



Effective removal and recovery of antimony using metal-loaded saponified orange waste

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ABSTRACT

Zr(IV) and Fe(III) ions were loaded onto an orange waste precursor to prepare a metal-loaded orange waste gel, which was investigated for the adsorptive removal and recovery of antimony (III and V) from an aqueous environment. The loading capacity of the orange waste for Zr(IV) and Fe(III) was found to be 1.40 and 1.87 mmol/g, respectively. The maximum batch mode sorption capacity of the Zr(III)-loaded saponified orange waste (SOW) gel was found to be 0.94 mmol/g for Sb(III) and 1.19 mmol/g for Sb(V). A nearly similar result was found for the Fe(III)-loaded SOW gel with the sorption capacity for Sb(III) and Sb(V) being 1.12 and 1.19 mmol/g, respectively. The presence of a variety of anionic species such as carbonate, chloride, nitrate and sulfate had no influence on the adsorption of both Sb(III) and Sb(V). A column adsorption–elution test demonstrated the utility of this system in continuous mode. Selective sulfide precipitation of antimony is one of the major findings in the present work, which clearly suggests a means of effective recovery of antimony from solution containing antimony and other metal ions. Due to their low cost, availability and significantly high adsorption capacity, the metal-loaded gels are expected to be effectively employed for the removal and recovery of antimony from aqueous solution, thus leading to the establishment of a greener environment.

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1. Introduction

Excessive release of toxic metals into the environment due to industrialization has created great global concern in recent years. Antimony is a toxic metal which has been extensively used in lead alloys, battery grids, bearing and power transmission equipment, ammunition, sheet and pipe [1]. This metal is finding increasing use also in semiconductors in the form of intermetallic compounds. However, the presence of antimony in the environment is a major concern due to its toxicity to many forms of life. Its toxicological effects depend on its chemical form and oxidation state [2]. Although few data address the speciation of antimony in water, these are presented together with thermodynamic predictions, indicating that the most favored form in water is the pentavalent antimonate oxoanion ($\text{Sb}(\text{OH})_6^-$), while the other common inorganic form of antimony is antimonite ($\text{Sb}(\text{OH})_3$) [3–5]. Because of the toxicological effects of antimony, its monitoring and subsequent removal from aqueous solution has been mandatory.

A number of methods have been proposed and reported for the removal of antimony. These include reduction and precipita-

tion [6,7], solvent extraction [8], ion exchange [9,10] and adsorption [11–13]. Although the precipitation method is predominant in antimony removal, this process requires the disposal of hazardous sludge. Solvent extraction is also an extensively used technique, but in this technique, it is sometimes not easy to regenerate the reagents by stripping. Ion exchange offers the ease of a column separation process but it poses some other processing problems such as low selectivity and slow kinetics. Adsorption of antimony has been studied on activated carbon [14], silica gel [15] and cellulose polymers [16]. Adsorption using such materials is sometimes found to be expensive and time consuming. Agriculture is one of the richest sources for low-cost adsorbents. Agricultural wastes like orange peels possess little economic value and create serious disposal problems. Natural, formaldehyde-treated and copolymer-grafted orange peels have been reported to remove lead ions from aqueous solutions [17]. Thus adsorption of antimony using agricultural by-products or biomass wastes has emerged as an option for developing an economic, efficient and eco-friendly method. It is noteworthy that biological materials as well as agricultural by-products represent potential sources of abundant low-cost adsorbents and there are no environmental or technical reasons which impede the use of these materials in the preparation of adsorbents.

From such a viewpoint, we have prepared an adsorption gel from orange waste, one of the major agricultural by-products in Japan,

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by carrying out a simple chemical process of saponification. Orange waste contains around 10% pectin in its cell wall as an intercellular cementing material. Pectin is a carboxylated polysaccharide in which pectic acid is partly esterified by a methyl group. It can be easily converted into pectic acid by saponification with alkali and can be loaded with metal ions to make an adsorption gel for capturing certain anionic species [18]. Since, hydrous zirconium has been reported to have a high resistance against acids, alkalis, oxidants and reductants and has been successfully loaded onto various polymers matrices to remove anions such as arsenic and selenium [19,20], Zr(IV) was loaded onto the orange waste to prepare an adsorption gel. Fe(III), on the other hand, was loaded considering its availability and low cost. In this study, we have focused on assessing the potential of such a prepared gel for the removal of antimony from aqueous solutions by examining the effect of pH, extent of sorption capacity, influence of coexisting anions and selectivity on the recovery of antimony.

2. Experimental

2.1. Materials

Crude orange waste was kindly donated by JA Saga Beverage Co., Ltd., Japan and was stored in a freezer at -20°C . Aqueous solutions of zirconium and iron were prepared by dissolving analytical grade zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 0.1 M ($M = \text{mol/l}$) hydrochloric acid. Stock solutions of antimony (III and V) were prepared by dissolving antimony trichloride (SbCl_3) and potassium hexahydroxoantimonate ($\text{K}[\text{Sb}(\text{OH})_6]$) in deionized water, respectively. However, if required, 0.1 M *N*-2-hydroxyethylpiperazine-*N*-2-ethanesulfonic acid (HEPES), a buffering agent, was added at an arbitrary volume ratio.

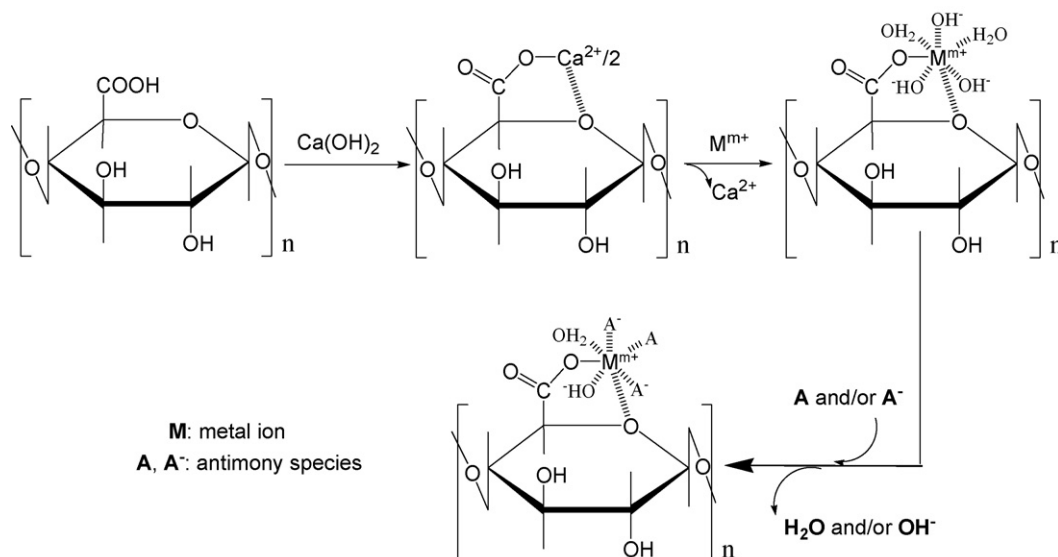
2.2. Preparation of saponified orange waste

