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Abstract: Orange waste has been chemically modified and loaded with lanthanum(III) and/or cerium(III) to examine its adsorption behavior to both As(V) and As(III). Arsenate removal was found to be favored over a pH range of $6 \sim 9.5$ while arsenite removal took place at pH values ranging from 9 to 11. The maximum sorption capacity of the gel for As(III) removal was evaluated as 43 mg/g, while that for As(V) was 42 mg/g. Column-mode tests using the La(III)-loaded gel confirmed a complete removal of As(V). A reasonably high adsorption potential within the design criteria makes the present gel an alternative choice for arsenic removal.

Keywords: Adsorption; Arsenic; Ligand substitution; Orange waste gel

INTRODUCTION

Arsenic, a toxic element, is known to be a risk to aquatic flora and fauna and human health even in relatively low concentration. It is the twentieth most abundant element in the earth's crust and, thus, it is widely distributed in the environment; especially as arsenopyrite or as metal arsenates (1). It is introduced into water through natural sources (1) e.g. volcanic emissions, dissolution of mineral ores, atmospheric deposition etc. as well as through anthropogenic sources (2) e.g. non-ferrous smelting, petroleum-refining, fossil fuel power plants and so forth. Naturally occurring arsenic

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is of great concern in some regions of Bangladesh, India, and Nepal, where hazardous concentrations of arsenic have appeared as a result of strong water-rock interactions and the physical and geochemical conditions for arsenic mobilization in aquifers (3). In water it is commonly found in inorganic species such as trivalent arsenite (predominant in groundwater) or pentavalent arsenate (predominant in well-oxygenated water), while organic arsenic species are rarely quantitatively important. Since 1993, the World Health Organization (WHO) has recommended a maximum contaminant level for arsenic (10 μg/l) in drinking water but many countries have retained the earlier WHO guideline of 50 μg/l including Bangladesh, India, and China (4,5). Therefore, processes to remove excess arsenic from drinking water are urgently required.

Numerous treatment techniques such as co-precipitation, liquid-liquid extraction, ion exchange, ultrafiltration, adsorption etc. have been so far proposed and employed for arsenic removal. A conventional approach for arsenic removal from an aqueous system is often by coprecipitation-coagulation with lime and ferric salts followed by adsorption onto the resulting ferric hydroxide flocs. However, a problem with this technique is the safe separation, and handling of the contaminated sludge. Anion exchangers are also very commonly used but they have low selectivity in the presence of other competing anions (6). Adsorption has evolved as a common treatment technique for removing arsenic to low concentration in water from which it cannot be removed by other techniques. Since adsorption with resins is expensive, hence improved, tailor-made, and inexpensive adsorbents are needed to cope with the current problem of arsenic removal. At this point adsorption of arsenic using natural products and biomass has emerged as an option for developing economic and eco-friendly wastewater treatment processes. Although a number of biological materials have been tested for removing toxic ions over the last two decades, only a limited number of studies have been made on the use of adsorbents obtained from biological sources e.g., bio-char (5), methylated yeast biomass (7), fungal biomass (8), chicken feathers (9) for the removal of arsenic. We have already investigated the binding capacity of orange waste gel for heavy metals (10).

Attention has already been paid to adsorption based on ligand substitution with metal loaded adsorbents in place of the conventional methods. Loaded metal cations with high positive charges can eventually uptake oxoanions such as arsenate, arsenite (11,12), phosphate (13), and fluoride (14) according to a ligand exchange mechanism. In previous work (15), we found that Fe(III)-loaded orange waste gel can effectively remove not only arsenate but also arsenite, which was verified in tests using actual mine water containing a high concentration of arsenic. Recently, rare earth elements such as lanthanum, yttrium (16), and cerium (17), which show specific affinity for arsenate, phosphate, fluoride, and selenite ions, have been found to be effective for the removal of such hazardous anions from aqueous solution. Therefore, our aim was to develop adsorbents by loading lanthanum(III) and/or cerium(III) onto orange waste, an agricultural by-product, and to investigate and evaluate the adsorption characteristics for arsenic by means of batch as well as column methods in the present work.

MATERIALS AND METHOD

Materials

All reagents and chemicals used in this study were of analytical grade and used without further purification. Arsenate and arsenite stock solutions (13.33 mmol/l) were prepared from sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) and arsenic trioxide (As_2O_3), respectively, by dissolution in deionized water. The stock solutions were diluted to prepare working solutions of the desired concentrations. Aqueous lanthanum and cerium solutions were prepared by dissolving analytical grade lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$) and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) in 0.1 M (M = mol/l) hydrochloric acid. If necessary, 0.1 M N-2-Hydroxyethylpiperazine-N-2-ethanesulphonic acid (HEPES), a buffering agent, was used to adjust the pH of the test solution.

Preparation of SOW Gel from Orange Waste

The saponified orange waste (SOW) gel was prepared according to the previous paper (13) as follows: about 100 g of orange juice residue was taken along with 8 g of $Ca(OH)_2$ in a juice mixer and crushed into small particles to make a suspension, which was then transferred into a beaker. After adding a substantial amount of deionized water, the suspension was stirred for 24 h at about 200 rpm at room temperature in order to facilitate the saponification. The initial pH of this suspension was maintained at around 12.5 by adding sodium hydroxide solution. After stirring, the suspension was repeatedly washed with deionized water until neutral pH by means of decantation and finally filtered to obtain a wet gel, which was dried in a convection oven for about 48 hours at 70°C to produce the dry SOW gel. The specific surface area of this gel was measured as 7.25 m^2/g by using Belsorp 18PLUS (BEL. JAPAN INC.) according to the BET method while leading pore size was found to be mesoporous with an average pore diameter of 14.3 nm.

