



Removal of arsenic from water using Fe-exchanged natural zeolite

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ABSTRACT

An elevated arsenic (As) content in groundwater imposes a great threat to people worldwide. Thus, developing new and cost-effective methods to remove As from groundwater and drinking water becomes a priority. Using iron/aluminum hydroxide to remove As from water is a proven technology. However, separation of As-bearing fine particles from treated water presented a challenge. An alternative method was to use coarse-grained sorbents to increase the flow rate and throughput. In this research, a natural zeolite (clinoptilolite) was exchanged with iron(III) to enhance its As removal. Batch test results showed a Fe(III) sorption capacity of 144 mmol/kg on the zeolite. The As sorption on the Fe-exchanged zeolite (Fe-eZ) could reach up to 100 mg/kg. Columns packed with Fe-eZ were tested for As removal from water collected from acid mine drainage (AMD) and groundwater containing high natural organic matter and high As(III). With an initial concentration of 147 µg/L in the AMD water, a complete As removal was achieved up to 40 pore volumes. However, the Fe-eZ was not effective to remove As from Chia-Nan Plain groundwater due to its high initial As concentration (511 µg/L), high amounts of natural organic matter, as well as its low oxidation–reduction potential, under which the As was in reduced As(III) form.

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1. Introduction

Arsenic (As) is a naturally occurring element present in soil and water. Chronic uptake of As resulted in numerous As poisonings. Although the major path for As intake is through drinking As-elevated water, the presence of clay minerals, many oxides and hydroxides, as well as natural organic matters (NOM) plays an important role in governing As sorption and release, transport and retardation.

A significant number of researches have been conducted to investigate the mechanism of As sorption and retention by soils, clays, and metal oxides [1–3], as well as As release by NOM [4–6]. The cation Ca²⁺ sorbed on kaolinite may form bridges between kaolinite negative surface sites and As(V) anions, resulting in an increase in As(V) sorption up to a capacity of 80 mg/kg [7]. Heterogeneous oxidation of As(III) to As(V) could be enhanced on kaolinite and illite surfaces [2]. More than one functional groups on peat humic acid and fulvic acid were attributed to the decrease of As(III) and As(V) sorption on goethite [5]. A competition between NOM and As resulted in increased bioavailability of As in soil and water systems [5].

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In parallel, developing cost-effective technologies to remove As from water also drew great attention in the last 20 years. Most of these technologies utilize the high adsorption and higher retention of As on iron oxide, iron hydroxides, and oxy(iron)hydroxide. The most effective methods to remove As from water include precipitation/coagulation or filtration, membrane separation, ion exchange and adsorption [8–12]. For adsorption, amorphous iron hydroxides, poorly crystalline hydrous ferric oxides and alums proved to be promising adsorbents for As(III) and As(V) removal from aqueous solution [13]. Conventional coagulation made of 30 mg/L of ferric sulfate or alum resulted in >90% removal of arsenate, and filtration could achieve an additional 5% removal with an optimal ratio of precipitant ion to arsenic ion varying from 1.5 to 4.0 [8]. For As removal using ion exchange resin, raising solution pH from 6 to 9 dramatically improved the resin's preference due to conversion of H₂AsO₄⁻ to HAsO₄²⁻ [8].

Although the above-mentioned sorbents are highly efficient, they were available only as fine powders or were generated *in situ* as gels, which could cause difficulties in separation during water treatment processes [14]. Thus, numerous researches were conducted to achieve better As sorption as well as efficient separation of As-bearing sorbent from water [15]. One of the inexpensive and yet effective method was to coat sand with iron hydroxide and use such modified sand as filtration media to remove As [16,17] and selenium [14]. Other substrates used for As removal after iron coating included polymers

[15] and activated carbon [18]. Nano Fe(II) particles were also used to coat kaolinite and zeolite to enhance sorption of As(V) [19].

Both natural and synthetic zeolites were studied for their sorption of As [20,21]. Natural clinoptilolite was able to adsorb up to 25 mg/kg of As(V) [20]. With an initial concentration of 100 µg/L, chabazite–phillipsite raw materials achieved 60–80% As removal efficiency while the efficiency was relatively low for clinoptilolite-bearing rocks [22]. For synthetic zeolite, a high aluminum content increased As removal [21].

