Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

ADSORPTIVE REMOVAL OF ARSENIC USING ORANGE JUICE RESIDUE

Kedar Nath Ghimire[a]; Katsutoshi Inoue[a]; Kenjiro Makino[b]; Tohru Miyajima[a]
[a] Department of Applied Chemistry and Chemistry, Saga University, Saga, Japan [b] Yamasoh Micron Inc., Sakai, Japan

To cite this Article Ghimire, Kedar Nath , Inoue, Katsutoshi , Makino, Kenjiro and Miyajima, Tohru(2002) 'ADSORPTIVE REMOVAL OF ARSENIC USING ORANGE JUICE RESIDUE', Separation Science and Technology, 37: 12, 2785 — 2799
To link to this Article: DOI: 10.1081/SS-120005466
URL: http://dx.doi.org/10.1081/SS-120005466

SEPARATION SCIENCE AND TECHNOLOGY, 37(12), 2785–2799 (2002)

ADSORPTIVE REMOVAL OF ARSENIC USING ORANGE JUICE RESIDUE

Kedar Nath Ghimire,[1] Katsutoshi Inoue,[1,*]
Kenjiro Makino,[2] and Tohru Miyajima[1]

[1]Department of Applied Chemistry and Chemistry, Saga
University, Honjo 1, Saga 840-8502, Japan
[2]Yamasoh Micron Inc., 1-21-12, Uenoshibamachi, Sakai
593-8301, Japan

ABSTRACT

A novel adsorbent has been prepared by simple chemical modification of orange juice residue (OJR) with the substitution of phosphate groups on the alcoholic analog of cellulose. Phosphorylated gel was further loaded with iron(III). The loading capacity for iron(III) on the gel was as high as 3.7 mol/kg. Adsorption studies on iron(III) loaded gel were carried out both batch wise and by using a column. Arsenic(III) adsorption was found to have been favored at alkaline condition ($\mathrm{pH} = 7-11$) while that of arsenic(V) was at acidic condition ($\mathrm{pH} = 2-6$). Maximum adsorption capacity for As(V) and As(III) was evaluated as 0.94 and 0.91 mol/kg at their optimum pH values 3.1 and 10.0, respectively. Experimental results indicate that iron-loaded phosphorylated OJR can be potentially applied for the removal and recovery of arsenic from various aqueous media.

---

[*] Corresponding author. E-mail: inoue@ccs.ce.saga-u.ac.jp

www.dekker.com

INTRODUCTION

Arsenic is a toxic unwanted chemical constituent thereby posing epidemiological problems to human health. Arsenic pollution has been seriously observed not only in various mineral and chemical processes but also in some ground water or hot spring water over the large area in Bangladesh, West Bengal in India, Inner Mongolia in China, and Japan as well. Most common arsenic species found in aqueous media are anionic species of arsenate and arsenite. To date, it has been removed by means of the following methods: precipitation of arsenic with lime, co-precipitation with ferric sulfate, alum precipitation, and precipitation of arsenic as sulfide using either sodium sulfide or hydrogen sulfide. Although, among these methods, iron co-precipitation method has been reported to be the most successful in lowering arsenic content to the drinking water standard level, it still suffers from a post treatment problem regarding the alkaline sludge produced after the treatment containing a mixture of gypsum, heavy-metal hydroxides, and carbonates in addition to a large amount of water, which may leak arsenic back to the environment after exposure with water and air. In addition, since it is difficult to remove As(III) directly by traditional methods, it should be oxidized into pentavalent state prior to their treatment by using suitable oxidizing agents like hydrogen peroxide.[1,2] Similarly, lime precipitation is in frequent use, but it suffers from the problem of gypsum formation and is not capable of reducing arsenic to the optimum level, which requires an additional ferric treatment. Furthermore, calcium arsenate formed in such process that has to be disposed in a landfill site may interact with carbon dioxide in air to form calcium carbonate releasing arsenic back into the solution/environment. Although alum precipitation is also in practice, its performance has not been considered satisfactory. Arsenic precipitation using sodium sulfide has been considered to be useful in reducing arsenic, however, it is very colloidal in nature causing a filtration problem and also gets readily oxidized when exposed to the atmosphere thereby making it difficult to dispose in a land fill site. Moreover, it is not possible to apply traditional methods for the treatment of arsenic in acidic medium.