Batchwise Adsorption Tests of La(III) and Ce(III) and Loading on SOW Gel for Arsenic Adsorption

To determine the loading capacity of La(III) and Ce(III) onto the SOW gel, batchwise adsorption tests were carried out. At first, batch tests were performed at varying pH to determine the optimum pH value for adsorption. The pH value thus determined was utilized to examine the adsorption isotherms for La(III) and Ce(III). Based on these isotherms, loading of these metal ions onto the SOW gel was carried out as follows: SOW gel (5 g) was equilibrated with 500 ml of 10 mM metal solutions for 24 h at pH 5.5 to obtain corresponding metal-loaded SOW gels. The suspensions were then filtered and washed with deionized water until neutral pH and finally dried at 70°C. The amount of metal ions loaded on the SOW gel was calculated from the difference in the concentration of the solution before and after loading. The gels were sieved to obtain a particle size between 75 and 150 μm, which was used in subsequent experiments.

Effect of pH on Arsenic Removal

Batch-wise adsorption tests for arsenic removal were carried out to examine the adsorption behavior of arsenic onto different metal-loaded SOW gels. Adsorption of arsenic as a function of pH was examined in a series of experiments where the initial arsenic concentration was maintained constant (0.0533 μmol/ml) at varying pH. Here, pH was adjusted by adding small amounts of NaOH or HCl. From such experiments, the optimum pH value for arsenic adsorption on the gels can be obtained. All batch adsorption experiments were carried out in 50 ml stoppered conical flasks by taking 25 mg (dry weight) of the gel together with 15 ml of arsenic solution. The flasks were then shaken in a thermostated shaker maintained at 30°C and 138 rpm for about 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1- μm filter paper and their equilibrium concentrations were measured. The amounts of adsorbed arsenic were calculated from the decrease in the arsenic concentrations.

Adsorption Isotherms of Arsenic

To evaluate the adsorption isotherms, the adsorption tests were carried out individually for arsenate and arsenite in the concentration range of 0.0133-12.0 μmol/ml at their optimum pH values. The adsorption isotherms for As(V) and As(III) were measured at pH values 6.5 and 10, respectively, for both La(III)- and Ce(III)-loaded gels. The procedure and calculation of the adsorbed amount of arsenic was the same as that mentioned in the preceding section. However, the reproducibility of all these batch adsorption experiments as well as column-mode experiments, which will be described later, was confirmed by carrying out the same adsorption tests in triplicate and the mean value was taken.

Kinetic Studies

The kinetics of As(V) and As(III) adsorption using the La(III)-loaded SOW gel have been studied as follows. Twenty-five mg of the gel was put into a 50 ml stoppered conical flask together with 15 ml of the arsenic working solutions at different initial concentrations, 0.2, 0.6 and 1.2 μmol/ml, where the pH of each solution was kept constant at 6.5 for As(V) and 10 for As(III). The flasks were then shaken in a thermostated shaker at 30°C at 138 rpm. The arsenic concentration was measured for different contact times. At the end of each contact time, the suspension was immediately filtered through a 1-μm filter paper and the filtrate analyzed. The amount of arsenic adsorbed at time t, q_t (mg/g of dry gel), was calculated from the mass balance between initial concentration and concentration at time t. The data were used to analyze the adsorption rates of As(V) onto the La(III)-loaded SOW gel. However, adsorption kinetics of As(V) and As(III) onto Ce(III)-loaded SOW gel has not been discussed here because of the similar kinetic behavior with La(III)-loaded SOW gel.

Column Studies: Adsorption Followed by Elution

Column adsorption tests of As(V) and As(III) onto a La(III)-loaded SOW gel were also individually carried out at 30°C using a transparent glass column of 0.8 cm inner diameter and 20 cm hight fitted with a glass filter at the bottom. The entire column was equipped with a jacket surrounding the column to keep the temperature constant at 30°C. Small glass beads having an average diameter of 1.35 mm were first packed up to an arbitrary height of the column and then a small amount of cotton, which acted as a support layer for the gel, was packed. Onto this cotton layer, the gel was tightly packed and pressed by another layer of cotton as well as glass beads in the remaining portion of the column at the top. The cotton layers ensured no drainage of gel throughout the operation. The solution was passed through from the bottom of the column and the effluent was taken from the top. Approximately 150 mg of La(III)-loaded SOW gel was first adequately soaked in deionized water to facilitate swelling and then packed into the column. The height of the fixed bed was measured as 1.2 cm. The test solution, containing 0.133 μmol/ml of arsenic, was percolated through the column using an EYELA model MP-3N micro tube pump. The pH of the feed solution was maintained at 6.5 and 10 for As(V) and As(III), respectively. Beforehand, the column was conditioned by passing water at the same pH for 24 h. A fraction collector (BIORAD Model 2110) was used to collect the fractions of effluent at definite intervals of time in 8 ml plastic tubes for the measurement of the arsenic concentration. After the complete breakthrough, elution tests for As(V) and As(III) were carried out using 1 M HCl and 1 M NaOH, respectively. Here, prior to the elution tests, the column was washed with de-ionized water to expel any unbound arsenic. The eluted arsenic concentration was measured as before.

Analysis

The pH of the sample solutions was measured using a DKK-TOA model HM-25G pH meter while the concentrations of lanthanum and cerium ions as well as arsenic were measured by using a Shimadzu model ICPS-8100 inductively coupled plasma-atomic emission spectrometer (ICP/AES). The linearity of calibration ranges from 2 μg/l up to 1000 μg/l with a detection limit of about 1 μg/l for each species measured. Standard solutions of arsenic and other metal ions (Wako Pure Chemical Industries, Ltd., Japan) of 1000 mg/l were diluted to the desired concentration and used for ICP/AES calibration.

