III) added to zeolite was in an amorphous form [26], rather than in any forms of FeO(OH) (Fig. 1c). The total Fe loading was about 3%. While the intended Fe loading was 60 mmol/kg. This amount is higher than the 110 mmol_c/kg, external CEC of the zeolite, but much lower than the total CEC of the zeolite [22].

3.2. Cr(VI) adsorption isotherm

Overall, the adsorption of a solute on a solid surface is governed by adsorption isotherm:

$$C_{\rm S} = \frac{K C_{\rm L}^{\beta}}{1 + \eta C_{\rm L}^{\beta}} \tag{2}$$

where C_S and C_L are solute concentration on solid (mass/mass) and in solution (mass/volume), *K*, η , and β are parameters to be determined. When ηC_L^β is very small, Eq. (2) becomes into the Freundlich isotherm. As β approaches to 1, Eq. (2) becomes into the Langmuir isotherm. And when ηC_L is very small and β approaches 1, Eq. (2) becomes into the linear isotherm.

The raw zeolite had no affinity for Cr(VI) oxyanion [16,27]. However, the adsorption of Cr(VI) on the Fe(III)-zeolite increased as the equilibrium Cr(VI) concentration increased. Fitting of adsorption data to both Freundlich and Langmuir isotherms resulted in the coefficients of regression being 0.94 and 0.71, respectively, suggesting that the Freundlich model described the data better (Fig. 2). Adsorption of Cr(VI) on kaolinite and illite also followed the Freundlich isotherm better [28]. In addition, the removal of As (III) and As(V) using Fe(III)-zeolite was better described by the Freundlich isotherm in comparison to the Langmuir isotherm [29]. Cr(VI) adsorption on soils was better fitted by the Freundlich isotherm over the Langmuir isotherm [30]. The good fits to the Freundlich adsorption isotherm could suggest a multi sites adsorption process [28]. In comparison to the Freundlich fit, Cr(VI) removal by surfactant-modified zeolite (SMZ) followed the Langmuir isotherm well [22]. The Cr(VI) adsorption capacity (S_m) determined by the Langmuir isotherm was 82 mg/kg, corresponding to 1.5 mmol/kg, in comparison to 0.8 and 1.3 mmol/kg for As(V) and As(III) adsorption on the same Fe(III)-zeolite [29] and 16 mmol/kg for chromate adsorption on SMZ [22]. However, the affinity of Cr(VI) on the Fe(III)-zeolite was 0.05 L/mg, in comparison to 0.0008–0.0010 L/mg for Cr(VI) adsorption on soils [30] and 0.23 L/mg for Cr(VI) adsorption on SMZ [22].

Fitting to these different adsorption models may also be attributed to different adsorption mechanisms. The removal of



Fig. 1. SEM image showing the integrity of the zeolite after Fe(III) modification (a); EDS spectrum showing the presence of Fe (b); and Mössbauer spectrum showing the amorphous Fe(III) on zeolite at 298 K (c).



Fig. 2. Cr(VI) adsorption by Fe(III)-zeolite. The data were fitted to the Freundlich (dashed line) and Langmuir (solid line) isotherm models.

Cr(VI) by SMZ was attributed to surface anion exchange with the ratio of Cr(VI) adsorbed to that of counterion bromide and chloride desorbed close to one [22], so was the removal of arsenate and arsenite by SMZ [31]. Similarly, the amount of Cr(VI) adsorbed on surfactant-modified clay minerals also followed stoichiometric relation with the counterion bromide desorbed [32]. In contrast, the adsorption of As(III) and As(V) by Fe(III)-zeolite was due to surface complexation [29]. Oxyanions, such as arsenate and chromate, tend to bind strongly to the surfaces of oxide minerals in soil, such as hydrous ferric oxide and goethite [33]. The similarity between the adsorption of Cr(VI) and As(V) by the Fe(III)-zeolite may indicate a similar type of mechanism, *i.e.* surface complexation. As reduction is not a major process, the capacity of Cr(VI) adsorption on SMZ [22].

3.3. Cr(VI) adsorption kinetics

Cr(VI) adsorption increased as the time of equilibration increased (Fig. 3). The data were well described by the pseudo-second-order kinetic model, which was used to describe chemisorption and has been widely applied to the sorption of pollutants from aqueous solutions in recent years. The integrated rate law of the pseudo-second-order kinetic model is [34]:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \tag{3}$$

where k (kg/mg h) is the rate constant of adsorption, q_e (mg/kg) the amount of Cr(VI) adsorbed at equilibrium, and q_t (mg/kg) is the



Fig. 3. Kinetics of Cr(VI) adsorption by Fe(III)-zeolite fitted to the pseudo-secondorder kinetics (solid line). The insert is the fit to Eq. (4) based on two segments (solid lines) and one segment (dashed line).



