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Adsorptive Separation of Metal Ions onto Phosphorylated Orange Waste

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Abstract: A highly selective and efficient biosorbent has been prepared from orange waste by introducing a phosphoric group at its polymer analog by simple chemical modification. Their adsorption behavior for several kinds of metal ions was studied and it was found to exhibit excellent selectivity towards several metal ions. As a typical example, a binary mixture of In(III) and Zn(II) was studied by using a packed column, indicating that In(III) ion can be selectively separated from its mixture with a concentration factor of 63 times. The maximum adsorption capacities evaluated in terms of mol/kg dry gel were 0.70 for In(III) and Ga(III), 0.97 for Cu(II), 1.15 for Pb(II) and Zr(IV), and 3.06 for Fe(III), respectively.

Keywords: Orange waste, phosphorylation, adsorption, ion exchange

INTRODUCTION

There is a growing concern for the recovery and recycling of valuable metals taking account of the shortage of mineral resources in future as well as the removal of toxic metals from the environment. Recently, the removal of toxic heavy metals has been already established after the serious disasters caused by the heavy metal pollution as, for example, the Minamata case in Japan. However, due to increasing human civilization with the fabrication of many chemical and pharmaceutical industries, heavy metal pollution in water and soil is a matter of utmost concern though they may not be severe

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compared with the case of Minamata. To date, the majority of heavy metals in wastewater are removed by means of precipitation by adding calcium hydroxide, in which large amounts of nontoxic metal compounds such as calcium sulfate are also precipitated together with heavy metals as a precipitated sludge, which are dumped in the landfill sites. It has become difficult not only to meet stringent environmental regulation by means of precipitation technique, but also landfill sites are expected to become unavailable in recent years as they have been already occupied by large amounts of polluted sludge in Japan. On the other hand, many heavy metals contained in these wastes are valuable and indispensable resources. Therefore, for a sustainable society in future, it is necessary to recover metal resources from various wastes instead of discarding in the landfill sites. Although adsorptive recovery and removal using ion-exchange chelating resin could be an alternative, such an approach is expensive taking account of the post-treatment of spent resin and, in addition, it also poses other environmental problems if such synthetic plastic materials are incinerated.

Recently, low cost adsorbents prepared from various wastes generated from forestry, fishery, and agriculture have attracted much attention to several workers. Some of the reported sorbents include peanut hulls (1), maize bran (2), sawdust (3), sugar beet pulp (4), crab shell (5), cornstarch (6), exhausted coffee (7), rice husk (8), chitin (9), orange waste (10, 16) and biological materials including bacteria (11), yeast (12), algal biomass (13, 14) and tuber bark waste (15) just to mention a few in the literature. These biomaterials have been recognized as the potential alternative to conventional technologies for the removal of heavy metals from the wastewater. Thus, it is possible to effectively recover valuable metals and remove toxic metals from wastewater by using low cost biomass wastes as such and, consequently, it would be a good solution for the difficult problems as mentioned above.

From such an economical viewpoint, we have prepared an adsorption gel from orange waste by making a simple chemical process of phosphorylation. In contrast to the ion-exchange chelating resin made of plastic, this gel is free from any refractory post-treatment after its use since the main components of the gel are natural polysaccharides, that is very easy to be incinerated. In the present investigation, we have attempted to evaluate the adsorption characteristics for several kinds of cationic metals onto the phosphorylated orange adsorption gel (POAG) in terms of selectivity and maximum adsorption capacities.

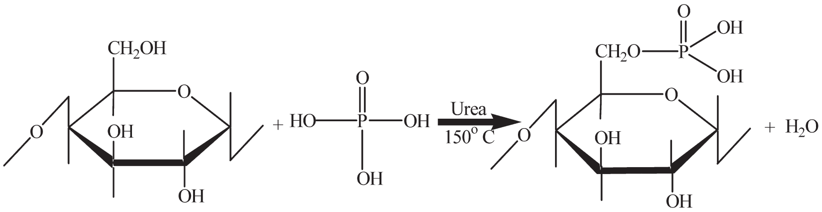
Indium is an indispensable metal for the production of liquid crystalline display. Accompanied by the rapid increase in the production of liquid crystalline display in recent years, the demands for indium is now increasing a lot and its cost is also rapidly rising. Consequently, the effective recovery process of indium from various resources including secondary resources is now strongly required. Since indium occurs in zinc ores at trace quantities $<1\%$ in nature (16), it has to be selectively recovered from zinc. For this provision, we have tried to employ POAG gel to effectively recover indium.

