Adsorption characteristics of As(V) on iron-coated zeolite

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ABSTRACT

The sorption characteristics of arsenic(As(V)) on iron-coated zeolite (ICZ) were investigated through batch and column studies. As(V) was completely removed within 30 min in a concentration of 2 mg/l, with a 100 g/l dose of ICZ. Optimum dose of ICZ was 33.3 g/l at a concentration of 20.12 mg/l and the effect of solution pH was negligible at a pH range of 3.0 < pH < 10.0. Langmuir Isotherm Model was suitable to explain the sorption characteristics of As(V) onto ICZ. The co-presence of sulfate ions inhibited sorption of As(V) because of competitive adsorption. The adsorption capacity of ICZ for As(V) was 0.68 mg/g. Based on the result, ICZ is a suitable material to treat the mine drainage or wastewater bearing As(V).

1. Introduction

Arsenic exists ubiquitously and it is well known that arsenic is toxic to humans [1]. Various minerals include arsenic, but arsenic contamination in groundwater is mainly caused by agricultural activities and industrial wastes [2]. Recently, arsenic contamination has come into the spotlight, because of its negative impact on humans and the environment [3]. As a result, the WHO and USEPA have strengthened standards against arsenic in drinking water at 10 ppb replacing the old standard of 50 ppb [4,5]. Although this standard has been implemented, arsenic poisoning has been on the increase. Arsenic is introduced into the human body through drinking water and food, causing lung, liver, kidney and bladder cancer [6,7].

Arsenic exists in both organic and inorganic forms in nature; inorganic arsenic is mostly found in natural water systems. Generally, inorganic arsenic has two different oxidation states, that is, trivalent and pentavalent, in natural aqueous systems [8]. The speciation of arsenic highly depends on solution pH. Pentavalent arsenic(As(V), arsenate) is stable in oxidative condition, while trivalent arsenic(As(III), arsenite) is stable in reductive condition [9]. Generally, inorganic arsenic is more toxic than organic arsenic, and As(III) is more toxic than As(V) [10]. In an aqueous system, heavy metals are easily removed by adsorption or pH adjustment while arsenic is not removed by pH control.

Adsorption, cation exchange, lime softening, reverse osmosis, coagulation and precipitation have been applied to remove arsenic from aqueous streams [11,12]. Among these technologies, adsorption technology is mainly used because it is very simple and cost effective [13]. Several sorbents for arsenic removal have been used including zero valent iron [14], activated alumina [15], red mud [16], coconut husk, rice bran and zeolite. Iron oxide has been a common sorbent for arsenic removal because of cost-effectiveness and high adsorption capacity [17].

In this study, sorption characteristics of arsenic on iron-coated zeolite, a new sorbent for arsenic, were investigated in an aqueous system. Adsorption kinetic and sorption capacity were studied in a batch test. The breakthrough of arsenic sorption on ICZ was evaluated in a column experiment.

2. Materials and methods

2.1. Materials

For the preparation of ICZ, 2000 g of zeolite (clinoptilolite) and 1 l of 10 wt% $FeCl_3$ solution were mixed, as well as, the pH of the mixture was adjusted to 10.0 using 0.1 M NaOH. The mixture was agitated in a rotary evaporator at 150 °C for 60 min. After a primary coating, the mixture was dried in a drying oven. The characterization of zeolite and ICZ was performed by using a scanning electronic