In order to overcome the drawbacks of traditional treatment process, many attempts have been made regarding the removal of arsenite and arsenate by using iron(III)-loaded chelating ion exchange resins having either acidic or basic moiety as the functional group.[3–6] But the treatment with these chelating ion exchange resins are expensive, originated from the cost of their materials associated with the removal process.

In view of such regard, an alternative adsorption gel prepared from cheap biomass has been explored in the present work. Effective use of biomass wastes has become one of the promising fields of investigation due to availability of the raw materials almost free of cost as well as their environmentally friendly nature.

To reach this goal, we have prepared an adsorption gel from orange juice residue (OJR) by means of simple chemical modification of phosphorylation followed by loading with iron(III) to examine their adsorption characteristics for arsenate and arsenite from various aqueous media.

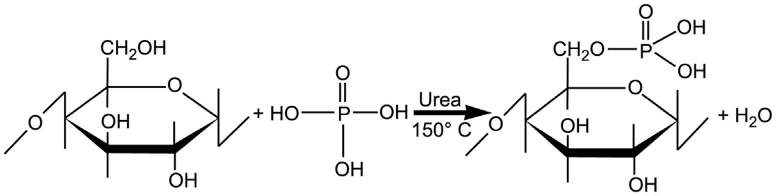
EXPERIMENTAL

Materials

Phosphorylated Crosslinked Orange Juice Residue

A sample of crude orange juice residue, hereafter abbreviated as OJR, was kindly provided from JA Saga Beverage, Japan, just after juicing. The crude OJR was dried for 72 hr in a convection oven at a temperature of 50°C and then dried in vacuo. The dried OJR was grounded into smaller particles with the aid of a ball-mill. The particle size of the powder was around 100–200 μm. The OJR principally consists of cellulose, pectin substances, hemi-cellulose, chlorophyll pigments, and other low molecular weight compounds like limonene and so on.[7] The active binding sites for metals are supposed to be functional groups of carboxylic acid in pectin substances. However, since the content of carboxylic groups in the original OJR was considered unsatisfactory to strongly load enough amount of iron(III) to adsorb arsenic, cellulose part of OJR was phosphorylated after crosslinking in order to convert their abundant hydroxyl groups into phosphate groups with high affinity to ferric iron to enhance the loading capacity for iron as follows. Twenty grams of dried OJR powder was stirred in 750 mL of 80% aqueous propanol for about 24 hr at room temperature and then vacuum filtered. The sample was repeatedly washed with propanol until it had no color in the filtrate. The thoroughly washed OJR sample was dried in vacuo for 24 hr.

Since OJR consists of pectin substances in addition to cellulose, the OJR sample has been crosslinked with epichlorohydrin to avoid its aqueous solubility under basic medium. Dried OJR weighing 8.5 g, thoroughly washed with propanol, was taken into a flask together with 300 mL of dimethyl sulfoxide (DMSO) and stirred for 24 hr at 25°C. Then, 40 mL of epichlorohydrin was added to the mixture to undergo the crosslinking reaction at 50°C for 5 hr. After cooling down to room temperature, it was filtered and washed with 70% aqueous propanol followed by 0.5 *M* HCl and finally with ethanol to neutral pH. The sample was kept for dry in vacuo for 24 hr. After crosslinking, the gel was phosphorylated according to the following reaction.



Cross-linked OJR weighing 8.6 g was soaked in 200 mL of dimethyl formamide (DMF) overnight and the dirty DMF was removed by vacuum filtration. The gel once again immersed in 200 mL of fresh DMF was taken in a flask along with 30 g of urea, and the mixture was stirred by the aid of a magnetic stirrer during which 18 g of phosphoric acid was added drop wise. After 1 hr of stirring, the temperature of the reaction mixture was raised to 150°C and further stirred for 2 hr. After cooling down to room temperature, it was washed with 70% aqueous propanol and then by water to neutral pH. Further, in order to activate the gel, it was washed with 0.1 HCl followed by water to neutral pH and the gel was kept to dry in vacuo for 2 days. The dry weight of phosphorylated gel was 7.8 g.

The elemental analysis of phosphorus content in phosphorylated crosslinked orange juice residue (POJR) was measured by using Shimadzu Model ICPS-5000 ICP/AES spectrometer as follows. POJR (83.3 mg) was slowly dissolved in 50 mL of concentrated sulfuric acid with gentle stirring. The acid solution was further diluted with water for the analysis by ICP/AES spectrometer, from which net elemental phosphorus concentration was found to be 254.40 ppm, i.e., equivalent to 1.2 mol of phosphorus per glucose unit of the chemically modified POJR.