Environmental pollution by arsenic has been seriously observed not only in various industrial effluents but also in some ground water or hot spring water over a large area in Asian countries. Arsenic species found in aqueous media are anionic species of arsenate and arsenite, which coexists together with large excess of other anionic species such as carbonate, sulfate, and chloride. Since usual anion exchange resins have no selectivity to arsenite and arsenate over the above-mentioned other anionic species, they are difficult to employ to selectively remove arsenic from environments. Yoshida et. al. proposed to use chelating resin loaded with ferric ion which has high a affinity to arsenate and arsenite (17). However, chelating resins are expensive and unsuitable for the recovery of arsenic, a valueless material. In addition chelating resins suffer from the drawbacks mentioned earlier. In the previous work (18), we found iron(III)-loaded POAG exhibits favorable adsorption behavior both for arsenate and arsenite. As will be mentioned later, since POAG was found to exhibit the highest selectivity to Zr(IV), we also studied the adsorptive separation of arsenic onto the zirconium-loaded POAG and compared with the iron(III)-loaded POAG in the present work.

EXPERIMENTAL

Preparation of Phosphorylated Orange Adsorption Gel (POAG)

The feed material employed in this study was wet crude orange waste, hereafter abbreviated as OW, provided from juice factory of JA Beverage Saga Co. Ltd., Japan. The OW was dried in an oven at a temperature of 60°C for 48 h and then crushed to a fine powder which passes the mesh size of 150 μm. Thus obtained powdered OW was washed with 70% methanol repeatedly until it had no color in the filtrate. The thoroughly washed OW sample was dried in an oven for 24 h at 60°C. The OW contains cellulose, hemicellulose, pectins, water soluble sugars, limonene, and other low molecular weight compounds (19). The cellulosic and hemicellulosic contents of OW was phosphorylated for the conversion of alcoholic hydroxyl groups at 6-th position in particular into phosphate groups that has high affinity for the binding of metal ions according to the following reaction.



10 g of dried OW was soaked in 200 mL of dimethyl formamide (DMF) overnight in a 500 mL three-necked flask equipped with a magnetic stirrer

and then 30 g of urea was added into the reactor followed by 18 g of phosphoric acid drop wisely. The suspension was stirred for a while maintaining the reaction temperature at 150°C. After cooling to room temperature, it was washed with 70% methanol followed by water washing till neutrality. The solid product was dried in a convection oven for 24 h at 60°C. Thus obtained dried product was termed as phosphorylated orange adsorption gel (POAG) and used for the subsequent adsorption tests of metal ions.

Chemicals

All chemicals used in this study were of pure analytical grade purchased from Katayama Chemical Co. Ltd. Japan, unless otherwise mentioned. Aqueous solutions of Fe(III), Al(III), In(III), Co(II), Ni(II), and Cu(II) were prepared from their chloride salt while Ga(III), Cd(II), Zn(II), and Pb(II) from their corresponding nitrate salt, and that of iron(II) from ferrous ammonium sulfate, Zr(IV) from zirconium oxychloride, and V(IV) from vanadyl sulfate, respectively. Arsenic solutions were prepared by dissolving a corresponding analytical grade arsenic trioxide and sodium arsenate as appropriately, in deionized water and dilute hydrochloric acid or sodium hydroxide solution. 0.1 M solution of 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulphonic acid (HEPES) was used for the purpose of buffering purchased from Sigma Aldrich.

