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Selective extraction of Pb(II) using triethylenetetramine-modified polystyrene-divinylbenzene resin

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Abstract

Polystyrene-divinylbenzene contained cyclic triethylenetetramine (TETA-PS-DVB) was prepared and employed as selective sorbent for the extraction of Pb(II) in aqueous solution. The sorption performance of Pb(II) in single metal solution was similar to that obtained by binary metal solutions (Pb(II) with Co(II), Cr(II), Cu(II), Ni(II), and Zn(II)) indicating the high selectivity of the sorbent. Under optimal conditions, 60 min was utilized for adsorption of Pb(II) on the sorbent in batch method and the kinetics of sorption fitted well with pseudo-second order rate. The adsorption isotherm obeyed the Langmuir model. The method could be applied for the extraction of Pb(II) from cement-base leachate sample with the percentage sorption of 82.3, the percentage of desorption of ~100% and the relative standard deviation of 2.2 %.

Keywords: Chelating resin; Polystyrene-divinylbenzene; Triethylenetetramine; Lead; Extraction; Adsorption; Cement-base leachate

1. Introduction

Lead is a heavy metal that is naturally found in small amounts. Currently, utilization of many products in daily life such as battery, solder, paint pigments, phosphate fertilizer, plastic stabilizer, and combustion of fossil fuel is the causes of contamination and accumulation of lead in our environment. Because lead is a very poisonous metal, it causes many health problems such as a growth inhibition and brain dysfunction in children, destructions of the central and the end of nervous connections especially in young children. Additionally, it causes weakness in fingers, wrists and ankle, and also affects on gastrointestinal tract, blood, urology, and ultimately death. Then, the determination of lead in various products should be taken into account [1]. Consequently, either separation and/or determination of Pb(II) in various products should be taken into account as well as in hazardous wastes [2].

There are many difficulties to selectively separate Pb(II) owing to really high matrix interferences in real samples. Several methods have been widely applied for the separation such as coprecipitation, solvent extraction, electrodeposition, membrane extraction, and solid phase extraction (SPE) [3-7].

Solid phase extraction (SPE) is one of the most generally used methods for extraction because there are several advantages for example, it has a good efficiency for removing a heavy metal from their matrices, and it can easily remove the sorbent from the solution. With the benefits of various sorbents, significant decrease in the amount of organic solvents, low cost, less labor and time, SPE is thus widely used for separation [8]. However, the commonly used solid sorbents in SPE had disadvantage of low selectivity [9-11]. The design and use of selective sorbents is of interest [12].

Polystyrene-divinylbenzene (PS-DVB) copolymers, commonly used as polymeric sorbent in SPE, have hydrophobic characters but they are non-selective towards lead ions resulting in difficulties for co-extraction from interferences. However, they have broader pH stability range than silica and can be often overcome their selectivity by chemical modification of their surface [7].

Thus, in this work, styrene-divinylbenzene copolymer beads modified with triethylenetetramine (TETA) in cyclic form was chosen as a sorbent in SPE for selective extraction of Pb(II) ions. The selection criteria of the solid sorbent was based on its high selectivity towards Pb(II) as previously reported by Nutthanara et al. [13].

The proposed protocol was applied to the extraction and elution of Pb(II) ions from aqueous solution and leachate of cement-based stabilized waste.

2. Materials and methods

2.1 Apparatus

The infrared spectra were obtained by Nicolet 6700 IR-spectrophotometer. The amount of Pb(II) in solution were determined by a flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin-Elmer).

2.2 Chemicals and reagents

Chloromethylated styrene/divinylbenzene copolymer (Cl-PS-DVB, 1% cross-linked, 100-200 mesh, 4.42 mmol Cl/g) and triethylenetetramine were purchased from Aldrich and Fluka, respectively. A stock standard metal solution (1000 mg/L) was purchased from Merck. Working metal solutions were prepared by stepwise dilution and adjusted pH with 1%HNO_3 and 1%KOH. Hydrochloric and nitric acid solutions used as desorption solutions were prepared by direct dilution from the concentrated solutions.