The preparation scheme for the adsorbent is shown in Scheme 1. The saponified orange waste gel was prepared according to the method described in our previous paper [18] as follows: about 100 g of frozen orange waste was taken together with 8 g of $\text{Ca}(\text{OH})_2$ in a juice mixer and crushed into small particles to make a suspension, which was then transferred to 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 h at 70°C to produce the dry gel. The specific surface area of this gel was measured as $7.25 \text{ m}^2/\text{g}$ by using a Belsorp 18PLUS-SP (BELJAPAN.INC.) according to the BET method.

2.3. Batchwise adsorption tests of Zr(IV) and Fe(III) and their loading on the SOW gel for antimony adsorption

To determine the loading capacity of the SOW gel for Zr(IV), batchwise adsorption tests were carried out. At first, adsorption tests were performed at varying pH values to determine the optimum pH value for adsorption. The pH value thus determined was utilized to obtain the adsorption isotherm for Zr(IV). Based on this isotherm, loading of Zr(IV) onto the SOW gel was carried out as follows: SOW gel (3 g) was equilibrated with 500 ml of 0.1 M zirconium solution at pH 2.11 for 24 h. The suspension was then filtered and washed with deionized water until neutral pH, followed by drying in vacuum to constant weight and finally sieved to produce a particle size fraction of between 75 and $150 \mu\text{m}$ for the antimony adsorption tests. The amount of metal ion loaded on the SOW gel was calculated from the difference in metal concentration of the solution before and after loading. The preparation of the Fe(III)-loaded SOW gel [21], on the other hand, has been carried out as follows: the iron solution was prepared by dissolving analytical grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in hydrochloric acid solution and the pH value maintained at 3. The pH of the solution was adjusted by using either 5 M HCl or 5 M NaOH. Approximately 5 g of the SOW was equilibrated with 1000 ml of the iron solution for 24 h at 30°C . The suspension was then filtered and washed with deionized water until neutral pH, and then dried in an oven at 60°C for about 2 days to obtain the Fe(III)-loaded SOW gel. However, the specific surface area of the gel after metal loading was not changed significantly ($2.0 \text{ m}^2/\text{g}$ after Zr(IV) loading). Since adsorption of antimony is supposed to be occurred via ligand exchange as will be described in Section 3.2, the extent of adsorption largely depends on the kind of metal ion loaded onto the gel.



Scheme 1. Preparation of the metal-loaded SOW gel followed by antimony adsorption via ligand exchange.

2.4. Adsorption tests of Sb(III) and Sb(V) on the metal-loaded gels and subsequent elution tests

SOW gel being a cation exchanger cannot adsorb antimony species and it is necessary to load metal ion, which facilitates to form hydroxyl and/or water ligands coordinated with the metal ion in hydrated condition. Since Zr(IV) ion tends to be extensively polymerized and hydrolyzed even at low concentration and it converts into tetranuclear $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ ions and octanuclear $[\text{Zr}_8(\text{OH})_{20}(\text{H}_2\text{O})_{24}]^{12+}$ species [22], a lot of water molecules as well as hydroxyl ions are, therefore, available for ligand exchange with antimony species. In aqueous solution, iron also gives $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ ion [22], which facilitates ligand exchange too. However, batchwise adsorption tests for Sb(III) and Sb(V) were individually carried out to examine the adsorption behavior of the Zr(IV)- and Fe(III)-loaded SOW gels for antimony. Adsorption of antimony as a function of pH was first examined in a series of experiments where the initial concentrations of Sb(III) and Sb(V) were maintained constant (15 mg/l) at varying pH values and thus the optimum pH for adsorption was determined. Once the optimum pH for adsorption was determined, adsorption isotherms were developed by varying the antimony concentration. All batch adsorption experiments were carried out in 50 ml conical flasks by taking 25 mg (dry weight) of the gel together with 15 ml of the antimony solution. The flasks were then shaken in a thermostated shaker (THOMAS thermostatic shaking incubator AT24R) maintained at 30 °C and 140 rpm for about 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1 μm filter paper and the equilibrium concentrations in the filtrates were measured. The amount of adsorbed Sb(III) and Sb(V) was calculated from the decrease in antimony concentration in the filtrate.

Elution tests of Sb(III) and Sb(V) from the Zr(IV)-loaded SOW gel were carried out by using various concentrations of NaOH at 30 °C. At the same time, the effect of the addition of tartaric acid was also tested to determine the change in the extent of elution of Sb(III) and Sb(V).

2.5. Continuous antimony adsorption and elution in a column operation

Continuous adsorption tests of Sb(V) and Sb(III) onto the Fe(III)-loaded SOW gel were individually carried out at 30 °C using a transparent glass column of 0.8 cm inner diameter and 20 cm height 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 to an arbitrary height in the column and then a small amount of cotton, which acted as a support layer for the gel, was packed on top. The gel was tightly packed onto this cotton layer and another layer of cotton pressed on top of the gel together with another layer of glass beads at the top of the column. The cotton layer ensured a uniform flow pattern through the gel during the operation. The solution was percolated through from the bottom of the column and the effluent was taken from the top. The Fe(III)-loaded SOW gel (100 mg) was first soaked in deionized water to facilitate swelling and then packed into the column. The gel volume was approximately 0.4 cm^3 . The test solution, containing 5.5 mg/l of Sb(III) or 3.5 mg/l of and Sb(V), was percolated through the column using an EYELA model MP-3N Micro Tube Pump at a flow rate of 4.7 and 4.5 ml/h, respectively. The pH of the solution was maintained at 5.4 for Sb(III) and 3.0 for Sb(V). Beforehand, the column was conditioned by passing water at the same pH for 24 h. A fraction collector (BIORAD Model 2110 Fraction Collector) was used to collect the fractions of effluent at selected time intervals in 8 ml plastic tubes for the measurement of the antimony concentration. Elution tests for both Sb(III) and Sb(V) were carried

out using 2 M HCl solution. Prior to the elution test, the column was washed with deionized water to expel any unbound adsorbate. The eluted antimony concentration was measured as before.