Evaluation of Exchangeable Cations

The evaluation of the exchangeable protons of POAG was carried out as follows. 50 mg of dried gel and 30 ml of 0.01 M of standardized sodium hydroxide was taken into five separate stoppered bottles for each sample and shaken for 24 h at 30°C. The decrease in basicity was evaluated by titrating the filtrate with standardized 0.01 M hydrochloric acid using phenolphthalein as the indicator. On the other hand, 50 mg of gel was dissolved with 30 mL of aqua regia for 24 h at 30°C. The concentration of phosphorus dissolved in the filtrate was measured by Shimadzu Model ICPS-8100 ICP/AES spectrometer.

Adsorption Tests

In the batchwise tests, 25 mg of dried adsorbent was taken into the 50 mL conical flask together with 15 mL of corresponding aqueous solution. The pH of the aqueous solutions was adjusted by adding small amounts of hydrochloric acid or sodium hydroxide solutions and 2-[4-(2-Hydroxymethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) was also used as a buffer reagent.

The flask was shaken vigorously in a thermostated shaker at 30°C at 150 rpm for 24 h to ensure the equilibrium to be attained. The initial and equilibrium concentrations of metal ions were measured by using Shimadzu Model ICPS-8100 ICP/AES spectrometer or Shimadzu AA-6650 atomic absorption spectrophotometer. The arsenic concentration of less than 1 mg/l was measured using the atomic absorption spectrophotometer equipped with Shimadzu model HVR-1 hydride vapor generator. The adsorption efficiency, A%, of the metal ion was calculated from

$$A\% = (C_i - C_i)/C_i \times 100 \tag{1}$$

The adsorption capacity of metal ions is the concentration of metal ions on the adsorbent and can be calculated based on the mass balance principle where

$$q = \{(C_i - C_e)/W\} \times (L/1000) \tag{2}$$

In the above equations, q represents the amount of metal uptaken per unit mass of the adsorbent (mol/kg), L the volume of the test solution (mL), W the dry mass of the adsorbent (g), C_i and C_e the initial and final concentrations (mol/dm^3), respectively.

Since arsenic can not be directly adsorbed onto the gel, it was loaded with Zr(IV) prior to arsenic adsorption. 2 g dried gel was shaken together with 1 L of 10 mM zirconium oxychloride solution at pH = 2.0 for 24 h at 30°C. The amount of zirconium loaded onto the gel was evaluated to be 1.04 mol/kg dry gel.

Adsorption Study Using a Packed Column

Mutual adsorptive separation of small concentration of In(III) from large excess of Zn(II) was carried out using a glass column of 8 mm internal diameter packed with 100 mg of POAG. The column was conditioned by passing water of pH = 1.30 overnight. The sample solution containing 7.30 mg/l of In(III) and 861 mg/l of Zn(II), whose pH was maintained at 1.30, was percolated into the column at a constant flow rate of 5.06 ml/h using a peristaltic pump (IWAKI PST-100 N, Japan). Effluent samples were collected at each one-hour interval of time by using a fraction collector (BIORAD Model 2110 Fraction Collector) to measure the corresponding metal ion concentrations.

For the elution tests, the column was pre-washed with deionized water so as to expel any unbound metal ions. 1 M hydrochloric acid solution used as the eluent was percolated into the column at the same constant flow rate of 5.06 ml/h using the peristaltic pump. The concentration of the eluted metal ions collected at each interval in the tube of fraction collector was measured by using a Shimadzu Model ICPS-8100 ICP/AES spectrometer.

RESULTS AND DISCUSSION

Characterization of POAG

The amount of exchangeable protons contained in POAG was evaluated as 2.36 mol/kg and the amount of phosphorus content as 37.16 mg of phosphorus per unit g of POAG, which is equivalent to 1.20 mol of phosphorus per kg gel. The number of exchangeable protons and the phosphorus content suggests that protons availed in phosphoric group are involved for the ion exchange process. The evaluated values are almost the same with the gel that was initially crosslinked and further phosphorylated as reported in the previous work (18). However, the result of the present work indicated that expensive processes like crosslinking and vaccum drying can be eliminated, thereby providing the possibility of a cheaper means of gel preparation process as compared to our earlier work.