Zeolite was also used as a substrate for Fe modification. Alkaline leaching could significantly increase the uptake of Fe on a zeolite ZSM5 [23]. Treating natural zeolites with Fe(II) improved their sorption selectivity for As(V) oxyanions [18]. However, significant increases of Fe(III) suggested that the adsorption of As was mainly due to accumulation of FeOOH and Fe(III) oxides during the Fe loading process [19]. Although many studies were conducted to evaluate arsenate and arsenite adsorption by zeolite modified with Fe(III) [15,24–26], the initial amounts of Fe(III) used to modify the zeolite varied from 0.02 mol/kg [24] to 4 mol/kg [25]. In addition, the solution pH for Fe modification varied from 3.6 [25] to 10 [26], while the temperature for Fe modification ranged from room temperature [24] to 150 °C [26]. Furthermore, at the equilibrium concentration of 10 g/L, the Fe(III) adsorption was only 8 mg/g, corresponding to only 14 mmol/100 g, much less than the CEC of 167 mequiv./100 g [24]. Thus, the inconsistent results on As removal by Fe-modified zeolite warrant further studies.

2. Experimental

2.1. Materials

The zeolite used was a clinoptilolite-rich tuff obtained from the St. Cloud mine (Winston, NM) with a particle size range of 1.4–2.4 mm. The major exchangeable cations were Na⁺, Ca²⁺, K⁺, and Mg²⁺ with an external cation exchange capacity (ECEC) of 90–110 mequiv./kg [27] and a total cation exchange capacity (TCEC) of 900 mequiv./kg [28]. The iron used for zeolite modification was FeCl₃·6H₂O from Katayama Chemical (Osaka, Japan). The artificial As water for batch study was made using Na₂HAsO₄·7H₂O and NaAsO₂ from Fisher Scientific (Pittsburg, PA).

2.2. Batch studies of Fe(III) uptake by zeolite

To each 50 mL centrifuge tube, 1.0 g of zeolite and 20.0 mL of Fe(III) solution at concentrations from 0.1 to 10 mmol/L were combined. The mixture was shaken at 150 rpm for 24 h at 25 °C, and then centrifuged at 5000 rpm for 10 min, and the supernatant was passed through a 0.45 µm syringe filter before being analyzed for equilibrium Fe concentrations. The amount of Fe adsorbed/exchanged was calculated from the difference between the initial and equilibrium concentrations.

2.3. Creation of Fe-exchange zeolite (Fe-eZ)

To each 500 mL centrifuge bottle, 120 g of zeolite and 360 mL of 20 mmol/L Fe(III) solution was combined. The mixture was shaken at 150 rpm for 20 h at 25 °C before pH was measured and 2 M NaOH solution was added to raise the pH. This procedure was repeated every 2 h for a total of three times to bring the final solution pH to 9. The mixture was allowed to settle and the supernatant removed, followed by washing the zeolite with de-ionized (DI) water. The chloride concentration of supernatant was checked with AgNO₃ until no white precipitation was observed, which was confirmed after the zeolite was washed with 6 portions of 360 mL DI water. The exchanged zeolite was allowed to dry naturally. Tests of Fe in

the supernatant were 0.15 mg/L less than 0.3 mg/L for the secondary water standard.

2.4. Batch studies of As(III) and As(V) removal by Fe-eZ

For As sorption, 1.0 g of Fe-eZ was mixed with 50 mL of As solutions in 50 mL centrifuge tubes with initial concentrations from 0.1 to 20 mg/L. The mixture tubes were shaken at 150 rpm for 24 h and then was allowed to settle. The supernatant was analyzed for equilibrium As solution concentrations. For kinetic study, 1.0 g of Fe-eZ was mixed with 20 mL of 0.5 mg/L As solution in 50 mL centrifuge tubes for varying amounts of time. The mixtures were centrifuged for 5 min and the supernatant passed through a 0.45 µm syringe filter before being analyzed for As concentration. For pH sorption edge study, 1.0 g of Fe-eZ was mixed with 20 mL of 0.5 mg/L As solution in 50 mL centrifuge tubes with final pHs from 3 to 11. The solution pH was checked every 4–6 h and adjusted by 1 M HCl or 1 M NaOH solutions. After 24 h of shaking at 150 rpm, the mixtures were centrifuged for 5 min and the supernatant passed through a 0.45 µm syringe filter before being analyzed.