2.6. Selective precipitation of antimony from the Fe(III)-containing antimony eluent

The elute from the column experiments contained antimony as well as the iron which was loaded on the sorbent. An attempt to selectively separate Sb(III) and Sb(V) from iron was made by means of a sulfide precipitation method. In this process, 0.5 ml of 20 mM sodium sulfide was added to 7 ml of the elute, which was kept in a test tube. After shaking the test tube for 5 min, the precipitate was allowed to settle for 24 h. Finally the supernatant was collected and the concentration of antimony as well as iron was determined.

2.7. Analyses and measurement of elements in the test solutions

The pH of the sample solution was measured by a DKK-TOA model HM-25G pH meter. The concentrations of antimony as well as other metal ions were determined using a Shimadzu model ICPS-8100 ICP/AES spectrometer. Standard solutions of antimony and other metal ions (Wako Pure Chemical Industries, Ltd., Japan) at a concentration of 1000 mg/l were diluted to the desired concentration and used for the ICP/AES calibration.

3. Results and discussion

3.1. Zr(IV) and Fe(III) loading on SOW gels

The optimum pH for loading of metal ions was first determined through a series of experiments where the % adsorption was calculated at varying pH values. Consequently, Zr(IV) and Fe(III) were loaded onto the SOW gel at optimum pH 2.5 and 2.7, respectively. Fig. 1(a) illustrates the adsorption isotherms for both metals, which shows that the adsorption increases with increasing metal concentration until reaching a plateau region, suggesting that the adsorption takes place according to the Langmuir adsorption mechanism. From the plateau regions of both metals, the maximum loading capacities of the SOW gel were determined to be 1.40 and 1.87 mmol/g for Zr(IV) and Fe(III), respectively. However, the presence of metal ions was confirmed by taking energy dispersive X-ray spectroscopy (EDS) of the metal-loaded SOW gel. Fig. 1(b) shows the EDS of Zr(IV)-loaded SOW gel where characteristic peak of zirconium compound was observed at around 183 eV, which is analogous to the findings of Sarma and Rao [23] and Moulder et al. [24].

3.2. Effect of pH on the adsorption of antimony onto Zr(IV)- and Fe(III)-loaded SOW gels

As mentioned earlier in Section 2.4 that the ligand exchange will not be possible for SOW, where calcium is originally present, owing to the fact that calcium does not exist as complexes that may render to be possible to anion exchange either in electrostatic form or through ligand substitution process. Rather, it will be leaked into solution after cation exchange process with various metal ions, which has been confirmed in our previous research [25]. Moreover, calcium perhaps forms an inner-sphere complex during hydration states so the attractive force between calcium and ligand is strong, which does not allow ligand exchange with target anions in the solution. Zirconium, on the other hand, has a high shielding effect, so the ligands (hydroxyl and/or water) coordinated with the Zr(IV) ion can easily be substituted. This is why metal-loaded SOW gel can adsorb anionic forms of antimony. However, the adsorption behavior of Sb(V) and Sb(III) onto both Zr(IV)- and Fe(III)-loaded SOW gels were studied from aqueous solutions over a range of pH values. The

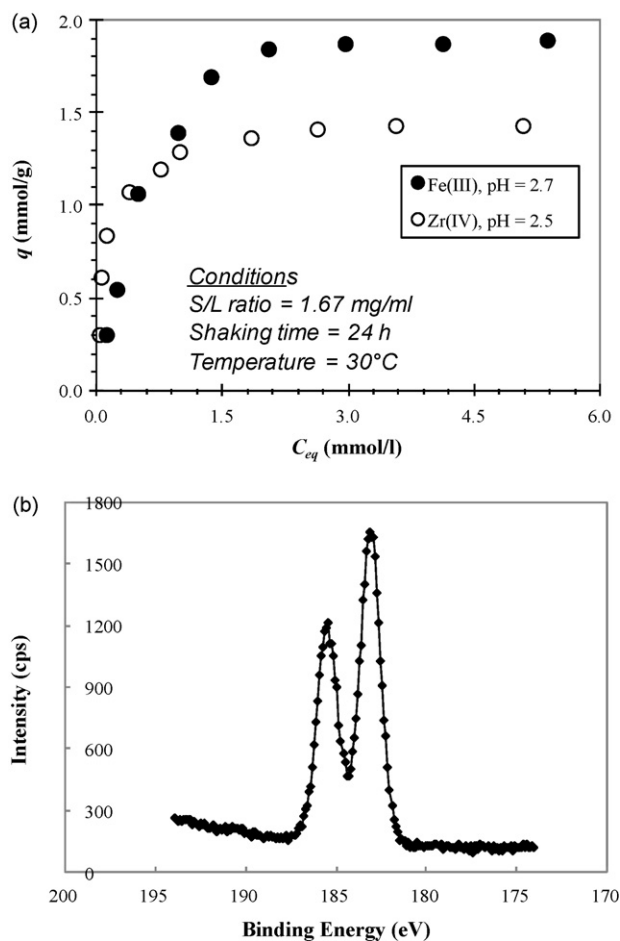


Fig. 1. (a) Isotherms for Zr(IV) and Fe(III) adsorption onto the SOW and (b) EDS spectra of Zr(IV)-loaded SOW gel.

percentage adsorptions of Sb(V) and Sb(III) are shown in Fig. 2(a) and (b), respectively. In the case of the Zr(IV)-loaded SOW gel, it was found that the % adsorption of Sb(V) increased with increasing pH at pH values lower than 2.0 and the maximum adsorption was observed over a wide pH range from 2.5 to 7.5. Similar adsorption behavior was reported for Sb(V) adsorption on activated carbon and graphite [26]. At pH values higher than 8, adsorption decreased with further increases in the pH of the solution. The adsorption behavior can be explained in terms of the distribution of antimony species. Sb(V) exists in different ionic forms depending on the solution pH [27] as shown in Fig. 3(a). In aqueous solution, two species of antimonous acid (Sb(OH)_5 , Sb(OH)_6^-) are believed to be in equilibrium

