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Sorption of Pb(II), Cd(II) and Zn(II) performed with the use of carboxyphenylresorcinarene-impregnated Amberlite XAD-4 resin

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ABSTRACT

A study on the adsorption characteristics of Pb(II), Cd(II) and Zn(II) cations onto carboxyphenylresorcinarene-impregnated resin in batch and fixed bed column systems has been conducted. Results of the batch and fixed bed column systems confirm that impregnated resin is a good adsorbent for Pb(II) and a poor one for Cd(II) and Zn(II) ions. Solid phase extraction (SPE) of Pb(II), Cd(II) and Zn(II) was conducted in batch system under various pH, interaction times, and metal concentrations. It was found that SPE of Pb(II) was optimal at pH 6.5 at contact time of 60 min, and at initial Pb(II) concentration equal to 10 mg/L. The extraction capacity for Pb(II) in the batch system was 107.6 mg/g, i.e. 99.7%. On the other hand, the SPE of Cd(II) and Zn(II) under optimal conditions has shown much smaller extraction capacities. Selectivity order of extracted metal ions was Pb(II) >> Cd(II), Zn (II). The values of correlation coefficients (R^2) indicated that the Langmuir isotherm model well-described the sorption equilibrium. Application of Temkin sorption model to the experimental data revealed that the mechanism of adsorption of metal ions onto resorcinarene-impregnated resin was physisorption. The column test also confirmed the results of batch tests and showed that the total uptake of Pb(II) was 104.4 mg/g. The carboxyphenyl resorcinarene derivative-impregnated resin has been found efficient and easily regenerative and can be used several times.

Keywords: Adsorption; Pb(II); Cd(II); Zn(II); C-4-Methoxyphenylcalix[4]resorcinarene impregnated resin; Batch system; Fixed bed column system

1. Introduction

The presence of heavy metals in the environment, due to their toxicity, is very harmful; to overcome this difficulty is now of a great importance. Contamination of water supplies by heavy metals, such as lead, zinc, and cadmium has steadily increased over the last years as a result of overpopulation and industrial activity [1]. There are various industries those are pertaining to heavy metals, such as pulp and paper, petrochemicals, refineries, explosive manufacturing, electronic, mining activities, automotive, coating, painting, storage batteries, alloy, and steel industries. Therefore, the elimination of toxic metals from aqueous solutions is important for the protection of

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public health [2]. Up to now, various techniques, including chemical precipitation, extraction [3], ion exchange [4–6], membrane separation [7,8], and sorption [9] have been developed for effective removal of heavy metals from different aqueous solutions of various concentrations. The adsorption/solid phase extraction (SPE) processes are the most attractive methods, due to their high efficiency, in a wide range of metal ion concentration, and easy handling under relatively flexible working conditions; one should also point out the selectivity and rapidity of these methods [10,11]. Moreover, adsorption processes offer a number of important benefits over conventional solvent extraction, such as reduction in solvent use and minimal cost due to low consumption of reagents, safety with respect to hazardous solvents and ease of automation [12]. In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and a high enrichment factor [13].

In recent years, resorcinarenes and their derivatives have received a growing attention as a versatile class of macrocyclic compounds [14,15], and have been studied as solvent extraction reagents for selective removal of metal ions [16,17]. However, the conventional solvent extraction processes using macrocyclic extractants are subjected to several limitations, such as tedious operation, emulsion formation, and low process efficiency as well as the toxicity of solvents and their cost [18,19]. For this reason, modification and impregnation techniques of solid phase have been employed to increase the surface adsorption capacity, and to enhance the removal efficiency and selectivity of the solid phase [13,20–24].

The aim of this work is to study the behavior of supported carboxyphenyl derivative of resorcinarene as solid extractant using solid–liquid extraction and sorption characteristics of impregnated resin for the Pb(II), Zn(II), and Cd(II) ions. For this purpose, C-(4-carboxyphenyl) resorcin[4]arene **1** was chosen; the impregnated resin was prepared by the combination of Amberlite XAD-4 with **1**.

2. Experimental part

2.1. Reagents

Metal solutions were prepared by diluting 1,000 mg/L $Pb(NO_3)_2$, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ standard solutions to the desired concentration. An adjustment of pH was carried out by adding slowly NaOH, or HNO_3 solutions into metal solutions followed by stirring until the desired pH was achieved. Chemicals for the synthesis of **1** were: resorcinol, carboxybenzaldehyde, methanol, and HCl. All reagent grade chemicals were purchased from Sigma-Aldrich.

2.2. Instruments

In experiments, the equipments involving a set of reflux utilities, Buchner funnels, and Fourier transform infra red spectrophotometer (FTIR, Nicolet Nexus 470) were used for resorcinarene **1** synthesis and characterization. In addition, other apparatus: thermostated shaker (IKA 4000i), atomic absorption spectrophotometers (AASs), i.e. flame system: Solaar 939, Unicam, GBC Avanta—graphite furnace system as well as pH meter (Accumet AR20, Fisher Scientific) were used for SPE and the determination of metal concentrations.

2.3. Synthesis and analysis procedures

C-(4-Carboxyphenyl)resorcinarene (**1**) was synthesized by the acid-catalyzed cyclocondensation reaction of resorcinol and p-carboxybenzaldehyde—(Fig. 1) according to the reported method [25].

The structure of the synthesized C-(4-carboxyphenyl)resorcinarene have been confirmed by FT-IR as well as by ^1H NMR, and ^{13}C NMR spectroscopy. IR spectra were recorded on Nexus Nicolet spectrometer. ^1H NMR and ^{13}C NMR spectra were measured on a DRX 300 spectrophotometer by operating at 300 MHz in $CdCl_3$ with TMS as an internal standard.

The FT-IR (KBr) spectrum of resorcinarene **1** displayed three sharp bands at 3,200, 1,620, and 900 cm^{-1}. The band at 3,200 cm^{-1} results from the O–H stretching vibration. It is known that O–H stretching vibrations bands occur at around 3,600 cm^{-1}; hydrogen bonding shifts these bands to lower frequencies. In **1** carboxyphenyl acids, the resorcinarene hydroxyl groups are situated very close to polar carbonyl groups. The band at 1,620 cm^{-1} is assigned to the C=O group of the carboxyl.

