

Effective Use of Orange Juice Residue for Removing Heavy and Radioactive Metals from Environments

Katsutoshi INOUE¹, Yushan ZHU¹, Kedar Nath GHIMIRE², Masayuki YANO¹,

Kenjiro MAKINO³ and Tohru MIYAJIMA²

¹Department of Applied Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan

²Department of Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan

³Yamasoh Micron Inc., 1-21-12, Uenoshibamachi, Sakai 593-8301, Japan

Large amounts of orange juice are produced in Japan every year. Accompanied by the production of orange juice, large amount of juice residues are also generated in nearly the same amounts with juice. Although, at present, some of these residues are marketed as a feed for cattle after drying and mixing with lime, the marketing price is lower than its production cost and the difference is paid by the consumers as a part of the price of orange juice. In the present work, we developed new innovative use of orange juice residue, a biomass waste, as adsorption gel for removing toxic heavy metals such as lead, arsenic, selenium and so on as well as radioactive elements such as uranium and thorium from environments.

The major components of orange juice residue are cellulose, hemicellulose and pectin, which are converted into pectic acid, an acidic polysaccharide, by means of saponification with concentrated sodium hydroxide solution. In the previous work, we found that crosslinked pectic acid gel strongly and selectively adsorbs lead over other metals such as zinc and copper. On the other hand, it is well known that polysaccharides such as cellulose can be easily phosphorylated and that phosphorylated polysaccharides have high affinity to uranium and thorium as well as some trivalent metals such as ferric iron and aluminum.

Taking account of the noticeable characteristics of these polysaccharides, 2 types of adsorption gels were prepared from orange juice residue: one is the gel which was prepared by saponifying the residue followed by crosslinking with epichlorohydrin and another is that prepared by crosslinking the residue followed by phosphorylation. The former gel exhibited excellent adsorptive separation behavior for lead away from zinc owing to high content of pectic acid while the latter gel exhibited that for uranium and thorium. Both types of adsorption gels exhibited high affinity to ferric iron, which enables selective and strong adsorption for some toxic oxo-anions of arsenic (V and III), selenium and so on via iron loaded on these gels.

These results demonstrate that biomass wastes such as orange juice residue can be effectively utilized for the purpose of removing toxic heavy or radioactive metals existing in trace or small amounts in environments.

Introduction

Recently, there is a growing interest of using biomass wastes for the removal and recovery of hazardous materials generated from mineral and chemical industries. The main advantage of using such materials is due to their environmental friendly nature in one hand and their highly selective nature on the other. Much attention has been paid for the separation of various metal ions by using biomass wastes derived from fishery industries like chitin and chitosan [1]. Similarly, apple juice residue has been studied as an adsorption gel for the removal and recovery of copper from the aqueous medium [2].

Cell walls of prokaryotes and eukaryotes contain polysaccharides as basic building blocks. The ion exchange

properties of natural polysaccharides have been extensively studied and it is a well-known fact that metal ions exchange with counter ions of the polysaccharides [3]. Pectic acid and alginic acid are natural acidic polysaccharide containing carboxylic groups existing in cell wall of all land plant tissues and of seaweeds, respectively, which functions as an intercell cementing material. Because of their non-toxicity nature and metal binding properties, they are suitable for adsorption of metals from aqueous solutions. Alginic acid has the highest complexation ability for lead among the natural biopolymers tested by Deans and Dixon [4]. The application of natural biopolymers as adsorbents for heavy metals have been extensively studied and its potentials have been appreciated [5-6].

Tsezos *et al.* have studied biosorption of uranium and thorium by using *R. arrhizus* and reached the conclusion that uranium and thorium can be removed 2-3 times and 20 times, respectively, more than the synthetic ion exchange resin [7].

In our previous work, we have studied four different forms of alginic acid and pectic acid regarding the adsorption of lead, copper and zinc and indicated that both of pectic and alginic acid gels strongly and selectively adsorb lead over other metals such as zinc and copper [8].

In the present work, we have explored orange juice residue itself, one of typical biomass, the major components of which are cellulose, hemicellulose, and pectin, rather than pure pectic acid or alginic acid from practical points of view.