RESULTS AND DISCUSSION

Adsorption of Metal Ions onto SOW Gel and Preparation of Metal-Loaded Gels

The effect of equilibrium pH on the adsorption of La(III) and Ce(III) onto SOW gel is illustrated in Fig. 1, which demonstrated that maximum adsorption for both metal ions occurred between pH 5.5 and 6.5. At pH values higher than 6.5, both metals were hydrolyzed to form precipitates, especially at concentrations greater than 1 mM. Consequently, pH 5.5 was selected as a suitable pH value for loading the individual metal ions onto the SOW gel.

Figure 2 illustrates the adsorption isotherms for both metals, which shows that the adsorption increases with increasing metal concentration and tends to approach a constant value, suggesting that adsorption takes place according to the Langmuir adsorption mechanism. Based on the

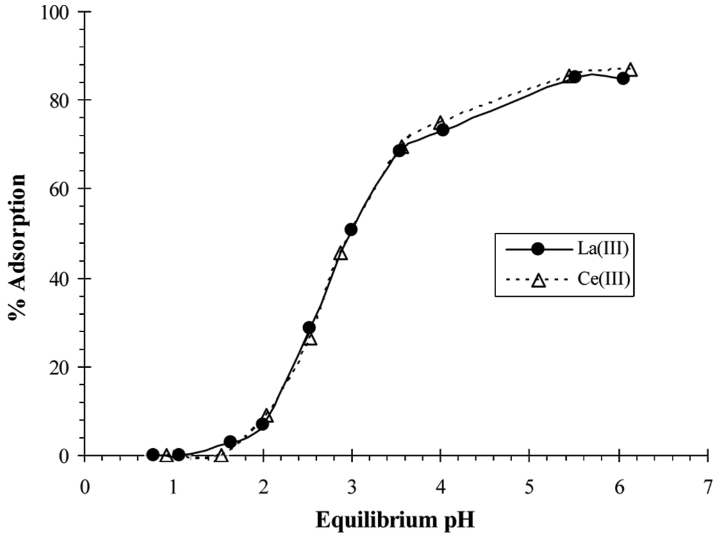


Figure 1. Adsorption of La(III) and Ce(III) onto modified orange waste at varying pH. Initial metal ion concentration = 1 mM (for each), solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C.

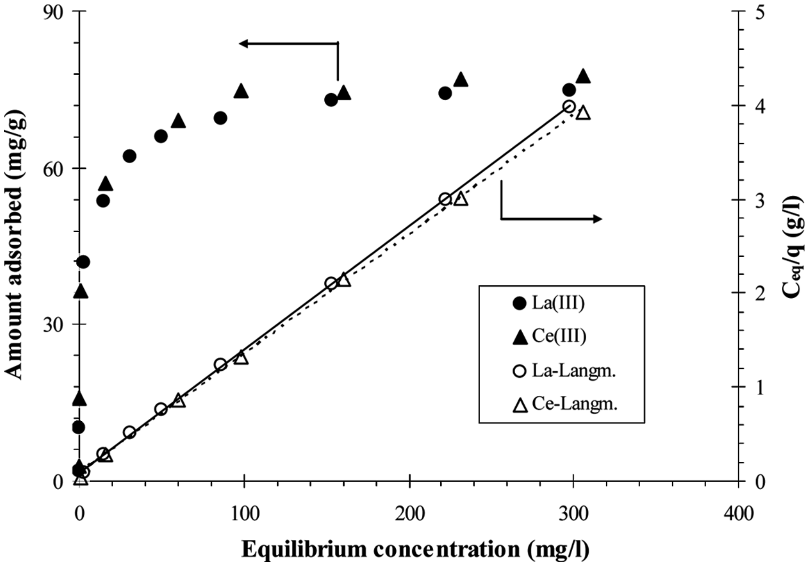


Figure 2. Adsorption isotherms for La(III) and Ce(III) ions on the SOW gel at pH 5 and 5.5, respectively. Solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C.

Langmuir equation (Eq. (1)), the adsorption isotherm data were replotted as shown by the open keys in Fig. 2. The replotted plots are in good linear relationship as expected from Eq. (1). From the slopes and the intercepts of the straight lines with the ordinate, the binding constants of La(III) and Ce(III) on the gel were evaluated as 1.58×10^2 and 1.81×10^2 l/kg, respectively. The preference in binding of Ce(III) to the gel compared to La(III) may be due to the difference in ionic radii of Ce(III) and La(III), which is well known phenomena in solvent extraction with acidic solvent extraction reagents (18). However, the maximum loading capacity of the SOW gel was evaluated as 76 mg La(III)/g (0.55 mol/kg) and 77 mg Ce(III)/g (0.55 mol/kg).

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{1}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), and q_0 and b are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

Kinetic Studies

In order to obtain kinetic data for As(V) and As(III) adsorption onto the La(III)-loaded SOW gel, the variation of the arsenic concentration with time was measured. The rate of As(V) and As(III) uptake by the gel from aqueous solution is depicted in Fig. 3 (a) and (b), respectively, which show that the amount of arsenic adsorption increases rapidly with increasing shaking time and it tends to approach a constant value after a certain shaking time depending on the initial arsenic concentration. It is seen that adsorption is rapid during the initial adsorption stages and then approaches equilibrium regardless of the initial arsenic concentration. However, 24 h was determined as optimum shaking time for the subsequent adsorption tests. A similar observation was reported by Singh et al. (19) for As(V) adsorption on hematite and feldspar. The initial rapid step may be attributed to diffusion controlled sorption onto the gel (20). All curves shown in Fig. 3 (a) and (b) are single, smooth and continuous leading to saturation, suggesting a monolayer coverage of the surface of the gel (21). Lalvani et al. (22) proposed an empirical rate expression described by Eq. (2) for the adsorption kinetics of hexavalent chromium on a carbon adsorbent.

$$R = k_t t^m \tag{2}$$

where R and t denote the % removal of solute from the aqueous solution and contact time, respectively, and k_t and m are constants. Figure 4