2.3 Preparation and characterization of sorbent

The preparation procedure was modified from our previous work [13]. In summary, Cl-PS-DVB (5 g) was oxidized with 2.1 g of $NaHCO_3$ in 40 mL of dimethyl sulfoxide (DMSO), stirred and refluxed at 155 °C for 6 hrs. Afterwards, the sorbent was filtered out, washed and rinsed with several types of organic solvents and dried (so called CHO-PS-DVB). Next, CHO-PS-DVB (1 g) was immersed in 10 mL of CH_2Cl_2 for 1 hr. Then, 2.64 mmol of triethylenetetramine (TETA) in 30 mL CH_2Cl_2 was slowly added dropwise and stirred for 6 hrs under N_2 atmosphere at room temperature. Then, the sorbent was filtered out and washed with solvents prior to vacuum dry at room temperature, the product was labelled as TETA-PS-DVB. The products of each step were characterized with attenuated total reflectance Fourier transforms infrared spectrometry (ATR-FTIR) and Ninhydrin test. The preparation procedure was depicted in Figure 1.

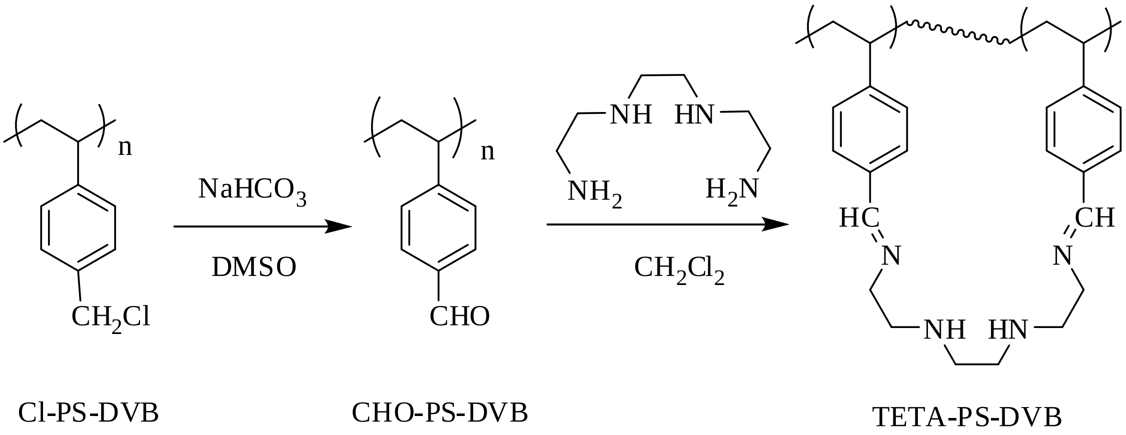

Figure 1: Preparation procedure of sorbent.

2.4 Adsorption procedure

2.4.1 Batch method

In batch method, sorption time and kinetics of Pb(II) sorption were studied. According to our previous study [13], the optimal pH for Pb(II) adsorption on TETA-PS-DVB was 4-6. A 5.00 mL aliquot of 5 mg/L Pb(II) solution after being adjusted its pH to 4 was mechanically shaken with 25 mg sorbent at sorption times ranging from 0-120 min. After the sorbent was separated, the remained amount of Pb(II) in the solution was determined by FAAS. In addition, selectivity of sorbent was tested by comparing the Pb(II) adsorption efficiency of sorbent between in a single Pb(II) solution pH 4 and binary solution of Pb(II) with other metal ions i.e. Zn(II), Ni(II), Cu(II), Co(II) or Cr(III). Sorption capacity and adsorption isotherm were performed by varying the Pb(II) concentration under the optimum sorption conditions.

2.4.2 Column method

A Curity® stomach tube (0.4 cm internal diameter, 2.5 cm length) was used for preparation of a laboratory-made mini-column. Each column was packed with 50 mg of sorbent and sealed with cotton at both ends. The effect of flow rate was studied by passing a 25.0 mL aliquot of 1 mg/L Pb(II) solution through the column over a flow rate ranging of 0.5-5.0 mL/min (controlled by a peristaltic pump). The remaining Pb(II) in the solution was determined by FAAS. Moreover, recirculation of solution was evaluated for improvement of the sorption efficiency by passing the remaining solution through the same column again and again at the same flow rate. The recirculation of solution was varied in the range of 2-7 cycles.