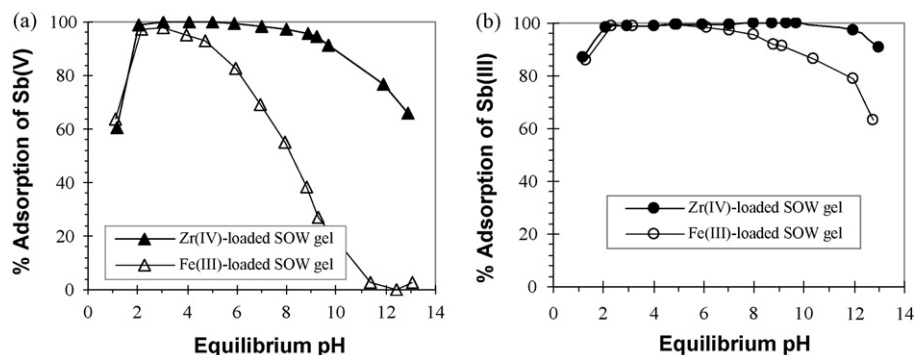


Fig. 2. Effect of equilibrium pH on the adsorption of (a) Sb(V) and (b) Sb(III) onto both gels. Conditions: S/L ratio = 1.67 mg/ml, C_{in} = 15 mg/l (for both Sb(V) and Sb(III)), shaking time = 24 h and temperature = 30 °C.

and it is apparent that the dissociation depends on the aqueous chemistry of the solution. However, at acidic pH values, the concentration of Sb(OH)_6^- increases with an increase in pH, which benefits the adsorption of antimony through substitution of hydroxyl ions coordinated with the metal ions loaded on the gel matrices.

In the case of the Fe(III)-loaded SOW gel, the increase in the % adsorption of Sb(V) was found to occur over a pH range of 1–3, and then it decreased with further increases in the pH. Consequently, pH 2.5 was selected to conduct further batch adsorption tests to determine the adsorption isotherm for this system, which will be discussed later in Section 3.3. However, there is a distinct difference in the adsorption pattern for the two gels which may be attributed to the differences in their physicochemical properties such as the solubility product of the loaded metal ions. In addition, the decrease in adsorption at $\text{pH} < 2$ may be attributed to a partial leakage of the loaded metal ions to the strong acidic solution, which is supported by the measured concentration of the leaked metal ions. Moreover, under strong acidic solution conditions ($\text{pH} < 2$), the increase in the concentration of Sb(OH)_5 may result in a decrease in antimony adsorption. A similar phenomenon of decreasing adsorption at low pH (< 2.8) has also been reported by Xu et al. for antimony adsorption by activated alumina [28].

Sb(III), on the other hand, showed quantitative adsorption for both gels over a wider pH range (Fig. 2(b)), which indicates that Zr(IV)- and Fe(III)-loaded SOW gels could be applied to treat waste water contaminated with antimony. A similar result had been also reported for Sb(III) adsorption onto adsorbents chemically modified with a pyrogallol moiety [12]. In the case of the Zr(IV)-loaded SOW gel, at pH values higher than 11, the % adsorption decreases with increasing pH, which can be attributed to the competition for the adsorption sites between hydroxyl ions, predominant at high pH, and the anionic antimony species (SbO_2^-), as depicted in Fig. 3(b) [29]. In the case of the Fe(III)-loaded SOW gel, although the decrease in the % Sb(III) adsorption starts at pH values higher than 7, a high adsorption (>80%) is still found at pH 10. Hence, it can be concluded that both Zr(IV)- and Fe(III)-loaded SOW gels have a strong affinity toward antimony species and the adsorption could, therefore, be due to the substitution of hydroxyl or water ligands, which are coordinated with the metal ion at hydrated condition (Scheme 1). This has been further supported by the fact that the pH has either increased or not quite changed after the adsorption of antimony at various initial pH. Similar results have also been reported for the adsorption of antimony on rice husks [13] and activated alumina [28].

3.3. Adsorption isotherms

Analysis of the adsorption isotherms in the present work was conducted on the basis of the Langmuir model to evaluate the

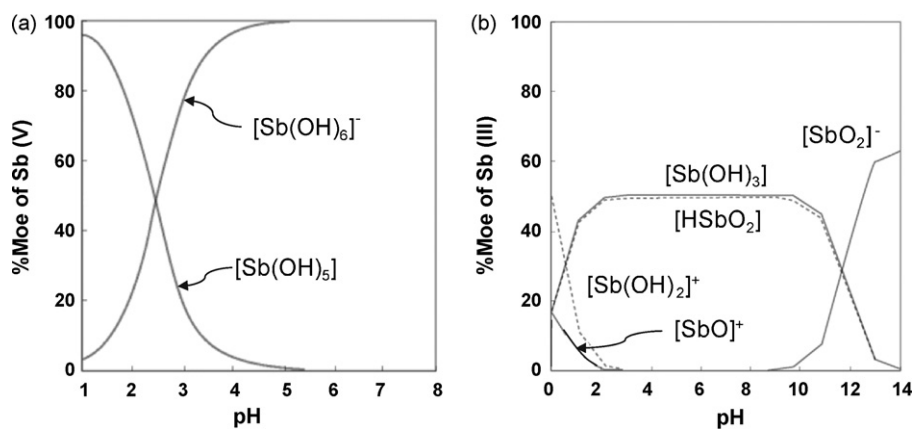


Fig. 3. Species distribution of (a) Sb(V) [27] and (b) Sb(III) [29] as a function of pH.

maximum adsorption capacity for antimony. That is, equilibrium adsorption data were plotted as a function of antimony concentration in aqueous solution at the optimum pH according to Eq. (1):

$$\frac{c_e}{q} = \frac{c_e}{q_m} + \frac{1}{b \times q_m} \quad (1)$$

where c_e is the equilibrium concentration (mmol/l), q is the amount adsorbed at equilibrium (mmol/g), and q_m and b are the Langmuir constants related to the adsorption capacity (mmol/g) and the binding energy of the sorption system (l/mg), respectively. The plots of antimony adsorption on both Zr(IV)- and Fe(III)-loaded SOW gels according to Eq. (1) have been illustrated in Fig. 4(a) and (b) and the corresponding results are summarized in Table 1. High correlation coefficients of the linearized Langmuir equation indicate that the model can quite satisfactorily explain the adsorption of antimony by the gels. Although it is difficult to directly compare the gels studied in the present work with other adsorbents because of the different experimental conditions used, still it is obvious that the maximum sorption capacities of the Zr(IV)- and Fe(III)-loaded SOW gels for antimony are significantly higher than other adsorbents reported in the literature as listed in Table 2. Because of this high adsorption capacity, the Zr(IV)- and Fe(III)-loaded SOW gels may be expected to be employed commercially in future for the removal of antimony from aqueous solution.