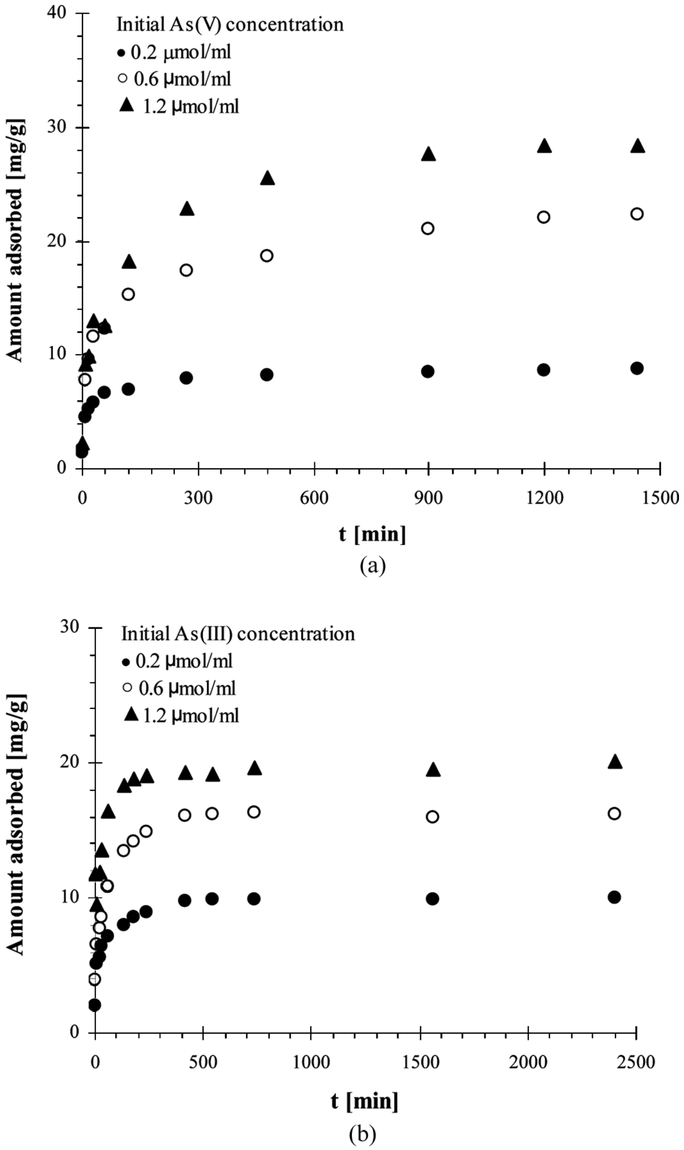


Figure 3. Effect of shaking time and initial concentration of (a) As(V) adsorption at pH 6.5 and (b) As(III) adsorption at pH 10 onto La(III)-loaded SOW gel. Solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C.

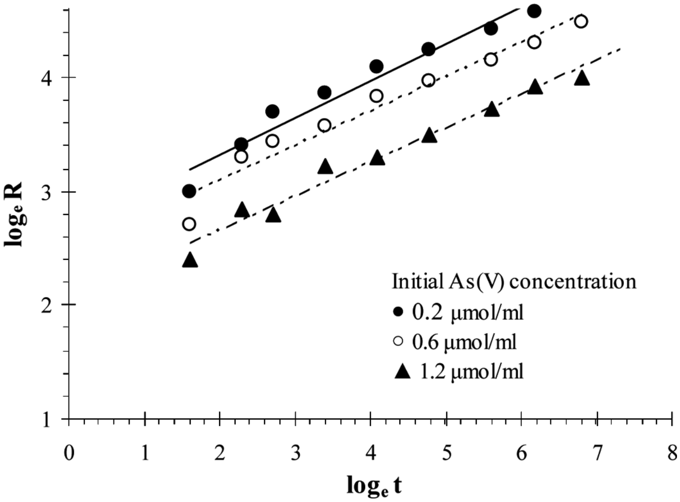


Figure 4. Logarithmic plot of As(V) removal efficiency versus time. Solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C, pH = 6.5.

shows the plot of log_eR against log_et for the data shown in Fig. 3 (a) according to Eq. 2. As expected, fairly linear plots are obtained for all three different initial arsenate concentrations. The numerical values of m are calculated to be 0.32, 0.30, and 0.29 for initial concentrations of 0.2, 0.6 and 1.2 μmol As(V)/ml, respectively. According to Lalvani et al. (22), the reaction order (n) is expressed as follows:

$$n = m^{-1} - 1 \tag{3}$$

From this equation, the reaction order was evaluated to be 2.08, 2.33, and 2.35 for 0.2, 0.6, and 1.2 μmol/ml initial As(V) concentrations, respectively. Therefore, it may be assumed that the kinetics of arsenate adsorption can be represented by a second order rate equation. Consequently, in the present work, the adsorption rate has been analyzed based on the pseudo-second-order rate equation proposed by Ho and McKay (23), expressed as follows.

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{4}$$

where k is the rate constant [g/(mg·min)], and q_t and q_e denote the amount of arsenic adsorbed (mg/g) at any time t and at equilibrium, respectively. Integration of Eq. (4) within the initial and boundary

Table 1. Kinetic parameters for the adsorption of As(V) and As(III) by the La(III)-loaded SOW gel

			Pseudo-2nd-order kinetic parameters			Non-linear regression	
Species	C_{in} (μmol/ml)	$q_{e,exp.}$ (mg/g)	k [g/(mg·min)]	R^2	$q_{e,cal}$ (mg/g)	$q_{e,cal}$ (mg/g)	R^2
As(V)	0.2	8.5	6.19×10^{-3}	0.99	8.8	8.41	0.963
	0.6	22.1	1.07×10^{-3}	0.99	22.5	21.07	0.958
	1.2	28.4	7.54×10^{-4}	0.99	29.2	28.13	0.974
As(III)	0.2	7.8	5.44×10^{-3}	0.99	8.0	7.64	0.957
	0.6	15.9	3.42×10^{-3}	0.99	16.3	16.29	0.961
	1.2	19.6	3.3×10^{-3}	0.99	20.1	19.77	0.985

conditions gives the relationship between q_t and t described by Eq. (5).