* Corresponding author. Tel.: +82 54 478 7635; fax: +82 54 478 7629.
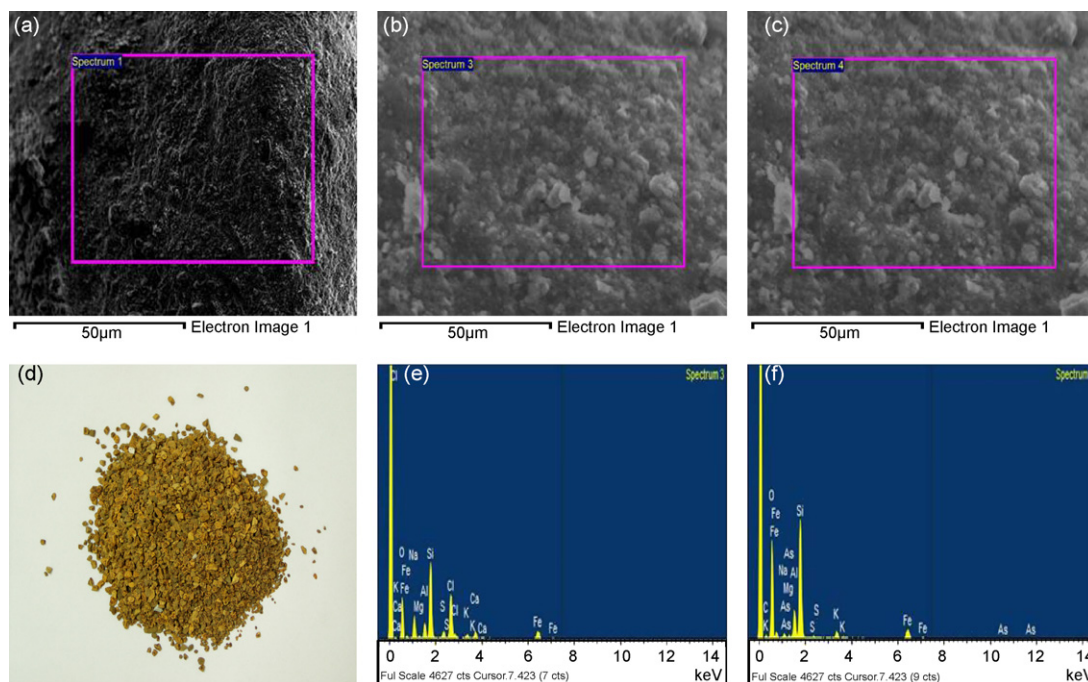E-mail address: kbaek@kumoh.ac.kr (K. Baek).

Fig. 1. SEM images and SEM-EDX. (a) Raw zeolite, (b) iron-coated zeolite, (c) iron-coated zeolite used for arsenic adsorption, (d) photo of iron-coated zeolite, (e) EDX of iron-coated zeolite, and (f) EDX of used zeolite.

microscope combined with X-ray energy dispersive spectrometer (SEM-EDX, S-3400N, Hitachi, Japan).

The stock solution of arsenic was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Sigma, USA) in deionized water. ICZ and solution mixtures were shaken in 50 ml polyethylene tubes by an over-head shaker. The pH of solution was adjusted using HCl and NaOH. Arsenic was analyzed by anodic stripping voltammetry (ASV, PDV6000, MTI, Australia).

2.2. Sorption kinetic study

The sorption kinetic study was carried out at a pH of 4.0 and 10.0. The initial concentration of arsenic was 2 mg/l and 0.01 M NaCl was used for adjustment of ionic strength. To investigate the effect of co-existing anions, sulfate was added to the arsenic solution. A mass of 3 g of ICZ were mixed with 30 ml of arsenic solution. The mixture was shaken with an over-head shaker for 24 h. At the desired time, interval samples were taken and centrifuged for 10 min at 3000 rpm.

2.3. Sorption isotherm study

A mass of 3.0 g of ICZ was mixed with 30 ml arsenic solution with various concentrations of As(V) in polyethylene tubes using an over-head shaker. After 12 h, the sample was taken and centrifuged, then the arsenic concentration in supernatant was analyzed using ASV.

2.4. Column experiment

Raw zeolite and ICZ were packed into a column that was 1.1 cm in inner diameter and 17 cm in height and fitted with glass wool at the bottom and top. An As(V) solution was continuously passed from the bottom of column at a constant rate (30 ml/h) at room temperature using a Masterflex L/S pump (Model No. 7524-45). The adsorption capacity of As(V) onto raw zeolite and ICZ was determined by evaluating breakthrough points.