The ^1H NMR (DMSO) spectrum of resorcinarene **1** shows five singlets at 7.2 and 7.4 ppm for aromatic

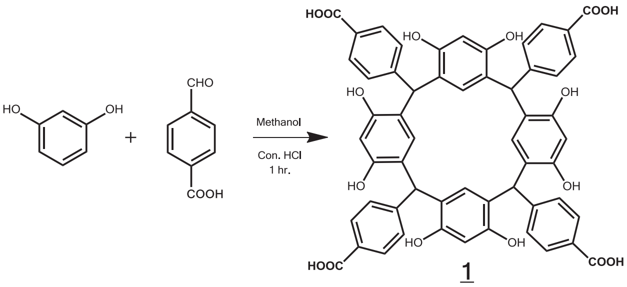

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Fig. 1. Synthesis of C-(4-carboxyphenyl [4]resorcinarene 1.

protons, 8.25 and 8.3 ppm for hydroxyl groups, and 8.8 ppm for carbonyl groups. In the spectrum, one quartet at 4.5 ppm for methine is also present.

The ^{13}C NMR ($CDCl_3$) spectrum of resorcinarene **1** displayed two singlets at 120–130 and 140–160 ppm for aromatic carbons, and one singlet at 170–180 ppm for carbonyl groups. In addition, the compound displayed one doublet at 35 ppm for bridged methine groups.

2.4. Impregnation of the stationary phase

A 1 g portion of dry Amberlite XAD-4 was placed in 50 mL methanol containing 1.0×10^{-4} mol **1** and stirred for 24 h. The resin was separated by filtration through a sintered glass funnel and washed with water to remove the solvent. The ligand content was evaluated by solvent evaporation using gravimetric analysis. The amount of ligand **1** impregnated onto dry resin was calculated from the material balance and its maximum was 1.0×10^{-5} mol g^{-1}. The resin impregnated with ligand **1** was used as an air-dried product.

2.5. Adsorption procedures

A batch experiment was conducted by adding 0.75 g of impregnated resin into 20 mL metal cation sample solution at a 10 mg/L concentration (up to 100 mg/L in the case of concentration change). The mixture was shaken at room temperature for a certain period of time, and the adsorbent was filtered and dried in a desiccator. The metal ions in aqueous phase were measured by AAS. The data obtained was compared and corrected by a blank solution. The blank solution was similar to the adsorption sample, except for the existence of the adsorbent. The amount of metal cation adsorbed was calculated from the difference between the metal cation concentration before and after the adsorption experiment. The metal uptake, q_e (mg metal ion/g resorcinarene **1**) was determined as follows: $q_e = (C_0 - C) \times V/m$, where C_0 and C are the initial and the final metal ion concentrations (mg/L), respectively; V is the volume of solution (mL); and m is the resorcinarene **1** weight (g) in dry form. For each metal cation, the experiment was done under three conditions, i.e. variation of pH, shaking time, and metal concentration.

2.6. The column experiments

Adsorption isotherm studies for resin impregnated with ligand **1** were carried out using solid–liquid extraction (column procedure). For the solid–liquid extraction, a Millipore column (1.0 cm I.D., 25.0 cm length) filled with 1.0 g of impregnated resin was used. It was cleaned by passing methanol and double distilled water. The 10 mL of aqueous metal solutions at the initial concentrations in the range 10–100 mg/L was passed through the column at a flow rate 1.0 mL min^{-1}. The analyte amounts in the effluents were determined by the flame atomic absorption spectrophotometry (Unicam Solaar 939).

The blank experiments for metal ions sorption when the ligand **1** was absent showed no significant adsorption capacity of Amberlite XAD-4 resin.

The fixed bed column adsorption experiment was done in a descendant flow, the apparatus used is shown in Fig. 2.

The metal solution at a 10 mg/L concentration was passed through the column in a down flow at a fixed flow rate. The solution which passed through the column was fractionated into 3.5 mL portions, and the effluent concentration was determined by AAS. Fractions of the effluent were collected until the ratio of effluent concentration (C) to initial concentration (C_0) was equal to one. After loading, the column was rinsed with demineralized water so that the metal ions, which were not sorbed could be removed. Metal ions sorbed on the resin were then eluted using the appropriate elution reagent. Preliminary regeneration tests were conducted with different regeneration agents (1 M HCl and 1 M HNO_3). The effluent was collected in fractions in which metal contents were

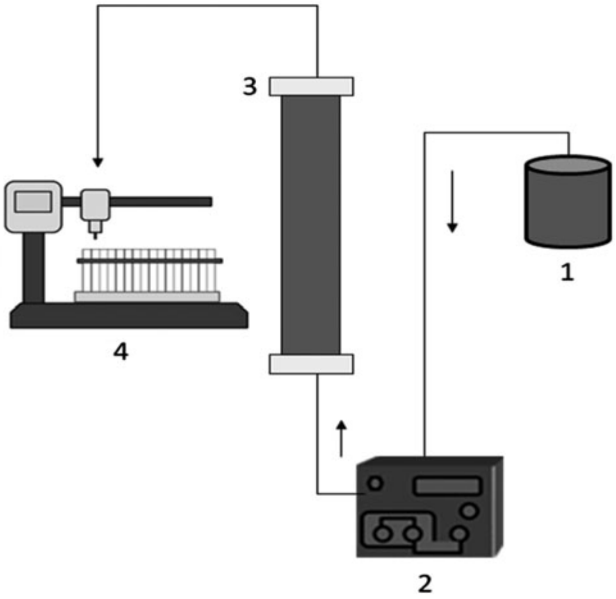

Fig. 2. Apparatus for fixed bed column adsorption experiment: (1) feed solution, (2) pump (flow rate 1 mL/min), (3) fractions of sample (3.5 mL), (4) column adsorption (5 cm × 1 cm).

determined by the AAS method, as in the case of the sorption mode.

