Extraction of heavy metal ions from leachate of cement-based stabilized waste using purpurin functionalized resin

Marisa Wongkaew, Apichat Imyim *, Ponwason Eamchan

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Abstract

A new chelating resin was synthesized by functionalization of a polymer support, Amberlite XAD-2 with purpurin through an azo linkage ($-N=N-$). The products were characterized by scanning electron microscopy, elemental analysis, Fourier transform infrared spectroscopy and thermogravimetric analysis. The optimum conditions for the extraction of Cd(II), Cr(III) and Pb(II) in two matrices; leachate from cement-based material and de-ionized water, were studied by batch and column methods. The determination of the metal ions was carried out by flame atomic absorption spectrometry. The optimum pH for the extraction of all metal ions in both matrices were at 4.0. Their sorption equilibrium was reached within 1 h. The sorbed Cd(II) and Pb(II) were eluted by 1% HNO_3 within 10 min with the desorption recovery of >90%. The elution of Cr(III) by 3% H_2O_2 in 0.1 M NaOH was achieved within 30 min with the desorption recovery of >80%. The sorption capacity of Cd(II), Cr(III) and Pb(II) onto the resin was 75.0, 68.2, 82.7 $\mu mol\,g^{-1}$ resin in DI water and 54.1, 46.5 and 55.7 $\mu mol\,g^{-1}$ resin in leachate, respectively. The extraction efficiency in the column method can be improved using the recirculation system. This new method gave a good accuracy in batch system with the recovery of 86.5 and 89.9% for Cd(II) and Pb(II) and R.S.D. less than 2.3% ($n = 14$).
© 2007 Elsevier B.V. All rights reserved.

Keywords: Pupurin; Amberlite XAD-2; Chelating resin; Cement-based stabilized waste

1. Introduction

The cement-based solidification/stabilization (s/s) process is a well-known method for the disposal of heavy metal contaminated hazardous wastes [1] because of its low operation and material cost, ability to improve physical characteristics (solidification) and to reduce the toxicity and mobility of contaminants (stabilization). The product from s/s process can be disposed in a landfill or used for construction purposes. However, the effectiveness of s/s treatment should be considered to prevent the release of heavy metals from the s/s waste to the environment, especially into water resources. In 1997, the Ministry of Industry of Thailand announced a regulation on the testing of toxicity of treated wastes from s/s process using the leaching extraction procedure, modified from the EPA method 1312 [2]. The leaching level of toxic heavy metals that has to be controlled in this regulation must be less than 5.0, 100.0, 1.0, 5.0, 5.0,

0.2, 1.0 and 5.0 $mg\,L^{-1}$ for As, Ba, Cd, Cr, Pb, Hg, Se and Ag, respectively.

Heavy metals in s/s products can be dissolved in a leachant (extraction fluid), the solution becomes a complicated leachate containing high concentration of calcium ions dissolved from the cement matrix and others elements such as Si, Al and Fe [3]. A common method for the determination of heavy metals is atomic absorption spectrometry (AAS), due to its accuracy and precision, high sensitivity, good selectivity and low operation cost [4]. However, concomitants in the leachate can affect the correct determination of the heavy metals because their concentration is much less than that of the concomitants such as calcium ions. There were some reports that showed the interference effect of calcium towards the decrease of the absorbance of investigated elements using electrothermal atomic absorption spectrometry (ETAAS) [5,6]. Extraction of heavy metals from the leachate matrix before the determination is thus suggested to overcome those problems. Several separation techniques used to isolate metal ions from the matrix interference consist of coprecipitation, liquid–liquid extraction [5] and flotation separation method [6] or solid phase extraction (SPE).

* Corresponding author. Tel.: +66 2 218 7607: fax: +66 2 2541309.
E-mail address: iapichat@chula.ac.th (A. Imyim).

SPE offers several advantages, such as selectivity, availability and easy recovery of sorbent, attainability of high preconcentration factors [7–9], ease of handling and eco-friendliness [10,11].

Employing chelating resin as solid sorbent is an attractive analytical tool as the selectivity of the sorbent is greatly improved. Chelating resin consists of two main parts, i.e. a polymeric solid support and a chelating ligand which is an important part involved in the extraction of metal ions. Styrene–divinylbenzene, being commercially available as Amberlite XAD resin series, was found to be a good solid support to load the chelating ligand due to its good physical and chemical properties such as porosity, high surface area, durability and purity [12]. The chelating ligand is a molecule bearing donor atoms or binding sites to form a complex with a metal ion. The improved selectivity can be attributed to the size of the chelate ring and the metal atom, type of donor atoms (hard or soft bases), oxidation state of the metal ion and pH of the solvent system [13]. The two means for attaching chelating ligands to polymer solid supports are impregnation and functionalization. The impregnation method involves a physical adsorption while the functionalization involves a chemical bonding based on covalent coupling of the ligand with the polymer backbone through a spacer arm, generally $-N=N-$ group [13–17]. The functionalized sorbent is a much more stronger system and hence free from chelating ligand leaching problem [14]. Several works on Amberlite XAD series, used as chelating solid support for metal ion extraction, have been reported in the recent years. The examples of the chelating agents employed are pyrocatechol [18], nitroso R salt [10], 2-(methylthio)aniline [19] and pyrocatechol violet [20], *o*-aminobenzoic acid [21], salicylic acid [22] and dithiocarbamates [23], 1,3-dimethyl-3-aminopropan-1-ol [24], (bis-2,3,4-trihydroxybenzyl)ethylene diamine [17] and phthalic acid [25].

Purpurin is one of chelating ligands that has many attractions for the extraction of metal ions from cement-based leachate. It can form complex with various metal ions [26,27]. Moreover, purpurin is highly selective towards certain metal ions in the presence of calcium ion and the selectivity towards each metal ion can be controlled by adjusting the solution pH [28,29]. To the best of our knowledge, the preparation of chelating resin functionalized with purpurin for the extraction of metal ions had not yet been reported.