Table 1

The Langmuir parameters for Sb(III) and Sb(V) adsorption on both Zr(IV)- and Fe(III)-loaded SOW gels.

Element	Gel	q_m (mmol/g)	b (l/mg)	R^2
Sb(III)	Zr(IV)-loaded SOW	0.94	0.124	0.9966
	Fe(III)-loaded SOW	1.12	0.073	0.9805
Sb(V)	Zr(IV)-loaded SOW	1.19	0.139	0.9913
	Fe(III)-loaded SOW	1.19	0.098	0.9745

Table 2

Maximum sorption capacities of various adsorbents.

Adsorbent	q (mmol/g)	Species	Refs.
Chemically bonded adsorbent	0.18	Sb(III)	[12]
Hydrous oxide of Mn	0.14	Sb(III)	[30]
Hydrous oxide of Fe	0.10	Sb(III)	[30]
Activated alumina of different mesh	0.051–0.774	Sb(V)	[28]
Aluminium-loaded Shirasu zeolite	0.0199	Sb(V)	[28]
Diphenylthiocarbazone-loaded polyurethane foam	0.22	Sb(V)	[31]

From the comparison of the maximum adsorption capacity for Sb(V) (1.19 mmol/g) to the loading capacity of zirconium (1.40 mmol/g) on the SOW gel, it is indicated that an approximately 1:1 molar binding ratio has been achieved between Sb(V) and Zr(V), which is much better than that (0.07:1) reported by Nishiyama et al. [32]. Since Fe(III) loading was quite high at 1.87 mmol/g, it is considered that binuclear complexation between iron and antimony might have taken place under the present experimental conditions.

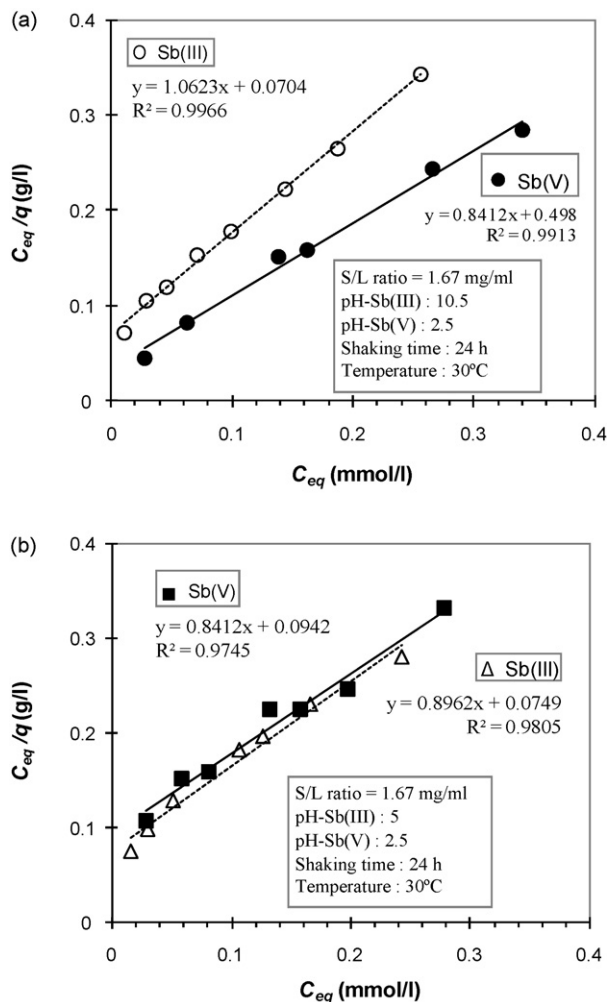


Fig. 4. Langmuir adsorption isotherm plots for both Sb(III) and Sb(V) for (a) the Zr(IV)-loaded SOW gel and (b) the Fe(III)-loaded SOW gel.

3.4. Effect of coexisting anions

The sorption efficiency of an adsorbent is usually affected by the presence of a number of coexisting ions in the aqueous solution [13,28,31]. Therefore, the effect of different anions on the adsorption of Sb(V) onto Zr(IV)- and Fe(III)-loaded SOW gels has been investigated to determine the sensitivity of this method. That is, the adsorption of Sb(V) onto both gels in the presence of excess concentrations of various foreign anions was examined over a wide pH range as shown in Fig. 5(a) and (b). As seen from these figures, the addition of 1.56 mM SO_4^{2-} , 2.42 mM NO_3^{2-} , 2.50 mM CO_3^{2-} and 4.23 mM Cl^- hardly affected the adsorption of 0.12 mM antimony, which signifies that the affinity of antimony towards the adsorption sites is much higher than that of the tested foreign anions. Similar results were found in case of Sb(III) adsorption onto both Zr(IV)- and Fe(III)-loaded SOW gels.

3.5. Elution of Sb(III) and Sb(V) from Zr(IV)-loaded SOW gel

Elution is an important process in determining the extent of recovery of antimony after its adsorption as well as the regeneration of the adsorbents for their repeated use. Elution of Sb(III) and Sb(V) was carried out by using varying concentrations of NaOH as shown in Fig. 6(a). The elution of Sb(III) increased from 20% to 44% with increasing NaOH concentration (from 0.1 to 1 M) while no significant change in the % elution of Sb(V) was observed in the above-mentioned NaOH concentration range. Moreover, elution of both Sb(III) and Sb(V) was carried out by using higher concentrations of NaOH (up to 5 M). However no more than 50% elution was achieved.