Experimental

Preparation of adsorption gel from orange residue

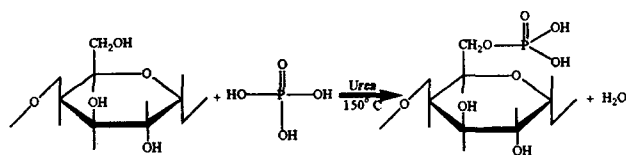
Two types of adsorption gels were prepared from orange juice residue, abbreviated as OJR hereafter, which was kindly provided from JA Bibberage Saga. One was saponificated gel and another was phosphorylated gel, which are abbreviated as SOJR and POJR, respectively, hereafter. Since pectin substances are water soluble at high pH, both gels were crosslinked with epichlorohydrin.

The former was prepared by the following method from dried OJR marketed as a feed for cattles, which is produced by drying together with lime at high temperature in rotary kiln. The sample of dried OJR was washed with 80% aqueous ethanol solution to remove some organic components like chlorophyll pigments and other low molecular-weight compounds such as limonene and so on [9]. Subsequently, it was saponificated by interacting for 1h at 25° C with 20 mM sodium hydroxide in 50% aqueous acetone solution for the purpose of increasing the content of pectic acid, the component which has strong binding affinity for lead(II) ion contained in OJR, by hydrolyzing methyl ester part of original pectin substance. The saponificated OJR was further crosslinked with epichlorohydrin in dimethyl sulphoxide (DMSO) containing 5N sodium hydroxide at 50° C and washed with ion-exchanged water at 50° C for 1h to remove water-soluble components.

The latter was prepared from crude OJR just after juicing as follows. The crude OJR was dried in a convection oven at a temperature of 50° C and then dried *in vacuo*. The dried OJR grounded into smaller particles with the aid of ball-mill. The particle size of the powder was around 100-200 µm. 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 to be unsatisfactory to strongly adsorb some metal ions except for lead(II), cellulose and hemicellulose parts of OJR was phosphorylated after crosslinking in order to convert their abundant hydroxyl groups into phosphate groups with high affinity to some metal ions as follows. 20g of dried OJR

powder was stirred in 750 ml of 80% aqueous propanol for about 24 h 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 subjected to be dry *in vacuo* for 24 h.

It was then crosslinked as follows. 8.5g of dried OJR thoroughly washed with propanol was taken into a flask together with 300 ml of dimethyl sulphoxide (DMSO) and stirred for 24 h at 25° C. Then 40 ml of epichlorohydrin was added to the mixture to undergo the crosslinking reaction at 50° C for 5 h. After cooling down to room temperature, it was filtered and washed with 70% aqueous propanol followed by washing with 0.5M HCl and finally with ethanol to neutral pH. The sample was kept for dry *in vacuo* for 24 h. After crosslinking, the gel was phosphorylated according to the following reaction.



8.6g of cross-linked OJR were soaked in 200 ml of dimethyl formamide (DMF) for overnight and removed the contaminated DMF by vacuum filtration. The gel once again immersed in 200 ml of fresh DMF was taken in a flask along with 30g of urea, and the mixture was stirred by the aid of magnetic stirrer during which 18g of phosphoric acid were added dropwise. After one hour stirring, the temperature of the reaction mixture was raised to 150° C and further stirred for 2 h. 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 kept the gel for dry *in vacuo* for 2 days. The dry weight of phosphorylated gel was 7.8g.

The phosphorus content in POJR was measured as the P_2O_5 mass% with the aid of Rigaku ZSX 100E fluorescence X-ray crystallography as 20%, which is equivalent to 1.15 mol of phosphorus per glucose unit of POJR.

SOJR gel was used for removing lead(II) ion separating away from zinc while POJR was used for recovering uranium and thorium or for removing heavy metals existing as oxoanions such as arsenate, arsenite, selenate, selenite and so on after loading ferric ion on the POJR gel.

Chemicals

All chemicals used in this study were of pure analytical grade purchased from Katayama Chemical Co. Ltd. Japan, unless and otherwise mentioned. Metal solutions were prepared by dissolving the corresponding analytical grade metal nitrate or chloride of lead(II), zinc(II), iron(III), thorium(IV), uranium(VI), antimony(III) in dilute nitric or hydrochloric acid solution.

Methods

Batch test

In the batchwise tests, 25 mg of dried adsorbent was taken into a conical flask together with a 15ml portion of corresponding aqueous solution. The pH of the aqueous solutions was adjusted by adding small amount of HCl or NaOH and in some cases 2-[4-(2-Hydroxyethyl)-1-piperazinyl] ethanesulphonic acid (HEPES) was used as the buffer reagent. The flask was shaken vigorously in a thermostated shaker at 30°C for about 24 h 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.

