Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded Shirasu-zeolite

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Abstract

The demand for effective and inexpensive adsorbents is to increase in response to the widespread recognition of the deleterious health effects of arsenic exposure through drinking water. A novel adsorbent, aluminum-loaded Shirasu-zeolite P_1 (Al-SZP$_1$), was prepared and employed for the adsorption and removal of arsenic(V) (As(V)) ion from aqueous system. The process of adsorption follows first-order kinetics and the adsorption behavior is fitted with a Freundlich isotherm. The adsorption of As(V) is slightly dependent on the initial pH over a wide range (3–10). Al-SZP$_1$ was found with a high As(V) adsorption ability, equivalent to that of activated alumina, and seems to be especially suitable for removal of As(V) in low concentration. The addition of arsenite, chloride, nitrate, sulfate, chromate, and acetate ions hardly affected the As(V) adsorption, whereas the co-existing phosphate greatly interfered with the adsorption. The adsorption mechanism is supposed as a ligand-exchange process between As(V) ions and the hydroxide groups present on the surface of Al-SZP$_1$. The adsorbed As(V) ions were desorbed effectively by a 40 mM NaOH solution. Continuous operation was demonstrated in a column packed with Al-SZP$_1$. The feasibility of this technique to practical utilization was also assessed by adsorption/desorption multiple cycles with in situ desorption/regeneration operation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic(V); Adsorption; Aluminum-loaded Shirasu-zeolite; Regeneration; Removal

1. Introduction

Arsenic is ubiquitous in the Earth's crust and ranks 20th among the elements in abundance. It is a carcinogen and toxic to man and other living organisms [1,2]. There will be an increase in the global cycling of arsenic due to the progressive industrialization of developing nations, which will pose potentially serious environmental problems throughout the world.

In Bangladesh, west Bengal region in India, Inner Mongolia region in China, Thai, and Taiwan, serious arsenic pollutions are running through. About 20 millions of people are suffering from arsenic poison. Also, 2–3% out of ca. 3000 wells that spread all over Japan showed excess values for arsenic over the Environmental Quality Standards for natural water (0.01 mg/l) (Environment Agency, 1993). Thus, it is urgently needed to develop some feasible techniques for arsenic removal.

Removal of arsenic is one of the most important areas of wastewater treatment. Usually, the requirements for a removal technique of arsenic from aqueous system are: (i) safe operation with respect to the maximum contaminant level, (ii) high efficiency, (iii) easy for application, and (iv) low cost.

The most common valence states of arsenic in water are oxidized (+V oxidation state, arsenate, arsenic(V) (As(V)) and reduced (+III oxidation state, arsenite, As(III)) forms. The former is less toxic than the latter and is a main species in natural waters [3]. Generally, As(V) is more prevalent in surface water while As(III) is more likely to occur in anaerobic ground waters. However, actual valence states depend on the redox environment in water systems and may vary from districts to districts. They may vary even from wells to wells. A total of 14.9% out of the ground water collected in 282 wells in Bangladesh was found to have arsenic concentration to a level above 0.5 mg/l, while the main species of it was determined as As(III) [4]. In another case, most arsenic in the ground water collected from two villages in Inner Mongolia of China was found to be As(V) with an average arsenic concentration of 0.4 mg/l [5].

Removal of As(III) from aqueous solutions is usually poor compared to that of As(V) by almost all of the technologies evaluated. It is because the predominant As(III) compound is neutral in charge, while the As(V) species are negatively charged in the pH range of 4–10. However, the achievement of enhanced As(III) removal is expected by converting As(III)–(V) through pre-oxidation.

Various treatment methods such as ion exchange, adsorption, ultrafiltration, reverse osmosis, and adsorption-coprecipitation by metals (predominately ferric chloride) followed by coagulation have been so far proposed and adopted for the removal of arsenic from aqueous media. In general, the removal of arsenic by precipitation is most effective for small quantities of highly concentrated arsenic waste liquid. The most common arsenic removal method is precipitation-coagulation with lime and iron(III) salts followed by adsorption onto the resulting iron(III) hydroxide flocs [6]. However, a problem with this technique is the safe separation, filtration, and the handling of the contaminated coagulant sludge. The cost effectiveness of precipitation is diminished when disposing of large quantities of low concentration arsenic wastes.