As mentioned above, the extraction of metal ions from leachate matrix shall be done prior to their determination using spectrometric techniques in order to reduce background interferences, obtain better results and longer lifetime of apparatus. Thus, this research is focused on the synthesis and characterization of a chelating resin using Amberlite XAD-2 functionalized with purpurin (XAD-P) through $-N=N-$ group followed by the studies on various parameters affecting the process of quantitative extraction of Cd(II), Cr(III) and Pb(II) from cement-based material leachate. These metals were selected from the list of toxic heavy metals in leachate since they are usually found in industrial hazardous wastes [3,30,31]. The practical applicability of the new chelating resin to extract metal ions from the synthetic leachate has been tested.

2. Experimental

2.1. Apparatus

Infrared spectra were recorded on a Fourier transform infrared spectrometer (FT-IR) model 410 (Nicolet Impact) with the KBr pellet method. A thermal analyzer model 409 (Netzsch) and a scanning electron microscope model JSM 5410LV (JEOL) were used for the characterization of all polymers. A CHNS/O analyzer PE 2400 Series II (Perkin-Elmer) was used for elemental analysis. A Mechanical shaker model SA-31 (Yamato shaker) was used for agitation of solution for cement extraction. pH measurements were made with digital pH meter (Hanna instruments Model pH211). A peristaltic pump REGLO Analog MS-4/8 model ISM 827 (ISMATEC®) was used for the control of the flow of solutions passing through the column. A flame atomic absorption spectrometer (FAAS) model AAnalyst 100 (Perkin-Elmer) was used for the determination of metal concentration using an air–acetylene flame. The instrumental parameters are the following; the wavelengths used were 228.8, 357.9 and 283.3 nm with the lamp current 4, 25 and 10 mA for Cd, Cr and Pb, respectively, the slit width was 0.7 nm for all three analytes.

2.2. Materials and reagents

All reagents and solvents were of standard analytical grade and used without further purification. De-ionized (DI) water with conductivity of less than $4 \, \mu S \, cm^{-1}$ was obtained from cation and anion exchange resin columns. Working standard solutions of Cd(II), Cr(III), and Pb(II) were prepared by stepwise dilution of $1000 \, mg \, L^{-1}$ stock standard solutions purchased from BDH Laboratory Supplies (Poole, England, UK) and Fisher Scientifics (Loughborough, Leics, UK). Purpurin was supplied by Fluka (Buchs, Switzerland). The solution pH was adjusted with 1% HNO_3 and 5% NH_3 (Merck, Darmstadt, Germany). Amberlite XAD-2 resin with surface area of $366.5 \, m^2 \, g^{-1}$ dry resin purchased from Supelco (Bellefonte, PA, USA) was washed with 4 M HCl (Merck) for 12 h before use. It was then washed with DI water until free from acid and washed finally with a small amount of methanol (Merck) and dried in air.

2.3. Synthesis of Amberlite XAD-2 functionalized with purpurin

The procedure reported by Kumar et al. [14] with some modifications was applied for the synthesis of the XAD-P chelating resin. Amberlite XAD-2 beads (10 g) were treated with 20 mL of concentrated HNO_3 and 50 mL of concentrated H_2SO_4 (Merck) and the mixture was stirred at 60 °C for 1 h in an oil bath. The nitrated resin ($XAD-NO_2$) was poured into ice-cold water. It was further filtered, washed repeatedly with DI water until free from acid. Then it was reduced with a mixture of 40 g of $SnCl_2$ (Fluka) in 45 mL of concentrated HCl and 50 mL of ethanol (Merck) and refluxed for 12 h at 90 °C. The amino resin ($XAD-NH_2$) was filtered and washed with DI water and 2 M NaOH (Merck).

The amino resin was firstly washed with 2 M HCl, then with DI water in order to remove excess of HCl and suspended in ice-cold water and treated with 1 M HCl and 1 M $NaNO_2$ (Merck) (added 1:1 mL each time until the reaction mixture showed a permanent dark blue color with starch-iodide paper). The diazotized resin was filtered, washed with ice-cold water and finally reacted with purpurin (1 g in 250 mL of 10% NaOH) at 0–5 °C for 24 h. The resulting dark red beads were filtered and washed with DI water until the solution free from the red color of excess purpurin, then washed with methanol and air dried.

2.4. Synthetic leachate

A blank cement-based mortar was prepared by mixing mixed cement (Tiger Cement, The Siam Cement Group, Thailand) and sand with a weight composition of 30:70. A small volume of DI water was added. The mixture was homogenized and the paste was molded in a plastic container. Thereafter, the blank cement-based mortar was cured for 28 days and then crushed and sieved to obtain particle size of less than 9.5 mm. And then 25 g of the crushed solid was extracted using 500 mL of leachant. The leachant or extraction fluid was simulated from natural precipitation. It was easily prepared by using a mixture of H_2SO_4:HNO_3 (80:20 by weight) to adjust pH of DI water to pH 5. This method was modified from the EPA method 1312 [32]. The mixture was shaken using a mechanical shaker for 18 h. The leachate was then filtered through a 0.45 μm membrane filter utilizing a pressure filtration unit. This filtrate was used as a representative synthetic leachate for further experiments.