2.5 Desorption procedure

The desorption step was performed and type and concentration of desorption solutions was studied by using HNO_3 or HCl solution with different concentrations. And desorption time was varied in the range of 0-60 min.

2.6 Application to real samples

The demonstration of the validity of this proposed method was performed in batch method, recovery was evaluated by using spiked Pb(II) to leachate (leachate from cement-based stabilized waste was prepared by following the procedure of Wongkaew et al. [7] adapted from EPA method 1312 (SPLP) [14]. The batch method was carried out by weighing 25 mg of sorbent with a 5.00 mL aliquot of leachate spiked with 5 mg/L Pb(II) solution (pH 4) and the extraction was done under optimal conditions.

3. Results and discussion

3.1 Characterization of the sorbent

To confirm the presence of TETA in the functionalized polymer, ATR-FTIR technique was used. ATR-FTIR spectra were shown in Figure 2. Comparing the ATR-FTIR spectra of Cl-PS-DVB with CHO-PS-DVB, CHO-PS-DVB showed two important characteristic peaks of aldehydic C-H stretching at 2726 cm^{-1} and C=O stretching at 1704 cm^{-1}. Moreover, comparing the spectra of CHO-PS-DVB with TETA-PS-DVB, the final product showed the presence of C-C stretching of aromatic moiety at 600-1000 cm^{-1}, C-N stretching at 1125 cm^{-1}, C=N stretching at 1650 cm^{-1}, N-H stretching at 3200-3500 cm^{-1}, and absence of C=O stretching at 1704 cm^{-1}. Ninhydrin test was applied to identify whether the surface of prepared polymeric materials contained free-terminal primary amine functional group [15,16]. The result of Ninhydrin test reveals that all of products were not positive with Ninhydrin, suggested that they did not contain any free amino group. From the IR and Ninhydrin test results, the successful preparation procedure of sorbent was assured.

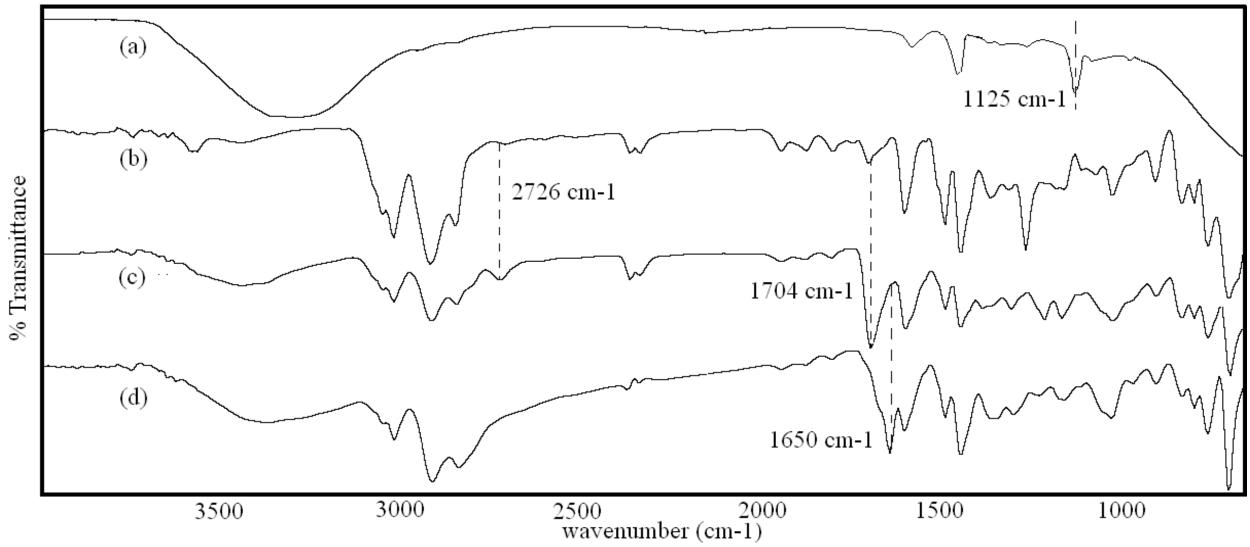

Figure 2: ATR-FTIR spectra of (a) TETA (b) Cl-PS-DVB (c) CHO- PS-DVB and (d) TETA-PS-DVB.