3. Results and discussion

3.1. SPE of Pb(II), Cd(II) and Zn(II)

3.1.1. Effect of pH

The pH value is an important parameter for the extraction of metal ions from aqueous solution because it affects the solubility of the metal ions concentration of the counterions on the functional groups of the extractor and the degree of ionization of the metal during process. To examine the effect of pH on the Pb(II), Cd(II), and Zn(II) removal efficiency, the pH was varied from 5 to 6.5. As shown in Fig. 3, the uptake of Pb(II) depends on pH where the optimal metal removal efficiency occurs at pH 6.5 and decreases at lower pH.

Fig. 3 shows that the differences of pH values in the case of Pb(II) caused significant differences of extraction capacity.

Generally, the increase of pH value accompanies the extraction, and low acidity results in the higher extraction capacity. This fact indicates that the predominant extracted species has a simple cation form.

In case of tetracarboxylated resorcinarenes, the first acidity is stronger. However, the second and the third acidities are slightly weaker; i.e. the removal of the second and the third proton of resorcinarenes is more difficult. This occurrence could be explained in terms of stabilization of the protonated species through hydrogen bonding with the additional oxygen atoms present in the macrocyclic array.

Recent reports for the applications of calixarenes/resorcinarenes, or their derivatives for SPE of metal ions are presented below. The adsorption capacities of the thiacalix[4]arene-loaded resin toward Cu(II), Pb(II), and Cd(II) ions were investigated using batch adsorption experiments by Hu et al. [26]. They found that the selective adsorption capacities of the thiacalix[4]arene-loaded resin are mainly attributed to the complex of the loaded thiacalix[4]arene with heavy metal ions. Moreover, they studied various factors affecting the adsorption capacities, such as contact time, temperature, pH, and initial concentration of metal ions. They observed that the removal percentage of three heavy metal ions increased sharply along with the increase of the solution pH from 2 to 7, and reached 94% at pH $\geqslant 6$. This means that the adsorption capacities of the thiacalix[4]arene-loaded resin in weak acidic, or neutral solution toward heavy metal ions are better than that in strong acidic solution. In the case of contact time, they found that the amount of heavy metal ions adsorbed onto the thiacalix[4]arene-loaded resin increased quickly with time, and after 60 min, slowly reached equilibrium.

3.1.2. Effect of contact time

The result of Pb(II) SPE at optimal pH as a function of the contact time is presented in Fig. 4. Some of extraction parameters, such as solution pH equal to 6.5 and agitation speed were kept at optimal level, and the experiments were performed at room temperature.

The adsorption capacities of resorcinarene **1** increase rapidly in the initial stage of contact time and reach equilibrium at 60 min. In the beginning, the

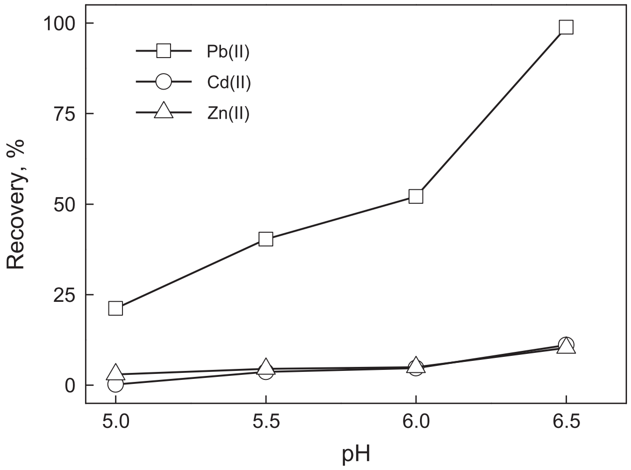

Fig. 3. The effect of solution pH on the metal ions separation with **1**.

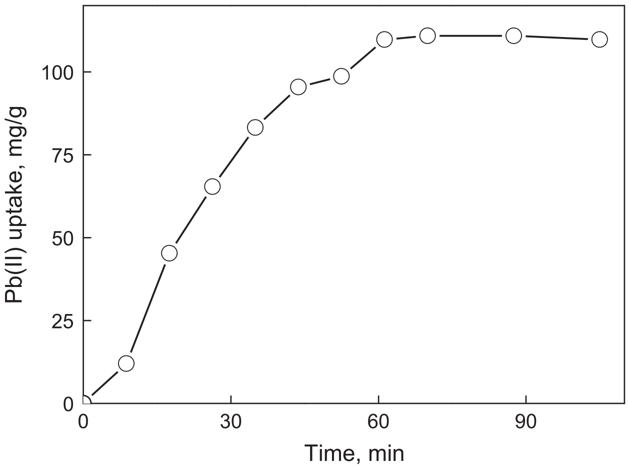

Fig. 4. Effect of contact time on the extraction of Pb(II) with **1**.

extraction rate was fast as the lead(II) was adsorbed/complexed by external surface site of **1**, i.e. carboxylic groups. When the adsorptions of the exterior surface reached saturation, the metal ions extracted onto cavity of the resorcinarene.

Similar results of shaking time study of p-tert-[(dimethylamino)methyl]-1,3-bisglycyl-calix[4]arene functionalized aminopropylpolysiloxane resin for separation of Cr(III), Cu(II), Ni(II), Co(II), and Zn(II) ions were obtained by Nie et al. [27]. This study showed the rapid adsorption kinetics, i.e. 20 min of stirring was enough to reach maximum values of simultaneous separation of all metals.

3.1.3. Effect of metal concentration

The effect of metal concentrations on extraction of Pb(II), Cd(II), and Zn(II) onto resorcinarene **1** is shown in Fig. 5. The amount of Pb(II) extracted consistently increased as the initial metal concentration increased. At initial metal concentration of 10 mg/L, the uptake of Pb(II) was 107.6 mg/g, whereas at initial concentration of 100, the uptake was 461.0 mg/g.