Alternatively, the P_2O_5 content in POJR was analyzed with the aid of Rigaku ZSX 100E fluorescence x-ray crystallography, which was 20 mass% as it was not possible to measure directly the elemental phosphorus by this method. The 20 mass% P_2O_5 content in POJR after conversion into elemental phosphorus is equivalent to 1.15 mol of phosphorus per glucose unit of chemically modified POJR. The results obtained from both the analytical methods are almost the same (below 5% error), indicating that phosphorylation has been accompanied within the network of POJR.

Chemicals

All chemicals used in this study were of pure analytical grade purchased from Katayama Chemical Co. Ltd., Japan, unless and otherwise mentioned.

Methods

The adsorption tests were carried out batchwise and by using a column for breakthrough and elution tests. In the batchwise tests, 25 mg of dried adsorbent was taken into a conical flask together with a 15 mL portion of corresponding aqueous solution. The pH of the aqueous solutions was adjusted by contacting with HCl or NaOH while in the case of iron(III) adsorption, 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid was used as the buffer reagent.

The flask was shaken vigorously in a thermostatic shaker at 30°C for about 24 hr to attain equilibrium. The metal concentrations before and after adsorption were measured by using Shimadzu Model ICPS-5000 ICP/AES spectrometer or Shimadzu AA-6650 atomic absorption spectrophotometer.

From the metal concentrations measured before and after adsorption (C_0 and C_e, respectively) and the dry weight of adsorption gel (W), as well as the volume of aqueous solution (V), the amount of adsorption of metals (q) was calculated according to Eq. (1). The removal percentage ($R\%$) defined as the ratio of the decrease in metal concentration before and after the adsorption ($C_0 - C_e$) to initial concentration of aqueous solution (C_0), was calculated according to Eq. (2).

$$q = \frac{C_0 - C_e}{W} V \quad [\text{mol/kg}] \tag{1}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

In the tests using a column, arsenic removal was carried out in a glass column of 8 mm diameter packed with 0.1 g of iron-loaded POJR. A schematic diagram of the column experimental set up is shown in Fig. 1. The column was conditioned by passing water of pH = 3.1 overnight. The sample solution containing 15.8 ppm of arsenate, whose pH was maintained at 3.1, was percolated into the column at a constant flow rate of 6 cm^3/hr using a peristaltic pump (IWAKI PST-100N, Japan). Effluent samples were collected at each one-hour

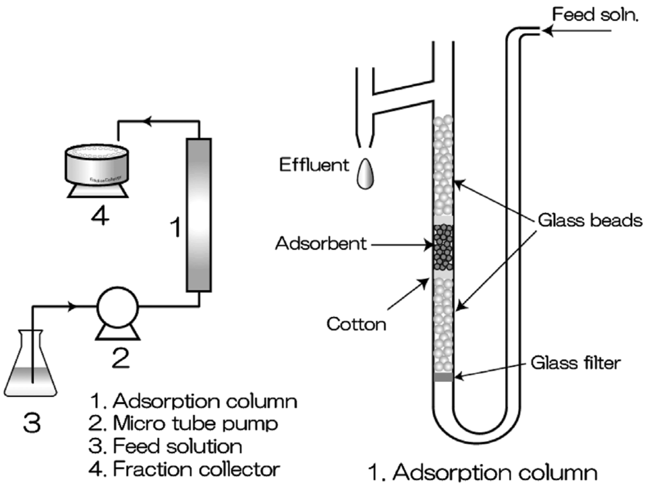


Figure 1. Schematic diagram of column experiment.

interval of time by using a fraction collector (BIORAD Model 2110 Fraction Collector). Effluent samples collected at each and subsequent hours were used for pH and arsenic concentration measurement.