3.2 Batch method

3.2.1 Effect of sorption time and kinetics of Pb(II) sorption

The sorption amount expressed in µmol/g resin and sorption (%) were calculated based on Equations 1 and 2, respectively.

$$sorption\,amount(\mu mol/g) = \frac{n_i - n_f}{m} \qquad (1)$$

where n_i is the initial amount of Pb(II) in the solution (µmol), n_f is the residual amount of Pb(II) in the solution at equilibrium (µmol), m is the amount of sorbent (g):

$$sorption(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

where C_i is the initial concentration of Pb(II) in the solution (mol/L), C_f is the residual concentration of Pb(II) in the solution at equilibrium (mol/L)

The result was shown in Figure 3. Obviously, Pb(II) adsorption was not complete within the short time. The adsorption equilibrium was reached within 60 min and increasing time did not affect the quantitative adsorbed amount of Pb(II). This could be explained that a coordination of metal ions with macrocyclic ligands is usually slower than that of open-chain ligands [17]. Then 60 min was used for all subsequent experiments.

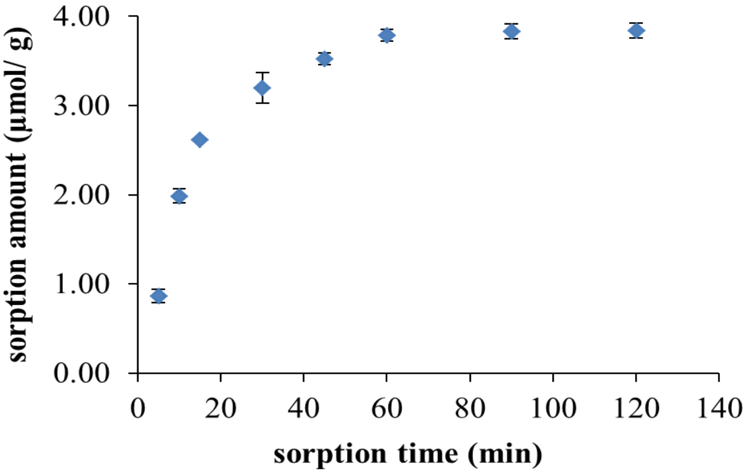

Figure 3 Influence of sorption time of Pb(II) on the sorbent (n=3).

The experimental kinetics data were fitted with pseudo-first-order rate and pseudo-second-order rate for determination of the value of rate constant of Pb(II) sorption using the following Equations 3 and 4, respectively [18].

$$log(q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e is the amount of Pb(II) adsorbed per gram of sorbent at equilibrium (mol/g), q_t is the amount of Pb(II) adsorbed per gram sorbent at any time (mol/g), k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the pseudo-second-order rate constant (g mol^{-1} min^{-1}), t is the sorption time (min).

Figure 4 shows that both pseudo-first-order rate and pseudo-second-order rate exhibited good linearity. But this mechanism was presupposed to be chemisorption. In chemisorptions process, the rate of reaction depends on both active sites on sorbent surface and sorbate ions. Then, the pseudo-second-order model should be more suitable than the pseudo-first-order one. The pseudo-first-order result might be as a result that the sorbent has so many active sites than the amount of Pb(II) in solution. The kinetics depends on only the sorbent. Consequently, better linearity from pseudo-second-order rate ($R^2 > 0.99$) was obtained. The similar results were achieved by El Bouchti et al. for the adsorption of Pb(II) and Cu(II) on the functionalized polyamide [11]. The rate constant k_2 derived from the graph was to be 18,425 g mol^{-1} min^{-1}.