Fig. 4. Effect of the pH on Cr(VI) adsorption by Fe(III)-zeolite.

amount of Cr(VI) adsorbed on Fe(III)-zeolite at any time, *t*. Eq. (3) can be re-arranged into a linear form [34]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t\tag{4}$$

where kq_e^2 is the initial rate (mg/kg h). The patterns of $(t/q_t vs. t)$ could be used to assess the surface heterogeneity of the adsorbent and the plot of t/q_t vs. t would fall into two segments if the surface was heterogeneous [35]. Fitting the kinetic data to Eq. (4) based on two segments resulted in an r^2 of 0.97 for both segments (solid lines in Fig. 3 insert). In contrast, a similar r^2 value of 0.97, an initial rate of 7 mg/kg-h, a rate constant of 0.05 kg/mg h, and a q_e of 12 mg/kg were obtained when the data were fitted to one segment (dashed line in Fig. 3 insert), in comparison to the initial rates of 1.4 and 3.6 mg/kg-h, the rate constants of 0.01 and 0.06 kg/mgh, and q_e of 11 and 8 mg/kg for As(V) and As(III) sorption on Fe(III)-zeolite, respectively [29]. The Cr(VI) adsorption rate constant in this study is higher than 0.12 kg/mg h for Cr(VI) adsorption on NaX zeolite [20], 0.0015 kg/mg h for Cr(III) adsorption on weathered basalt andesite products [12], and much higher than the first-order rate constant of 0.001 h⁻¹ for Cr(VI) removal from soil [36]. The similarity between the adsorption kinetics of Cr(VI) and As(V) or As(III) again suggested a similar mechanism for Cr(VI) and As(V) or As(III) uptake and retention by Fe(III)-zeolite. The equal goodness of fitting to one segment and two segments indicates that the surface heterogeneity may not play a major role. In comparison to pseudo-second-order kinetics, fitting of the observed data to pseudo-first-order kinetic, Elovich, and parabolic diffusion models resulted in r^2 values of 0.75, 0.63, and 0.92, respectively.

Confirmations of the pseudo-second-order kinetics suggested that the Cr(VI) adsorption on Fe(III)-zeolite was mass transfer limited and the mass transfer coefficient can be determined by [37]:

$$K_{\rm f} = \frac{mkq_{\rm e}^2}{(C_0 A)} \tag{5}$$

where *m* is the mass of adsorbent, C_0 is the initial concentration of Cr(VI), and *A* is the external surface area. Using a surface area of 10 m²/g, the calculated mass transfer coefficient was 8 × 10⁻⁹ cm/s.

3.4. Effects of pH and ionic strength on Cr(VI) adsorptions

As solution pH increased from 3 to 7, Cr(VI) adsorption decreased by 50% from about 20 mg/kg to 10 mg/kg. Beyond pH 7, a further increase in pH to 11 only resulted in a slight decrease in Cr(VI) adsorption (Fig. 4). A similar result was observed for Cr(VI) sorption on hematite and goethite [8] and As(V) adsorption on Fe(III)-zeolite [29]. However, for Cr(VI) adsorption on hematite and goethite, the influences of solution pH began at pH 5 and 3, respectively, beyond which, further increasing pH drastically decreased Cr(VI) adsorption was minimal



Fig. 5. Effect of the ionic strength on Cr(VI) adsorption by Fe(III)-zeolite.

[8]. The pK_{a2} of chromate is 6.5 [36]. Thus, at pH less than the pK_{a2} , the Cr(VI) would be present in mono-anionic form, while above the pK_{a2} , it was in divalent anionic form. Thus, when the solution pH was higher than the pK_{a2} the extra negative charge of Cr(VI) might prevent further interactions with Fe(OH)₃ formed on zeolite surfaces.

In comparison to pH, ionic strength of the solution had essentially no effects on Cr(VI) adsorption when the background electrolyte increased from 0.001 to 0.1 mmol/L of NaCl (Fig. 5). Previous study on adsorption of Cr(VI) on hematite and goethite also showed strong dependency on the pH, but independency of ionic strength [8]. In general, the sorption mechanism of surface complexation is significantly affected by pH, whereas the sorption mechanism of ion exchange is influenced by ionic strength [8]. The strong pH dependence and ionic strength independence of Cr(VI) adsorption suggested that surface complexation rather than ion exchange was the dominant mechanism with the formation of an inner-sphere complex.