As it is easy to remove the adsorbent from aqueous media after treatment, adsorption technique is generally considered to be a promising method and has been studied for arsenic removal as well. Adsorption is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. So far, various adsorbents for arsenic removal have been developed which include metal-loaded coral limestone [7,8], hematite and feldspar [9], sandy soils [10], activated carbon [11,12], activated alumina [13,14], lanthanum-loaded silica gel [15], and hydrous zirconium oxide [16], etc. But for most of them, there is a problem in terms of either in efficiency (especially for the former four) or in cost (especially for the later three). New

techniques are required that can effectively reduce arsenic concentration to environmentally acceptable level at affordable costs.

A new adsorbent, aluminum-loaded Shirasu-zeolite P_1 (Al-SZP$_1$), was developed for adsorption and removal of As(V) from aqueous solution, which has been reported briefly in our previous paper [17]. Al-SZP$_1$ was prepared by treating a P_1 type Shirasu-zeolite (SZP$_1$) with aluminum sulfate solution. Shirasu is of volcanic origin and is located in southern Kyushu area of Japan in large quantities, and SZP$_1$ is easily synthesized by one-step reaction from Shirasu. By use of Al-SZP$_1$, removal of arsenate, phosphate, and fluoride ions was investigated [18]. Al-SZP$_1$ was found effective to the adsorption of not only As(V), but also phosphate and fluoride ions.

In the present work, using the Al-SZP$_1$, studies are focused on the adsorption of As(V) from natural aqueous system like drinking water and are conducted in detail in both batch and continuous experiments. The Al-SZP$_1$ was found to work as an excellent adsorbent for As(V).

2. Materials and methods

SZP$_1$ was donated by Sankei Kagaku Co., Ltd. (Kagoshima, Japan). The composition of SZP$_1$ is $Na_2O \cdot Al_2O_3 \cdot 3.3SiO_2 \cdot 4.3H_2O$ to $Na_2O \cdot Al_2O_3 \cdot 5.3SiO_2 \cdot 5.7H_2O$; while the average particle size, effective pore size, and specific surface area are 35–45 μm, 0.35 nm, and ca. 15.6 m^2/g (measured in our laboratory), respectively.

The preparation of Al-SZP$_1$ was carried out as shown in our previous work [17]. The specific surface areas of SZP$_1$ and Al-SZP$_1$ were determined by Micromeritics Gemini 2375. The morphology of the microparticles of SZP$_1$ and Al-SZP$_1$ was observed by scanning electronic microscopy (SEM) (Hitachi H-7010).

Analytical-reagent grade chemicals (Wako Pure Chemical Industries) were used for the preparation of all solutions with deionized water obtained from an Organo G-10B cartridge. Stock solutions of As(V) ion (13.4 mM), As(III) ion (10 mM), nitrate ion (10 mM), chloride ion (10 mM), sulfate ion (10 mM), acetate ion (10 mM), and phosphate ion (10 mM) were prepared by dissolving disodium hydrogen arsenate ($Na_2HAsO4 \cdot 7H_2O$), $NaAsO_2$, $NaNO_3$, NaCl, Na_2SO_4, CH_3COONH_4, K_2CrO_4, and $Na_2HPO_4 \cdot 12H_2O$ in deionized water, respectively. These solutions were further diluted to suitable concentrations on the day of use.

2.1. Batch experiment

An aqueous solution (20 ml) containing a suitable concentration of As(V) ion was shaken with a suitable amount of adsorbent at 24 °C in an air-conditioned room for a definite period. A suitable volume of acid (hydrochloric acid) or base (sodium hydroxide) solution was added to adjust pH that was measured with a digital pH meter (TOA Electronics Ltd., HM-35 V). After removal of the adsorbent by centrifugation, the concentration of the anion remaining in the supernatant was determined by atomic absorption spectrophotometry using a Nippon Jerrel Ash AA-890 with FLA-1000 flameless atomizer unit. Kinetic study was carried out at different intervals of time according to the above procedure. The adsorption isotherms

were studied with varying doses of adsorbent at a fixed initial concentration of As(V). The adsorption density, which is given in mmol As(V)/g Al-SZP$_1$, was calculated from the residual concentrations of As(V), the known initial concentrations of As(V) ion, and the amount of used Al-SZP$_1$(g). Freundlich parameters were obtained by linear regression of the logarithm of the data.

To investigate the possibility of recycle of the adsorbent, Al-SZP$_1$ desorption and regeneration process was also studied. Desorption tests were carried out using sodium hydroxide or hydrochloride acid solution in batch operation. Al-SZP$_1$ pre-adsorbed a known amount of As(V) ions was added to desorption solutions (HCl or NaOH) in various concentrations. The mixture was shaken for 2 h followed by a centrifugation for separation. The desorption efficiency was evaluated by determination of As(V) concentration in the supernatant. After desorption, Al-SZP$_1$ was regenerated with loading treatment using aluminum sulfate solution under the same conditions as those in the original loading treatment. The regenerated Al-SZP$_1$ was reused again, and thus yielded adsorption capacity was compared with that by the virgin Al-SZP$_1$. The adsorption capacity for the Al-SZP$_1$ without regeneration was also investigated for comparison.