3. Results and discussion

3.1. Characterization of iron-coated zeolite

The surface and chemical composition of zeolite and ICZ determined by the SEM-EDX analysis, is shown in Fig. 1 and Table 1. The major constituents of zeolite are silicate and alumina, and Fe_2O_3 content was 2.32 wt%. The superficial iron contents of raw zeolite and ICZ were 5507 and 22,266 mg/kg, respectively. Iron content of ICZ increased 4 times compared with raw zeolite. Fig. 1(a)–(c) show the surfaces of raw zeolite, iron-coated zeolite and used iron-coated zeolite, respectively. As shown in Fig. 1(b) and (c), ICZ and used ICZ surfaces contained rod shapes of iron oxide particles. SEM-EDX shows that the used ICZ contains arsenic on the surface. Except for the arsenic peak, the overall pattern of used ICZ is similar to that of fresh ICZ.

3.2. Adsorption study

3.2.1. Effect of adsorbent dose

The effect of the adsorbent dose on the removal of As(V) is shown in Fig. 2, which indicates that the removal efficiency of As(V) increased from 28% to 99.9% as the adsorbent dose increased from 10 to 100 g/l. The increase may be attributed to the increase in the adsorption sites which were provided by the surface area of ICZ. Beyond 33.3 g/l, the As(V) removal reached plateau values at an initial As(V) concentration of 20.12 mg/l. Even though the removal efficiency of arsenic above 33.3 g/l of ICZ was saturated at 2 mg/l of initial concentration of arsenic, an adsorbent dose of 100 g/l of ICZ was selected for all further experiments considering high contamination level.

Table 1
Chemical composition of the raw zeolite

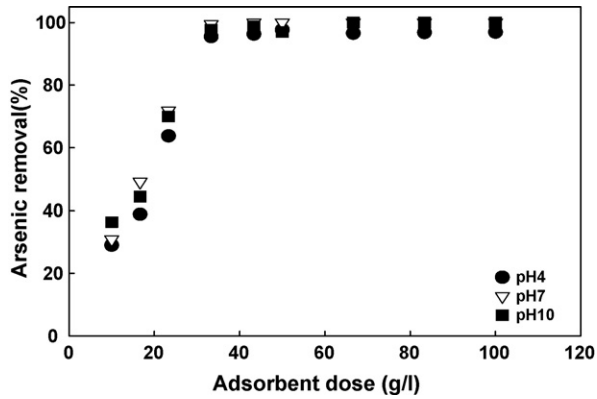|	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2
wt%	11.24	70.63	2.32	1.61	1.24	2.16	0.84	0.12	0.25

Fig. 2. The effect of adsorbent dose of ICZ on adsorption of As(V). Initial concentration of As(V) was 20.12 mg/l and mixing time was 6 h.
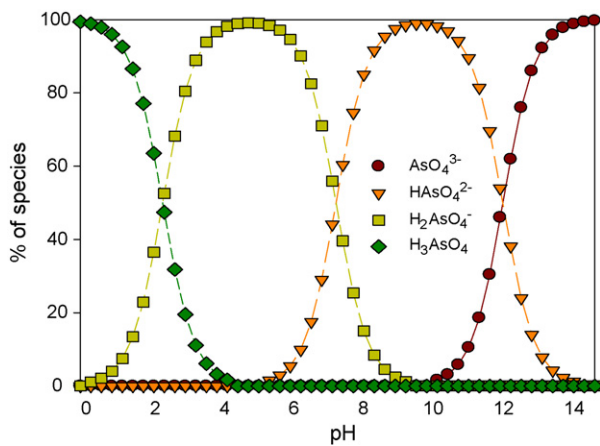

Fig. 3. The speciation of As(V) at various pH. (Calculated using MINTEQ.)