2.5. Extraction procedure

2.5.1. Batch method
The effect of various parameters influencing the extraction efficiency was investigated in both matrices: leachate and DI water. In addition, the adsorption isotherm of the metals was studied. An individual metal solution (5.0 mL) containing 1.0 mg L^{-1} for Cd(II) and 5.0 mg L^{-1} for Cr(III) and Pb(II) in leachate and 5.0 mg L^{-1} for all the metal ions in DI water was placed in a test tube after pH adjustment. XAD-P was added to the test tube and the mixture was stirred. The resins were separated. The effects of pH and extraction time were investigated. Nitric acid and hydrogen peroxide were used as eluents; their concentration was varied from 1 to 5%. The elution time was varied in the range of 2–60 min. The study of the adsorption isotherm was investigated by varying the concentration of metal solution under optimum conditions for each metal at 25.0 ± 1.0 °C. All the experiments were performed in triplicate. The residual metal concentration in the supernatant and the amount of metal in the stripped solution was determined by FAAS.

2.5.2. Column method
A polyethylene mini-column with 0.4 cm i.d. was packed with XAD-P. A leachate solution at optimum pH (5.0 mL) containing 1.0 mg L^{-1} for Cd(II) and 5.0 mg L^{-1} for Cr(III) and Pb(II) was separately passed through the prepared column, at varying flow rates from 0.5 to 5.0 mL min^{-1} (controlled with a peristaltic pump). The recirculation of sample solution was adopted for higher extraction efficiency. 5 mL of metal ion solution at optimum pH was passed and recirculated (5–40 cycles) through the column at a fixed flow rate of 5.0 mL min^{-1}. The remaining metal ion in the solution after the recirculation was determined by FAAS.

2.6. Method validation

In order to demonstrate the validity of this method in the batch system, the accuracy and precision were investigated using the leachate spiked with a known amount of each metal ion. The spiked concentrations of each metal ion were set at the regulatory levels of heavy metal in leachate. An individual solution (5 mL) containing 1.0 mg L^{-1} for Cd(II) and 5.0 mg L^{-1} for Cr(III) and Pb(II) was stirred with XAD-P, the sorbed metal was then eluted with 1% HNO_3 (5.0 mL) for Cd(II) and Pb(II) and 3% H_2O_2 in 0.1 M NaOH for Cr(III). Under the optimum conditions, the method validation was performed by repeating the same experiment 14 times. The accuracy and precision were calculated as a recovery and R.S.D., respectively.

3. Results and discussion

3.1. Characterization of Amberlite XAD-2 functionalized with purpurin

The SEM micrographs (Fig. 1) reveal that the XAD-2 surface is rougher than XAD-P surface, implying that the substrate surface was changed after the functionalization with purpurin. The EA results are illustrated in Table 1. The nitrogen content appeared in the XAD-NO_2 indicating the successful synthesis of nitration. The EA calculated value based on one repeating unit of XAD-P ($C_{22}H_{14}N_2O_5$) is C 68.39, H 3.63 and N 7.25%. These values were not in good agreement with those obtained experimentally with XAD-P, probably due to the incompleteness of each synthesis step.

The resin from each synthesis step was characterized by FT-IR (Fig. 2). The IR bands of $\nu(N=O)$ at 1526, 1348 cm^{-1}; $\nu(N-H)$, $\delta(N-H)$ and $\nu(=C-NH_2)$ at 3430, 1626 and 1383 cm^{-1}; $\nu(C=O)$ and $\nu(C-O)$ at 1704, 1347 cm^{-1} were observed for XAD-NO_2, XAD-NH_2 and XAD-P, respectively.

The TGA curves (Fig. 3) showed that each resin exhibited different decomposition temperature. The final product XAD-P

Table 1
Elemental analysis of resins

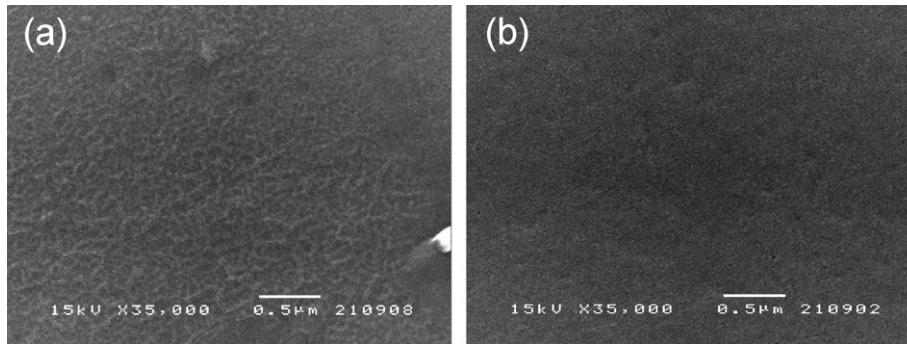| Sample	%C	%H	%N
XAD-2	90.63	7.93	nd
XAD-NO_2	61.15	5.75	8.53
XAD-NH_2	67.24	7.14	6.47
XAD-P	71.56	7.63	6.71

nd, Not detectable.

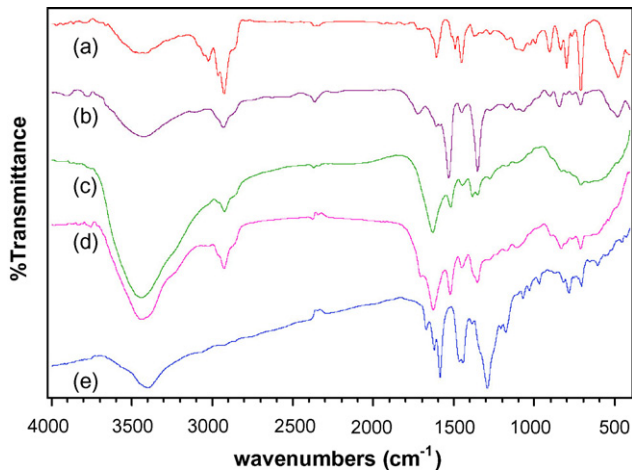Fig. 1. SEM photographs of (a) XAD-2 and (b) XAD-P surface.