2.5. Column tests

To each column (5 cm in diameter and 70 cm in length), 400 g of Fe-eZ was packed to a height of 22 cm. Groundwater collected from Chia-Nan Plain aquifer in Southwestern Taiwan and surface water from an acid mine drainage (AMD) collected at the bottom of a tailing pile in the Chinkuashih gold–copper mining area, Northeastern Taiwan were fed into the columns at a flow rate of 125 mL/min. The groundwater had a pH of 7.8, an oxidation–reduction potential (ORP) of –179 mV, a dissolved oxygen content of 0.73 mg/L, a total dissolved solid of 438 mg/L, and an As concentration of 511 µg/L with 90% of the As as As(III). The AMD water had a pH of 2.9, an ORP of 374 mV, and contained 147 µg/L of As, 995 mg/L of sulfate, and 101 mg/L of total dissolved Fe (Fe^{TOT}), among which 91 mg/L was Fe(II). The column tests were conducted within 5 h after water collection. The effluent water from the columns was sampled every 0.5 L, corresponding to 2 pore volumes (PVs), for a total of 40 PVs.

2.6. Chemical analysis

The Fe^{TOT} was determined using a Lovibond MutiDirect Photometric System (The Tintometer Ltd., Dortmund, Germany) with an analytical range of 0.02–1.0 mg/L. Proper dilution was made for higher Fe^{TOT} concentrations. The As analysis was made on an PE Optima 7000 DV ICP-OES with a detection limit of 1 µg/L and a linear range of 1–1000 µg/L.

2.7. Scanning electron microscope observation and X-ray diffraction analyses

Samples were coated with Au for scanning electron microscope observation and C for element analysis. The SEM observation was performed on JEOL JSM-840A (Japan) at a voltage of 15 kV and a beam current of 0.4 nA while the element analyses were conducted with an energy dispersion X-ray spectrometer using a Bruker XFlash detector 5010 attached to the SEM.

Powder XRD analyses were performed on a Rigaku D/Max-IIIa diffractometer with Ni-filtered Cu Kα radiation at 30 kV and 20 mA. Randomly orientated samples were collected from 2° to 80° 2θ with a scanning rate of 1°/min at 0.01° per step. A 1° divergent slit, 1° receiving slit, and 0.3 mm scatter slit were used.

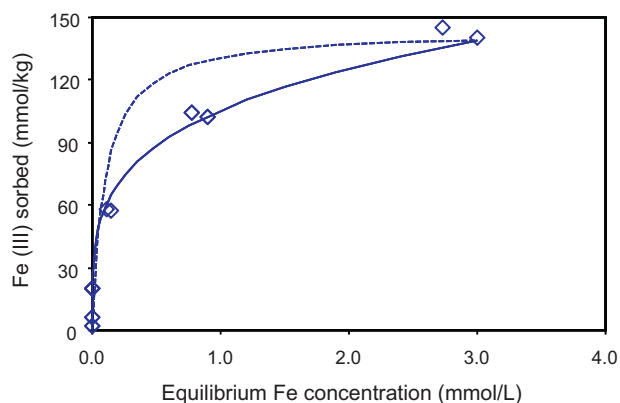


Fig. 1. Sorption of Fe(III) on zeolite. The dashed and solid lines were the Langmuir and Freundlich fits to the experiment data.

3. Results and discussion

3.1. Batch Fe(III) sorption on zeolite

Batch tests showed good sorption of Fe(III) on the zeolite (Fig. 1). Both Langmuir and Freundlich sorption isotherms modeled the Fe(III) adsorption well with a coefficient of determination $r^2 = 0.99$ and 0.98 , respectively. The calculated Fe(III) sorption capacity was 144 mmol/kg . Even though with a trivalent charge, the amount of Fe(III) sorbed was much less than the TCEC of 900 mequiv./kg [28], but was about four times to the ECEC [27] of the zeolite, suggesting that internal sorption sites were partially responsible for the Fe(III) uptake. The amount of Fe(III) sorbed was similar to that on a zeolitic tuff collected from Romania, on which Fe(III) sorption capacity was 8 mg/g , corresponding to 140 mmol/kg [24]. The Fe sorption from AMD water on a zeolite collected from Princeton, British Columbia, Canada, was $5\text{--}6 \text{ g/kg}$, corresponding to 100 mmol/kg [29].