For elution test, the column was washed with de-ionized distilled water prior to the elution tests so as to expel any residual arsenic by physical adsorption. Hydrochloric acid (1 *M*) was used as the eluent, which was percolated into the column at the same constant flow rate of 6 cm^3/hr using the peristaltic pump. The concentration of the eluted arsenic effluents collected at each interval of time in the tube of fraction collector were measured by using a Shimadzu Model ICPS-5000 ICP/AES spectrometer or a Shimadzu AA-6650 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Batch Experiment

Adsorption of Iron(III)

Adsorption of iron(III) on POJR at varying pH is shown in Fig. 2, where the initial concentration of iron(III) was 55.85 ppm (1 *mM*). It is seen from this figure that the iron(III) is almost adsorbed and constant until $pH = 3$ and decreases after $pH > 3$. This is due to the hydrolysis of iron(III) at those pH region. Figure 3 shows the adsorption isotherm of iron(III) for POJR gel at its optimum pH of 2.9. In this figure, the adsorption appears to take place according to Langmuir-type

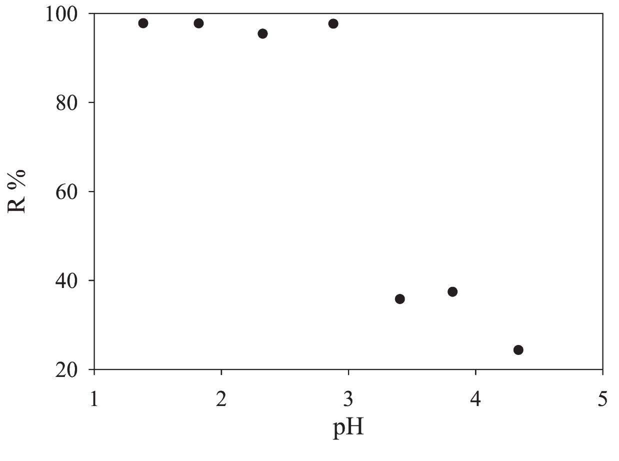


Figure 2. Adsorption of Fe(III) on POJR as a function of pH.

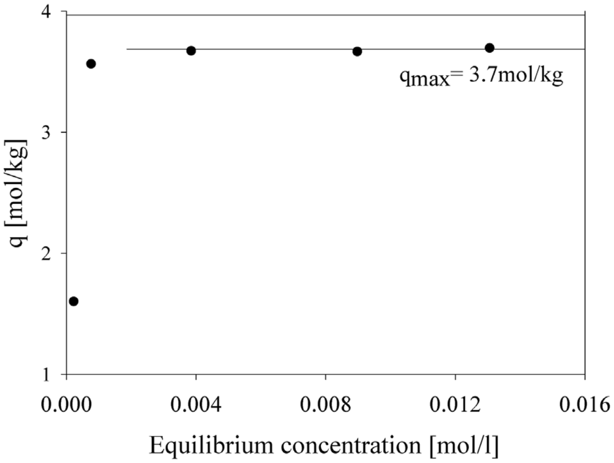


Figure 3. Adsorption isotherm of Fe(III) on POJR at varied concentration.

adsorption, that is, it increases with increasing iron concentration in the low concentration region and reaches a constant value, from which the maximum iron uptake capacity was evaluated as high as 3.7 mol/kg dry gel. The high value of iron(III) uptake capacity by the POJR gel may be due to synergistic effect of additional carboxyl functionalities present within the polymer matrix, which in turn could accommodate more metal ions. After knowing the maximum loading capacity of those, corresponding gels were loaded with iron(III) at their optimum concentration and pH range in order to further investigate their adsorption characteristics for As(V) and As(III).

Effect of pH on Arsenic Distribution

Before going through the discussion about the adsorption characteristics for arsenite and arsenate, a simple picture of their chemical speciation calculated based on their stability constants have been outlined in Fig. 4.[9] The monovalent anionic species of arsenate are dominant at pH ranging from 2 to 6 while in the case of arsenite, are significant at an alkaline region of pH $= 9-12$.

Effect of Contact Time on Adsorption

Figure 5 shows the time variation of the amount of adsorption of arsenate on iron(III)-loaded POJR gel at an initial concentration of 18 ppm. From this