The adsorption capacity of the resorcinarene **1** increases with the increasing metals concentration and reaches a value: 2.22, 1.62 and 1.01 mmol/g for lead, zinc and cadmium, respectively. The amount of Pb(II) adsorbed onto resorcinarene **1** was significantly higher compared with the other metals. In order to explain dependencies observed in this work, the simplest metal cation resorcinarene cavity size matching approach may be used. The best fitting metal cation is Pb(II) which, indeed, was preferentially adsorbed by resorcinarene derivative **1**. The outer-sphere complexation of metal ions with receptors plays a major role in recognition. The excellent sorption behavior of applied resorcinarene **1** towards Pb(II) ions results probably from better fitting of large Pb(II) cations to cavity size of resorcinarene than in the case of smaller cations, i.e. Cd(II) and Zn(II).

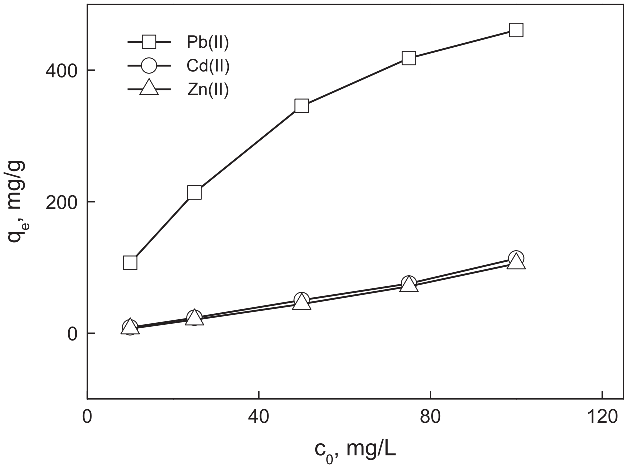

Fig. 5. The effect of Pb(II), Zn(II), and Cd(II) concentrations on the extraction capacity with **1**.

According to their large cavity size, calix[4]resorcinarenes and their derivatives can be regarded as artificial receptors for large metal ions. The selectivity of inner-sphere complexation of metal ions by macrocycles is known to be mainly determined by "size-match rule". The outer-sphere complexation between metal ions and calix[4]resorcinarene was found to be also selective for Pb(II) over Cd(II) and Zn(II).

In literature data, a new p-tert-[(dimethylamino) methyl]-1,3-bisglycyl-calix[4]arene functionalized aminopropylpolysiloxane resin (APPS-CA) has been investigated for selective SPE of Cr(III), Cu(II), Ni(II), Co(II), and Zn (II) trace amounts [27]. The results obtained by Nie et al. [27] have shown that adsorption capacity of various heavy metal ions was different due to their size, degree of hydration, and value of their binding constant to the adsorbent. Moreover, they observed that the adsorption capacity of APPS-CA is much higher than APPS; this fact indicates the high binding abilities of the calix[4]arene derivative units.

3.2. Adsorption isotherms

Results obtained for the adsorption of Cd(II), Zn (II), and Pb(II) ions onto impregnated resin were analyzed with well-known Langmuir, Freundlich and Temkin adsorption models.

3.2.1. Langmuir model

The Langmuir isotherm is a commonly applied model for adsorption on a completely homogenous surface with negligible interaction between the adsorbed molecules [28]. The model assumes uniform adsorption energies onto the surface and maximum adsorption depending on saturation level of monolayer.

Langmuir model can be represented with the following linear equation [29]:

$$\frac{C_e}{q_e} = \frac{1}{k\,V_m} + \frac{C_e}{V_m} \tag{1}$$

where q_e represents the mass of adsorbed heavy metal per unit resin (mg/g), V_m is the monolayer capacity, k is the equilibrium constant, and C_e is the equilibrium concentration of the solution (mg/L). k and V_m were determined from the slope and intercept of the Langmuir plot (Fig. 6).

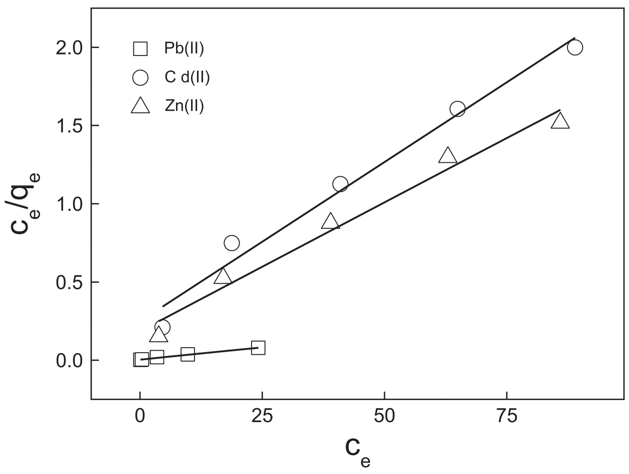

Fig. 6. Application of Langmuir model to the experimental data.

3.2.2. Freundlich model

The Freundlich model is known as the earliest empirical equation and is shown to be consistent with exponential distribution of active centers characteristic of heterogeneous surfaces [30,31].

The Freundlich equation (linear form) is [32]:

$$\log q_{\mathrm{e}} = \log K_{\mathrm{f}} + \frac{1}{n}\log C_{\mathrm{e}} \tag{2}$$

where K_{f} and n represent adsorption capacity and intensity, respectively. K_{f} is an important constant used as relative measure for adsorption efficiency. The magnitude of the n indicates the favorability of adsorption [33].

The plot of log q_{e} against log C_{e} shows data for adsorption of Cd(II), Zn(II), and Pb(II) on impregnated resin (Fig. 7).

3.2.3. Temkin isotherm

Temkin isotherm shows that the decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed by the following equation:

$$q_{\mathrm{e}} = \frac{RT}{b}\ln(K_{\mathrm{T}}C_{\mathrm{e}}) \quad \text{or} \quad q_{\mathrm{e}} = B_1 \ln K_{\mathrm{T}} + B_1 \ln C_{\mathrm{e}} \tag{3}$$

where K_{T} is equilibrium binding constant (L mg^{-1}), b is related to heat of adsorption (kJ mol^{-1}), R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}), and T is the absolute temperature (K), and for investigated metal ions is shown in Fig. 8.