3.2.2. Effect of initial pH

The surface charge of ICZ is changed by deprotonation and protonation reactions of iron-hydroxide coated onto zeolite. Under acidic condition, surface charge becomes more positive, because of the protonation of the ICZ surface area, which provides more adsorption sites for arsenic. Also, As(V), that is, arsenate, is an oxyanion and the net valence of As(V) is affected by solution pH due to the protonation reaction of AsO_4^{3-} (Fig. 3). As a result, adsorption of As(V) highly depends on the solution pH. As shown in Fig. 4, the
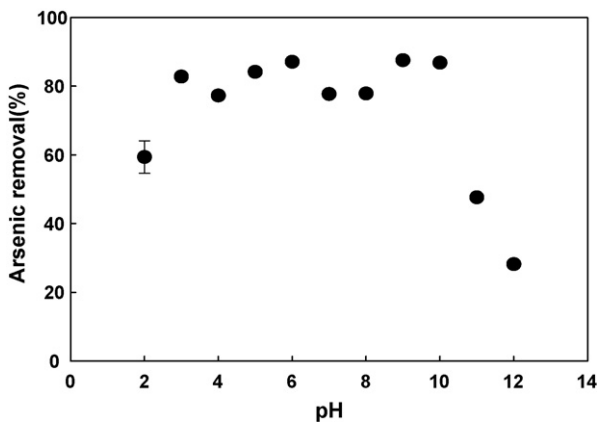

Fig. 4. The effect of solution pH on adsorption of As(V) onto ICZ. Initial concentration of As(V) was 10.24 mg/l, dose of ICZ was 10 g/l and mixing time was 6 h.
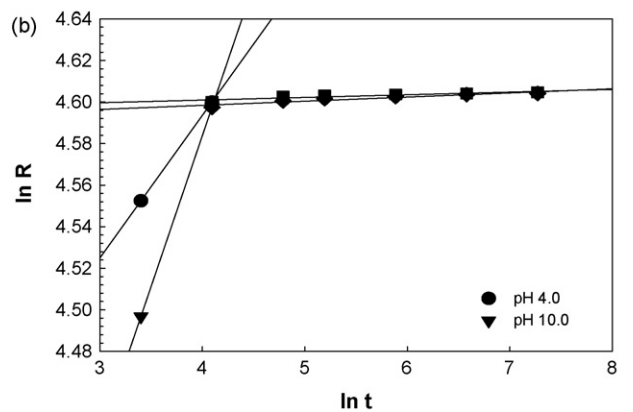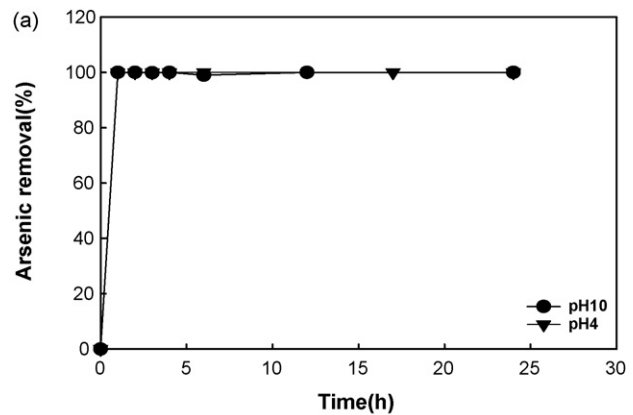

Fig. 5. Adsorption kinetics of As(V) onto ICZ. (a) Time course of As(V) removal and (b) linearized plot of adsorption kinetics of As(V) onto ICZ. Initial concentration of As(V) was 2.0 mg/l, 0.01 M NaCl was used to adjust ionic strength and dose of ICZ was 100 g/l.

effect of solution pH on the adsorption of As(V) onto ICZ was negligible at pH values of 3 < pH <10. At the strong alkaline condition (pH 12.0), the ICZ surface becomes negatively charged and electrostatic repulsion between ICZ and $[H_2AsO_4]^-$ resulted in a decrease of adsorption. At a strong acidic condition (pH 2.0), arsenate competed with hydrogen ions for the adsorption onto ICZ.

3.2.3. Adsorption kinetics

Fig. 5(a) shows adsorption kinetics of arsenic onto ICZ. A study of the adsorption kinetics shows a rapid uptake of As(V) within the first 30 min to achieve the equilibrium condition. Therefore, an optimum agitation time of 6 h was chosen for further experiment.