3.2.2 Selectivity of sorbent

The selectivity of sorbent for Pb(II) adsorption in binary mixture solution was assessed. The result in Table 1 reveals that the same amount of Zn(II), Ni(II), Cu(II), Co(II) and Cr(III) with Pb(II) did not considerably change the adsorption ability towards Pb(II). The Pb(II) adsorpability increased slightly when the competing metal ions were present in the solution. It could be explained according to Le Chatelier's Principle, when a dynamic equilibrium of the system was disturbed by changing the concentration, the equilibrium position will shift in the way to counteract the change. The binary mixture solutions had either higher concentration of ions. Then, the alteration of the system was neutralized by decreasing ions concentration in consequence of increasing sorption efficiency.

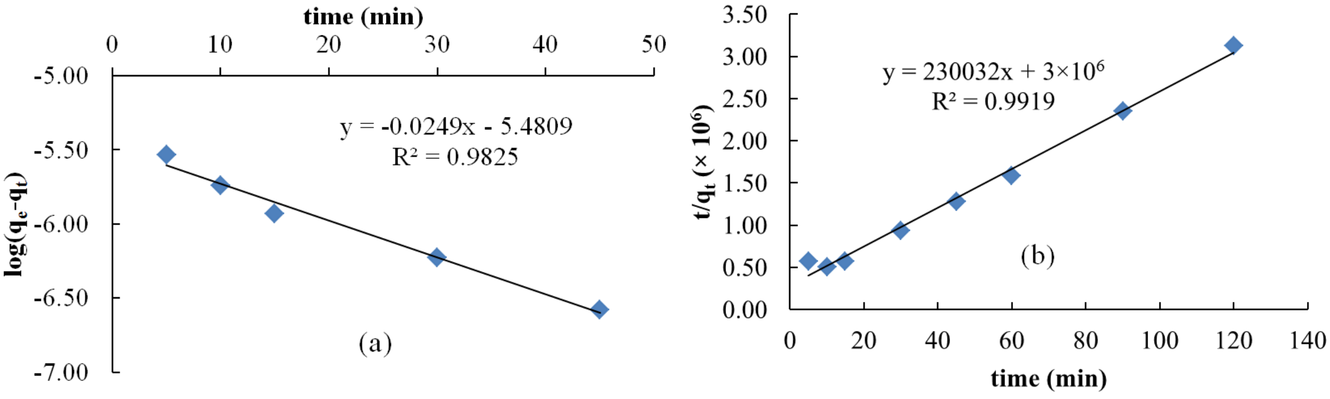

Figure 4: (a) Pseudo-first-order and (b) Pseudo-second-order sorption kinetics of Pb(II) on the sorbent.

Table 1: Amount of Pb(II) adsorbed on the sorbent

Metal ions in solution	Sorption of Pb(II) (μmol/g)*	Sorption of competing ions (μmol/g)*
Pb(II)	3.85 ± 0.07	-
Pb(II) / Co(II)	4.12 ± 0.12	0.00 ± 0.00
Pb(II) / Cr(III)	4.19 ± 0.06	4.10 ± 0.06
Pb(II) / Cu(II)	3.92 ± 0.06	0.70 ± 0.05
Pb(II) / Ni(II)	4.10 ± 0.00	0.00 ± 0.00
Pb(II) / Zn(II)	4.29 ± 0.07	0.10 ± 0.07

*mean±SD (n=3)

According to the hard soft acid base principle, R_2NH could be classified as borderline-soft Lewis base. Therefore, Cr(III) in single metal solution might not prefer to form complex with amine groups on the sorbent as reported by Nutthanara et al. [13]. But from the experiment data, Cr(III) in binary mixture solution could be adsorbed on the sorbent. This abnormal phenomenon might be described that, at the pH 4 Cr(III) was hydrolyzed to $[Cr(OH)]^{2+}$ [19], and Cr(III) could form bimetallic complexes with amine-phenolate ligands [20] or quadridentate amines [21] using a hydroxyl group (μ-OH) as a bridge between two Cr(III) centers. From these supporting data, we proposed that a bimetallic complex based on Pb−(μ-OH)−Cr might presumably form on the sorbent surface. As a result, Cr(III) in the binary solution could be retained on the sorbent.