2.2. Column experiment

Al-SZP$_1$ was packed into a column that was 1 cm in inner diameter by 44 cm in height and fitted with a sintered glass filter at the bottom. An As(V) aqueous solution was continuously passed through the column at a constant rate at room temperature (24 °C). By use of a super fraction collector (Advantec Toyo, SF-2120), the fraction of effluent was collected at a definite interval time in 8 ml glass tubes for the analysis of As(V).

The adsorption capacity of As(V) ions onto Al-SZP$_1$ was determined by performing breakthrough studies. In situ desorption and regeneration experiments were carried out using a caustic soda solution in optimal concentration or by aluminum loading treatment, respectively. Multiple adsorption/desorption cycles were also executed to investigate storage stability and operational stability for As(V) ions adsorption onto Al-SZP$_1$.

3. Results and discussion

3.1. Kinetic study

Adsorption of As(V) onto Al-SZP$_1$ was found time dependent as seen in Fig. 1a. An aqueous solution (20 ml) of 0.13 mM As(V) was shaken with 0.1, 0.05, 0.025 g of Al-SZP$_1$ at 24 °C, respectively. It was revealed that the adsorption was rapid in the first 30 min and then slowed considerably as the reaction approached equilibrium. The adsorption rate was found to accelerate with an increase in the amount of Al-SZP$_1$. The adsorption rate was described by a first-order equation, as demonstrated by the results in Fig. 1b, plotted in a semilogarithmic diagram. The rate equation can be expressed for As(V) ions as follows:

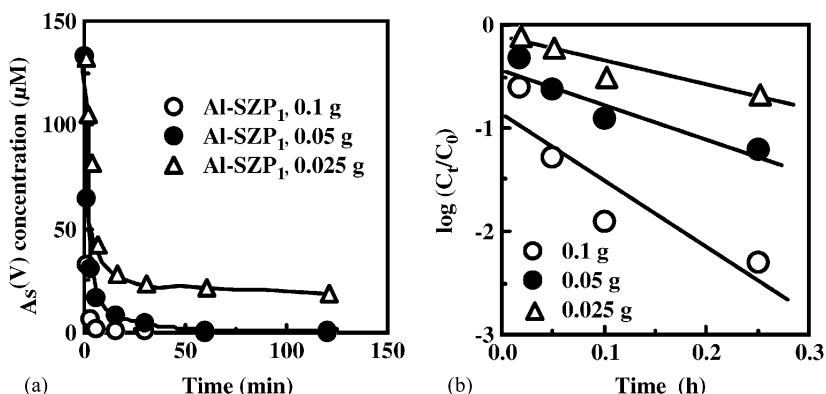$$\log\left(\frac{C_t}{C_0}\right) = -kt + b \tag{1}$$

Fig. 1. Time dependence of As(V) ion adsorption onto Al-SZP$_1$. (a) Time courses; (b) kinetic study. As(V) initial concentration, 0.13 mM; 20 ml; Al-SZP$_1$, 0.1, 0.05 and 0.025 g, respectively.

where C_0 and C_t are initial As(V) ions concentration and concentration at time t, respectively, t the time (h), and k the rate constant. The values for K, calculated from the slope of the respective linear plot of $\log(C_t/C_0)$ versus t are 6.4, 3.4, 2.3 h^{-1}, respectively. This rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy.

3.2. Adsorption capacity and comparison with some other adsorbents

To investigate the adsorption capacity, an aqueous solution of 1.3 mM As(V) was shaken with the adsorbent Al-SZP$_1$ varied from 0.05–0.75 g at 24 °C for 16 h. After removal of the adsorbent, the As(V) concentration was determined. Furthermore, the adsorption ability of adsorbent Al-SZP$_1'$, Al-SZP$_1$ loaded with aluminum sulfate solution once again, was also investigated at the same conditions as described above.

It was found from the results that the adsorption percentage increased with an increase in the amount of Al-SZP$_1$ up to 0.35 g; beyond this dosage the adsorption percentages were almost constant. The data for the dosages from 0.05–0.35 g were analyzed in the light of the Freundlich mode of adsorption. The Freundlich isotherm was tested in the following linearized form:

$$\log\left(\frac{x}{m}\right) = \log K + \left(\frac{1}{n}\right)\log C_e \tag{2}$$

where x/m is the amount of As(V) ions adsorbed at equilibrium (mmol/g), C_e the equilibrium concentration of As(V) in solution (mM), K and $1/n$ the Freundlich constants.