Fig. 2. Infrared spectra of (a) XAD-2, (b) XAD-NO$_2$, (c) XAD-NH$_2$, (d) XAD-P and (e) purpurin.

exhibited two stages of mass loss up to 500 °C. In the first stage, a mass loss of 10.16% at 130 °C seems to be due to sorbed water evaporation. The second mass loss started after 200 °C, corresponding to the first decomposition stage of purpurin that began around 250 °C. The presence of water molecule in this resin showed that XAD-P was more hydrophilic than the starting solid support (XAD-2). Consequently, the rate of metal ion phase transfer from solution onto the chelating resin will be increased [17]. Overall, the results from all characterization techniques indicated the success of the XAD-P synthesis.
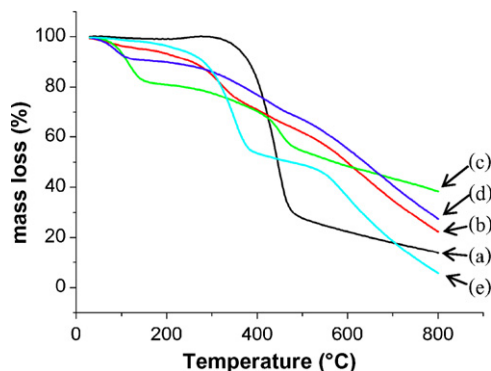

Fig. 3. Thermograms of (a) XAD-2, (b) XAD-NO$_2$, (c) XAD-NH$_2$, (d) XAD-P and (e) purpurin.

3.2. Extraction study

3.2.1. Batch method

In the batch method, the effect of various parameters influencing the extraction efficiency of Cd(II), Cr(III) and Pb(II) were investigated in both matrices. After that, the optimization conditions from the batch method were applied for the column method.

3.2.1.1. Effect of pH on metal extraction. The metal sorption (mg g^{-1} resin) of the metal retained on the sorbent was calculated according to Eq. (1).

$$\text{sorption capacity} = \frac{n_s - n_f}{m} \tag{1}$$

where n_s is the starting amounts of each metal (mg), n_f the amount of metal remaining in the solution after extraction (mg) and m is the mass of sorbent (g).

The results of each metal sorption are illustrated in Fig. 4. The maximum sorption capacity for Cd(II), Cr(III) and Pb(II) were observed at pH 4.0 in both matrices. The pH of less than 4.0 were not suitable for the extraction because the binding site of purpurin was possibly protonated. At pH above 4.0, the sorption capacity decreased gradually. This observation can be attributed to the decrease of appropriate extractable metal species in higher pH medium.

3.2.1.2. Kinetics of metal extraction. The variation of sorption as a function of time for all metal ions at pH 4.0 is shown in Fig. 5. It was observed that an equilibration time of about 30 and 20 min were required for Pb(II) and Cd(II) in both matrices and that of about 10 min in DI water and 40 min in leachate for Cr(III). The rate of metal sorption onto XAD-P was quite rapid. This showed that the metal ions can easily form complex with XAD-P.

3.2.1.3. Effect of eluent. The selection criterion was based on the result of the effect of pH observed that no metal ion could be sorbed onto XAD-P at pH 1–2. Nitric acid, which is compatible with the determination by FAAS, was firstly selected as an eluent. Its concentration was varied in the range of 1–5% (v/v) in order to achieve the enough of proton for protonating chelation sites (proton exchange mechanism was purposed). The results
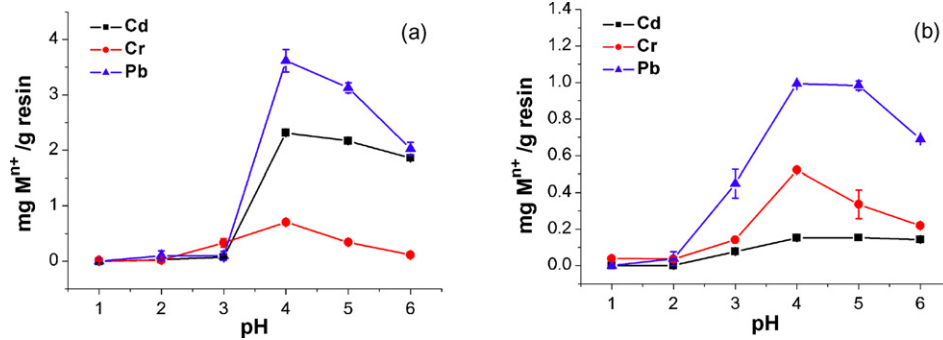
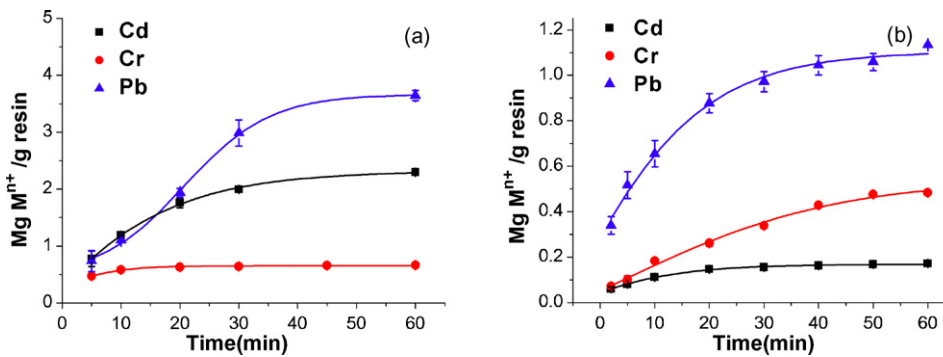Fig. 4. Effect of pH on metal extraction (a) in DI water and (b) in leachate.