3.5. Temperature effects

The free energy (ΔG) of adsorption on Fe(III)-zeolite is related to the distribution coefficient K_d (the ratio of the amount of Cr(VI) adsorbed to the equilibrium Cr(VI) solution concentration) by:

$$\ln K_{\rm d} = -\frac{\Delta G}{RT} \tag{6}$$

where *R* and *T* are gas constant and temperature in *K*. The ΔG is also related to ΔH , the change in enthalpy, and ΔS , the change in entropy, by:

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

Thus, the ΔS and ΔH values can be obtained from the slope and intercept when ΔG is linearly regressed against *T*. In comparison to ΔH of 20 kJ/mol, ΔS of 0.1 kJ/mol-K, and ΔG of -12 to -16 kJ/mol for Cr(VI) adsorption on goethite [38], the ΔG values for Cr(VI) adsorption on Fe(III)-zeolite are in the range of -2.37 to -3.02 kJ/mol, indicating weak net attractive interactions, thus a spontaneous adsorption. The small positive change in ΔS (0.02 kJ/mol K) also indicated spontaneous adsorption, while the negative ΔH value (-9.1 kJ/mol) suggested an exothermic process for Cr(VI) adsorption by Fe(III)-zeolite.

3.6. Column transport of Cr(VI)

Raw zeolite columns showed no retention of Cr(VI) as the retardation factor *R*, as defined by the number of PVs at which the effluent Cr(VI) concentration equals to 50% of the input concentration, was 1 (Fig. 6a). Fitting of the experimental data by HYDRUS-1D resulted in a dispersion of 0.5 cm at r^2 = 0.95 (Table 1).



Fig. 6. Breakthrough curve of Cr(VI) for a column packed with (a) raw zeolite and (b) Fe(III)-zeolite. Solid lines correspond to the adjusting of the experimental data with the HYDRUS-1D model and dashed lines represent a reduction term of Cr(VI) to Cr(III).

In the presence of Fe(III), the Cr(VI) breakthrough curve became asymmetric (Fig. 6b). At $C/C_0 = 0.5$, the number of PVs is about 3, suggesting some retardation in Cr(VI) transport. Fitting the experimental data by HYDRUS-1D with a reaction term resulted in a dispersion of 57 cm, K=2, $\beta=0.85$, and a reaction rate in liquid phase μ_L of $0.09 h^{-1}$ with $r^2 = 0.98$ as indicated by the dashed line (Fig. 6b). Alternatively, fitting the experimental data in the absence of a reduction term resulted in K=2.7, $\eta=0.1$, $\beta=0.83$, and $r^2=0.97$ as indicated by the solid line (Fig. 6b). The K value obtained from the batch test was 4.1, showing a reasonable match between the batch results that the Cr(VI) adsorption on Fe(III)-zeolite followed the Freundlich isotherm better. The similar r^2 values suggest that Cr(VI) reduction is minimal.

Column experiment of Cr(VI) transport through goethiteembedded polyacrylamide gel beads resulted in an *R* of 6 at an input Cr(VI) concentration of 5.2 mg/L and a goethite to gel ratio of 4.44 g goethite per liter of gel [39]. On the other hand, Cr(VI) transport through columns packed with cationic hydrogels, a highly selective material for Cr(VI) anion exchange, resulted in a *R* up to 200 [40]. Compared to these specially manufactured anion exchangers, Fe(III)-zeolite had weak adsorption for Cr(VI). Nevertheless, the inexpensive cost of zeolite and small dosage of Fe(III) for zeolite modification, may make the materials inexpensive for the removal of Cr(VI) from water.

3.7. Conclusions

As Cr(VI) is very mobile in the environment, it is difficult to immobilize it in soils and subsurface sediments. However, in the presence of Fe(III), complexation of Cr(VI) on Fe₂O₃ surfaces could retard Cr(VI) transport in soils. The treatment of zeolite by Fe(III) increased the Cr(VI) adsorption capacity to 82 mg/kg. The Cr(VI) adsorption on Fe(III)-zeolite followed a pseudo-secondorder kinetics and Freundlich adsorption isotherm. Fitting the column experimental data to HYDRUS-1D resulted in a Cr(VI) retardation factor of 3 in comparison to 5 as determined from batch tests. Due to the inexpensive cost, zeolite modified with Fe could serve as medium to remove Cr(VI) from water.