As shown in Fig. 2, the plots of $\log(x/m)$ versus $\log C_e$ give straight lines for both Al-SZP$_1$ and Al-SZP$_1'$, which supports the applicability of the Freundlich isotherm model to the present study. The values of Freundlich constants K and $1/n$ represent the adsorption capacity (mmol/g) and adsorption intensity of these adsorbents, respectively. The constants K and $1/n$ were evaluated from the intercept and the slope of the straight lines using a least-square
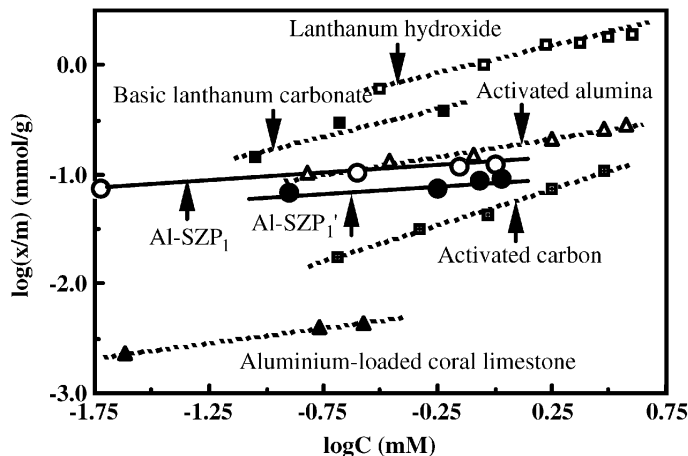
Fig. 2. Adsorption isotherms of As(V) onto Al-SZP$_1$, Al-SZP$_1'$ and several existent adsorbents. For Al-SZP$_1$ and Al-SZP$_1'$, As(V) initial concentration, 1.3 mM, 20 ml; Al-SZP$_1$, 0.05–0.35 g; shaking time, 16 h.

fit program and were found to be 0.122, 0.088 mmol/g and 0.13, 0.14, for Al-SZP$_1$ and Al-SZP$_1'$, respectively. Theses results revealed that the adsorption capacity for As(V) was reduced by the multiloading treatment of aluminum.

For comparison with that of Al-SZP$_1$, the Freundlich isotherms for several existent adsorbents were cited and also illustrated in the Fig. 2 [19]. It is apparently that both lanthanum hydroxide and basic lanthanum carbonate are of higher adsorption capacity than Al-SZP$_1$. But the former two adsorbents are more costly. Al-SZP$_1$ presented much higher adsorption ability than activated carbon and aluminum-loaded coral. The adsorption capacities of Al-SZP$_1$ and activated alumina cited here seem well matched while Al-SZP$_1$ appears more suitable for adsorption of As(V) in low concentration as in drinking water.

Moreover, as described in our preliminary investigation [17], Al-SZP$_1$ shown apparently higher adsorption capacity than an activated alumina (300 mesh, Wako Pure Chemical Industries) under the pH of the adsorption system without adjustment, which may be due to the higher pH values in the later system than in the former system. Compared to the basic pH natured activated alumina, the weak acidic pH natured Al-SZP$_1$ presented another practical benefit, that is, Al-SZP$_1$ can be effectively employed in As(V) adsorption from aqueous solution without pH adjustment. In consideration of adsorption capacity, actual feasibility, and cost, Al-SZP$_1$ appears to be superior to activated alumina and a very suitable adsorbent for As(V) adsorption.

3.3. Effect of pH on As(V) adsorption

The dependence of removal percentage for As(V) upon pH of the aqueous solution is shown in Fig. 3 by using two dosages of Al-SZP$_1$. The adsorption by Al-SZP$_1$ is found slightly dependent on the initial pH in the range 3–10.
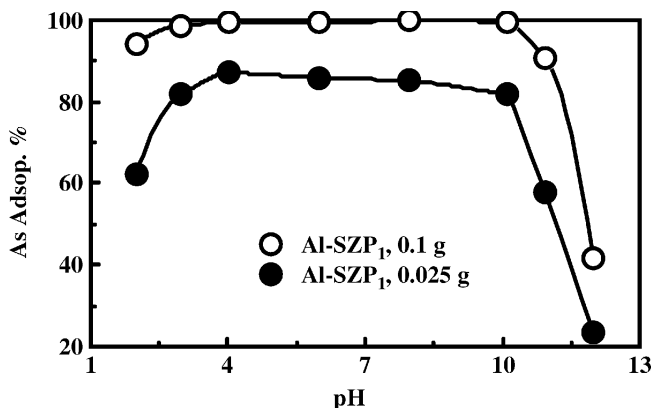
Fig. 3. The dependence of As(V) removal percentage upon pH of the aqueous solution. As(V) initial concentration, 0.13 mM, 20 ml; Al-SZP$_1$, 0.1 and 0.025 g, respectively; shaking time, 16 h.