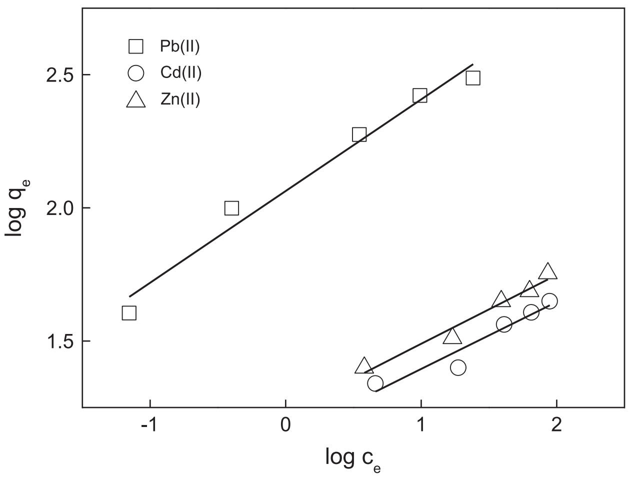

Fig. 7. Application of Freundlich model to the experimental data.

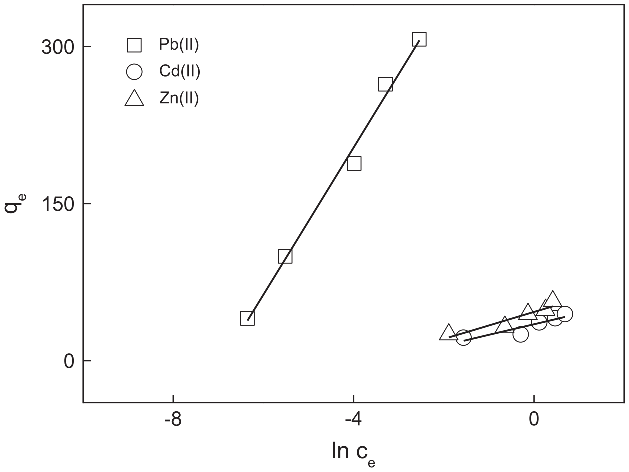

Fig. 8. Application of Temkin model to the experimental data.

All value constants determined from Langmuir, Freundlich, and Temkin isotherms are given in Table 1.

The adsorption parameters of Cd(II), Zn(II), and Pb(II) ions onto impregnated resin are satisfactorily described by the Langmuir model. The values of the R^2 are regarded as a measure of the good fit of experimental data to the isotherm model. These values for Cd(II), Zn(II), and Pb(II) ions are very close to 1. Therefore, determination coefficients indicate the following order to fit isotherms: Langmuir > Freundlich > Temkin for adsorption of Cd(II), Zn(II), and Pb(II) ions onto impregnated resin. Values of Freundlich constant,n, larger than 1 show the favorable nature of adsorption.

The Temkin isotherm indicates that (1) the heat of adsorption of all the molecules in the layer decreases

Table 1
Isotherm parameters calculated for metal ions onto resin impregnated with ligand **1**

Metal ions	Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants		
	V_m	k	R^2	K_f	n	R^2	K_T	b	R^2
Cd(II)	49.02	0.08	0.981	13.9	4.0	0.925	2.5	0.31	0.901
Zn(II)	60.98	0.09	0.978	17.00	3.9	0.970	2.6	0.25	0.929
Pb(II)	322.6	0.74	0.993	115.64	2.9	0.976	26.6	0.05	0.984

linearly with coverage due to adsorbent—adsorbate interactions, and that (2) the adsorption is characterized by a uniform distribution of binding energies. Typical binding energy for ion-exchange mechanism is reported to be in the range of 8–16 kJ mol^{-1}, while physisorption processes are reported to have low adsorption energies [34]. Very low values of b (0.05–0.31 kJ mol^{-1}) obtained for all metals in the present study show weak ionic interactions between sorbates and the sorbent indicating the physisorption of metal ions.

Based on the data, Pb(II) adsorption by **1** was dominated by physisorption, but chemisorption ruled adsorption mechanism to moderate extent. In the range of pH 5–6, the partial deprotonation occurred and therefore Pb(II) was poorly adsorbed. Pb(II) was significantly associated with **1** via formation of mononuclear 1:1 inclusion complexes. However, it was difficult to determine the stoichiometries by interacting Pb(II) with ionizable (carboxylic) groups, especially when they were partially deprotonated.

A wide variety of sorbents used to remove metal ions from aqueous solutions have been reported in the literature. Table 2 presents a brief list of the published maximum sorption capacity of various sorbents, including also the results obtained in this work.

As Table 2 shows, the sorption capacity of the resin impregnated with C-(4-carboxyphenyl) resorcin[4]arene for Pb^{2+} ions is much more higher than that reported for other sorbents [26,35–41]. The effectiveness of the impregnated resin for Pb^{2+} ions is only comparable with that reported for hydrous manganese dioxide [42], methylene-crosslinked calix[6]arene hexacaarboxylic acid resin [43] and polyvinylcalix[4]arene tetraacetic acid resin [10]. The relatively higher adsorption capacity of polyvinylcalix[4]arene tetraacetic acid resin [10] is attributable to the cyclic structure of calix[6]arene with predefined cavity and aggregating effect of larger number of carboxyl functional groups which are responsible for the uptake of lead ion. The sorption capacities of the impregnated resin for Zn^{2+} and Cd^{2+} ions is mostly comparable with that reported for other sorbents. The higher sorption capacities for Cd^{2+} and Zn^{2+} ions is noted only in case of hydrous manganese dioxide [42] and Mg(II)-doped goethite [38], respectively.