In addition to ionic radius, there are significant differences in ionic radius between Pb(II) and Co(II), Ni(II), Cu(II), and Zn(II) [22]. From the experimental result, it suggests that the cavity site of the sorbent should be suitable for the ionic radius of Pb(II). The chelate structure of Pb(II) with TETA-PS-DVB was proposed in Figure 5.

3.2.3 Sorption capacity and adsorption isotherms

The equilibrium experimental data under optimal sorption conditions were fitted with Langmuir which is described by Equations 5 [23].

$$\frac{C}{N_f} = \frac{1}{bN_s} + \frac{C}{N_s} \qquad (5)$$

where C is the residual concentration of Pb(II) in the solution at equilibrium (mol/L), b is the Langmuir constant related to energy of adsorption (L/mol), N_f is the amount of Pb(II) adsorbed per gram sorbent (mol/g), N_s is the maximum amount of Pb(II) adsorbed per gram sorbent (mol/g)

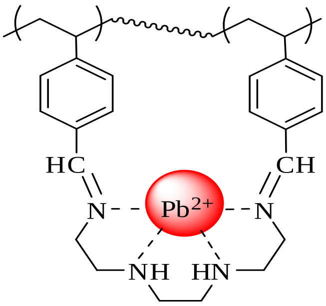

Figure 5: Proposed chelate structure of Pb(II) with TETA-PS-DVB.

The Freundlich, and Temkin models which are described by Equations 6-7, respectively [24-25] were used for assessing the adsorption isotherm.

$$\log N_f = \log K - \frac{1}{n}\log C \tag{6}$$

where C is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1}), N_f is the amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1}), n is the Freundlich constant related to adsorption intensity, and K is the Freundlich constant related to adsorption capacity.

$$N_f = \frac{RT}{b}\ln K_T - \frac{RT}{b}\ln C \tag{7}$$

where C is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1}), N_f is the amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1}), K_T is equilibrium binding, R is the gas constant (8.314 J mol^{-1}), T is the absolute temperature, b is related to the heat of adsorption.

From the results in Figure 6, the regression correlation coefficient (R^2) from Langmuir adsorption isotherm was obtained more than 0.99. While the R^2 of the linearized Freundlich, and Temkin plots (data not shown) were 0.87 and 0.89, respectively. It exposes that Pb(II) adsorption on the preparative sorbent obeyed Langmuir adsorption isotherm. It could be assumed that the surface has homogeneous active sites, Pb(II) adsorbed as monolayer on the sorbent and there are no other interactions for instance sorbent and adsorbate interactions or interaction between adsorbate on contiguous sites [26]. The calculated maximum adsorption capacity and Langmuir constant were 4.04 µmol/g and 4.37 × 10^6 L/mol, respectively. The high value of Langmuir constant signifies that Pb(II) was easily and directly coordinated with the active site on the sorbent.

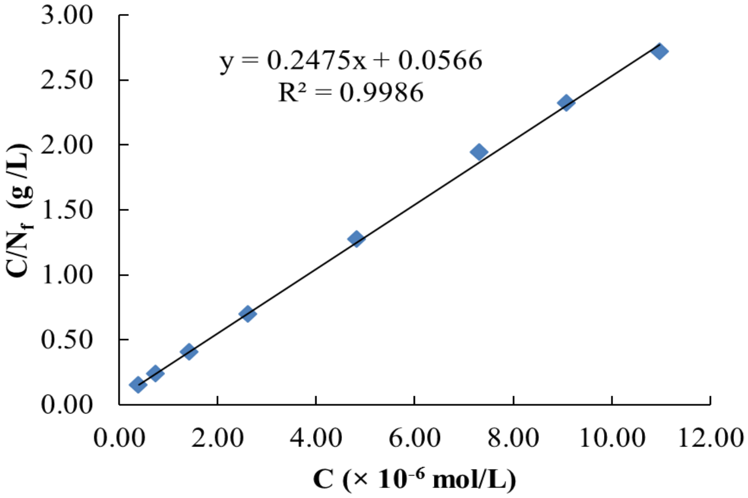

Figure 6: Langmuir isotherm of Pb(II) on the sorbent.