It has been reported that at pH range between 3 and 6, As(V) ion occurs mainly in the form of $H_2AsO_4^-$, while a divalent anion $HAsO_4^{2-}$ dominates at higher pH values (between 8 and 10.5); in the intermediate region, i.e. at pH range between 6 and 8, both species co-exist [20]. It is evident that both species of $H_2AsO_4^-$ and $HAsO_4^{2-}$ can be effectively adsorbed by Al-SZP$_1$. Compared with some other adsorbents such as La(III)- and Y(III)-impregnated alumina (optimum pH range 6–8) [21] and molybdate-impregnated chitosan beads (optimum pH range from 2–4) [22], the adsorption for As(V) by use of Al-SZP$_1$ is of a wide optimum pH range, which should be of great advantage for practical operation.

3.4. Adsorption mechanism study

It is suggested that the As(V) adsorption mostly occurs at active sites on aluminum species (aluminum hydroxide) deposited on the surface and/or in the cavity of SZP$_1$ by loading treatment. The As(V) adsorption is enhanced with increasing the amount of these active sites which is dependent on the effective surface area of the bound aluminum species. As shown in Table 1, by using the Al-SZP$_1$ loaded by aluminum sulfate solution of 7.3 mM, the As(V) adsorption increases abruptly from 4.0 to 99% although its specific surface area decreases from 16.6 to 9.3 m^2/g, which infers that the effective specific surface area (specific surface area effective to As(V) adsorption) actually increased with this loading treatment. However, when the Al-SZP$_1$ is loaded once again, the specific surface area reduces significantly as being observed in Table 1 (from 9.3 to 3.8 m^2/g), which leads to the drop of the As(V) adsorption capacity (as shown in Table 1 and Fig. 2). The significant decrease of effective specific surface area for Al-SZP$_1'$ is probably due to the clogging of the micropores by the excess deposit of the bound aluminum species.

Fig. 4 shows the SEM micrographs for SZP$_1$washed by deionized water and sodium nitrate solution (A), Al-SZP$_1$ loaded by 7.3 mM aluminum sulfate solution (B), and Al-SZP$_1$ loaded by 7.3 mM aluminum sulfate solution twice (C), respectively. It is evident that there are many microcavities in the sample (A), and some of them remained in the sample (B),

Table 1
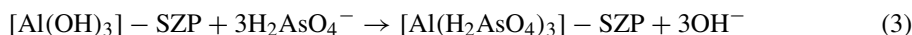As(V) adsorption percentages[a] and specific surface areas of adsorbents[b]

	Aluminum sulfate concentration in the loading solution (mM)					
	0.0	1.5	2.9	7.3		8.8
				Loaded once Al-SZP$_1$	Loaded twice Al-SZP$_1'$	
As(V) adsorption percentages (%)	4	52	91	99	93	97
Specific surface area (m^2/g)	16.6	10.3	9.8	9.3	3.8	8.7

[a] The adsorption test was performed under conditions of As(V) initial concentration, 0.13 mM; 20 ml; adsorbent, 0.05 g; shaking time, 16 h.
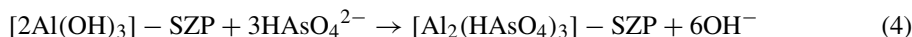
[b] The specific surface area of untreated SZP$_1$ was 15.6 (m^2/g).

but almost all of them disappeared in the sample (C), which responds to the specific surface area decreases.

It is proposed that the adsorption of As(V) ion onto the Al-SZP$_1$ proceeds from the formation of aluminum hydroxide on the surface of the Al-SZP$_1$, followed by the replacement of the hydroxide anion by the As(V) ion in aqueous media, which can be described as follows:

$$[Al(OH)_3] - SZP + 3H_2AsO_4^{-} \rightarrow [Al(H_2AsO_4)_3] - SZP + 3OH^{-} \tag{3}$$

and/or

$$[2Al(OH)_3] - SZP + 3HAsO_4^{2-} \rightarrow [Al_2(HAsO_4)_3] - SZP + 6OH^{-} \tag{4}$$

Similar mechanisms have been reported in the adsorption of As(V) by a lanthanum-loaded silica gel [15] and that of phosphate by an aluminum-loaded alumina [23].