According to Deorkar and Tavlarides [12] antimony can be successfully eluted with tartaric acid from a sorbent containing the pyrogallol moiety. Therefore, a mixture of tartaric acid together with NaOH was used to elute Sb(III) and Sb(V) from the Zr(IV)-loaded SOW gel. As depicted in Fig. 6 (b), Sb(III) elution increased from 20% to 72% with the addition of 0.05 M tartaric acid to 0.1 M NaOH. In the same way, elution of Sb(V) was also increased from 27% to 60%. However, loaded zirconium was also eluted to some extent. Similar results were also observed for the elution of antimony from the Fe(III)-loaded SOW gel. Since the selective elution of the adsorbed antimony free from leakage of the loaded metal ions was found to be impossible, the adsorbed antimony was eluted together with the loaded metal by washing with hydrochloric acid solution in the view of recovering antimony by selective precipitation, which will be described in latter part (Section 3.7). From economic considerations, it was

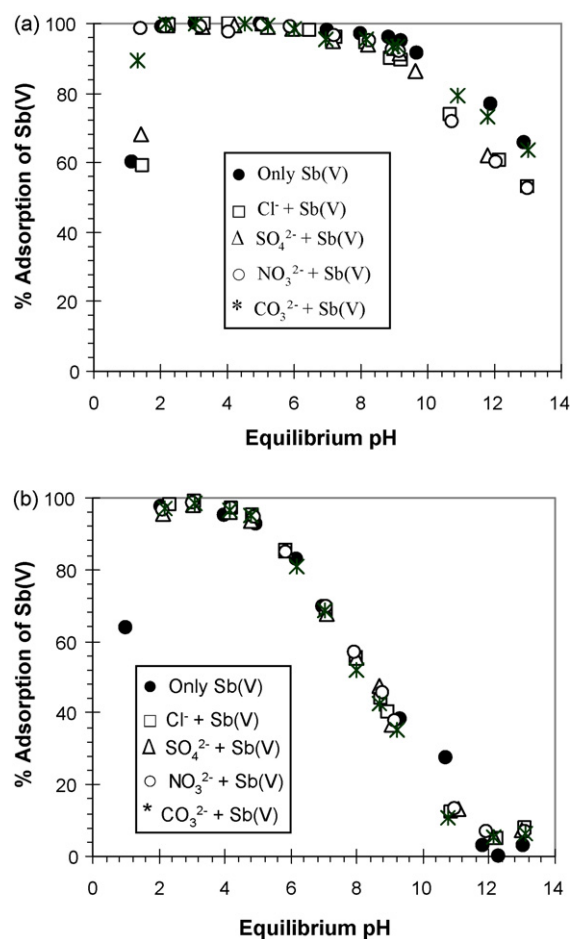


Fig. 5. Effect of coexisting anions on Sb(V) adsorption on (a) the Zr(IV)-loaded SOW gel and (b) the Fe(III)-loaded SOW gel. Conditions: solid/liquid ratio = 1.67 mg/ml, shaking time = 24 h and temperature = 30 °C.

decided to use Fe(III) as the loaded metal ion in the subsequent experiments.

3.6. Continuous Sb(III) and Sb(V) adsorption–elution in a column packed with the Fe(III)-loaded SOW gel

The performance of the gel in continuous operation was studied by percolating antimony solutions through a column as described

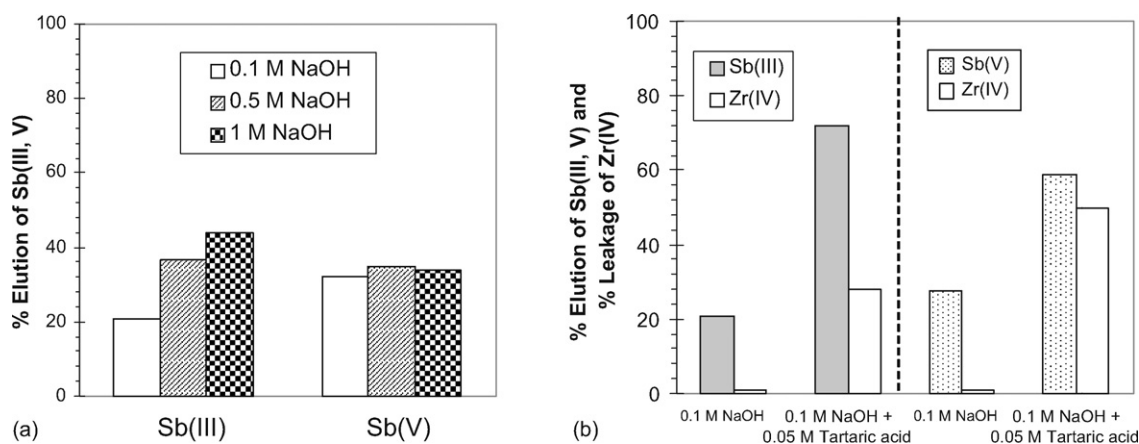


Fig. 6. % elution of Sb(III) and Sb(V) from the Zr(IV)-loaded SOW gel by using (a) different concentrations of NaOH and (b) a mixture of tartaric acid and 0.1 M NaOH. Conditions: S/L ratio = 1.67 mg/ml, shaking time = 24 h and temperature = 30 °C.

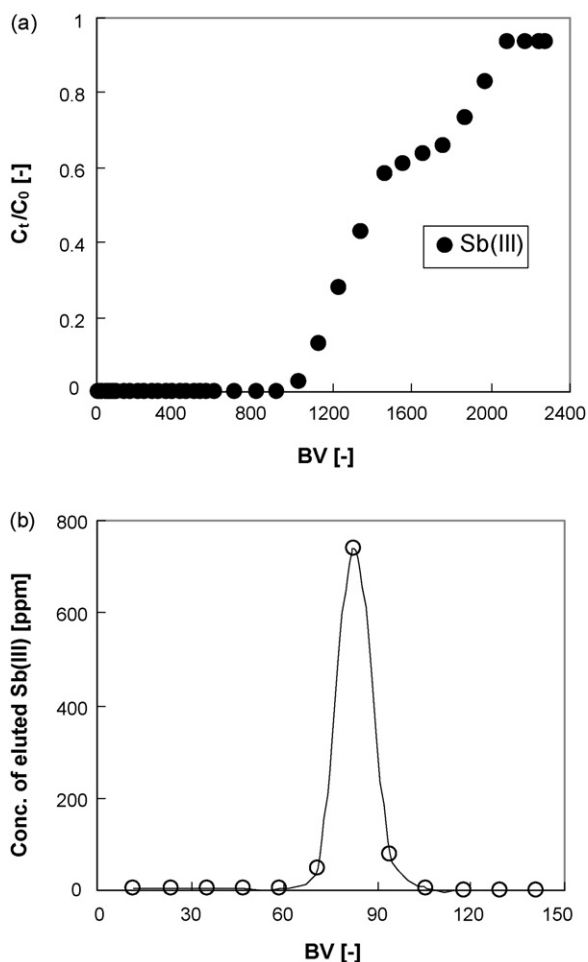


Fig. 7. (a) Breakthrough profile for Sb(III) adsorption on the Fe(III)-loaded SOW gel. Conditions: $C_{in} = 5.5$ mg-Sb(III)/l, pH = 5.4, gel volume = 0.4 cm^3 , feed rate = 4.7 ml/h , and (b) subsequent elution curve. Condition: eluent = 2 M HCl .