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{kq_e^2} \tag{5}$$

It is noted that k and q_e can be evaluated from the intercept and slope for the linear relationship between t/q_t and t (from Eq. (5)). However, these kinetic parameters have also been evaluated from nonlinear regression by using XLSTAT, a statistical analysis package, developed by Kovach Computing Services (24). The kinetic parameters thus evaluated and the correlation coefficients calculated at different concentrations are listed in Table 1. The values of kinetic parameters obtained from nonlinear regression resemble to that of linear regression. Since the adsorption rate process follows a pseudo-second-order model, it can be surmised that a chemisorption process may have taken place for arsenic sorption onto the gel (23,25).

Effect of pH on Adsorption of Arsenic Species

Figure 5 shows the effect of equilibrium pH on arsenic removal over a pH range of 1–13 by using La(III)- and Ce(III)-loaded gels. The arsenic adsorption behavior of Fe(III)-loaded gel, investigated in our previous work (15), has also been incorporated here for comparison. It is obvious from this figure that the pH of the aqueous solution plays an important role in the adsorption. Figure 5(a) shows that As(V) can be effectively adsorbed by using the La(III)- and Ce(III)-loaded SOW gels over a pH range from 6 to 9.5 while Fe(III)-loaded gel (15) is effective only at acidic

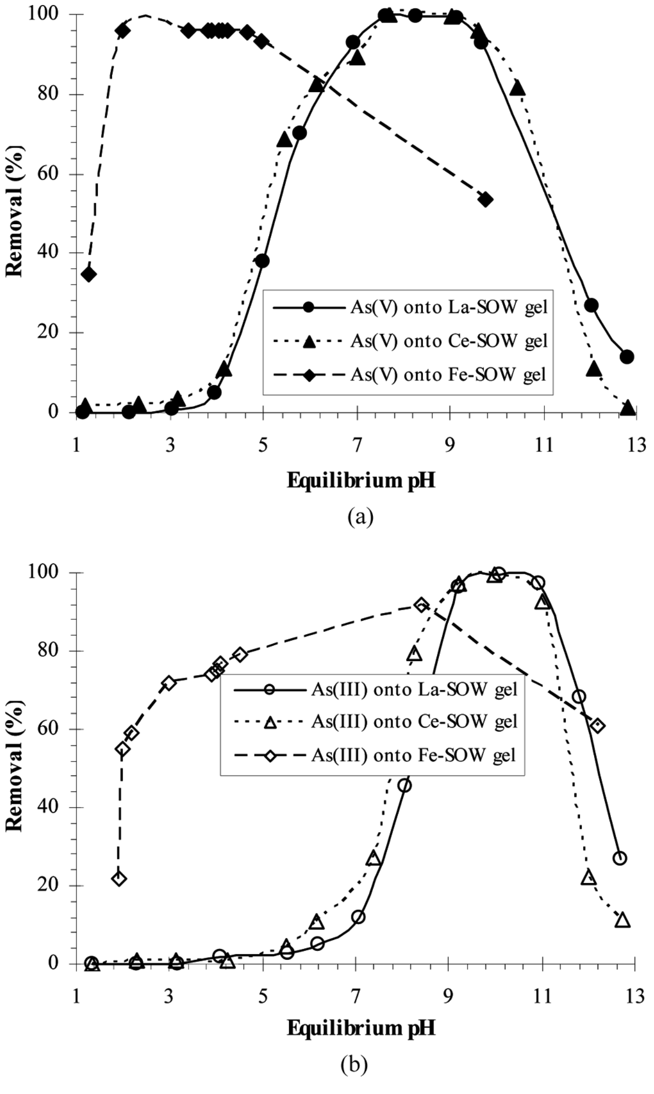
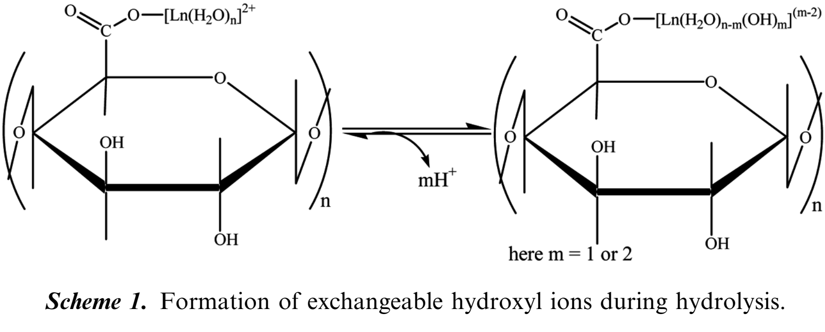


Figure 5. Removal of (a) As(V) and (b) As(III) onto La(III)-, Ce(III)- loaded gels and Fe(III)-loaded gel (Ref. 15) as a function of equilibrium pH. Initial concentration of arsenic = 0.0533 μmol/ml, Solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C.