Column test

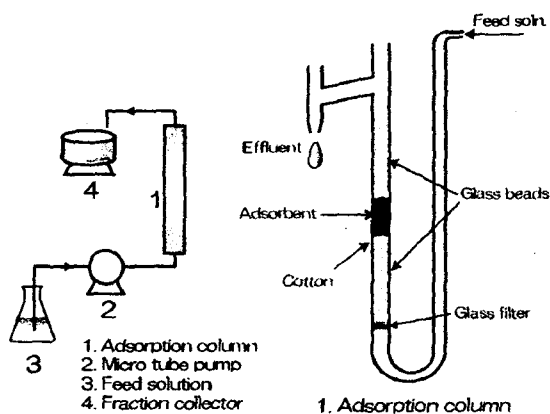


Fig. 1 Schematic diagram of adsorption column.

Adsorption tests were carried out also by using a glass column of 8 mm diameter packed with 0.1 g of SOJR gel or iron-loaded POJR gel as shown in Fig.1. In the case of adsorptive removal of arsenic by using iron loaded POJR gel, 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 cm³/h using a peristaltic pump (IWAKI PST-100N, Japan). Effluent samples were collected at each one-hour interval of time by using 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. 1M hydrochloric acid was used as the eluent, which was percolated into the column at the same constant flow rate of 6 cm³/h using the peristaltic pump.

Similarly, in the case of the separation of lead away from zinc by using SOJR gel, the adsorption column packed with SOJR was conditioned by passing water of pH = 2.6. A feed containing 102.3 and 95.95 ppm of lead(II) and zinc(II), respectively, were percolated into the column at a

constant flow rate of 5.5 cm³/h using a peristaltic pump. The pH of the feed solution was maintained at 2.6. Effluent samples collected at each interval of time were used for their residual concentration measurement. Subsequently, the adsorbed lead(II) and zinc(II) were eluted at a flow rate of 5.5 cm³/h using 1M nitric acid as the eluent.

The concentration of the eluted arsenic(V), lead(II) and zinc(II) effluents collected at each interval of time in the tube of fraction collector were measured by using Shimadzu Model ICPS-5000 ICP/AES spectrometer or Shimadzu AA-6650 atomic absorption spectrophotometer.

Results and Discussion

Adsorption of lead(II)

Figure 2 shows the adsorption behavior of SOJR gel and DIAION WK11 resin, a weakly acidic cation-exchange resin containing carboxylic groups, for comparison, for lead and zinc as a function of pH. It is seen that lead is selectively and strongly adsorbed on SOJR gel over zinc and, at the same time, the selective adsorption of lead on SOJR gel is much superior to WK11 resin, which is considered to be owing to high content of pectic acid in SOJR gel [10].

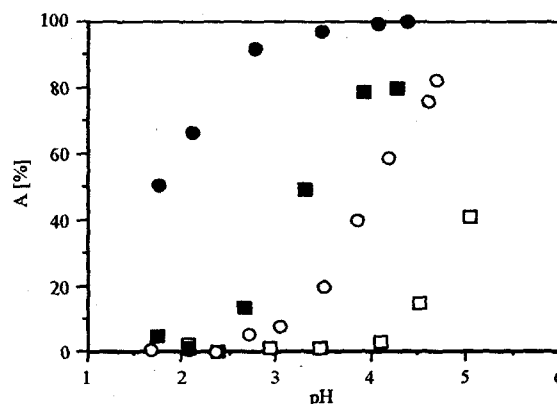


Fig. 2 Adsorption of lead(II) and zinc(II) as a function of pH.

- : SOJR gel - Pb(II)
- : SOJR gel - Zn(II)
- : WK11 resin - Pb(II)
- : WK11 resin - Zn(II)

Adsorption of iron(III)

Iron(III) was nearly quantitatively adsorbed from aqueous solution containing 55.85 ppm iron over the pH region of 1 to 3. Adsorption isotherm of iron(III) on POJR at varying equilibrium concentration is shown in Fig.3. The maximum iron uptake capacity was evaluated as high as 3.7 mol/kg dry gel. The high value of Fe(III) uptake capacity by the POJR gel may be due to synergistic effect of additional carboxyl functionalities present within the polymer matrix which could accommodate more metal ions. After knowing the maximum loading capacity of those corresponding gels were loaded with Fe(II) at their optimum concentration and pH range in order to further investigate their adsorption

characteristics for arsenic, selenium and antimony.