Characterization of POAG was accomplished by IR spectroscopy. The spectrum of unmodified OW and POAG are given in Fig. 1. The spectrum of POAG displayed two strong bands at 1258 and 1172 cm^{-1} in relation to that of unmodified OW, which demonstrated the presence of two types of phosphorus environment; one relative to phosphate ester and another relative to aliphatic phosphine oxides. There is also a broad band assigned for single -OH at 1600 cm^{-1} from the O═P-OH vibration of the phosphoric acid group contained in the POAG (20).

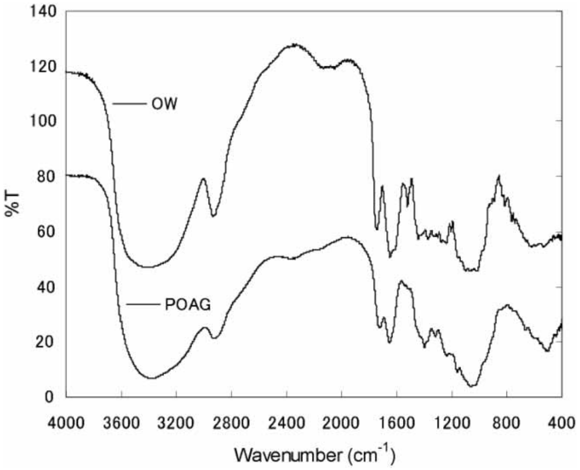


Figure 1. IR spectrum of orange waste (OW) and phosphorylated adsorption gel (POAG).

Effect of pH on the Adsorption of Metal Ions

Figure 2 shows the % adsorption of Cd(II), Zn(II), Cu(II), Fe(III), Fe(II), Ni(II), Pb(II), Co(II), Al(III), Ga(III), In(III), Zr(IV), and V(IV), ions as the function of equilibrium pH. As seen in this figure, the adsorption of metal ions increases with the increase in pH, suggesting that metal ions are adsorbed according to a cation exchange mechanism, releasing protons from the phosphoric analog of POAG gel. This is further supported by the fact that the pH of the aqueous solution had been decreased after the adsorption of metal ions.

Almost all metal ions are adsorbed to the extent of almost 80–100% at weakly acidic conditions except for vanadium. Although the adsorption of Ga(III) increases with the increase in pH till 3.0, it decreased rapidly with the further increase in pH, which is inferred to be attributable to the hydrolysis of Ga(III). A similar trend has been observed for V(IV). According to Fig. 2, the order of adsorption among the tested metal ions is as follows; Zr(IV) > Fe(III) > Ga(III) = In(III) > Al(III) > Pb(II) > Fe(II) > V(IV) > Cd(II) > Zn(II) > Cu(II) > Co(II) > Ni(II). The highest adsorption strength for Zr(IV) and other trivalent metal ions onto POAG gel was owing to its higher binding affinity for those metal ions with phosphoric acid group (18).

Adsorption Isotherms

Figure 3 shows the adsorption isotherms of In(III), Ga(III), Cu(II), Pb(II), Fe(III), and Zr(IV). It appears that the adsorption increases with the

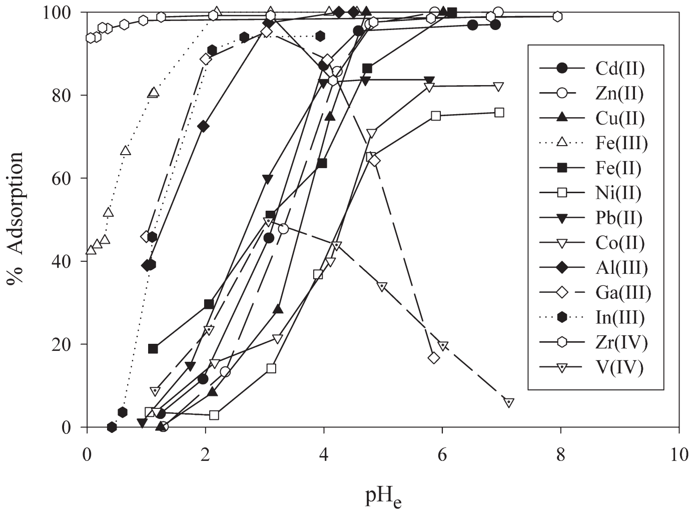


Figure 2. Effect of pH on adsorption of several metal ions onto POAG gel.