3.2. Batch As sorption on Fe-eZ

Overall, As(III) had a higher sorption on Fe-eZ than As(V) (Fig. 2). The experimental data were modeled with both Langmuir and Freundlich sorption isotherms. The Freundlich sorption isotherm fitted the experimental data better than the Langmuir sorption isotherm for both As(III) and As(V) sorption with $r^2 = 0.99$ and 0.85 , respectively. The calculated As(III) and As(V) sorption capacity on Fe-eZ was 100 and 50 mg/kg , respectively (Fig. 2). In similar studies, the As(V) sorption capacity was 40 mg/kg and 44 mg/kg on an Fe(II)-modified clinoptilolite [18] and on an Fe(III)-modified clinoptilolite, respectively [15]. However, the result from this study was lower

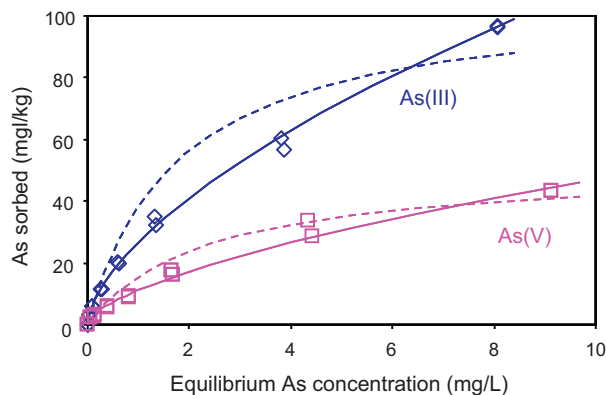


Fig. 2. Sorption of As(III) and As(V) on Fe-eZ. The dashed and solid lines were the Langmuir and Freundlich fits to the experiment data.

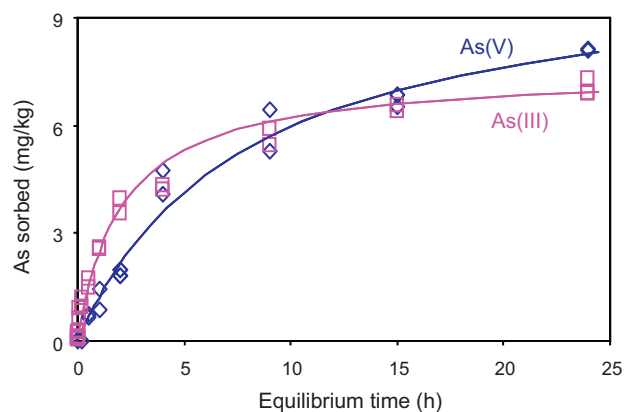


Fig. 3. Kinetics of As sorption on Fe-eZ. The lines are pseudo-second order fits to the observed data.

than the As(V) and As(III) sorption on a different iron-coated zeolite (ICZ), on which the amount of Fe loading was not specified while the amount of ICZ used was 100 g/L [26] much larger than 20 g/L used in this study. The result from this study was also smaller than As(V) sorption on Fe(III)-modified zeolitic tuff with an Fe(III) loading of 3.3 mg/g , corresponding to 60 mmol/kg [24]. The As sorption capacity on Fe-eZ was much smaller than that on zeolite modified by long chain cationic surfactants to a bilayer surface coverage [27,30].

The As sorption kinetic data were fitted to both pseudo-first order and pseudo-second order reactions and the latter fitted the experimental data better (Fig. 3). The initial rates were 1.4 and 3.6 mg/g h and the rate constants were 0.01 and 0.06 g/mg h for As(V) and As(III) sorption on Fe-eZ, respectively. A fast As(V) sorption within 30 min was reported on ICZ [26] and on Fe(III)-modified zeolitic tuff [24], and film diffusion instead of pore diffusion was attributed to the limiting step of As(V) sorption [26]. On the contrary, a much slower rate of As sorption on Fe(II)-modified clinoptilolite with equilibrium as long as 48 h was observed and was attributed to surface complexation and pore diffusion [18]. Studies of As(V) and As(III) sorption onto amorphous iron oxide, goethite, and magnetite at varying solution compositions were modeled with a diffuse double layer surface complexation model [13].