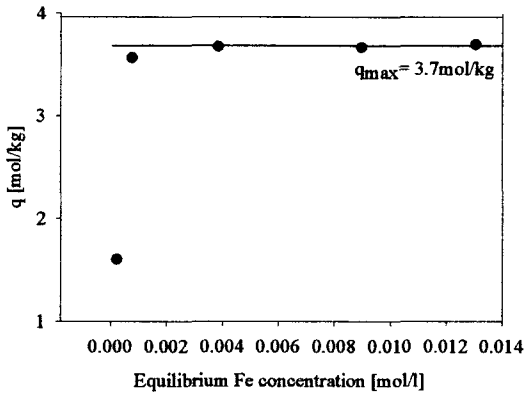


Fig.3 Adsorption isotherm of iron(III) at varying concentration on POJR gel.

Adsorption of Thorium and Uranium

Figure 4 shows adsorption percentage of thorium and uranium as a function of equilibrium pH at an initial concentration of 15 ppm. Thorium was quantitatively adsorbed over whole pH tested selectively over uranium. Since radiowaste has to be treated at very low pH, the POJR gel seems to be effective for such purpose. The adsorption of thorium and uranium is considered to take place with the release of proton on the phosphorylated part of the alcoholic analog of orange juice residue according to a cation exchange mechanism.

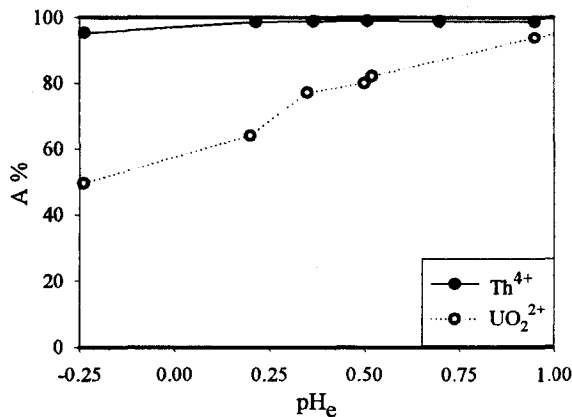


Fig.4 Adsorption of thorium and uranium as a function of pH.

Adsorption of Arsenic

Figure 5 shows the relationship between % adsorption and equilibrium pH in the adsorption of arsenate and 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 on POJR gel 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. 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. The 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% and 85% in the case of As(V) and As(III), respectively.

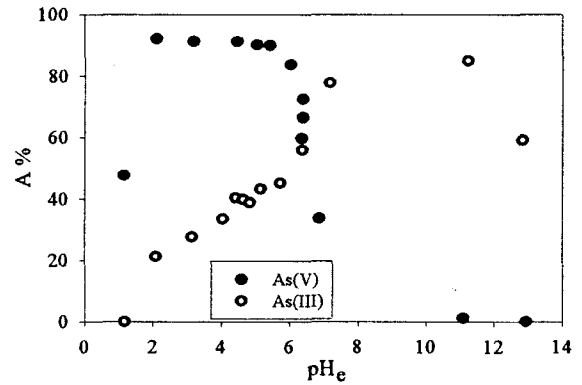


Fig.5 Adsorption of As(III & V) on iron-loaded POJR as a function of pH.

Adsorption of Selenium

Figure 6 shows the adsorption percentage of selenate and selenite as a function of equilibrium pH. The optimum adsorption condition for selenite is acidic within the pH range 2-6 and a highest adsorption of 85% has been achieved at pH=3. In contrary, selenate are not effectively adsorbed, only up to the extent of 36% at the same pH of 3, as can be seen in Fig.6.

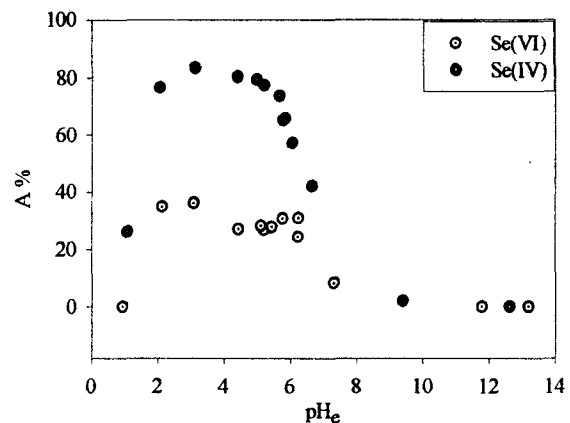


Fig.6 Adsorption of Selenium(IV and VI) on iron-loaded POJR as a function of pH.