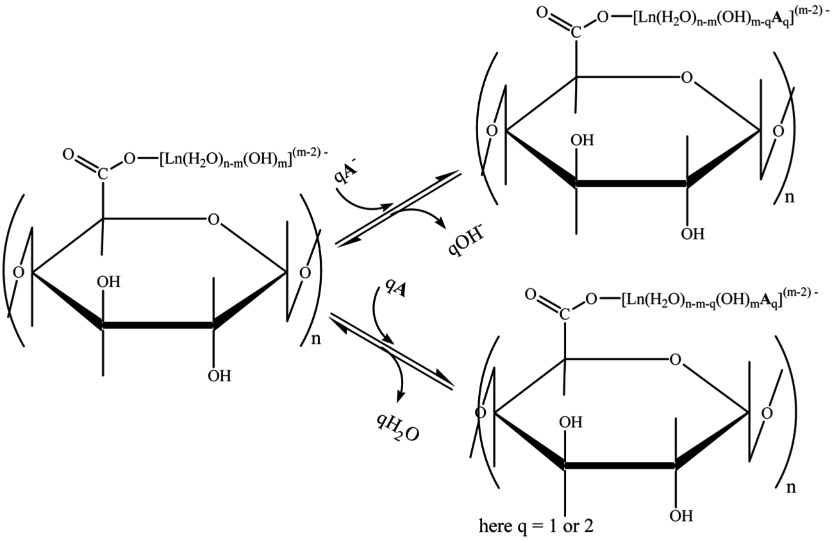
condition. However, pH 6.5 was selected for further batch adsorption tests. According to Wasay et al., La(III) and Y(III) impregnated alumina can effectively remove As(V) in the optimum pH range of 6 to 8, (16), compared with which the adsorption onto the La(III)- or Ce(III)-loaded SOW gel has a wider optimum pH range for As(V) removal, which should be of great advantage for practical operation. Arsenic(V) can exist in different ionic species depending on solution pH (26). The dominant species in the above mentioned pH range are $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions which can be adsorbed on the gel by substituting hydroxyl ions from the coordination sphere of the loaded lanthanide ions as will be described in detail later in this section. Since lanthanides tend to be extensively hydrolyzed, a numbers of hydroxyl ions are therefore available for ligand exchange with arsenic anions (Scheme 1).

In contrast to the removal of As(V), adsorption of As(III) was the most favorable at pH 9 ~ 11 for both the La(III)- and Ce(III)-loaded SOW gels as shown in Fig. 5(b). However, pH 10 was selected for further batch-mode adsorption tests for As(III). In solution, up to pH 8, arsenite exists principally as undissociated H_3AsO_3, which accounts for the lack of adsorption. The predominant monoanionic ($H_2AsO_3^-$) and neutral (H_3AsO_3) species are thus considered to be responsible for the adsorption of As(III) by substitution of the hydroxyl ions or water molecules at pH 9 ~ 11.

As mentioned earlier, arsenate and arsenite are inferred to be adsorbed onto the gel according to the ligand exchange reaction as shown in Scheme 2. Ligands involved in such exchange processes may be hydroxyl ions or neutral water molecules existing in the lanthanides coordination spheres. These mechanisms have been further supported by the fact that the pH of the solution had been increased or almost no change had taken place after arsenic adsorption in the present experiments. Similar mechanisms have been reported for the adsorption of As(V) on aluminum-loaded Shirasu-zeolite (27), As(V) as well as As(III) on Fe(III)-loaded crosslinked seaweed gel (12) and that of fluoride on various La(III)-loaded adsorbents (14). Figure 5(a) and (b) also show that % removal of arsenic decreases with a further increase in pH. The decrease in arsenic adsorption can be attributed to the competition between



Scheme 1. Formation of exchangeable hydroxyl ions during hydrolysis.



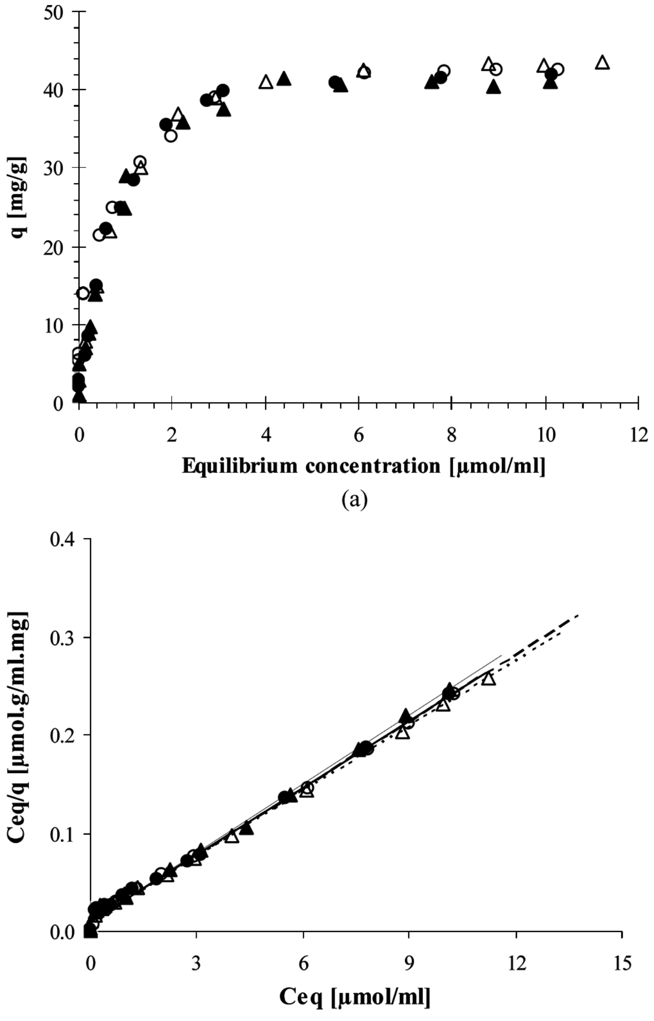
Scheme 2. Ligand exchange reaction, where *A* stands for arsenic.

hydroxyl ions, predominant at higher pH, and arsenic species for the adsorption sites.