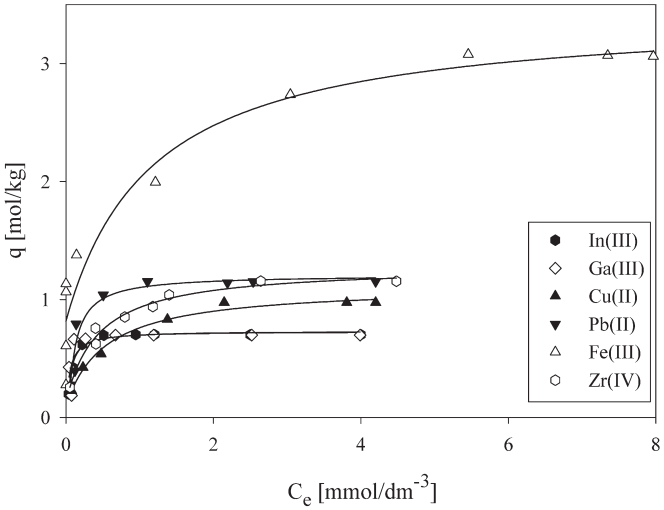


Figure 3. Adsorption isotherms of some metal ions onto POAG gel. The pH of the solutions containing In(III), Ga(III), Cu(II), Pb(II), Fe(III), and Zr(IV) ion were adjusted to 2.0, 2.5, 4.5, 4.4, 2.0, and 2.2, respectively.

increase in equilibrium concentration at low metal ion concentration and tends to approach constant values for each metal ion at their high concentration, suggesting that these metal ions are adsorbed onto the gel according to the Langmuir adsorption. From adsorption isotherm plots at which it tends to approach constant values, the maximum adsorption capacities evaluated in terms of mol/kg dry gel were 0.70 for In(III) and Ga(III), 0.97 for Cu(II), 1.15 for Pb(II) and Zr(IV), and 3.06 for Fe(III), respectively. Figure 4 shows the plots of the experimental data shown in Fig. 3 rearranged according to the Langmuir equation expressed by Eq. (3), from which parameters were evaluated as listed in Table 1(a).

$$C_{eq}/q = C_{eq}/q_m + 1/b.q_m \tag{3}$$

The solid lines in Fig. 3 are the calculated lines by Eq. (3) using these parameters. The plots are in good agreement with the calculated lines. The evaluated maximum adsorption capacities of POAG investigated in this work are much higher than the values reported about several kinds of biomass in the literatures (2, 4, 8, 14, 15). Since the POAG has exhibited the maximum adsorption capacity comparable with commercially available chelating resins, it is expected to be employed in commercial processes for the recovery and removal of some metal ions from various actual solutions.

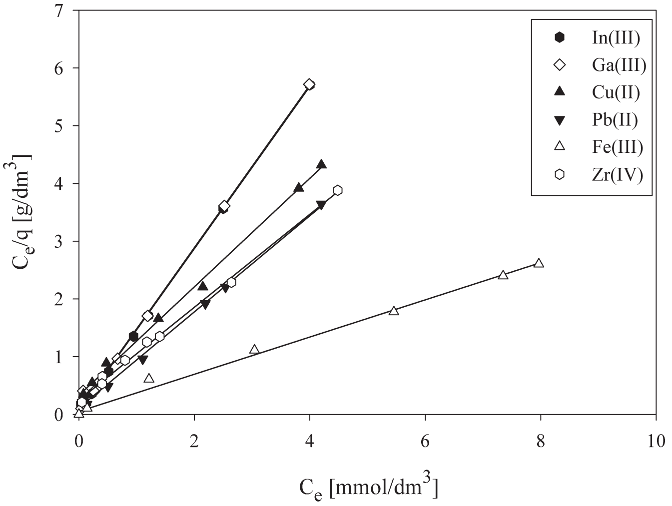


Figure 4. Langmuir plot for the adsorption of metal ions on POAG at 30°C.