Fig. 5. Rate of metal extraction on XAD-P at pH 4 (a) in DI water and (b) in leachate.

were plotted between the percent desorption that was calculated from Eq. (2), versus the concentration of nitric acid, as shown in Fig. 6.

$$\text{desorption}(\%) = \frac{n_e}{n_a} \times 100 \tag{2}$$

where n_a is the amount of metal ions (mg) adsorbed on resin and n_e is the amount of metal ions (mg) eluted from resin.

1% (v/v) HNO₃ was sufficient for quantitative elution with more than 90% for all metal ions within 10 min, except for Cr(III) of which the percent desorption was only 50% even when eluted with 5% (v/v) HNO₃. This may be explained by the charge density of metal ion. Cr(III) has the highest charge density and was sorbed strongly onto the resin, therefore it is difficult to elute from XAD-P surface by a simple acid solution. The H_2O_2 in
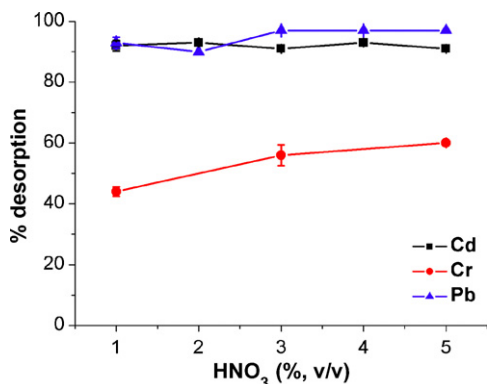

Fig. 6. Effect of HNO₃ concentration on metal desorption.

0.1 M NaOH was selected to elute Cr(III) because it can act as an oxidizing agent, so Cr(III) on XAD-P might be oxidized to Cr(VI) [33]. The dominant species of Cr(VI) is chromate ion (CrO_4^{2-}) which has a negative charge and would not be retained on XAD-P. 3% H_2O_2 in 0.1 M NaOH was able to quantitatively elute Cr(III) with more than 80% desorption within 30 min.

3.2.1.4. Adsorption isotherm. The distribution of metal ions between liquid and solid phases can be described by Langmuir adsorption isotherm. This isotherm is based on the assumptions that metal ions are chemically adsorbed on a fixed number of well-defined sites. Each site can hold only one ion (monolayer adsorption), all sites are energetically equivalent (homogeneous surface), and there is no interaction between the ions [34,35]. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant. The model is described by Eq. (3).

$$\frac{C}{N_f} = \frac{1}{bN_s} + \frac{C}{N_s} \tag{3}$$

where C is the residual metal concentration in solution at equilibrium (mol dm⁻³), N_f the amount of metal ions adsorbed per gram of sorbent (mol g⁻¹), N_s the maximum sorption capacity of sorbent (mol g⁻¹), and b is the Langmuir constant related to energy of adsorption (L mol⁻¹).

The results in Fig. 7 showed that the correlation coefficients (r^2) of the linear regression line of Langmuir isotherm were more than 0.99 for all metal ions in both matrices (Table 2). This indicated that the sorption of the metal ions onto XAD-P was agreeable with the Langmuir isotherm. Considering the
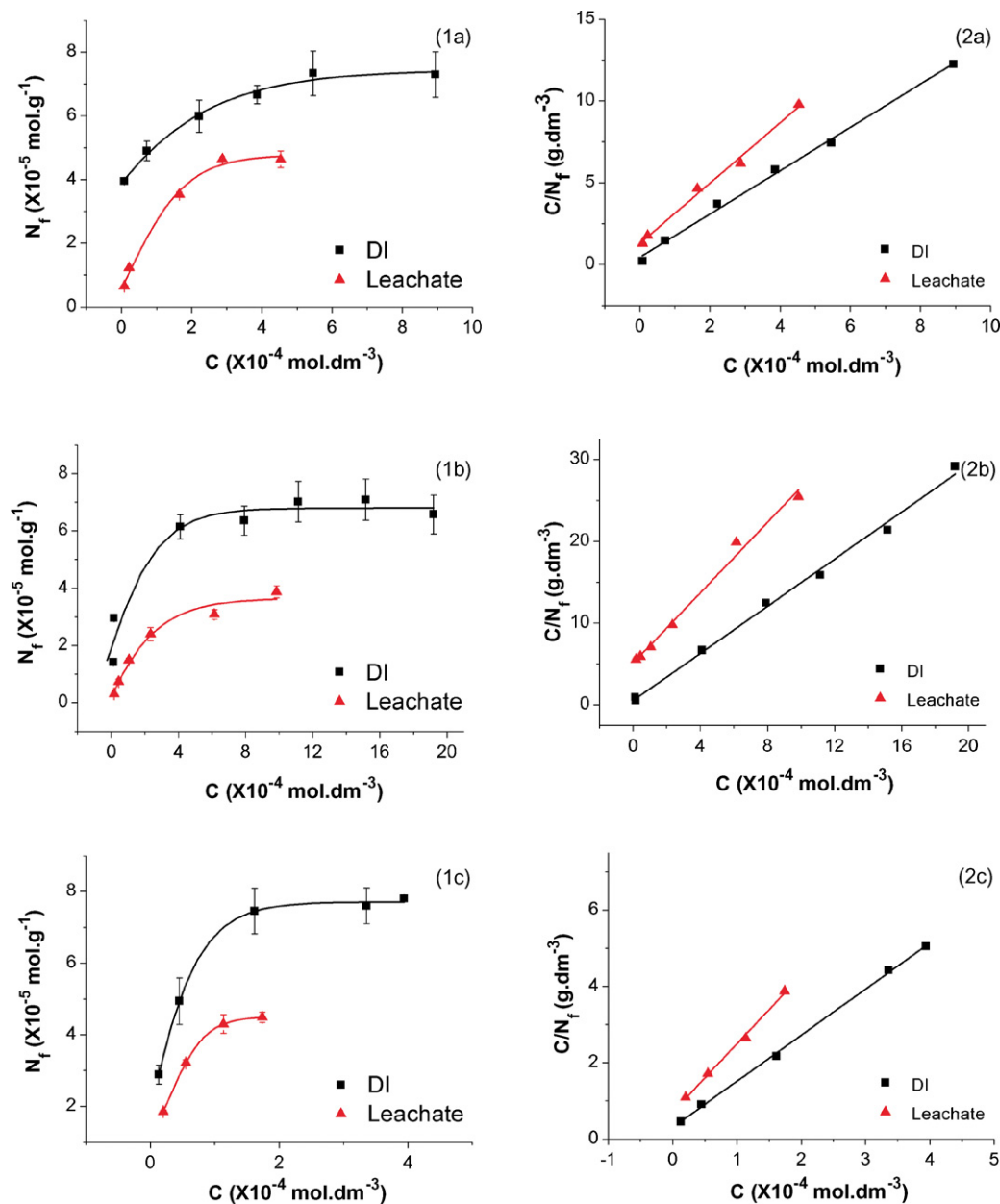
Fig. 7. Adsorption isotherm of (1a) Cd(II), (1b) Cr(III) and (1c) Pb(II) and Langmuir adsorption model fit of (2a) Cd(II), (2b) Cr(III) and (2c) Pb(II) in DI water and leachate at pH 4 and $25 \pm 1\,^\circ$C.