Comparing the data presented in Table 2, we may conclude that the resin impregnated with C-(4-carboxyphenyl)

Table 2
Comparison of theoretical sorption capacities (q_{max}, mg/g) for heavy metal ions of different sorbents

Sorbent	q_{max} mg/g			Reference
	Metal ion			
	Pb^{2+}	Cd^{2+}	Zn^{2+}	
Polyvinylcalix[4]arene tetraacetic acid resin	377.10	–	–	[10]
Thiacalix[4]arene-loaded resin	47.9	44.9	–	[26]
CG.Dh cryogel	–	18.47	8.28	[35]
Lignite	39.03	5.18	15.21	[36]
Iron ore slime	105.26	48.07	–	[37]
Mg(II)-doped goethite	98.03	–	158.73	[38]
Cross-linked metal-imprinted chitosan with epichlorohydrin	74.07	–	14.74	[39]
Mango peel waste	96.32	67.08	–	[40]
HBS-SH (thiol-functionalized silica)	117.51	33.72	–	[41]
Hydrous manganese dioxide	326.96	140.40	54.47	[42]
Methylene-crosslinked calix[6]arene hexacaarboxylic acid resin	269.36	–	–	[43]
Resin impregnated with C-(4-carboxyphenyl) resorcin[4]arene	322.6	49.02	60.98	This study

resorcin[4]arene is a promising sorbent for the selective removal of heavy metal ions from aqueous solutions.

3.3. Fixed bed column system

Column operations do not have sufficient contact time for attainment of equilibrium. Hence, in addition to equilibrium studies, there was a need to perform sorption studies using a column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determination of the operation and the dynamic response of adsorption column. The breakthrough curves show the loading behavior of metal to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed metal concentration (C_{ad} = inlet metal concentration (C_0)—outlet metal concentration (C_t)) or normalized concentration defined as the ratio of effluent metal concentration to inlet metal concentration (C_t/C_0) as a function of time, or volume of effluent for a given bed height [44]. Effluent volume (V_{eff}) can be calculated from the following equation:

$$V_{\mathrm{eff}} = Qt \tag{4}$$

where t and Q are the total flow time (min) and volumetric flow rate (ml min^{-1}), respectively. The area under the breakthrough curve (A) is obtained by integrating the adsorbed concentration (C_{ad}; mg l^{-1}) vs. t (min). Plot can be used to find the total adsorbed metal quantity (maximum column capacity).

Total adsorbed metal quantity (q_{total}; mg) in the column for a given feed concentration and flow rate is calculated from the following equation:

$$q_{\mathrm{total}} = QA/1000 \tag{5}$$

Equilibrium metal uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by the total amount of metal sorbed (q_{total}) per gram of sorbent (X) at the end of total flow time:

$$q_{\mathrm{eq}} = q_{\mathrm{total}}/x \tag{6}$$

The breakthrough is usually defined as the point when the effluent concentration from the column is about 3–5% of the influent concentration [45].

The breakthrough curves of Pb(II), Cd(II), and Zn (II) adsorption are presented in Fig. 9. It can be seen that in the case of Pb(II), a 5% breakthrough point (BT), 50% BT, and a 100% BT occurred after the passing of the feeding solution of about 21, 56, and 118 mL. Shorter breakthrough points took place in the Cd(II) and Zn(II) case wherein 5% BT, 50% BT, and 100% BT occurred after the feeding solution reached up to 1, 5, and 11 mL. The value of adsorption column capacity for Pb(II) was significantly higher compared with the value of adsorption capacity for cadmium and zinc, which practically are not extracted. The total uptake of Pb(II) was 104.4 mg Pb(II) per g of resorcinarene **1**. This value was similar to that obtained in batch experiment at the same initial concentration of the metal solution (10 mg/L).

As expected from the result of the batch experiment, cadmium and zinc ions were immediately eluted through after the starting of the feed without being trapped in the bed. On the contrary, the breakthrough of lead began to take place late which was about 21 mL. This observation suggested clearly that the complete separation of lead from other metals can be achieved successfully by using a column packed with the resin impregnated with resorcinarene **1**.

It is known that both resorcinarenes and calixarenes are suitable macrocycles, which were immobilized on the resins for selective separation of Pb(II) from various aqueous solution systems. For example, the adsorption behavior of lead ion using calix[4]arene tetracarboxylic acid-impregnated resin was studied [46]. It was found that the selectivity of this resin toward Pb(II) over other metal ions was superior to those of commercial resins. The selectivity order of metal ions is as follows: Pb >> Cu > Zn > Ni, Co. Therefore, it is evident that the resin described by Ohto et al. [46] is effective for the removal of trace amount of lead from large amount of other metals.

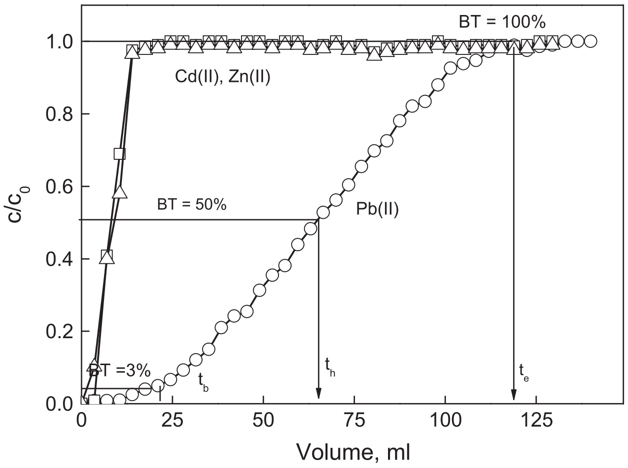

Fig. 9. Breakthrough curves of Pb(II), Zn(II), and Cd(II) adsorption by **1** immobilized into Amberlite XAD-4 (C_0 = initial metal ion concentration, C = metal ion concentration in the effluent).

3.4. Desorption studies

For real time application, the impregnated resin should be recyclable, i.e. it should not only adsorb the target metal ion but also be able to conveniently and quantitatively release the adsorbed metal cation in response to mild changes in the environment, such as pH. The desorption process not only regenerates the resin but also recovers the loaded metal in preconcentrated form. Consequently, the desorption test of loaded lead on the impregnated resin was examined by contacting the lead-loaded resin with 1.0 M HCl and 1.0 M HNO_3 solutions. The results of desorption test indicate that 1.0 M HNO_3 solution is effective for this process and can be used as a regeneration agent. The desorption process is rapid during 7.0 mL of the effluent volume when more than 98% of lead were desorbed.