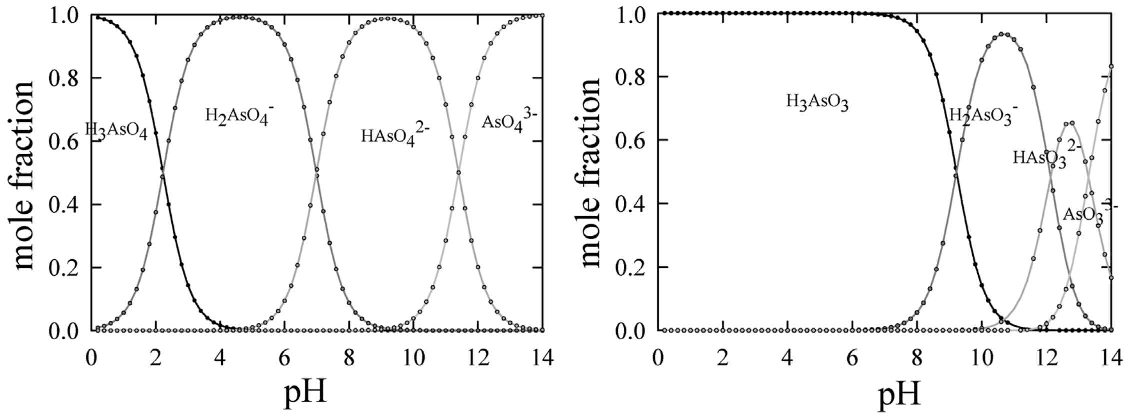


Figure 4. Distribution of As(V) and As(III) as a function of pH.

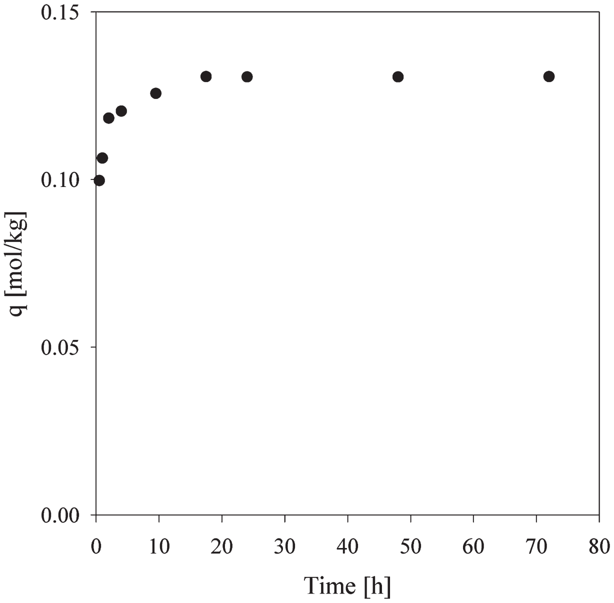


Figure 5. Effect of contact time for removal of As(V) on POJR.

figure, it is evident that adsorption was very fast at the beginning till half-an-hour and slowed down markedly after 1 hr. Adsorption continued to increase till 18 hr after which it became constant, reaching equilibrium. In view of ensuring enough equilibration time, 24 hr of contact was continued throughout the batch experiment.

Effect of pH on Arsenic Adsorption

Figure 6 shows the relationship between removal percentage and equilibrium pH in the adsorption of arsenate/arsenite on iron(III)-loaded POJR gel at an initial concentration of 15 ppm. It is seen from this figure that the pH of the aqueous solution plays as the important variable for adsorption. It is considered that iron(III) is adsorbed by releasing protons from the phosphorylated unit of cellulose according to cation exchange mechanism. The adsorbed iron will coordinate octahedrally with hydroxyl ions and neutral water molecules that are available in aqueous medium. The adsorption of As(III and V) will take place by releasing hydroxyl anion from the above-mentioned coordination sphere. For this reason, the adsorption of anionic species on

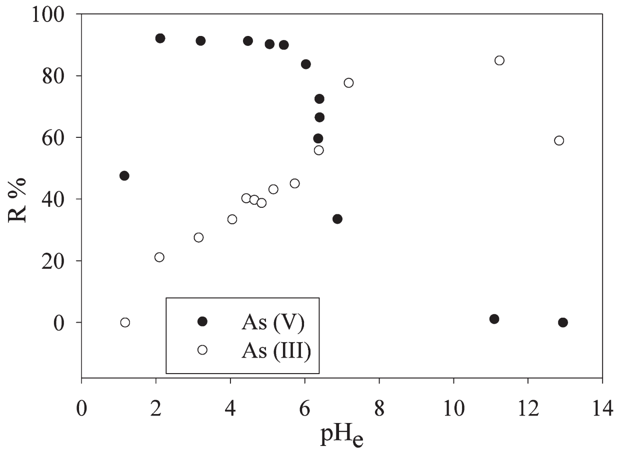


Figure 6. Removal of As(III) and As(V) on POJR as a function of pH.

metal-loaded gel is termed as ligand exchange adsorption.[5] But the fate is decided only in the presence of iron(III). This is the reason why iron(III)-loaded materials are being used for arsenic removal.