References

- L.E. Eary, D. Rai, Chromate removal from aqueous waters by reduction with ferrous ion, Environ. Sci. Technol. 22 (1988) 972–977.
- [2] J.S. Fruchter, J.E. Amonette, J.E. Szecsody, J.D. Istok, M.D. Humphrey, C.R. Cole, M.D. Williams, V.R. Vermeul, Creation of a subsurface permeable treatment zone for aqueous chromate contamination using *in situ* redox manipulation, Ground Water Monit. Remed. 20 (2000) 66–77.
- [3] R.W. Puls, C.J. Paul, R.M. Powell, The application of *in situ* permeable reactive (zero-valent iron) barrier technology for the remediation of chromatecontaminated groundwater: a field test, Appl. Geochem. 14 (1999) 989–1000.
- [4] S. Loyaux-Lawniczak, P. Lecomte, J.-J. Ehrhardt, Behavior of hexavalent chromium in a polluted groundwater: redox processes and immobilization in soils, Environ. Sci. Technol. 35 (2001) 1350–1357.
- [5] D.L. Bond, S. Fendorf, Kinetics and structural constraints of chromate reduction by green rusts, Environ. Sci. Technol. 37 (2003) 2750–2757.
- [6] F. dos, S. Coelho, J.D. Ardisson, F.C.C. Moura, R.M. Lago, E. Murad, J.D. Fabris, Potential application of highly reactive Fe(0)/Fe₃O₄ composites for the reduction of Cr(VI) environmental contaminants, Chemosphere 71 (2008) 90–96.
- [7] Y. Li, G.K.-C. Low, J.A. Scott, R. Amal, The role of iron in hexavalent chromium reduction by municipal landfill leachate, J. Hazard. Mater. 161 (2009) 657–662.
- [8] O. Ajouyed, C. Hurel, M. Ammari, L.B. Allal, N. Marmier, Sorption of Cr(VI) onto natural iron and aluminum (oxy)hydroxides: effects of pH, ionic strength and initial concentration, J. Hazard. Mater. 174 (2010) 616–622.
- [9] Y.M. Tzou, M.K. Wang, R.H. Loeppert, Sorption of phosphate and Cr(VI) by Fe(III) and Cr(III) hydroxides, Arch. Environ. Contam. Toxicol. 44 (2003) 445–453.
- [10] M. Villalobos, M.A. Trotz, J.O. Leckie, Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on goethite, Environ. Sci. Technol. 35 (2001) 3849–3856.
- [11] C.M. Zvinowanda, J.O. Okonkwo, P.N. Shabalala, N.M. Agyei, A novel adsorbent for heavy metal remediation in aqueous environments, Int. J. Environ. Sci. Technol. 6 (2009) 425–434.
- [12] B.A. Shah, A.V. Shah, R.R. Singh, Sorption isotherms and kinetics of chromium uptake from wastewater using natural sorbent material, Int. J. Environ. Sci. Technol. 6 (2009) 77–90.
- [13] M.A.S.D. Barros, E.A. Silva, P.A. Arroyo, C.R.G. Tavares, R.M. Schneider, M. Suszek, E.F. Sousa-Aguiar., Removal of Cr(III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX, Chem. Eng. Sci. 59 (2004) 5959–5966.
- [14] F.C. Gazola, M.R. Pereira, M.A.S.D. Barros, E.A. Silva, P.A. Arroyo, Removal of Cr³⁺ in fixed bed using zeolite NaY, Chem. Eng. J. 117 (2006) 253–261.
- [15] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, J. Hazard. Mater. B127 (2005) 89–101.
- [16] H. Faghihian, R.S. Bowman, Adsorption of chromate by clinoptilolite exchanged with various metal cations, Water Res. 39 (2005) 1099–1104.
- [17] M.V. Mier, R.L. Callejas, R. Gehr, B.E.J. Cisneros, P.J.J. Alvarez, Heavy metal removal with mexican clinoptilolite: multi-component ionic exchange, Water Res. 35 (2001) 373–378.
- [18] R.S. Bowman, Z. Li, S.J. Roy, T.A. Burt, T.L. Johnson, R.L. Johnson, Surface-Altered Zeolites as Permeable Barriers for *in situ* Treatment of Contaminated Groundwater, USDOE report, 1999, 49 pp.
- [19] S. Lee, K. Lee, J. Park, Pb and Cr (VI) removal using Fe-loaded zeolite, Environ. Eng. Res. 9 (2004) 249–255.