4. Conclusions

Resorcinarene **1** appears to have good capability and efficiency for the selective extraction of heavy metals from aqueous medium. The obtained results can be summarized as follows:

- The highest percent removal of Pb(II) ions (99.7%) was obtained at initial metal concentration of 10 mg/L under optimal conditions.
- The amount of Pb(II) extracted consistently increased with the increase of initial pH, and reached optimum value at the initial pH 6.5. However, the increase of the initial pH to a value higher than 6 negatively influences the selectivity since simultaneous increase of Cd(II) and Zn(II) extraction capacity occurs.
- The breakthrough curve of Pb(II) adsorption at initial metal concentration of 10.0 mg/L presented in Fig. 6 shows that a 3% breakthrough point (BT), 50% BT, and a 100% BT occurred after the passing of feeding solution of about 21, 65 and 118 mL, respectively. The column test showed that the total uptake of Pb(II) was 104.4 mg Pb(II) per g of **1** and this value was similar to that obtained in batch experiment.
- The use of sorption models to the experimental data shows that the mechanism of removal of metal ions onto resorcinarene-impregnated resin is physisorption.
- These results are promising since they suggest that the resorcinarene **1** may be useful in achieving a selective and effective removal of trace amounts of lead from the polluted water. Moreover, it is important that the resorcinarene **1** is regenerative and can be used several times.

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References

[1] S. Kocaoba, Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals, J. Hazard. Mater. 147 (2007) 488–496.

[2] E. Pehlivan, T. Altun, Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution by Lewatit CNP 80, J. Hazard. Mater. 140 (2007) 299–307.

[3] C.W. Lim, K. Song, S.H. Kim, Synthesis of PPy/silica nanocomposites with cratered surfaces and their application in heavy metal extraction, J. Ind. Eng. Chem. 18 (2012) 24–28.

[4] B. Pan, Q. Zhang, W. Du, W. Zhang, B. Pan, Q. Zhang, Z. Xu, Q. Zhang, Selective heavy metals removal from waters by amorphous zirconium phosphate: Behavior and mechanism, Water Res. 41 (2007) 3103–3111.

[5] D. Kavak, M. Demir, B. Başsayel, A.S. Anagün, Factorial experimental design for optimizing the removal of lead ions from aqueous solutions by cation exchange resin, Desalin. Water Treat. 51 (2013) 1712–1719, doi:10.1080/19443994.2012.714640.

[6] I. Zawierucha, C. Kozlowski, G. Malina, Heavy metals removal from contaminated groundwater using permeable reactive barriers with immobilized membranes, in: P. Małoszewski, S. Witczak, G. Malina (Eds.), Groundwater Quality Sustainability, IAH Book series: Selected papers on hydrogeology 17, CRC Press/Balkema Taylor and Francis Group, London, UK, 2013, pp. 79–88 (Chapter 6).

[7] C.A. Kozlowski, W. Walkowiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, Water Res. 36 (2002) 4870–4876.

[8] A.O. Acosta, C. Illanes, J. Marchese, Removal and recovery of Cr (III) with emulsion liquid membranes, Desalin. Water Treat. 7 (2009) 18–24.

[9] K.C. Kang, S.S. Kim, J.W. Choi, S.H. Kwon, Sorption of Cu^{2+} and Cd^{2+} onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples, J. Ind. Eng. Chem. 14 (2008) 131–135.

[10] B.B. Adhikari, M. Kanemitsu, H. Kawakita, Jumina, K Ohto, Synthesis and application of a highly efficient polyvinylcalix[4]arene tetraacetic acid resin for adsorptive removal of lead from aqueous solutions, Chem. Eng. J. 172 (2011) 341–353.

[11] Ö.Ö. Karakuş, S. Elçin, M. Yilmaz, H. Deligöz, Removal of heavy metal ions from aqueous solution by azocalix[4]arene, Desalin. Water Treat. 26 (2011) 72–78.

[12] T. Rao, P. Metilda, J.M. Gladis, Preconcentration techniques for uranium(VI) and thorium(IV) prior to analytical determination—An overview, Talanta 68 (2006) 1047–1064.

[13] M. Ghaedi, B. Karami, S. Ehsani, F. Marahel, M. Soylak, Preconcentration–separation of Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} in real samples by solid phase extraction of a calix[4]resorcinarene modified Amberlite XAD-16 resin, J. Hazard. Mater. 172 (2009) 802–808.

[14] C. Kozlowski, W. Kudelska, J. Konczyk, New trends in modifications and applications of resorcinarenes, in: D.W. Fitzpatrick, H.J. Ulrich (Eds.), Macrocyclic Chemistry: New Research Developments, Nova Science Publishers, New York, NY, 2010.

[15] W. Sliwa, C. Kozlowski, Calixarenes and Resorcinarenes Synthesis, Properties and Applications, Wiley-VCH, Weinheim, 2009.

[16] V.K. Jain, S.G. Pillai, R.A. Pandya, Y.K. Agrawal, P.S. Shrivastav, Molecular octopus: Octafunctionalized calix[4]resorcinarene-hydroxamic acid [C4RAHA] for selective extraction, separation and preconcentration of U(VI), Talanta 65 (2005) 466–475.

[17] A.R. Mustafina, I.Y. Zagidullina, V.I. Maslennikova, O.S. Serkova, T.V. Guzeeva, A.I. Konovalova, Liquid extraction of LaIII, GdIII, and YbIII ions by phosphorylated calix[4] resorcinarene derivatives, Russ. Chem. Bull. 56 (2007) 313–319.

[18] E.M. Thurman, M.S. Mills, Solid-phase Extraction: Principle and Practice, John Wiley and Sons, New York, NY, 1998.

[19] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta, Part B 58 (2003) 1177–1233.

[20] C. Gok, S. Seyhan, M. Merdivan, M. Yurdako, Separation and preconcentration of La, Ce and Y using calix[4]resorcinarene impregnated on polymeric support, Microchim. Acta 157 (2007) 13–19.