maximum sorption capacity (N_s) of XAD-P in two matrices in Table 2, the results showed that the N_s in leachate were lower than in DI water. This can be explained by the binding competition between calcium ions and the heavy metal ions in the

leachate. The selectivity order of XAD-P towards the metal ions that is $Pb(II) > Cd(II) > Cr(III)$ is in the same direction as the sequence of the N_s and b values. The different sorption capacity for each metal ion can be explained by the Hard Soft Acid Base

Table 2
Langmuir parameters for the adsorption of metal ions at $25 \pm 1\,^\circ$C

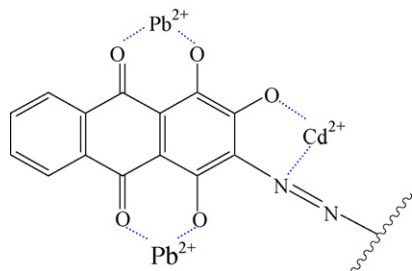| Metal	Matrix	Equation	r^2	$b \times 10^4$ (L mol^{-1})	N_s (µmol g^{-1})
Cd(II)	DI	$y = 13342x + 0.4436$	0.9966	3.01	75.0
	Leachate	$y = 18497x + 1.2998$	0.9933	1.43	54.1
Cr(III)	DI	$y = 14672x + 0.5073$	0.9957	2.89	68.2
	Leachate	$y = 21506x + 5.1648$	0.9904	0.42	46.5
Pb(II)	DI	$y = 12095x + 0.3188$	0.9988	3.79	82.7
	Leachate	$y = 17966x + 0.7063$	0.9976	2.01	55.7

Fig. 8. Proposed three chelation sites on XAD-P and the selectivity of each site towards Pb(II) (borderline cation) and Cd(II) (soft cation).

Fig. 9. Effect of solution flow rate on metal sorption at pH 4.

principle. Three effective binding sites in the purpurin structure can be separated into two types that are (O,O) and (O,N). The oxygen atoms act as borderline base because of the delocalization of electrons onto the coplanar structure of anthraquinone, while nitrogen atoms in the azo group act as soft base. The specific binding sites for metal ions were proposed in Fig. 8. Consequently, purpurin has two suitable binding sites for Pb(II) which is a borderline acid and one suitable binding site for Cd(II) which is a soft acid. The sorption capacity of XAD-P and other reported functionalized XAD-2 in DI water is summarized in Table 3. This comparison data showed that XAD-P has a good sorption capacity, especially for Pb(II) probably resulting from the two appropriate binding sites (Fig. 8). The sorption capacity for Cd(II) was moderate, while, from our knowledge, any sorption capacity data for Cr(III) had not been found. There is no literature data for leachate matrix.

3.2.2. Column method

In column method, the experiment was progressed only in leachate matrix using a homemade column packed with XAD-P.

3.2.2.1. Effect of flow rates.
The degree of sorption was studied at different flow rates and reported by the percent extraction that was calculated from Eq. (4). The results are illustrated in Fig. 9. The percent extraction was very low even though a very slow flow rate at $0.5 \, \text{mL} \, \text{min}^{-1}$ was applied. Moreover, at flow rates greater than $0.5 \, \text{mL} \, \text{min}^{-1}$, the percent extraction decreased. This can be explained by the insufficient contact time between the metal ions and XAD-P. Therefore, the dynamic system in
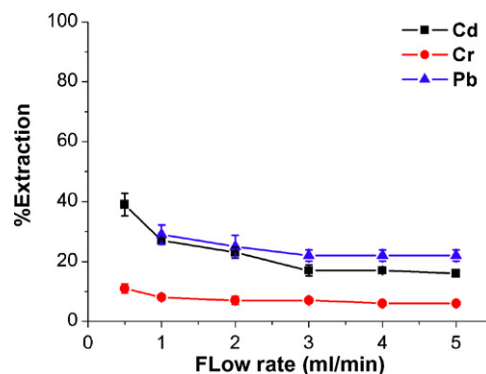
the column method was not recommended for XAD-P.

$$\text{extraction}(\%) = \frac{n_a}{n_s} \times 100 \qquad (4)$$

3.2.2.2. Recirculation of sample solution.
The very low percent extraction of metal ions can be improved using the recirculation of sample solution. To reduce the experiment time, the flow rate at $5 \, \text{mL} \, \text{min}^{-1}$ was chosen. The results are shown in Fig. 10. The recirculation system could raise the percent extraction that was directly proportional to the cycle number. The percent extraction of Cd(II) and Pb(II) increased up to 80% when using 30 cycles of sample solution recirculation. Similarly, the percent extraction of Cr(III) could be improved but still relatively low at around 50% after 40 cycles of recirculation. Although the percent extractions could be improved using the recirculation system, time consumption is a main drawback for this system. Therefore, XAD-P is still unsuitable for uses in the column method.