- [20] P.K. Pandey, S.K. Sharma, S.S. Sambi, Kinetics and equilibrium study of chromium adsorption on zeolite NaX, Int. J. Environ. Sci. Technol. 7 (2010) 395–404.
- [21] Y.-H. Xu, T. Nakajima, A. Ohki, Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasu-zeolite, J. Hazard. Mater. B92 (2002) 275–287.
- [22] Z. Li, R.S. Bowman, Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite, Environ. Sci. Technol. 31 (1997) 2407–2412.
- [23] Z. Li, Chromate extraction from surfactant-modified zeolite surfaces, J. Environ. Oual, 27 (1998) 240–242.
- [24] Z. Li, Y. Zou, A comparison of chromate analyses by AA, UV-vis spectrophotometric, and HPLC methods, Adv. Environ. Res. 3 (1999) 125-131.
- [25] J. Šimůnek, M. Sejna, M.Th. van Genuchten, The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media, U.S. Salinity Laboratory, USDA-ARS, Riverside, CA, 1998.
- [26] A.M. Fedoseev, M.S. grigoriev, N.N. Krot, A.Yu. Garnov, N.A. Budantseva, V.P. Perminor, A.A. Bessonov, L.N. Astafurova, M.V. Nikonov, Interaction of Pu(IV,VI) hydroxides/oxides with metal hydroxides/oxides in alkaline media, Pacific Northwest National Laboratory, 1998, PNNL-11900.
- [27] R.S. Bowman, E.J. Sullivan, Z. Li, Uptake of cations, anions, and nonpolar organic molecules by surfactant-modified clinoptilolite-rich tuff, in: C. Collela, F.A. Mumpton (Eds.), Natural Zeolites for the Third Millennium, De Frede Editore, Napoli, Italy, 2000, pp. 287–297.
- [28] O. Ajouyed, C. Hurel, N. Marmier, Evaluation of the adsorption of hexavalent chromium on kaolinite and illite, J. Environ. Prot. 2 (2011) 1347–1352.
- [29] Z. Li, J.-S. Jean, W.-T. Jiang, P.-H. Chang, C.-J. Chen, L. Liao, Removal of arsenic from water using Fe-exchanged natural zeolite, J. Hazard. Mater. 187 (2011) 318–323.
- [30] A.A. Khan, M. Muthukrishnan, B.K. Guha, Sorption and transport modeling of hexavalent chromium on soil media, J. Hazard. Mater. 174 (2010) 444-454.
- [31] Z. Li, R. Beachner, Z. McManama, H. Hong, Sorption of arsenic by surfactantmodified zeolite and kaolinite, Microporous Mesoporous Mater. 105 (2007) 291–297.
- [32] Z. Li, R.S. Bowman, Sorption of chromate and PCE by surfactant-modified clay minerals, Environ. Eng. Sci. 15 (1998) 237–245.
- [33] S. Fendorf, M.J. Eick, P. Grossl, D.L. Sparks, Arsenate and chromate retention mechanisms on goethite. 1. Surface structure, Environ. Sci. Technol. 31 (1997) 315–320.
- [34] Y.S. Ho, G. McKay., The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.
- [35] S. Azizian, A novel and simple method for finding the heterogeneity of adsorbents on the basis of adsorption kinetic data, J. Colloid Interface Sci. 302 (2006) 76–81.
- [36] B. Fonseca, A. Teixeira, H. Figueiredo, T. Tavares, Modelling of the Cr(VI) transport in typical soils of the North of Portugal, J. Hazard. Mater. 167 (2009) 756–762.
- [37] W.T. Tsai, C.Y. Chang, C.H. Ing, C.F. Chang, Adsorption of acid dyes from aqueous solution on activated bleaching earth, J. Colloid Interface Sci. 275 (2004) 72–78.
- [38] N.K. Lazaridis, Ch Charalambous, Sorptive removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate-goethite beads, Water Res. 39 (2005) 4385–4396.
- [39] W. van Beinum, J.C.L. Meeussen, W.H. van Riemsdijk, Competitive sorption and diffusion of chromate and sulphate in a flow system with goethite in gel beads, J. Contam. Hydrol. 86 (2006) 262–278.
- [40] S.C.N. Tang, K. Yin, I.M.C. Lo, Column study of Cr(VI) removal by cationic hydrogel for *in situ* remediation of contaminated groundwater and soil, J. Contam. Hydrol. 125 (2011) 39–46.