Fe(III)-loaded SOW gel was used to compare the adsorption behavior as shown in Fig. 5 as mentioned earlier. Different sorption behavior is observed for Fe(III)-loaded SOW gel compared to the La(III)- and Ce(III)-loaded SOW gels, which may be attributed to the loaded metal ions and their physicochemical properties. The extremely low value of the solubility product of $Fe(OH)_3$ compared to those of $La(OH)_3$ and $Ce(OH)_3$ may be responsible for the adsorption behavior of arsenic. Since lanthanides have coordination numbers of 6, 8, 9 (28), or even more, e.g. 10 or 11, which allow to take various geometries while iron has a coordination number of 6 in general (29), the differences in the coordination spheres may also be responsible for the different adsorption behavior between the Fe(III)-loaded and lanthanides(III)-loaded SOW gel systems. However, more detailed investigation using more different types of metal ions will be necessary to reasonably explain these differences.

Adsorption Isotherm

Adsorption isotherms were measured for As(V)and As(III) on the La(III)- and Ce(III)-loaded SOW gels under the optimized conditions as shown in Fig. 6(a). It is clear that at low arsenic concentration the



(a)

(b)

Figure 6. (a) Adsorption isotherms of As(III) at pH 10 on (○) the La(III)-loaded SOW gel, (△) the Ce(III)-loaded SOW gel and that for As(V) on (●) the La(III)-loaded SOW gel, (▲) the Ce(III)-loaded SOW gel at pH 6.5 and (b) corresponding Langmuir plots. Solid/liq ratio = 1.67 mg/ml, shaking time = 24 h, temperature = 30°C.

adsorption of both As(III) and As(V) increases with increasing arsenic concentration and reaches a plateau region, suggesting that the adsorption takes place according to the Langmuir mechanism. The linear plots (Fig. 6(b)) according to the Langmuir equation fit nicely with the experimental data with binding constants of 2.12 l/mmol and 2.96 l/mmol for As(III) and As(V), respectively, for the La(III)-loaded SOW gel while for the Ce(III)-loaded SOW gel the values were 2.19 and 2.38 l/mmol, correspondingly. Non-linear regression analysis using XLSTAT, a statistical package, has also been performed to obtain the model parameters. It was found that the values obtained from such non-linear regression were nearly the same as that obtained from linearization method. However, these values are much higher than that reported by Balaji et al. (30) for a Zr-loaded lysine diacetic acid chelating resin. The excellent correlation coefficients (>0.99) for the linear plots signify a homogeneous distribution of active sites on the gel surface (31). In these adsorption tests, we confirmed that there was no leakage of the loaded lanthanides from the gel under the mentioned experimental conditions.

The maximum adsorption capacities of both gels (La(III)- and Ce(III)-loaded gels) were found to be the same e.g. 43 mg/g (0.57 mol/kg) for As(III) removal and 42 mg/g (0.56 mol/kg) for As(V). Although it is difficult to directly compare the La(III)- and Ce(III)-loaded SOW gels with other adsorbents because of the different experimental conditions, it was found that the adsorption capacities of these gels are significantly higher than those for other adsorbents e.g. 12.88 mg As(V)/g for La(III)-impregnated alumina (16), 16.0 mg As(V)/g for Ce(III)-doped iron oxide (17), 28.2 mg As(V)/g for Lessonia nigrescens, an algae (32), 1.05 mg As(V)/g for activated carbon (33), 0.74 mg As(III)/g for polymetallic sea nodules (34), 0.69 mg As(III)/g for iron oxide coated cement (35). From the comparison as such, we can conclude that the adsorption gel with reasonably high adsorption capacity for arsenic can be prepared by a simple modification of orange waste by loading La(III) or Ce(III). The comparison between the maximum adsorption capacity for arsenic ($\approx$0.56 mol/kg) and the loading capacity of lanthanum or cerium on the SOW gel ($\approx$0.55 mol/kg) suggests that 1:1 complexation might take place between the loaded metal ion and arsenic under the present experimental conditions.

Column Adsorption and Elution Tests

The performance of the La(III)-loaded SOW gel in continuous operation for the removal of As(V) and As(III) was studied using a packed column. Figure 7 (a) and (b) show the breakthrough profiles of As(V) and As(III) at their optimum pH values, which are 6.5 and 10, respectively. From this figure, it is seen that the breakthrough for As(V) and As(III) started at 120 and 100 bed volumes (BV), indicating that As(V) and As(III) can be completely retained on the gel up to these bed volumes, while complete saturation was achieved at 690 and 280 BV, respectively. Here, the bed volume (BV) represents the volume ratio of the solution passed through the column to that of the packed gel. However, before reaching the complete saturation of the bed, the pH of the effluent increased slightly, which conforms to that of batch-mode adsorption. Once the bed is completely saturated, there was no change in pH. The effective adsorption capacities calculated from the breakthrough profiles were 14.2 mg/g g for As(V) and 10.5 mg/g for As(III), which were only 35% and 25% of their corresponding equilibrium sorption capacities evaluated from the batch-wise adsorption tests. The low extent of adsorption capacity may be attributable to various phenomena such as channeling and too short a contact time between the gel and the arsenic solution to allow equilibrium to be attained in the column. Similar results have also been reported