3.3. Method validation

The method validation should be investigated in order to check the accuracy and precision of the new proposed extraction method. The results are shown in Table 4. The accuracy (recovery that was calculated using Eq. (5)) and the precision (R.S.D.) of this method were acceptable for Cd(II) and Pb(II), according to the criteria of analyte recovery and precision at different concentrations [36]. Therefore, XAD-P resin was suitable to extract

Table 3

Comparison of sorption capacities of XAD-P with other azo spacer linkage functionalized Amberlite XAD-2 in DI water

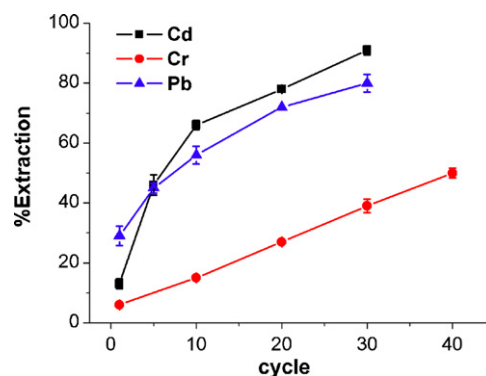| Chelating ligand	Sorption capacity ($\mu\text{mol} \, \text{g}^{-1}$)		
	Cd(II)	Cr(III)	Pb(II)
Purpurin [this work]	75.0	68.2	87.7
o-Vanillinthiosemicarbazone [13]	–	–	9.7
o-Aminophenol [14]	30.4	–	16.0
Tiron [15]	84.5	–	0.3
Alizarin Red-S [16]	1.1	–	1.5
Pyrocatechol [18]	40.9	–	–
2-Aminoacetylthiophenol [37]	190.4	–	–
Thiosalicylic acid [38]	197.5	–	–

Fig. 10. Effect of recirculation of sample solution at pH 4.

Table 4
Recovery and precision of the proposed method

Metal	Spiked concentration (mg L^{-1})	Recovery[a] (%)	R.S.D. (%)
Cd(II)	1	86.5	2.1
Cr(III)	5	56.9	4.8
Pb(II)	5	89.9	2.3

[a] Mean value ($n = 14$).

Cd(II) and Pb(II) from leachate without interfering from high content of calcium ions.

$$\text{recovery}\ (\%) = \frac{n_e}{n_s} \times 100 \qquad (5)$$

4. Conclusions

This newly developed chelating resin, Amberlite XAD-2 functionalized with purpurin was successfully applied for the extraction of Cd(II) and Pb(II) from cement-based leachate matrix in batch method. Many advantages of this method have been concluded as follows, the resin was easily synthesized and exhibited high sorption capacity and high selectivity towards for Pb(II) and Cd(II) and the elution was successful using 1% HNO_3 within 10 min. However, the main disadvantage of XAD-P is the insufficient extraction kinetics in leachate matrix, so the application in column method is still limited.

Acknowledgements

References

[1] B. Batchelor, Overview of waste stabilization with cement, Waste Manage. 26 (2006) 689–698.

[2] The Ministry of Industry of Thailand, The notification of the Ministry of Industry No.6 [B.E. 2540 (1997)] issued pursuant to the factory act B.E. 2535(1992) subject: disposal of wastes or unusable materials, 1997.

[3] R.A. Shawabkeh, Solidification and stabilization of cadmium ions in sand-cement-clay mixture, J. Hazard. Mater. 125 (2005) 237.

[4] D.A. Skoog, F.J. Holler, S.R. Crouch, Principles of Instrumental Analysis, sixth ed., Thomson Brooks/Cole, USA, 2007.

[5] T. Stafilov, D. Zendelovska, Determination of cobalt, copper, lead and nickel in gypsum by zeemzn electrothermal atomic absorption spectrometry, Acta Chim. Slov. 47 (2000) 381.

[6] T. Stafilov, D. Zendelovska, G. Pavlovska, K. Cundeva, Determination of trace elements in dolomite and gypsum by atomic absorption spectrometry: overcoming the matrix interference by flotation separation, Spectrochim. Acta B 57 (2002) 907.

[7] M. Soylak, L. Elci, M. Dogan, Determination of trace amounts of cobalt in natural water samples as 4-(2-thiazolylazo) recorcinol complex after adsorptive preconcentration, Anal. Lett. 30 (1997) 623.

[8] I. Narin, M. Soylak, K. Kayakirilmaz, L. Elci, M. Dogan, Preparation of a chelating resin by immobilizing 1-(2-pyridylazo) 2-naphtol on Amberlite XAD-16 and its application of solid phase extraction of Ni(II), Cd(II), Co(II), Cu(II), Pb(II), and Cr(III) in natural water samples, Anal. Lett. 36 (2003) 641.

[9] M. Tuzen, K. Parlar, M. Soylak, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction, J. Hazard. Mater. 121 (2005) 79.

[10] V.A. Lemos, J.S. Santos, S.L. Nunes, M.B. Carvalho, P.X. Baliza, R.T. Yamaki, Amberlite XAD-2 functionalized with Nitroso R salt: synthesis and application in an online system for preconcentration of cobalt, Anal. Chim. Acta 494 (2003) 87.

[11] G. Venkatesh, A.K. Singh, 2-{[1-(3,4-Dihydroxyphenyl)methylidene] amino}benzoic acid immobilized Amberlite XAD-16 as metal extractant, Talanta 67 (2005) 187.