3.3. Influence of solution pH on As sorption on Fe-eZ

With an initial As concentration of 0.5 mg/L and a liquid to solid ratio of $20:1$, the solution pH had a drastic influence on As uptake (Fig. 4). The As(V) sorption was more or less constant at 11 mg/kg when the pH was between 3 and 6 . Further increase in pH caused

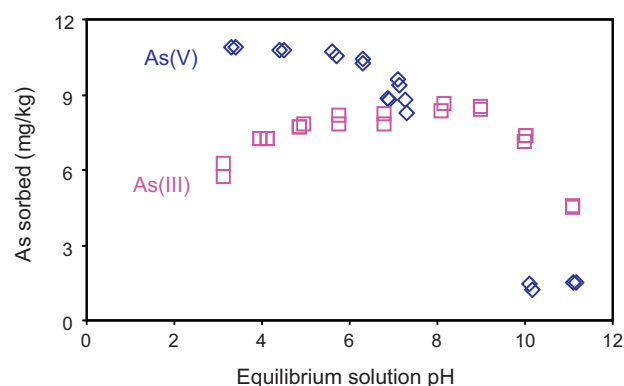


Fig. 4. Influence of equilibrium solution pH on As sorption on Fe-eZ.

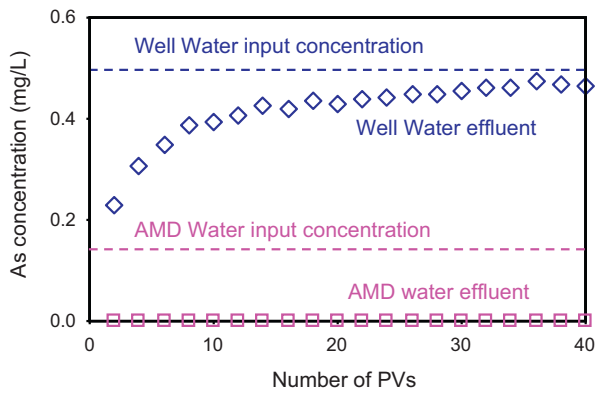


Fig. 5. Effluent As concentrations from a large Fe-eZ column with input AMD water and groundwater.

significant reduction in As sorption. At pH 10, the amount of As(V) sorbed was only 2 mg/kg (Fig. 4). Sorption of As(III) on Fe-eZ was somehow slightly different. Higher As(III) sorption was found at pH 6–9, above which significant decrease in As(III) sorption was also observed. However, the As(III) sorption was lower at solution pH 3–5 compared to 6–9 (Fig. 4). The pH effect on As(V) was similar to a previous observation of As(V) sorption on ICZ [26], but completely different from that on Fe(II)-modified clinoptilolite [18], in which peak As(V) and As(III) adsorption occurred at pH 7 and 8, respectively. Sorption of As(V) onto amorphous iron oxide and goethite was more favorable than that of As(III) below pH 5–6, whereas, above pH 7–8, As(III) had a higher affinity for the solids [13]. In a batch experiment it was found that ~99% of As(V) was removed at a pH of 6, 55.5% was removed at a pH of 7, and only 2% was removed at a pH 8 after 9 h of mixing of arsenic-bearing water with zero valent iron [31].

3.4. Column study

The effluent of AMD water leached from the Fe-eZ column showed zero As concentration while that of groundwater showed substantial As concentration (Fig. 5). The AMD water contained more than 100 mg/L of dissolved Fe^{TOT} and had a pH of 2.9 and an ORP of 374 mV. At pH 6.8 with a dissolved oxygen content of 9 mg/L the half-life of Fe(II) in water was only 0.36 min based on the kinetic rates [32]. As long as the dissolved oxygen concentration in solution was higher than 3 mg/L, oxidation of Fe(II) and precipitation of ferric hydroxides would not be expected to be the rate limiting step [33]. When passing through the Fe-eZ column, the dissolved Fe and sulfate may interact with the alkaline zeolite to induce $\text{Fe}(\text{OH})_3$ (Fig. 6) or oxyhydroxysulfate precipitation, which could enhance As removal due to sorption of $\text{Fe}(\text{OH})_3$ or oxyhydroxysulfate on the zeolite. Furthermore, although plot of As in AMD water on the pH-Eh diagram [34] fell in the As(III) region, it could be readily oxidized into As(V) when solution pH increased from 2.9 to 8 (Fig. 6).