[21] F. Marahel, M. Ghaedi, A. Shokrollahi, M. Montazerozohori, S. Davoodi, Sodium dodecyl sulfate coated poly (vinyl) chloride: An alternative support for solid phase extraction of some transition and heavy metals, Chemosphere 74 (2009) 583–589.

[22] M. Ghaedi, M. Montazerozohori, M. Soylak, Solid phase extraction method for selective determination of Pb(II) in water samples using 4-(4-methoxybenzylidenimine) thiophenole, J. Hazard. Mater. 142 (2007) 368–373.

[23] G. Azimi, J. Zolgharnein, M.R. Sangi, S. Ebrahimi, Solid phase selective and extractive preconcentration of silver ion from aqueous samples on modified silica gel with 5-(4-dimethylaminobenzylidene)-rhodanine, prepared by sol–gel method, Anal. Sci. 25 (2009) 711–716.

[24] E.M. Soliman, S.A. Ahmed, Selective separation of silver(I) and mercury(II) ions in natural water samples using alumina modified thiouracil derivatives as new solid phase extractor, Int. J. Environ. Anal. Chem. 89 (2009) 389–406.

[25] L.M. Tunstad, J.A. Tucker, E. Daicanale, J. Weiser, J.A. Bryant, J.C. Sherman, R.C. Helgeson, C.B. Knobler, D.J dan Cram, Host-guest complexation 48. Octol building blocks for cavitands and carcerands, J. Org. Chem. 54 (1989) 1305–1312.

[26] X. Hu, Y. Li, Y. Wang, X. Li, H. Li, X. Liu, P. Zhang, Adsorption kinetics, thermodynamics and isotherm of thiacalix[4] arene-loaded resin to heavy metal ions, Desalination 259 (2010) 76–83.

[27] R. Nie, X. Chang, Q. He, Z. Hu, Z. Li, Preparation of *p*-tert [(dimethylamino)methyl]-calix[4]arene functionalized aminopropylpolysiloxane resin for selective solid-phase extraction and preconcentration of metal ions, J. Hazard. Mater. 169 (2009) 203–209.

[28] Z. Temocin, M. Yigitoglu, Studies on selective uptake behavior of Hg(II) and Pb(II) by functionalized poly(ethylene terephthalate) fiber with 4-vinyl pyridine/2-hydroxyethylmethacrylate, Water Air Soil Pollut. 210 (2010) 463–472.

[29] K.G. Sreejalekshmi, K.A. Krishnan, T.S. Anirudhan, Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies, J. Hazard. Mater. 161 (2009) 1506–1513.

[30] Y.S. Ho, Effect of pH on lead removal from water using tree fern as the sorbent, Bioresour. Technol. 96 (2005) 1292–1296.

[31] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[32] M.R. Mehrasbi, Z. Farahmandkia, B. Taghibeigloo, A. Taromi, Adsorption of lead and cadmium from aqueous solution by using almond shells, Water Air Soil Pollut. 199 (2009) 343–351.

[33] A. Agrawal, K.K. Sahu, B.D. Pandey, Systematic studies on adsorption of lead on sea nodule residues, J. Colloid Interface Sci. 281 (2005) 291–298.

[34] I. Qureshi, S. Memon, M. Yilmaz, Estimation of chromium (VI) sorption efficiency of novel regenerable *p-tert*-butylcalix [8]areneoctamide impregnated Amberlite resin, J. Hazard. Mater. 164 (2009) 675–682.

[35] D.F. Apopei, M.V. Dinu, A.W. Trochimczuk, E.S. Dragan, Sorption isotherms of heavy metal ions onto semi-interpenetrating polymer network cryogels based on polyacrylamide and anionically modified potato starch, Ind. Eng. Chem. Res. 51 (2012) 10462–10471.

[36] L. Doskocil, M. Pekar, Removal of metal ions from multicomponent mixture using natural lignite, Fuel Process Technol. 101 (2012) 29–34.

[37] M. Mohapatra, K. Rout, B.K. Mohapatra, S. Anand, Sorption behavior of Pb(II) and Cd(II) on iron ore slime and characterization of metal ion loaded sorbent, J. Hazard. Mater. 166 (2009) 1506–1513.

[38] M. Mohapatra, K. Rout, S. Anand, Synthesis of Mg(II) doped goethite and its cation sorption behaviour, J. Hazard. Mater. 171 (2009) 417–423.

[39] C. Chen, C. Yang, A. Chen, Biosorption of Cu(II), Zn(II), Ni (II) and Pb(II) ions by cross-linked metal-imprinted chitosans with epichlorohydrin, J. Environ. Manage. 92 (2011) 796–802.

[40] M. Iqbal, A. Saeed, S.I. Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste, J. Hazard. Mater. 164 (2009) 161–171.

[41] X. Liang, Y. Xu, G. Sun, L. Wang, Y. Sun, X. Qin, Preparation, characterization of thiol-functionalized silica and application for sorption of Pb^{2+} and Cd^{2+}, Colloids Surf. A 349 (2009) 61–68.

[42] Q. Su, B. Pan, S. Wan, W. Zhang, L. Lv, Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water, J. Colloid Interface Sci. 349 (2010) 607–612.

[43] B.B. Adhikari, M. Gurung, H. Kawakita, Jumina, K Ohto, Methylene crosslinked calix[6]arene hexacaarboxylic acid resin: A highly efficient solid phase extractant for decontamination of lead bearing effluents, J. Hazard. Mater. 193 (2011) 200–208.

[44] Z. Aksu, F. Gonen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: Prediction of breakthrough curves, Process Biochem. 39 (2004) 599–613.

[45] J.P. Chen, X. Wang, Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed bed columns, Sep. Purif. Technol. 19 (2000) 157–167.

[46] K. Ohto, S. Inoue, N. Eguchi, T. Shinohara, K. Inoue, Adsorption behavior of lead ion on calix[4]arene tetracarboxylic acid impregnated resin, Sep. Sci. Technol. 37 (2002) 1943–1958.