The comparison of sorption capacities for Pb(II) with other functionalized polystyrene-divinylbenzene sorbent was shown in Table 2. The sorption capacity was higher than those of PS-DVB containing Alizarin Red-S and salicylic acid but lower than the others. However, the sorbent showed obviously its selectivity towards Pb(II).

Table 2: Comparison of sorption capacities of TETA-PS-DVB for Pb(II) with other functionalized polystyrene-divinylbenzene sorbent

Solid support	Sorption capacity of Pb(II) (μmol/g)
TETA (this work)	4.04
purpurin [7]	82.7
functionalized polyamide fiber [11]	38.9
diethyldithiocarbamate [27]	31.1
o-aminobenzoic acid [28]	60.0
2-hydroxy-propiophenone-4-phenyl-3-thiosemicarbazone [29]	35.0
Alizarin Red-S [30]	1.5
salicylic acid [31]	2.2

3.3 Column method

3.3.1 Effect of flow rate

Even the solution was passed through the column at the lowest flow rate at 0.5 mL/min, the efficiency of Pb(II) sorption was quantitatively very low with only 32% sorption. So it was not useful to study at higher flow rates. The flow rate at 0.5 mL/min was set for sub-experiments.

3.3.2 Recirculation of solution

The result (data not shown) indicated a little increase of sorption of Pb(II). The sorption percentage depended additionally on the number of cycles. The solution was passed through the column for 7 cycles. However, the sorption efficiency was still low (<50%). The possible reason of this phenomenon was the very slow kinetics of sorption. The sorption did certainly not reach the equilibrium in the column.

3.4 Desorption procedure

3.4.1 Effect of type and concentration of desorption solutions

The result was given in Figure 7, all of the desorption solutions could desorb Pb(II) which previously retained on the sorbent. But only 10% (v/v) HNO_3 could quantitatively desorb Pb(II) with around 100 % desorption.

3.4.2 Effect of desorption time

The result was shown in Figure 8. It is clearly observed that the desorption of Pb(II) was high at the beginning and approached rapidly the equilibrium. The desorption of close to 100% was obtained within 30 min and increasing time provided similar results. Then 30 min was used for further experiments.

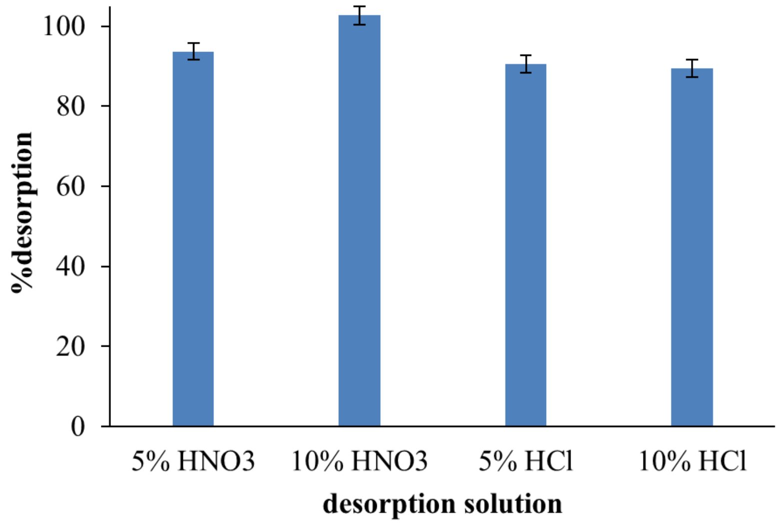

Figure 7: Effect of type and concentration of desorption solutions (n=3).