Adsorptive Separation of In(III) from Zn(II) by Using a Packed Column

Since good separation of In(III) from Zn(II) was expected from the batch wise adsorption test at pH = 1.3, we have carried out their adsorptive separation at the same pH using a POAG packed column. Figure 5 shows the breakthrough curves of In(III) and Zn(II) from the column at an initial concentration of 7.3 and 861 mg/L, respectively. This figure shows that breakthrough of In(III) occurred at 198 bed volumes while that of Zn(II) took place initially, suggesting very easy mutual separation between these metal ions by using the column packed with POAG. The amount of In(III) adsorbed onto the gel packed in the column was evaluated as 0.22 mol/kg dry gel (25 mg/g), which is lower than that evaluated in the batchwise adsorption test. This is reasonably attributed to a short space time of the metal solution to reach

Table 1a. Langmuir adsorption isotherm model parameters and experimental Q_{max}

Metal	Q_{max} [mol/kg] langmuir model	Q_{max} [mol/kg] experimental	b [dm^3/mmol]	R^2
In(III)	0.71	0.7	24.36	0.99
Ga(III)	0.71	0.7	18.91	0.99
Cu(II)	1.06	0.97	2.87	0.99
Pb(II)	1.20	1.15	7.68	0.99
Fe(III)	3.10	3.06	6.71	0.99
Zr(IV)	1.24	1.15	3.29	0.99

equilibration on the one hand and too low pH compared to the condition of the adsorption isotherm experiment on the other. The adsorbed indium ion was completely eluted at 18 bed volumes by using 1 M hydrochloric acid solution while only trace concentration of zinc was detected in the effluent as shown in Fig. 6. The In(III) eluted from the column was evaluated as 2.50 mg, while that evaluated from the breakthrough curve shown in Fig. 5 was 2.55 mg, suggesting that 98% of In(III) was recovered. Thus the present adsorbent is quite efficient for the separation of binary mixture into its individual components of In(III) and zinc(II).

Arsenic Adsorption

Figure 7 shows the relation between % adsorption and equilibrium pH in the adsorption of As(III and V) on Zr(IV)-loaded gel at an initial concentration of 15 mg/L. It is obvious from the figure that the pH of the aqueous solution plays an important role for adsorption. Arsenic(V) was quantitatively adsorbed over wide pH range ~1.5–8, while As(III) at alkaline range ~8–11. This may be attributable to the pH-dependant anionic form of each kind of arsenic species. This trend of arsenic adsorption is in good agreement with our previous work (18). It is inferred that neutral or anionic form of As(III and V) were adsorbed onto the Zr(IV)-loaded gel according to the ligand exchange adsorption mechanism with the substitution of water

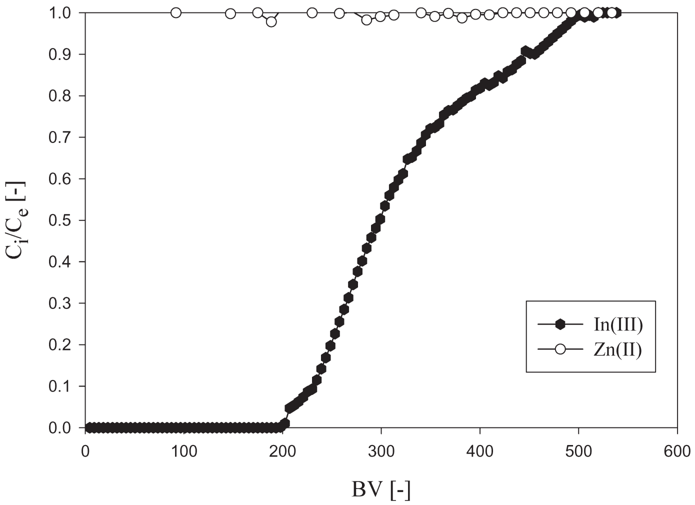


Figure 5. Breakthrough curve in the adsorption of In(III) and Zn(II) on POAG loaded column at an initial concentration of 7.3 and 861 mg/L, respectively. The pH of the solution containing both the metal ions was maintained at 1.3 with a flow rate of 5.06 ml/h, while the dry weight of the loaded gel was 100 mg.