Adsorption of Antimony

Figure 7 shows the pH dependency of the adsorption of antimony(III) on three different kinds of adsorbents: iron-loaded POJR, iron-loaded DIAION CRP-200, a phosphonic acid type chelating resin, and activated alumina. It is observed from the figure that iron-loaded DIAION CRP-200 is prevalent at acidic pH condition up to 4 and on the other hand activated alumina only at highly alkaline condition for the removal of antimony. In contrary, POJR is effective over wide pH ranging from 2-11, showing very high antimony removal capacity even at neutral condition.

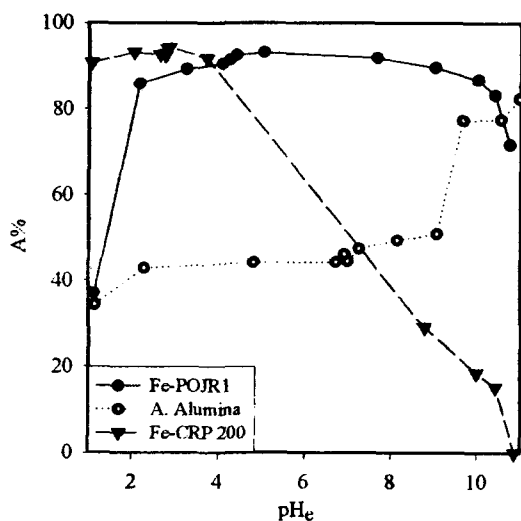


Fig.7 Adsorption of Sb(III) on three different adsorbents as a function of pH.

Column experiment

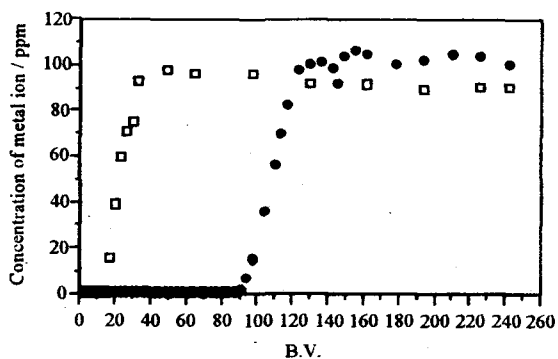


Fig.8 Breakthrough curves of Pb(II) and Zn(II) from the column packed with SOJR gel. ●: Pb(II), □: Zn(II).

Feed concentration, Pb(II):102.3ppm, Zn(II) : 95.95ppm.
pH of feed solution = 2.60. Flow rate = $5.5\text{cm}^3\text{ h}^{-1}$
Dry weight of the packed gel = 100mg.
Volume of the packed gel = 2.83cm^3

Figure 8 shows the breakthrough curves of lead(II) and zinc(II) from the column at an initial concentration of 102 and 96 ppm, respectively. This figure shows that breakthrough of lead(II) occurred at 90 bed volumes and the bed was completely saturated at 160 bed volumes, while that of zinc(II) takes place at 20 bed volumes, suggesting very easy mutual separation between these metal ions by using the column packed with SOJR gel. The adsorbed lead ion was completely eluted at 6 bed volumes by using 1M nitric acid solution while only negligible concentration of zinc was detected in the effluent, as seen in Fig.9.

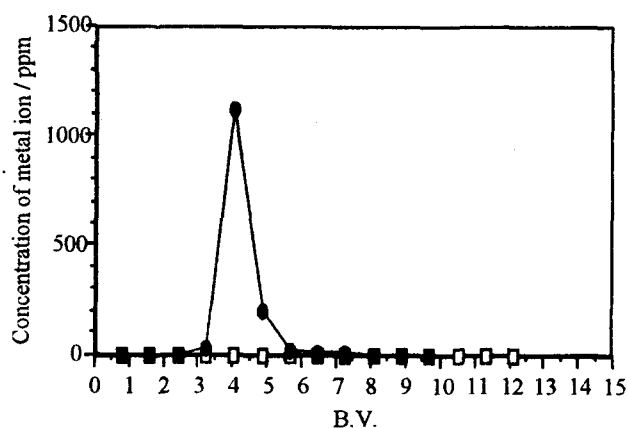


Fig.9 Elution curves of Pb(II) and Zn(II) from the column.
● : Pb(II) □ : Zn(II). Eluent = 1M of nitric acid solution.
Flow rate = 5.5ml h^{-1}

Figure 10 shows the breakthrough curve of As(V) from the column packed with the iron(III)-loaded POJR at an initial concentration of 15.8 ppm. The breakthrough began at 80 bed volumes and the bed was completely saturated at 342 bed volumes.