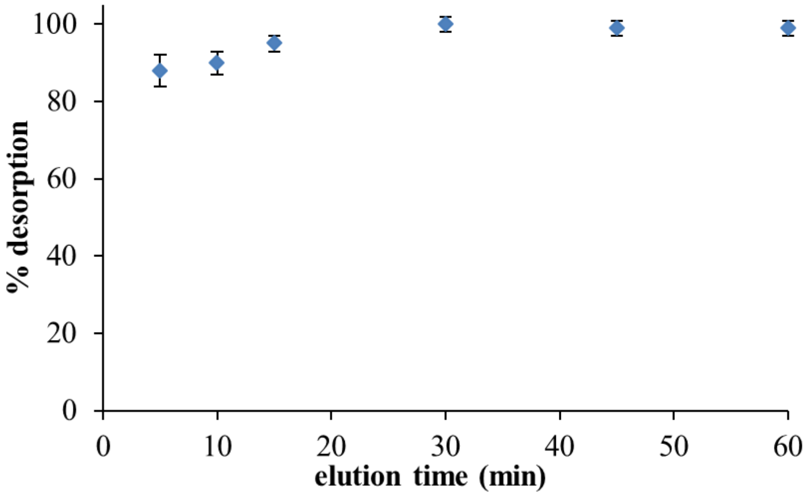

Figure 8: Effect of desorption time (n=3).

3.4.3 Reuse of adsorbent after desorption

The reusability of the sorbent after being used for Pb(II) desorption was investigated. The ability of Pb(II) sorption decreased brutally to 2 %. The decline of sorption efficiency suggests that the active sites of the sorbent might probably be destroyed by the desorption solution; 10% (v/v) HNO_3. This severe desorption solution might break the imine bonds (C=N) between TETA and PS-DVB. Therefore, the sorbent could be used only once.

3.5 Extraction of Pb(II) from the leachate

The capability of Pb(II) sorption onto 25 mg of TETA-PS-DVB was significantly different in two mediums (deionized water and leachate). It meant that high concentration of main interfering ions in the leachate *i.e.* Ca^{2+}, Mg^{2+}, K^+, and Na^+ could probably affect the capability of the sorbent. The increase in sorbent dose was investigated. The result in Table 3 showed that increasing the dose of sorbent could improve the extraction efficiency of Pb(II).

The blank extraction was also done using the similar conditions in order to evaluate the effect of interfering ions that might interfere or be extracted by TETA-PS-DVB. The concentration of the interfering ions presented in the desorption solution was determined by ICP-OES. The result showed in Table 4 that other ions were not removed from the leachate. Thus, Pb(II) could be successfully separated from their matrices.

Table 3: Effect of sorbent amount to percentage sortion of Pb(II) in the leachate sample (n=3)

Sorbent (mg)	Sorption (%)	RSD (%)
25	65.4	3.3
50	79.0	2.7
75	82.3	2.2

Table 4: Concentration of interfering ions from the analysis by ICP-OES

Solution	Concentration of interfering ions (mg/L)			
	Ca^{2+}	K^+	Na^+	Mg^{2+}
Leachate sample	671	529	179	27
Desorption solution	3	0.8	9	0.6

Conclusion

The preparative sorbent based on polystyrene-divinylbenzene functionalized with triethylenetetramine has been favorably used for selective extraction of Pb(II) from aqueous solution. The adsorption kinetics followed the pseudo-second-order model with the rate constant of 18,425 g mol^{-1} min^{-1}. The adsorption behavior fitted the Langmuir model with the maximum adsorption capacity of 4.04 μmol/g. 10% (v/v) HNO_3 was a good desorbing solution that could totally eluted Pb(II) from the sorbent. Ca^{2+}, Mg^{2+}, K^+, and Na^+ ions could not be adsorbed on the sorbent and did not interfere the adsorption efficiency towards Pb(II). The propose protocol could be efficiently applied for Pb(II) extraction from cement-based stabilized waste leachate with over 80% extraction. The sorbent has hold great assurance for solid phase extraction applications owing to many advantages including high selectivity, simple and inexpensive operation.

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