It should be pointed out, that the Al(OH)$_3$ given here is just an example of aluminum species present on the surface of the Al-SZP$_1$, while some other aluminum species, including
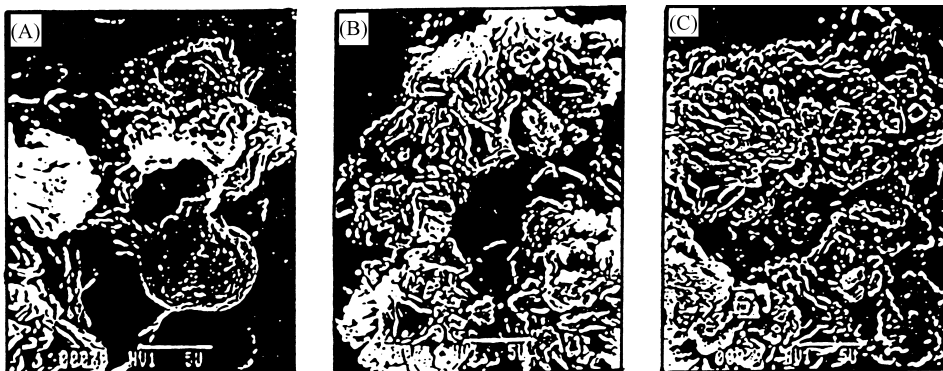

Fig. 4. SEM micrographs of SZP$_1$, Al-SZP$_1$, and Al-SZP$_1'$. (A) SZP$_1$ treated by deionized water and 0.1 M NaNO$_3$ solution; (B) Al-SZP$_1$, SZP$_1$ loaded with 7.3 mM aluminum sulfate solution; (C) Al-SZP$_1'$, Al-SZP$_1$ loaded with 7.3 mM aluminum sulfate solution once again.

several polynuclear hydrolysis products, such as $AlOH^{2+}$, $Al(OH)_2^+$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al(OH)_4^-$, etc. may also emerge in the adsorption system [24].

As described in our previous work [17], the Al-SZP_1 was prepared under the conditions of loading treatment with 7.3 mM aluminum sulfate solution as well as of pH values (approximately 4) in the loading. As the hydrolysis products of $Al(III)$, both Al^{3+} and the polynuclear species of $Al(III)$ may exist under these conditions. Therefore, it is supposed that aluminum was loaded by either cation exchange of Al^{3+} for cations in SZP_1 or deposition of the polynuclear species onto the surface of SZP_1. When the Al-SZP_1 prepared is subjected to $As(V)$ solution as an adsorbent, $Al(OH)_3$ tends to be the main species on its surface since the adsorption system is generally of neutral pH. Thus, $As(V)$ adsorption will proceed subject to Eqs. (3) and (4).

$As(V)$ adsorption efficiency depends on pH levels in solutions as shown in Fig. 3. In acidic pH range, $AlOH^{2+}$, $Al(OH)_2^+$, and $Al_{13}O_4(OH)_{24}^{7+}$ seem to be the predominant aluminum species present on the surface of Al-SZP_1. Consequently, a coulombic attraction can readily take place in conjunction with specific chemical adsorption due to an exchange reaction between $As(V)$ ions and hydroxide ions as Eq. (5), which attributed to the enhanced adsorption. The adsorption reaction will proceed as Eqs. (3) and (4) along with an increase in pH values. An increase of pH will cause an increase in hydroxide ions in the systems and cause the Eqs. (3) and (4) equilibrium move toward the left, thus results in a reduced $As(V)$ adsorption. In alkaline pH range, $Al(OH)_4^-$ is the prevalent species on the surface of SZP_1. The surface of the adsorbent becomes negative and the adsorption is depressed significantly due to coulombic repulsions. The enhanced decrease in adsorption in the extremely alkaline pH range may be highly competitive nature of the hydroxyl anions.

$$[Al_{13}O_4(OH)_{24}^{7+}] - SZP + xH_2AsO_4^- \rightarrow [Al_{13}O_4(OH)_{24-x}(H_2AsO_4)_x^{7+}]$$
$$-SZP + xOH^- \qquad (5)$$
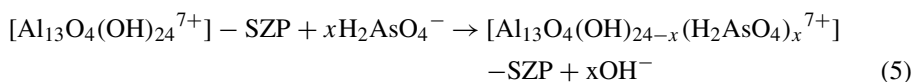
3.5. Influence of coexisting anions upon the adsorption