It can be seen from Fig. 6 that optimum adsorption conditions for arsenate is acidic ($pH = 2-6$) while that for arsenite is significant at weakly alkaline condition. The maximum removal percentage was around 90% in the case of As(V) and 85% in the case of As(III), respectively.

Since the pH range where monovalent arsenate species is predominant as shown in Fig. 4 are almost identical to that where high removal of arsenate is achieved as shown in Fig. 6, it can be concluded that an effective removal of monovalent As(V) can be accompanied by using iron(III)-loaded POJR gel. On the other hand, since, as can be seen in Fig. 4, monovalent arsenite ion is predominant only at $pH > 8$, which means As(III) adsorption on POJR gel taking place at $pH < 8$ is attributable to the adsorption of neutral arsenite species while at $pH > 8$ the adsorption of monovalent arsenite anions is taking place.

Figures 7 and 8 show the adsorption isotherm of As(V) and As(III) with respect to their respective equilibrium concentration. Initially, the adsorption increases and approaches a constant value with an increase in the concentration, suggesting the Langmuir-type of adsorption. The maximum amount of adsorption of As(V) and As(III) were evaluated as 0.94 and 0.91 mol/kg, respectively, which is quite high compared to 0.74 and 0.84 mol/kg, respectively, reported for the synthetic chelating resins.[6]

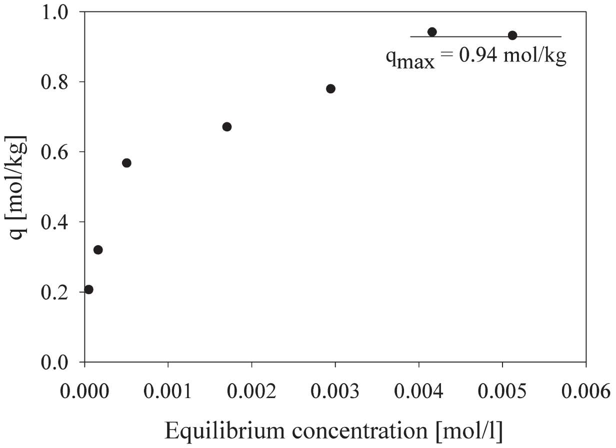


Figure 7. Adsorption isotherm of As(V) on Fe(III)-loaded POJR.

Column Experiment

As a model experiment, adsorptive removal of As(V) by using a column packed with the iron(III)-loaded POJR has been tested. Figure 9 shows the breakthrough curve of As(V) from the column at an initial concentration of 15.8 ppm. The volume of the adsorbent was 1.105 cm^3. Bed volume (abbreviated as B.V.) represents the volume ratio of the solution, which passed through the

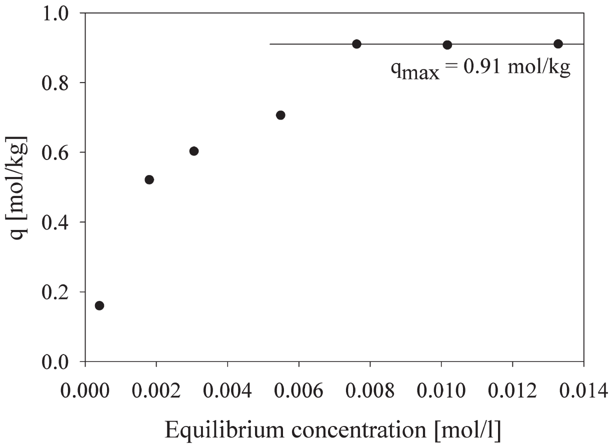


Figure 8. Adsorption isotherm of As(III) on Fe(III)-loaded POJR.

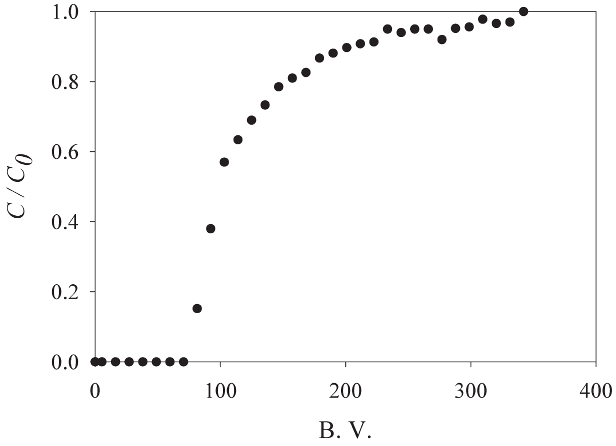


Figure 9. Breakthrough profile of As(V) on Fe(III)-loaded POJR. ($C_0 = 15.8\,\text{ppm}$).

column to the packed resin. The breakthrough began at 81.4 bed volumes and the bed was completely saturated at 342.1 bed volumes.