[12] V.A. Lemos, D.G. Silva, A.L. Carvalho, D.A. Santana, G.S. Novaes, A.S. Passos, Synthesis of Amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry, Microchem. J. 84 (2006) 14.

[13] V.K. Jain, S.S. Sait, P. Shrivastav, Y.K. Agrawal, Application of chelate forming resin Amberlite XAD-2-*o*-vanillinthiosemicarbazone to the separation and preconcentration of copper(II), zinc(II) and lead(II), Talanta 45 (1997) 397.

[14] M. Kumar, D.P.S. Rathore, A.K. Singh, Amberlite XAD-2 functionalized with o-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II), Talanta 51 (2000) 1187.

[15] M. Kumar, D.P.S. Rathore, A.K. Singh, Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: analytical applications, Analyst 125 (2000) 1221.

[16] R. Saxena, A.K. Singh, S.S. Sambi, Synthesis of a chelating polymer matrix by immobilizing Alizarin Red-S on Amberlite XAD-2 and its application to the preconcentration of lead(II), cadmium(II), zinc(II) and nickel(II), Anal. Chim. Acta 295 (1994) 199.

[17] D. Prabhakaran, M.S. Subramanian, Selective extraction and sequential separation of actinide and transition ions using AXAD-16-BTBED polymeric sorbent, React. Funct. Polym. 57 (2003) 147.

[18] P.K. Tewari, A.K. Singh, Synthesis, characterization and applications of pyrocatechol modified Amberlite XAD-2 resin for preconcentration and determination of metal ions in water samples by flame atomic absorption spectrometry (FAAS), Talanta 53 (2001) 823.

[19] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, M. Tian, Preconcentration of trace metals with 2-(methylthio)aniline-functionalized XAD-2 and their determination by flame atomic absorption spectrometry, Anal. Chim. Acta 504 (2004) 319.

[20] R. Saxena, A.K. Singh, Pyrocatechol Violet immobilized Amberlite XAD-2: synthesis and metal-ion uptake properties suitable for analytical applications, Anal. Chim. Acta 340 (1997) 285.

[21] S.D. Cekic, H. Filik, R. Apak, Use of an *o*-aminobenzoic acid-functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal(II) ions, Anal. Chim. Acta 505 (2004) 15.

[22] P. Vanloot, J.L. Boudenne, P.C. Brach, M. Sergent, B. Coulomb, An experimental design to optimize the flow extraction parameters for the selective removal of Fe(III) and Al(III) in aqueous samples using salicylic acid grafted on Amberlite XAD-4 and final determination by GF-AAS, J. Hazard. Mater. 147 (2007) 463–470.

[23] A. Ramesh, K.R. Mohan, K. Seshaiah, Preconcentration of trace metals on Amberlite XAD-4 resin coated with dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry in saline matrices, Talanta 57 (2002) 243.

[24] D. Prabhakaran, M.S. Subramanian, A new chelating sorbent for metal ion extraction under high saline conditions, Talanta 59 (2003) 1227.

[25] S.Q. Memon, S.M. Hasany, M.I. Bhanger, M.Y. Khuhawar, Enrichment of Pb(II) ions using phthalic acid functionalized XAD-16 resin as a sorbent, J. Colloid Interface Sci. 291 (2005) 84.

[26] A.A. Ramirez, C.J. Linares, F.A. Barrero, M.R. Ceba, Study of the mixed-metal lanthanummagnesium-purpurin complex: spectrophotometric determination of yttrium and lanthanides, Talanta 33 (12) (1986) 1021.

[27] A. Arrebola, M.G. Bagur, M.S. Vinas, D. Gazquez, R. Romero, M. Camino, Indirect determination of total yttrium and lanthanides by flame atomic

absorption measurement of magnesium after extraction of their ternary complexes with purpurin (1,2,4-trihydroxyanthraquinone) and magnesium into isobutyl methyl ketone, J. Anal. Atom. Spectrom. 13 (1998) 765.

[28] K.A. Idriss, H. Sedaira, M.S. Abdel-Aziz, H.M. Ahmad, Rapid test methods for minor components analysis of hydraulic cement: spectrophotometric determination of manganese oxide content of Portland cement and cement raw meal, Talanta 50 (1999) 913.

[29] K.A. Idriss, H. Sedaira, H.M. Ahmad, An insight into the solution equilibria of magnesium(II) with purpurin and spectrophotometric determination of magnesium, Talanta 54 (2001) 369.

[30] C. Jing, S. Liu, G.P. Korfiatis, X. Meng, Leaching behavior of Cr(III) in stabilized/solidified soil, Chemosphere 64 (2006) 379.

[31] C.Y. Yin, M.G. Shaaban, H.B. Mahmud, Stabilization/solidification of lead-contaminated soil using cement and rice husk ash, J. Hazard. Mater. 137 (2006) 1758.

[32] United States Environmental Protection Agency, Synthetic precipitation leaching procedure (SPLC) (US EPA Method 1312), 1994.

[33] J.E.T. Andersen, Introduction of hydrogen peroxide as an oxidant in flow injection analysis: speciation of Cr(III) and Cr(VI), Anal. Chim. Acta 361 (1998) 125.

[34] S. Meesri, N. Praphairaksit, A. Imyim, Extraction and preconcentration of toxic metal ions from aqueous solution using benzothiazole-based chelating resins, Microchem. J. 87 (2007) 47.

[35] J.C. Igwe, A.A. Abia, Adsorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob, Eclet. Quim. 32 (1) (2007) 33.

[36] R.L. Mark, Validation and Qualification in Analytical Laboratories, Interpharm Press, IL, USA, 1999.

[37] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry, Talanta 62 (2004) 209.

[38] P.K. Tewari, A.K. Singh, Thiosalicylic acid-immobilized Amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame absorption spectrometry, Analyst 125 (2000) 2350.