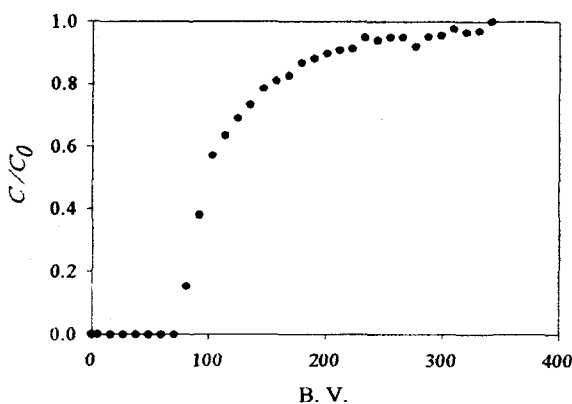


Fig.10 Breakthrough curve of As(V) from the column packed with Fe(III)-loaded POJR.

Arsenate adsorbed onto the column bed can be recovered by eluting either with alkaline or by acidic eluent. Since stripping using alkaline eluent still leaves the As(V) to a considerable extent in the column, it was recovered using 1M HCl as the eluent. As seen in the elution profile in

Fig. 11, the elution was completed within 38 bed volumes. Since the loaded Fe(III) was also eluted together with arsenate, it is necessary to load iron(III) once again onto the gel for the next operation.

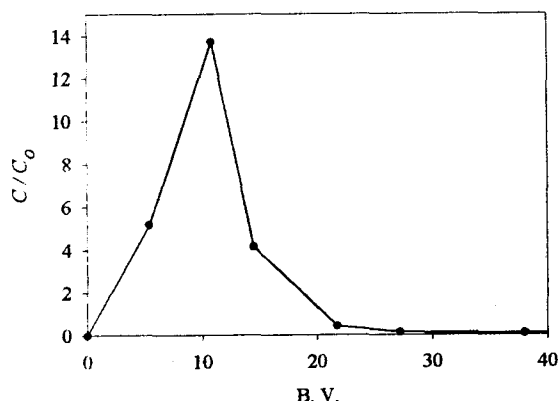


Fig.11 Elution profile of As(V) by using 1M HCl.

Conclusions

Effective use of orange juice residue as the adsorbents has been achieved to remove heavy as well as radioactive metals like thorium and uranium from aqueous environments. The technology offered in this paper provides an insight of the fact that biomass waste can be converted into valuable resources for the effective cleaning of aqueous environment contaminated with heavy metals and radioactive metals.

Acknowledgement

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.

References

- [1] Inoue, K., 1998. *Application of Chitosan in Separation and Purification of Metals*. Recent Advances in Marine Biotechnology : Oxford & IBH Publishing Pvt. Ltd.
- [2] Lee, S. H. and Yang, J. W., 1997. *Separation Science and Technology*. 32, 1371-1387.
- [3] Tanaka, Y., and Skoryna, S., 1970. *Organic Macromolecular Binders of Metal Ions*. Gastrointestinal Research Laboratory of Mc Gill University, Montreal.
- [4] Deans, J. R. and Dixon, B. G., 1992. *Water Research*. 26, 469-472.
- [5] Jang, L. K., Geesay, G.G., Lopez, S. L., Eastman, S. L., and Wichlacz, P. L., 1990. *Water Research*. 24, 889-897.
- [6] Chen, D., Lewandowski, Z., Roe, F., and Surapaneni, P., 1993. *Biotechnology and Bioengineering*. 41, 755-760.
- [7] Tsezos, M., Volesky, B., 1981. *Biotechnology and Bioengineering*. 23, 583-604.
- [8] Yano, M. and Inoue, K., 1997. *Analytical Sciences*. 13 (suppl.), 359-360.
- [9] Nagy, S., Shaw, P. and Veldhuis, M. K., 1977. *Citrus Science and Technology, Nutrition, Anatomy, Chemical Composition and Bioregulation*, The AVI Publishing Company, Inc., Westport, Connecticut, , vol.1, 74-479.
- [10] Yano, M., Inoue, K. Makino, K., and Baba, Y., 2001. *Environmental Science* (in press).