Arsenate adsorbed onto the column bed can be recovered by eluting either with alkaline eluent or by acidic eluent. Since stripping, using alkaline eluent, still leaves the As(V) to a considerable extent in the column, it has been recovered using 1 *M* HCl as the eluent. The elution profile is shown in Fig. 10. As seen in the elution profile in Fig. 10, the elution was completed within 38 bed volumes of 1 *M* HCl. So far, iron(III) has been eluted together with arsenate. It is necessary to load iron(III) once again onto the gel for the next operation.

Adsorption Reaction Mechanism

The chemical species of iron(III) involved in the loading mechanism is the hydrolyzed form of iron(III) at acidic condition.[10] Iron(III) is considered to be adsorbed on phosphate groups of gel according to cation exchange mechanism. This is supported by the fact that the initial pH of the solution had decreased after adsorption. As mentioned in "Column Experiment," arsenic can be adsorbed on the iron(III) immobilized onto POJR gel by the mechanism of ligand exchange. Both dependence of the chemical species on pH as illustrated in Fig. 4 and their subsequent removal, as shown in Fig. 6, suggests that As(III) removed at $\text{pH} > 8$ is due to the contribution of monovalent arsenite anions, which can be represented by mechanism 1 in the following adsorption reaction mechanism while the adsorption at $\text{pH} < 8$ is due to that of their neutral species accompanied

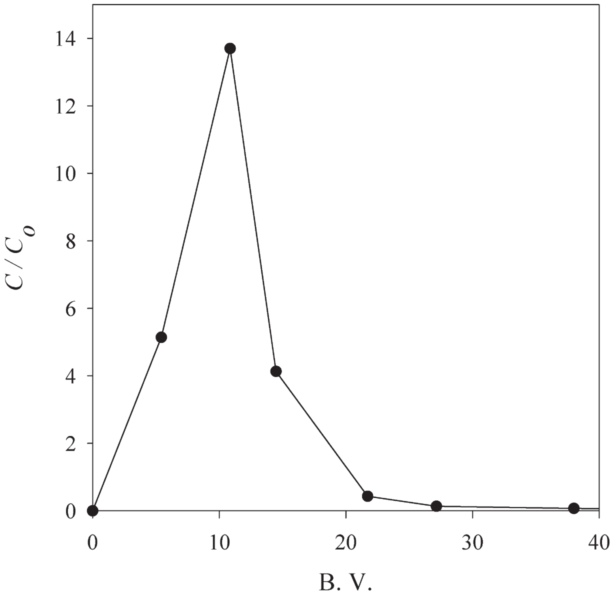
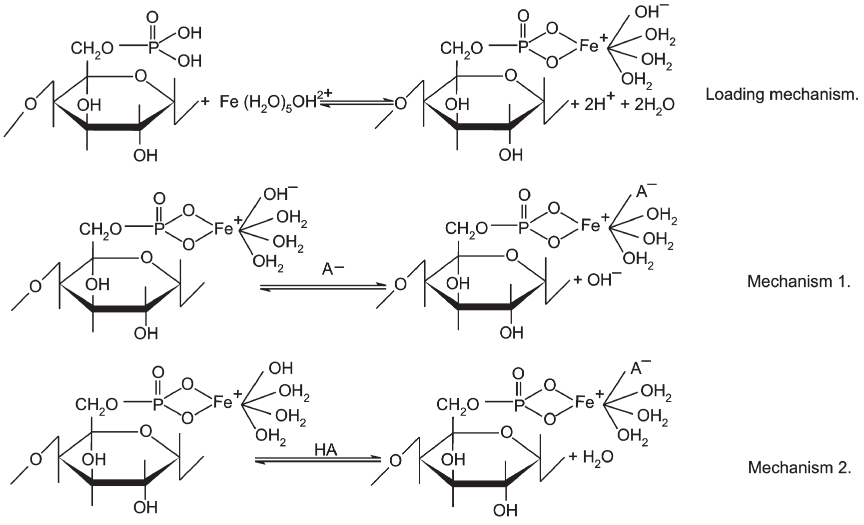


Figure 10. Elution profile of As(V) by using 1 *M* HCl. ($C_0 = 15.8$ ppm).

by the release of water molecule according to mechanism 2. In the case of As(V), monovalent arsenate anions are considered to be adsorbed according to mechanism 1 as evidenced by the distribution diagram as shown in Fig. 4.