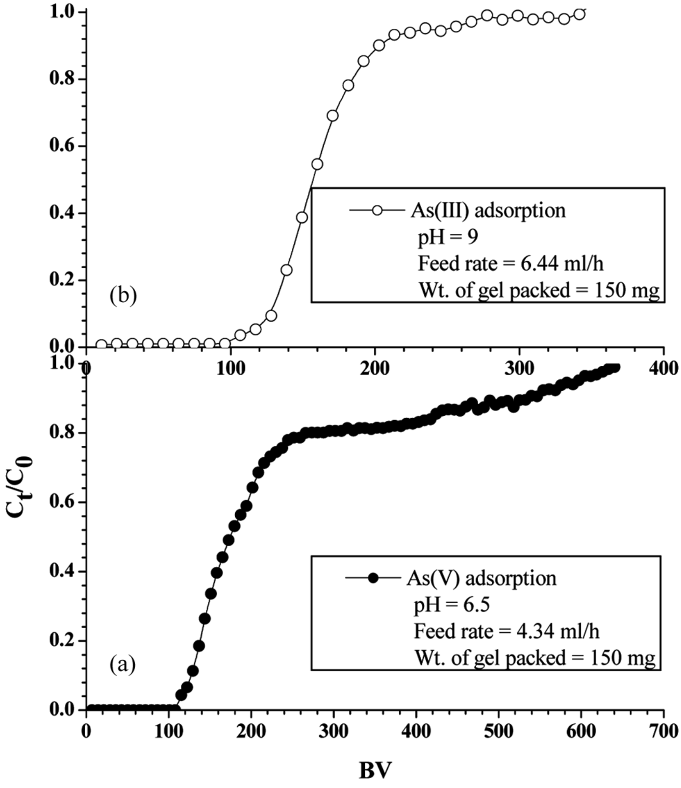


Figure 7. Breakthrough curves for (a) As(V) and (b) As(III) sorption onto the La(III)-loaded SOW gel.

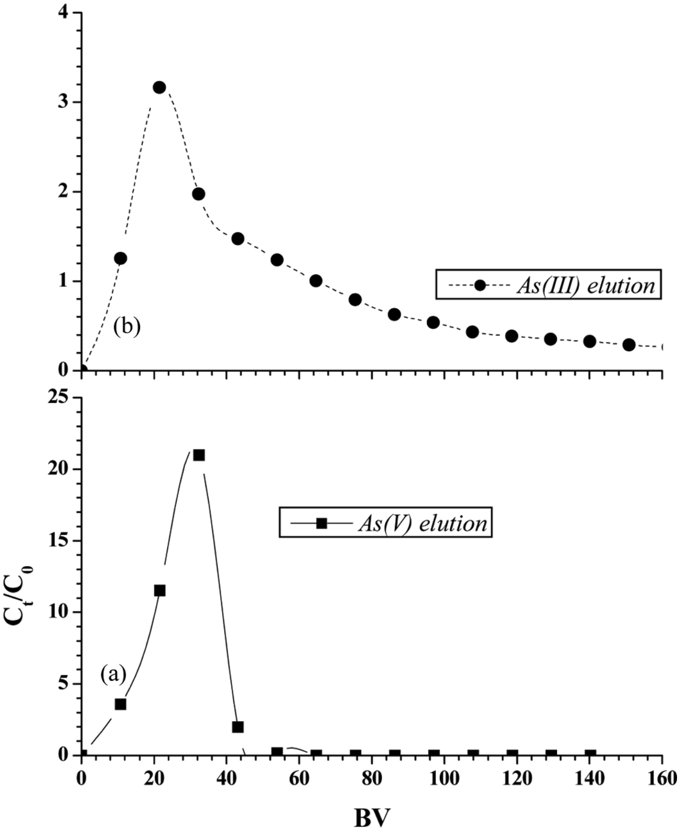


Figure 8. Elution profiles for (◆)As(V) and (○)As(III) by using 1 M hydrochloric acid and 1 M sodium hydroxide respectively. Corresponding feed rates are 4.34 ml/h and 6.44 ml/h.

by Lenoble et al. (1) for arsenic removal on MnO_2-loaded resin and by Zouboulis and Katsoyiannis (36) for arsenic removal using iron oxide loaded alginate beads. However, column adsorption studies showed that the adsorption of As(V) is a little bit more favorable compared to that of As(III), which may be due to the slower kinetics of As(III). Balaji et al. (30) reported a similar behavior for As(V) and As(III) adsorption using Zr-loaded lysine diacetic acid chelating resin.

Empty bed contact time (EBCT) is a useful process parameter for designing column. In this work EBCT was measured for arsenic removal, which were 8.3 and 5.6 min for As(V) and As(III), respectively. The obtained results resemble to that of AdEdge Technologies, Inc. (Atlanta based company) who has used a resin (commercial name: ID-33) to remove arsenic since 1999 (37).

After complete saturation of the column, elution tests were carried out using 1 M HCl for As(V) and 1 M NaOH for As(III) as depicted in Fig. 8(a) and Fig. 8(b), respectively, which show that more than 20 fold enrichment was attained for As(V), while the preconcentration for As(III) was less than 4 fold. These results are in agreement with those reported by Chanda et al. (38,39) for arsenate and arsenite adsorption on chelating resins. The elution of As(V) in the present study was very efficient since more than 95% of the adsorbed arsenic was eluted within less than 5 h by using less than 25 ml of eluent while that of As(III) took a fairly long time (longer than 20 h). La(III) was not detected in the effluent during elution of arsenite, while during elution of arsenate, it was eluted together with the arsenate, suggesting that it is necessary to load the metal again onto the gel for the next operation.

CONCLUSIONS

The present study shows that orange waste loaded with La(III) and Ce(III) metal ions are effective adsorbents for the removal of arsenic from aqueous systems. Quantitative arsenic removal over a wide pH range suggests that the lanthanide(III)-loaded SOW gel may have the possibility of practical application in waste water treatment while the gel loaded with Fe(III) shows its effectiveness only under acidic conditions for As(V) adsorption. The kinetics of adsorption of arsenic(V) onto the La(III)-loaded SOW gel was found to be interpreted by the pseudo-second-order kinetic model. Adsorption equilibrium was reasonably described by the Langmuir isotherm. In dynamic column experiments, the retention capacities for both As(V) and As(III) were less than the maximum sorption capacities obtained in batch experiments. However, complete adsorption was achievable with column-mode tests resulting in the permissible limit for arsenic to be attained under the present experimental conditions. Taking account of the low cost and easy availability of the starting material (orange waste), and reasonably high adsorption capacity of the prepared metal-loaded gel, it can be potentially used for arsenic removal from wastewater.

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