On the other hand the Chia-Nan Plain groundwater contained a higher amount of NOM. The concentration of humic substances was 34–468 QSU (mean = 128 ± 126.8 QSU) (quinine standard unit), which was higher than in Lanyang Plain groundwater of Northeastern Taiwan (16–211 QSU, mean = 53.4 ± 9.6 QSU) and Bengal Delta Plain groundwater (13–38 QSU, mean = 17.8 ± 4.6 QSU) [35]. The presence of NOM such as humic acid and fulvic acid dramatically decreased As(III) and As(V) sorption on goethite [5]. In addition, in the presence of NOM, arsenite was consistently desorbed or prevented from sorbing to a greater extent than arsenate [6]. The As in Chia-Nan Plain groundwater is dominant by As(III). The presence of high NOM together with the As(III) speciation resulted in reduced

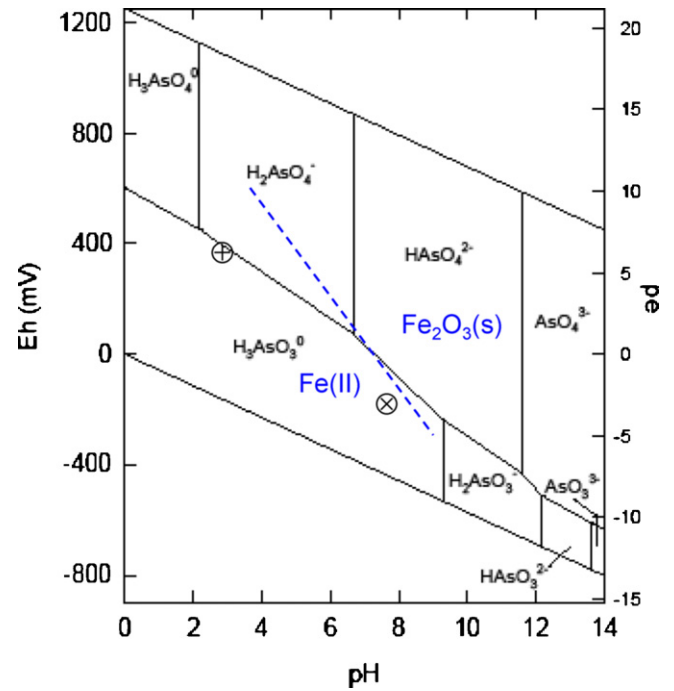


Fig. 6. Plot of AMD water (⊕) and groundwater (⊗) on pH-Eh diagram. The dashed line is the boundary between Fe(II) and Fe_2O_3 (s).

retention of arsenic by the Fe-eZ column (Fig. 5). Furthermore, the ORP of the groundwater was –179 mV. Under such a low ORP, As sorption might not be favored.

3.5. Material characterization after As sorption

SEM showed euhedral zeolite crystals with particle sizes in the range of 10 μm (Fig. 7). The crystal morphology did not change after Fe-exchange and As sorption (Fig. 7). The XRD patterns clearly showed crystalline clinoptilolite after Fe-exchange and after As sorption (Fig. 8). The invariance of crystallinity and crystal morphology suggested that the Fe-eZ was physically stable and could be used as filtration medium with no disintegration.