Fig. 5a shows the influence of adding coexisting anions upon the adsorption capacity of $As(V)$, which was tested by batch operation at various initial molar ratios (IMR) of these anions to $As(V)$ ions. Two $As(V)$ solutions with initial concentrations of 0.09 and 0.27 mM were used for phosphate ion, and only 0.27 mM $As(V)$ solution for the other anions. The IMR varied between 0 (no coexisting anions) and 20. The addition of $As(III)$, chloride, nitrate, sulfate, chromate, and acetate ions hardly affected the $As(V)$ adsorption, while the adsorption was significantly depressed by the addition of phosphate ion.

It was found that $As(V)$ adsorption density decreases with the IMR of phosphate ion to $As(V)$ ion in a hyperbolic dependence. A linearization is plotted in Fig. 5b by using the ratio of Q_0 to Q as ordinate parameter. Q_0 and Q are the adsorption densities without and with phosphate added, respectively. The linearization is quite good, while the gradients are 0.61 and 0.83 for $As(V)$ in initial concentrations of 0.09 and 0.27 mM, respectively. Both of the gradient values are <1, which implies that the adsorption of phosphate is lower than that of $As(V)$. However, as a possible major water constituent in some water systems, coexisting
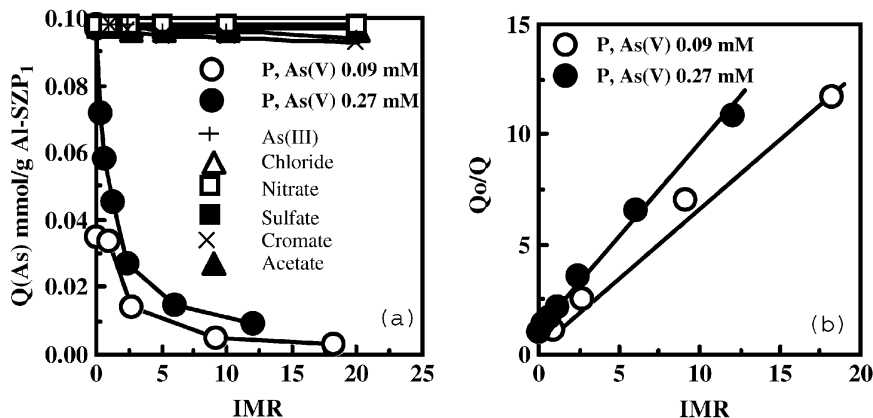
Fig. 5. Competition of coexisting anions on As(V) ion onto Al-SZP$_1$. (a) As (V) adsorption capacity Q(As) at different initial molar ratios (IMR) of coexisting anions to As(V) ion. Phosphate ion (P), As(III) ion, chloride ion, nitrate ion, sulfate ion, chromate ion, and acetate ion for As(V) initial concentration, 0.27 mM, 20 ml; and phosphate ion (P) for As(V) initial concentration, 0.09 mM, 20 ml; Al-SZP$_1$, 0.05 g; shaking time, 16 h. (b) Linearized plot of the ratios of adsorption capacities vs. IMR.

phosphate ions at high levels may compete strongly for adsorption sites with As(V) ions, resulting in a substantial reduction of As(V) removal.

3.6. Desorption of As(V) ions and regeneration of Al-SZP$_1$

As illustrated in Fig. 3, low adsorption for As(V) was presented in extremely pH range especially in strong alkaline pH, which implies that adsorbed As(V) ion can be desorbed from Al-SZP$_1$ by both acidic and alkaline media. Therefore, desorption tests were carried out using sodium hydroxide and hydrochloride acid solution in batch operation. As demonstrated in Table 2, 0.04 M NaOH appears to be the most suitable desorption agent. After desorption operation, the adsorption percentage of As(V) onto the Al-SZP$_1$ was reduced to ca. 71%, which may be due to partial dissolution of the aluminum precipitated

Table 2
Desorption and regeneration of Al-SZP$_1$[a]

	Desorption agent						
	NaOH (M)				HCl (M)		
	0.0	0.04	0.1	0.25	0.01	0.04	0.1
Desorption %	42	91	97	99	50	87	98
Adsorption % after deposition	45	71	30	18	42	25	11
Adsorption % after desorption and regeneration	53	94	92	84	51	85	81