in Section 2.5. Fig. 7(a) shows the breakthrough profile of Sb(III) from the column packed with the Fe(III)-loaded SOW gel at pH 5.4. From this figure, it is seen that Sb(III) breakthrough started after 1000 bed volumes (BV), which means that the bed can retain antimony very well up to the aforementioned BV. However, the column was almost saturated at 2000 BV. The dynamic adsorption capacity of the Fe(III)-loaded SOW gel for Sb(III) adsorption was calculated from the area of the breakthrough profile as 0.26 mmol/g , which is only 23% of its equilibrium sorption capacity (1.12 mmol/g) evaluated from the batchwise adsorption tests. The low adsorption capacity in the column operation compared to that in batch mode may be attributable to various phenomena such as slow adsorption of Sb(III) on the gel. Similar results have also been reported by the authors [33] for arsenic adsorption on a Zr(IV)-loaded orange waste gel and by Lenoble et al. [34] for arsenic removal by a MnO_2 -loaded resin. After the adsorption of antimony, an elution test was carried out from the Fe(III)-loaded SOW gel using 2 M HCl as shown in Fig. 7(b), which demonstrates that 136-fold preconcentration was achieved compared to the feed solution. Similar result for Sb(V) adsorption on the Fe(III)-loaded SOW gel was observed where the adsorption capacity was $0.30 \text{ mmol-Sb(V)/g}$.

3.7. Selective precipitation of antimony

Precipitation is a useful technique for the recovery of elements from solution. Precipitating antimony as a sulfide provides a practical route to lower the antimony concentration in antimony-

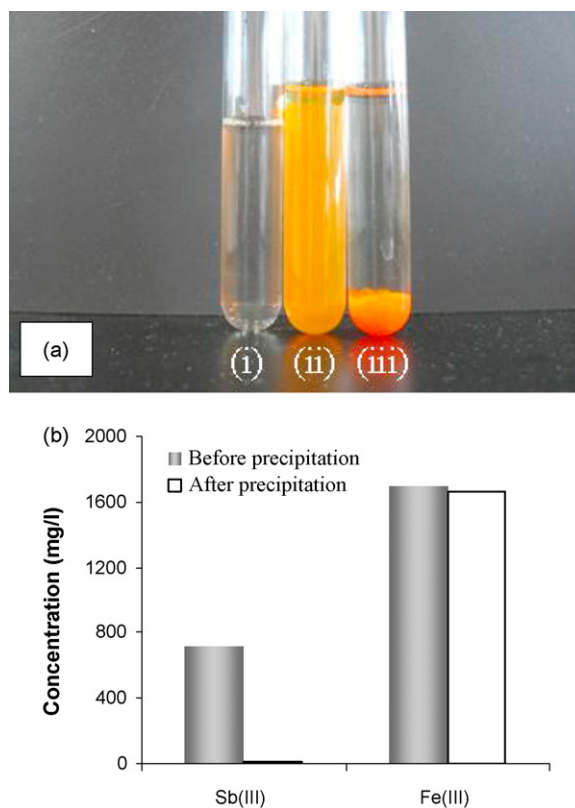


Fig. 8. Selective precipitation of Sb(III) (a) (i) before adding Na_2S , (ii) after adding Na_2S and (iii) after 24 h of settling, (b) graphical demonstration of the decrease in the concentrations of Fe(III) and Sb(III) before and after the precipitation.

containing solutions. An attempt was made to selectively recover antimony from the elute containing antimony together with a high concentration of iron. For this purpose, 0.5 ml of 20 mM of Na_2S was added to 7 ml of the solution containing a high concentration of antimony (810 mg/l) as well as iron (1845 mg/l). Fig. 8(a) shows three test tubes showing the solution before and just after adding Na_2S as well as simultaneous shaking for about 5 min followed by 24 h of settling. The figure clearly shows that the antimony sulfide precipitate is sedimented in a small volume at the bottom of the test tube. The supernatant at the top was collected to measure the concentrations of antimony and iron. It was found that the iron concentration has hardly decreased while that of antimony has significantly decreased as depicted in Fig. 8(b), which demonstrates the successful selective separation of Sb(III) by means of sulfide precipitation. More than 98% of Sb(III) was found to be precipitated in this test. A similar result was also found in the case of Sb(V) where the concentration of Sb(V) was decreased by almost 99%, which was a much better result than that reported by Gannon and Wilson [6] who achieved only 84% decrease in antimony concentration after precipitation using a solution containing 25 mg/l of Sb(III) and 1000 mg/l of Fe(III). Such a high degree of precipitation suggests a possible recovery route for antimony from the elute obtained in the continuous elution system in the column operation.

4. Conclusions

The present study has demonstrated that a gel prepared from orange waste, modified with Zr(IV) and Fe(III), is very effective for the adsorptive removal of antimony from aqueous media. The adsorption process can be satisfactorily explained by a ligand exchange mechanism. Significantly high adsorption capacities of the Zr(IV)- and Fe(III)-loaded SOW gels indicate promising and

potentially attractive adsorbents for environmental remediation. The adsorption was found to occur selectively even in the presence of a variety of foreign anions. A study of column adsorption followed by elution using a fixed bed suggested that the metal-loaded gel can be used in a continuous mode to remove antimony from industrial effluents. The selective precipitation of antimony, performed by adding Na_2S into a solution containing iron and antimony, showed a high degree of antimony recovery from solutions containing other metal ions. It therefore can be concluded that cheap and abundantly available orange waste, which has practically no utility at present, can be used to prepare a cheap adsorption gel for the treatment of aqueous solutions contaminated with dilute concentrations of antimony.