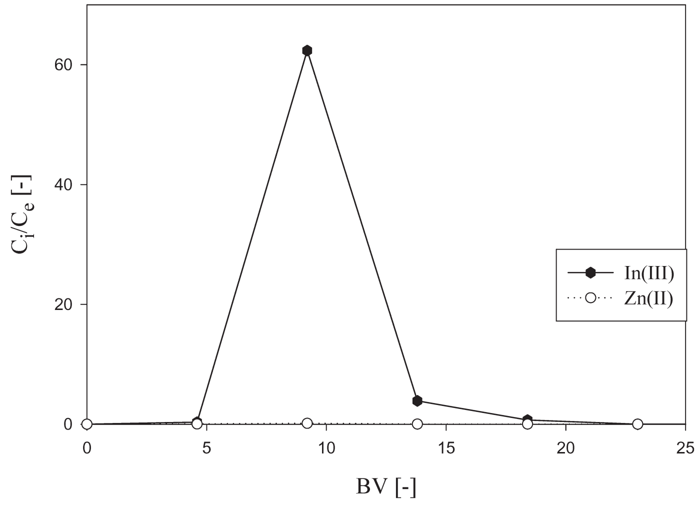


Figure 6. Elution profile of In(III) and Zn(II) from the column by 1 M HCl.

molecules or hydroxyl anions in the coordination sphere of the pre-loaded Zr(IV) as shown in Scheme 1. At highly acidic conditions ($[H+] \geq 0.6$ M), the tetranuclear species is the dominant species and at conditions with $[H+] \leq 0.5$, the octanuclear species becomes predominant (16). Since Zr(IV) was loaded onto the POAG gel at pH = 2, the adsorbed Zr(IV) species is considered to be octanuclear.

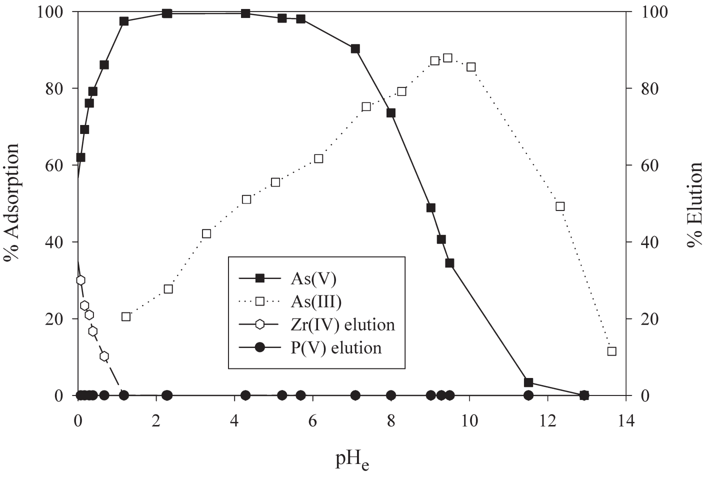
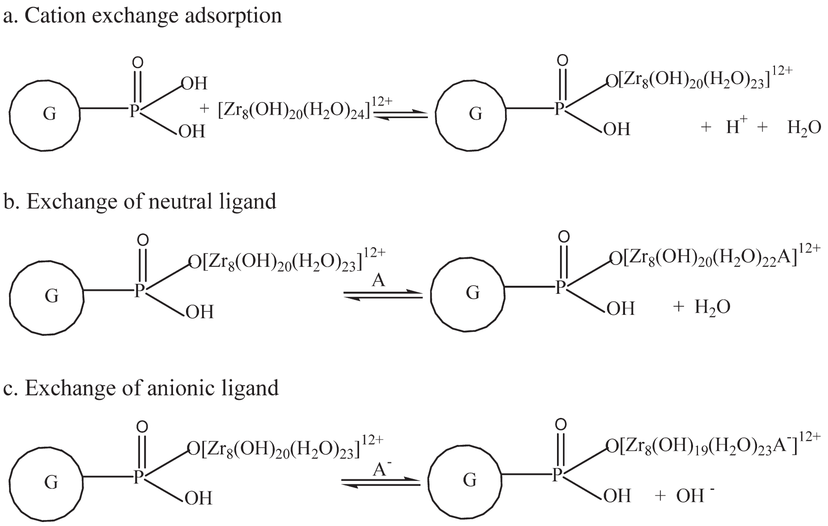


Figure 7. Effect of pH on adsorption of As(III and V) onto Zr(IV)-loaded POAG.