The adsorption kinetics may be expressed as,

$$R = k_t t^m$$

The equation can be expressed in linearized form as

$$\ln R = \ln k_t + m \ln t$$

where R is the As(V) concentration on ICZ (amount of As(V) adsorbed onto ICZ), t is the contact time (h) and k_t and m are the constants. A plot of $\ln R$ versus $\ln t$ shows that the sorption kinetics can be divided into two linear stages: (i) the first stage is the rapid removal phase and (ii) the second stage, where the removal reached a plateau indicating a steady state. In the first stage, the values of m were 0.07 and 0.15, respectively, for pH 4.0 and pH 10.0. For pore diffusion to be the rate limiting step, the value of m should have been 0.5 [18]. However, in the present study, the value was less than 0.5, which means that pore diffusion is not the rate limiting step (Fig. 5(b)). Therefore, the rate limiting step may be film

Table 2
Langmuir isotherm parameters and regression coefficients for adsorption of arsenic

pH	Sulfate	Q_{max} (mg/g)	R^2
4.0	400 mg/l	0.53	0.98
	0	0.68	0.94
7.0	400 mg/l	0.58	0.98
	0	0.60	0.99

diffusion. The overall pattern of adsorption kinetics at a pH of 4.0 was similar to that at pH 10.0.
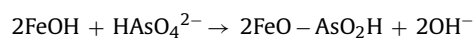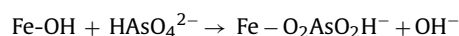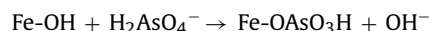
3.2.4. Sorption isotherm study

To evaluate the adsorption capacity of ICZ for As(V), and to investigate the characteristics of adsorption, the equilibrium adsorption isotherms are of fundamental importance. The Langmuir Isotherm Models were studied to determine the isotherm constants and regression coefficients of the adsorption experimental results. These models assume monolayer adsorption onto a homogeneous surface with a finite number of identical sites [19]. The Langmuir Isotherm Equation is,

$$q_e = \frac{Q_{max}K_aC_e}{1 + K_aC_e}$$

q_e (mg/g) is the adsorbed amount of arsenic by ICZ, Q_{max} is the maximum adsorbed amount, K_a is the Langmuir isotherm constant, and C_e (mg/s) is the equilibrium concentration.

The co-existence of sulfate decreased adsorption capacity of ICZ for arsenic, because arsenate ions competed with sulfate ions for the adsorption onto ICZ. The presence of sulfate reduced the adsorption capacity of ICZ for arsenate from 0.68 to 0.53 mg/g at a pH of 4.0 and from 0.60 to 0.58 mg/g at a pH of 7.0 (Table 2). Those adsorption capacities are fifteen times higher than those of iron oxide-coated sand [9]. Arsenic was removed by ICZ through the following mechanism:

$$Fe\text{-}OH + H_2AsO_4^- \rightarrow Fe\text{-}OAsO_3H + OH^-$$

$$Fe\text{-}OH + HAsO_4^{2-} \rightarrow Fe - O_2AsO_2H^- + OH^-$$

$$2FeOH + HAsO_4^{2-} \rightarrow 2FeO - AsO_2H + 2OH^-$$

The adsorption of As(V) onto ICZ occurred by ligand exchange reactions, and most of the hydroxide groups are involved in ligand exchange reactions. The adsorption of As(V) by iron-hydroxide resulted in the release of hydroxide. The cumulative hydroxide group release per amount of arsenic adsorbed was related with amount of arsenic adsorbed [20]. The amount of ferrihydrite on the surface of ICZ is proportional to the removal of arsenic. As shown in Fig. 6, the Langmuir Isotherm Model fits the experimental data well, because iron-hydroxide plays as an adsorption site for arsenic.