The arsenic adsorption on the site of iron has been reported as ligand exchange adsorption by the previous researchers,[5,8] which is in harmony with our proposed adsorption reaction mechanism. The lower ligand exchange capacity of arsenic on POJR as compared to the adsorbed iron may be due to coulombic interaction between the anions of arsenic and the hydrolyzed iron(III) surface itself. Further investigations are necessary to interpret the interactions completely.

CONCLUSIONS

A new alternative adsorption gel for arsenic removal has been explored by making simple essential chemical modifications of OJR. The most important aspects of this gel are as follows; direct removal of both arsenate and arsenite without oxidizing As(III) to As(V), which is necessary by traditional methods and, at the same time, this gel is cheaper and more efficient compared with the commercially available synthetic chelating resin. Since the biomass materials are environmentally friendly, it can be easily burnt in incineration plants. One of the most advantageous fact behind this technology is that a cheaper or almost free of cost bio-waste can be converted into valuable resources for the improvement of environment. Hence, the promising technology offered in this article could be potentially applied for both As(V) and As(III) removal from aqueous medium with a greater separation efficiency.

ACKNOWLEDGMENTS

The present work was conducted by the aid of the financial support from Japan Science Technology Corporation as the Modeling Project for New Concept of Technology. We would also like to acknowledge Saga Ceramics Research Center (SCRC), Arita, Japan for their kind assistance in providing x-ray crystallography measurement.

REFERENCES

1. Mirza, A.H.; Ramachandran, V. Second International Symposium on Extraction and Processing for the Treatment and Minimization of Wastes. In *Removal of Arsenic and Selenium from Waste Waters—A Review*; Ramachandran, V., Nesbitt, C.C., Eds.; The Minerals, Metals and Materials Society: Salt Lake City, Utah, 1996; 563–582.

2. Lawrence, R.W.; Higgs, T.W. Removing and Stabilizing As in Acid Mine Water. J. Occup. Med. **1999**, 27–29.
3. Yoshida, I.; Ueno, K.; Kobayashi, H. Selective Separation of Arsenic(III) and (V) Ions with Ferric Complex of Chelating Ion-Exchange Resin. Sep. Sci. Technol. **1978**, *13* (2), 173–184.
4. Egawa, H.; Nonaka, T.; Maeda, H. Studies of Selective Adsorption Resins. XXII. Removal and Recovery of Arsenic Ion in Geothermal Power Waste Solution with Chelating Resin Containing Mercapto Groups. Sep. Sci. Technol. **1985**, *20* (9 & 10), 653–664.
5. Chanda, M.; Odriscoll, K.F.; Rampel, G.L. Ligand Exchange Sorption of Arsenate and Arsenite Anions by Chelating Resins in Ferric Ion Form: II. Iminodiacetic Chelating Resin Chelex 100. React. Polym. **1988**, *8*, 85–95.
6. Matsunaga, H.; Yokoyama, T.; Eldridge, R.J.; Bolto, B.A. Adsorption Characteristics of Arsenic(III) and Arsenic(V) on Iron(III)-Loaded Chelating Resin Having Lysine-N^{α}, N^{α}-Diacetic Acid Moiety. React. Func. Polym. **1996**, *29*, 167–174.
7. Nagy, S.; Shaw, P.; Veldhuis, M.K. Nutrition, Anatomy, Chemical Composition and Bioregulation. *Citrus Science and Technology*; AVI Publishing Company, Inc.: Westport, Connecticut, 1977; Vol. 1, 74–479.
8. Haron, M.J.; Wan Yunus, W.M.Z.; Yong, N.L.; Tokunaga, S. Sorption of Arsenate and Arsenite Anions by Iron(III)–Poly(Hydroxamic Acid) Complex. Chemosphere **1999**, *14* (39), 2459–2466.
9. Bard, A.J.; Parsons, R.; Jordan, J. Arsenic. *Standard Potentials in Aqueous Solution*; Marcel Dekker, Inc.: New York, 1985; 162–171.
10. Cotton, F.A.; Wilkinson, G. The Elements of the First Transition Series. *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley and Sons: New York, 1988.

Received August 2001
Revised January 2002