Scheme 1. Adsorption of Zr(IV) onto the gel and subsequent ligand exchange mechanism for As(III and V) as the neutral (A) or anionic species (A^-).

Figure 8 shows adsorption isotherms of As(III) and As(V) onto Zr(IV)-loaded POAG measured at pH = 10.0 and 3, respectively. According to Eq. (3), Langmuir parameters were evaluated together with maximum adsorption capacities as listed in Table 1(b). The solid lines in Fig. 8 represent the calculated plots according to Eq. (3).

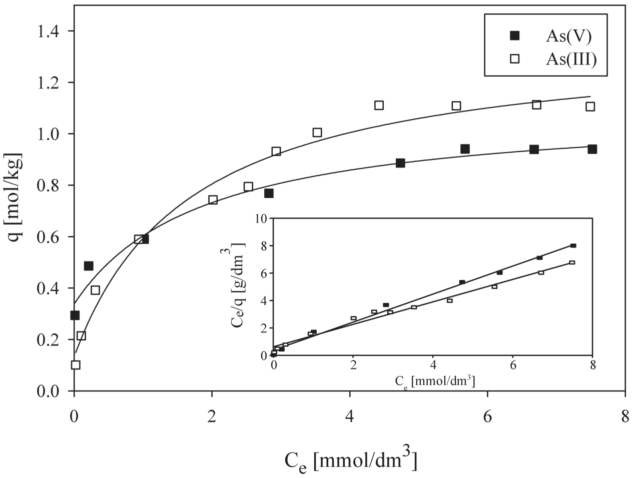


Figure 8. Adsorption isotherm of As(III and V) onto Zr(IV)-loaded POAG gel. The pH of As(III) and As(V) metal ions solution were adjusted at 10 and 4, respectively. A linearized Langmuir plot can also be seen in the figure.

Table 1(b). Langmuir adsorption isotherm model parameters and experimental Q_{max}

Metal	Q_{max} [mol/kg] langmuir model	Q_{max} [mol/kg] experimental	b [dm^3/mmol]	R^2
As(III)	1.22	1.11	1.30	0.98
As(V)	0.98	0.94	2.68	0.99

Since the gel contained phosphoric acid groups as the active binding group, any breakage of phosphorus during adsorption was also monitored. The experimental observation revealed as shown in Fig. 7 that there is no breakage of the phosphoric acid group under the condition from very acidic to alkaline aqueous environment. But small amounts of loaded Zr(IV) has been leaked into the solution at a highly acidic condition; however, there is no leakage at $pH > 2$ afterwards.

CONCLUSIONS

Adsorption behaviors of non-conventional and cost-effective adsorbent prepared from orange waste has been investigated for various metal ions. Separation factors for Fe(III) and Zr(IV) over Zn(II) at around pH 2 derived from individual adsorption isotherm by fitting a linear curve are 1×10^2 and 1.2×10^3, respectively, suggesting that there is an excellent selectivity for transition metals over alkaline/alkaline earths. Since the gel is chemically modified through phosphorylation, strong resistance was evidenced towards its aqueous solubility, which is considered as one of the fatal drawbacks of usual biomaterials. The prepared gel is found not only to be applicable for cationic metal ions, but also has shown its potential ability for the adsorption of anionic metal ion by loading the gel with Zr(IV) prior to its adsorption. Thus it can be concluded that the adsorbent prepared from orange waste revealed to be simple, cost-effective, and promising for the removal and recovery of metals ions from the aqueous medium.

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