3.2.5. Column experiment

Fig. 7 shows the adsorption of arsenic onto ICZ in a column. The influent with As(V) concentration of 2.0 mg/l was continuously passed through a column, packed with 11.7 g ICZ, at a rate of 30 ml/h and at a pH of about 4.0. In a raw zeolite column (Fig. 7(a) and (b)), effluent concentration of arsenic reached the influent concentration immediately, because the raw zeolite did not have any adsorption capacity for arsenic. However, almost 100% removal of As(V) from the influent at initial dozens of fractions was obtained, while the breakthrough for As(V) concentration of 0.01 mg/l in the effluent occurred at about 300 bed volumes at the absence of sulfate and 250 bed volumes at the presence of sulfate (400 mg/l). The As(V) adsorption capacity was calculated to be
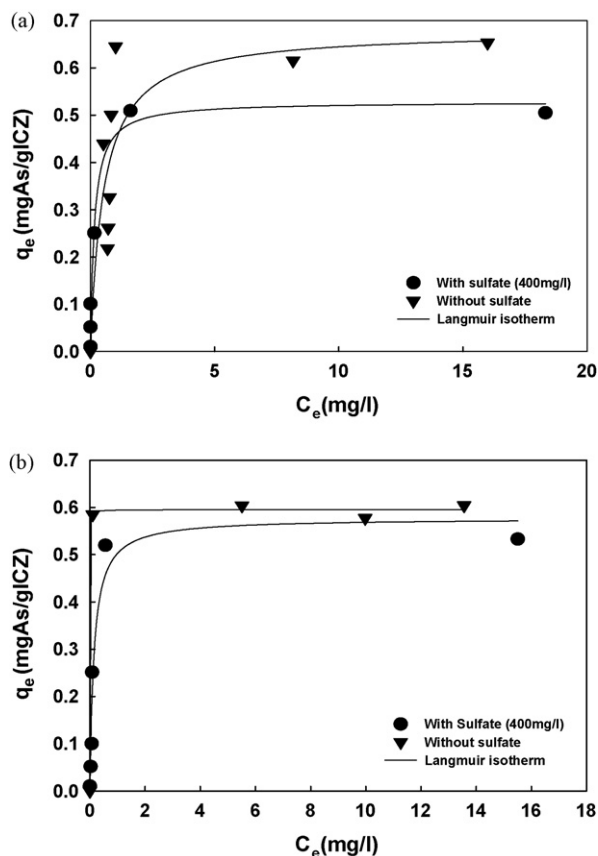

Fig. 6. Isotherms of As(V) onto ICZ. (a) At pH 4.0 and (b) at pH 7.0. Dose of ICZ was 100 g/l and mixing time was 12 h.
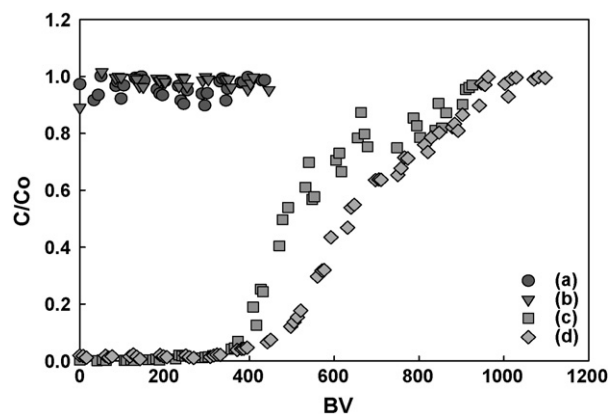

Fig. 7. Column experimental result of As(V) adsorption onto ICZ. (a) Raw zeolite with 400 mg/l sulfate, (b) raw zeolite without sulfate, (c) ICZ with 400 mg/l sulfate and (d) ICZ without sulfate. Initial concentration of As(V) was 2.0 mg/l.

0.69 mg/g in the absence of sulfate and 0.57 mg/g in the presence of sulfate. The capacities calculated in column experiments (Table 3) were similar to the capacities in the batch adsorption experiments (Table 2).

Table 3
Break trough points and adsorption capacity in column study

Adsorbent	Sulfate	Break through point	Adsorption capacity
Zeolite	400 mg/l	0 BV	0
Zeolite	0	0 BV	0
ICZ	400 mg/l	250 BV	0.58 mg/g
ICZ	0	300 BV	0.69 mg/g

4. Conclusion

In this study, adsorption characteristics of As(V) were studied under batch and column experiments. Arsenic was completely removed within 30 min at an initial concentration of 2.0 mg/l with 100 g/l of ICZ dose. The equilibrium data were well fitted to the Langmuir Isotherm Model. Adsorption capacity of ICZ in the absence of sulfate, co-anion, was higher than that in the presence of sulfate because SO_4^{2-} and arsenic were competitively adsorbed onto ICZ. The adsorption capacities in column experiments were similar to those in batch experiments.

Acknowledgement

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