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References

- [1] M. Meltzer, M. Callahan, T. Jensen, *Metal-Baeling Waste Streams: Minimizing Recycling and Treatment*, Noyes Data Corporation, Park Ridge, NJ, USA, 1990.
- [2] M. Fiella, N. Belzile, M.-C. Lett, Antimony in the environment: a review focused on natural waters. III. Microbiota relevant interaction, *Earth-Sci. Rev.* 80 (2007) 195–217.
- [3] T. Gebel, Arsenic and antimony: comparative approach on mechanistic toxicology, *Chem. Biol. Interact.* 107 (1997) 131–144.
- [4] M. Fiella, N. Belzile, Y.-W. Chen, Antimony in the environment: a review focused on natural waters. II. Relevant solution chemistry, *Earth-Sci. Rev.* 59 (2002) 265–285.
- [5] WHO, *Guidelines for Drinking-Water Quality*, 3rd edition, incorporating first addendum, vol. 1—Recommendations, WHO, Geneva, 2006.
- [6] K. Gannon, D.J. Wilson, Removal of antimony from aqueous solutions, *Sep. Sci. Technol.* 21 (1986) 475–493.
- [7] S. Nakashima, R.E. Sturgeon, S.N. Willie, S.S. Berman, Determination of trace elements in sea water by graphite-furnace atomic absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation, *Anal. Chim. Acta* 207 (1988) 291–299.
- [8] W.M. Mok, C.M. Wai, Distribution and mobilization of arsenic and antimony species in the Coeur D’Alene River, Idaho, *Environ. Sci. Technol.* 24 (1990) 102–108.
- [9] F. Nelson, D.C. Michelson, Cation exchange in HBr solutions, *J. Chromatogr.* 25 (1996) 414–441.
- [10] R. Guin, S.K. Das, S.K. Saha, The anion exchange behavior of Te and Sb, *J. Radioanal. Nucl. Chem. Art.* 230 (1998) 269–271.
- [11] S.M. Hasany, M.H. Chaudhary, Sorption potential of Haro river sand for the removal of antimony from acidic aqueous solution, *Appl. Radiat. Isot.* 47 (1996) 467–471.
- [12] N.V. Deorkar, L.L. Tavlarides, A chemically bonded adsorbent for separation of antimony, copper and lead, *Hydrometallurgy* 46 (1997) 121–135.
- [13] N. Khalid, S. Ahmad, A. Toheed, J. Ahmed, Potential of rice husk for antimony removal, *Appl. Radiat. Isot.* 52 (2000) 31–38.
- [14] B.M. Vanderborcht, R.E. van Grieken, Water analysis by spark source mass spectrometry after preconcentration on activated carbon, *Talanta* 27 (1980) 417–422.
- [15] M. Matsui, K. Matsumoto, K. Terada, Preconcentration of antimony (III) from water with thionalide loaded on glass beads with the aid of collodion, *Anal. Chim. Acta* 193 (1987) 381–385.
- [16] S. Imai, M. Muroi, A. Hamaguchi, R. Matsushita, M. Koyama, Preparation of dithiocarbamatecellulose derivatives and their adsorption properties for trace elements, *Anal. Chim. Acta* 113 (1980) 139–147.
- [17] V. Lugo-Lugo, S. Hernández-López, C. Barrera-Díaz, F. Ureña-Núñez, B. Bilyeu, A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous mode, *J. Hazard. Mater.* 161 (2009) 1255–1264.
- [18] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, The adsorption of phosphate from an aquatic environment using metal-loaded orange waste, *J. Colloid Interface Sci.* 312 (2007) 214–223.
- [19] T.M. Suzuki, J.O. Bomani, H. Matsunaga, T. Yokoyama, Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic, *React. Funct. Polym.* 43 (2000) 165–172.
- [20] T.M. Suzuki, M.L. Tanco, D.A.P. Tanaka, H. Matsunaga, T. Yokohama, Adsorption characteristics of oxo-anions of arsenic and selenium on the porous polymers loaded with monoclinic hydrous zirconium oxide, *Sep. Sci. Technol.* 36 (2001) 103–115.
- [21] K. Inoue, K.N. Ghimire, T. Hayashida, T. Oshima, K. Ohto, K. Makino, E. Kuboki, K. Hashimoto, Removal of arsenic from mine water by the effective use of biomass. Shigen-to-Sozai, *J. Min. Mater. Process. Inst. Jpn.* 119 (2003) 767–771 (in Japanese, with English abstract).
- [22] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., John Wiley and Sons, Inc., Singapore, 1999.
- [23] D.D. Sarma, C.N.R. Rao, XPS studies of oxides of second- and third-row transition metals including rare earths, *J. Electron Spectrosc. Relat. Phenom.* 20 (1980) 25–45.
- [24] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, Physical Electronics, Inc., USA, 1995.
- [25] R.P. Dhakal, K.N. Ghimire, K. Inoue, Adsorptive separation of heavy metals from an aquatic environment using orange waste, *Hydrometallurgy* 79 (2005) 895–900.
- [26] S. Ambe, Separation of trace elements, In(III), Sn(IV), Sb(V) and Te(IV) by adsorption on activated carbon and graphite, *J. Radioanal. Nucl. Chem. Art.* 81 (1984) 77–87.
- [27] C.F. Baes Jr., R.E. Mesmer, *The Hydrolysis of Cations*, Wiley, NY, USA, 1976, pp. 370–375.
- [28] Y.-H. Xu, A. Ohki, S. Maeda, Adsorption and removal of antimony from aqueous solution by an activated alumina. I. Adsorption capacity of adsorbent and effect of process variable, *Toxicol. Environ. Chem.* 80 (2001) 133–144.
- [29] R. Watkins, D. Weiss, W. Dubbin, K. Peel, B. Coles, T. Arnold, Investigations into the kinetics and thermodynamics of Sb(III) adsorption on goethite ($\alpha\text{-FeOOH}$), *J. Colloid Interface Sci.* 303 (2006) 639–646.
- [30] P. Thanabalasingam, W.F. Pickering, Specific sorption of antimony(III) by the hydrous oxides of Mn, Fe and Al, *Water Air Soil Pollut.* 49 (1990) 175–185.
- [31] M.M. Saeed, M. Ahmed, A. Ghaffar, Adsorption modeling of antimony(V) on diphenylthiocarbazon loaded polyurethane foam, *J. Radioanal. Nucl. Chem.* 256 (2003) 121–126.
- [32] S.-Y. Nishiyama, K. Saito, K. Saito, K. Sugita, K. Sato, M. Akiba, T. Saito, S. Tsuneda, A. Hirata, M. Tamada, T. Sugo, High-speed recovery of antimony using chelating porous hollow-fiber membrane, *J. Membr. Sci.* 214 (2003) 275–281.
- [33] B.K. Biswas, J. Inoue, K. Inoue, K.N. Ghimire, H. Harada, K. Ohto, H. Kawakita, Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel, *J. Hazard. Mater.* 154 (2008) 1066–1074.
- [34] V. Lenoble, C. Chabrouillet, R. Al-Shukry, B. Serpaud, V. Deluchat, J.-C. Bollinger, Dynamic arsenic removal on a MnO_2 -loaded resin, *J. Colloid Interface Sci.* 280 (2004) 62–67.