[a] The adsorption conditions, Al-SZP$_1$, 0.05 g; As(V), 0.13 mM, 20 ml; 16 h; the adsorption % for the virgin A1-SZP$_1$ was ca. 99%; desorption agent, 10 ml, 2 h.
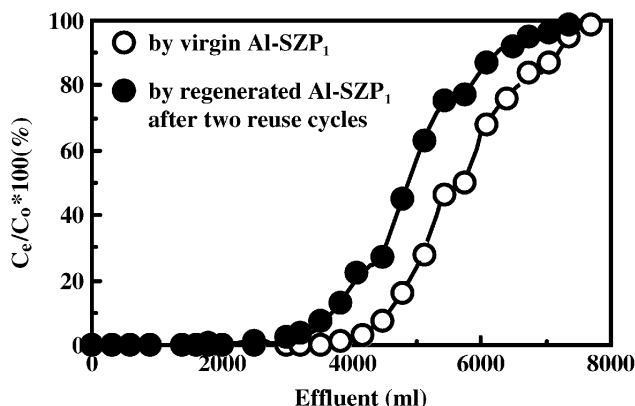
Fig. 6. Column experiment for the removal of As(V) by virgin Al-SZP$_1$ or Al-SZP$_1$ after two adsorption/desorption cycles. Adsorption condition: C_0, As(V) initial concentration, 6.7 μM; C_e, As(V) concentration in effluent, μM; Al-SZP$_1$, 0.5 g; flow rate, 0.5 ml/min; desorption condition: 40 mM NaOH solution, 165 ml; flow rate, 1.0 ml/min; regeneration condition: 7.3 mM aluminum sulfate solution 50 ml; flow rate, 0.1 ml/min.

on the surface of Al-SZP$_1$. However, the adsorption capacity of Al-SZP$_1$ was favorably restored to 94% by regeneration operation, that is, loaded again with aluminum sulfate solution.

3.7. Column experiment

Column operation of As(V) adsorption with Al-SZP$_1$ was performed. The influent with As(V) concentration of 6.7 μM was continuously passed through a column packed with 0.5 g Al-SZP$_1$ at a rate of 0.5 ml/min in the pH about 7.3. The breakthrough curve for As(V) was shown in Fig. 6. Almost 100% removal of As(V) from the influents at initial dozens of fractions was obtained, while the breakthrough for As(V) concentration of 0.13 μM (0.01 mg/l) in the effluents occurred at about 3200 ml. The As(V) adsorption capacity was calculated to be 75 μmol/g.

After complete saturation ($C_e/C_0 = 1$, influent volume, 7700 ml), the column was desorbed by 0.04 M NaOH solution at a flow rate of 1.0 ml/min. As(V) concentration in effluent was also determined. Recovery of As(V) ca. 98% was obtained by desorption with about 165 ml NaOH solution. Being washed with deionized water, the column was fed 50 ml of 7.3 mM aluminum sulfate solution for Al-SZP$_1$ regeneration. The adsorption test for the regenerated Al-SZP$_1$ was performed as the same procedure as the above for the virgin Al-SZP$_1$. After two adsorption/desorption cycles, the third time adsorption breakthrough curve was also demonstrated in Fig. 6. The adsorption capacity was found to be 64 μmol/g, which means ca. 85% of the adsorption capacity remained after two reuse cycles.

For As(V) actually removal process, a two-column alternative operation technology with adsorption/desorption/regeneration multiple cycle should be an alternative approach. However, since the Al-SZP$_1$ is very cheap, after being saturated with As(V), it can be disposed of directly or via stabilized with cement-mortar.

4. Conclusions

This study shows that Al-SZP$_1$ is an effective adsorbent for the removal of As(V) from aqueous systems like drinking water. As(V) ion adsorption on Al-SZP$_1$ follows first-order kinetics and the adsorption mode is of a Freundlich isothermal nature. The adsorption of As(V) is just slightly dependent on the initial pH over a wide range (3–10) and the Al-SZP$_1$ can be directly and effectively employed to common water systems without pH adjustment. Al-SZP$_1$ presented a quite high As(V) adsorption ability, equivalent or superior to that of activated alumina, and seems to be especially suitable for removal of As(V) in low concentration. Al-SZP$_1$ was quite selective towards As(V). The coexisting anions, except phosphate, hardly interfered with the adsorption of As(V) ions. The adsorbed As(V) ions were effectively desorbed by 40 mM NaOH solution and Al-SZP$_1$ was reused successfully after regeneration. In column tests, about 85% of the adsorption capacity was found remained after two adsorption/desorption/regeneration cycles. The easy availability of this adsorbent, fast adsorption rate, excellent adsorption capacity, wide optimum pH range, and sludge-free operation are expected to cut down the operating costs and render this removal technique attractive.

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