3.6. Possible mechanism of As sorption on Fe-eZ

Thorough investigations showed that the arsenic removal mechanisms using Fe(III) oxides involved in both mono- and biden-

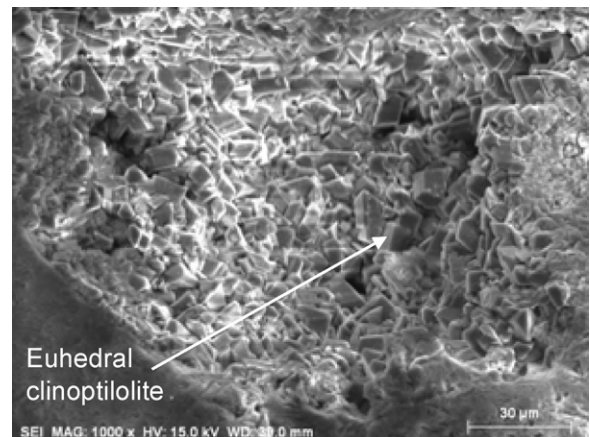


Fig. 7. SEM photo showing the euhedral clinoptilolite crystals after Fe-exchange and As sorption.

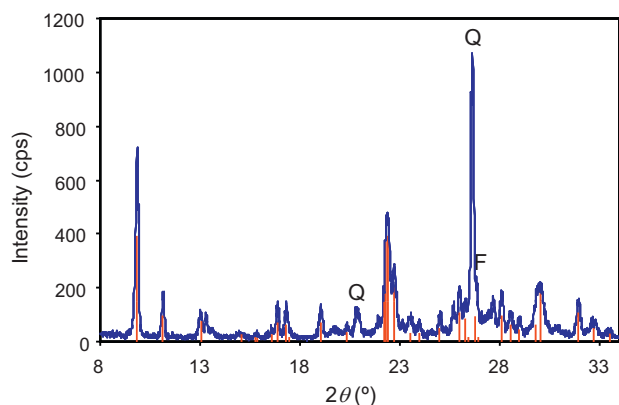
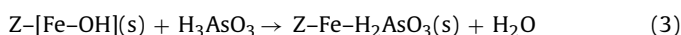
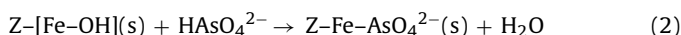
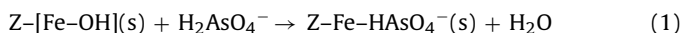


Fig. 8. An X-ray diffraction pattern showing the crystalline clinoptilolite after Fe-exchange and As sorption.

tate complex formation with ferric oxyhydroxides [3,36,37]. Under acidic condition the clinoptilolite was stable while the uptake of Fe(III) by clinoptilolite was attributed to cation exchange and was affected by valence charge, the free energy of hydration, and the hydrated size of Fe(III) [29]. The increase of solution pH after Fe(III) sorption during the modification stage could shift the chemical equilibrium of Fe(III) to the formation of Fe(OH)₃.

The pK_a values for arsenic acid were 2.2, 6.97, and 11.53, while those of arsenous acid were 9.22, 12.13, and 13.4 [38]. Thus, under most of the experimental conditions, the arsenic species would be H₂AsO₄⁻, HAsO₄²⁻ and H₃AsO₃. If the As sorption surface were assumed to be inner-sphere complexes, the surface complexation reactions for arsenate and arsenite adsorption would follow [3,18]:



The amounts of Fe and zeolite used for the large batch modification of Fe-eZ would result in a Fe loading about 60 mmol/kg, or 3 g/kg. At the As(III) and As(V) sorption capacity of 100 and 50 mg/kg, the amount of As sorption normalized to the mass of Fe would be about 3% and 1.5% for As(III) and As(V) adsorption, agreeing well for As(V) adsorption on amorphous iron oxide [3]. Thus, the enhanced As removal by Fe-eZ would be attributed to the formation of Fe oxyhydroxide on the zeolite surfaces that complexed with As(V) and As(III).

4. Conclusions

Removal of As from water can be achieved fairly effectively using Fe-eZ. The loading of Fe(III) on the zeolite could be up to 140 mmol/kg, while the uptake of As on Fe-eZ was as high as 100 mg/kg. Arsenic sorption on Fe-eZ followed second order kinetics with the initial rates of 1.4 and 3.6 mg/g h and the rate constants of 0.01 and 0.06 g/mg h for As(V) and As(III), respectively. Arsenic complexation with iron oxyhydroxide formed on zeolite surfaces would be attributed to its removal. The materials work better for water collected from acid mine drainage in which higher amount of dissolved Fe was present and work less favorable for water under extremely reduced condition that contains higher amount of dissolved organic matter.

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