



Preconcentration and Determination of Cadmium in Natural Water using Amberlite XAD-4/4-(2-Pyridylazo) Resorcinol Resin Prior to Flame Atomic Absorption Spectrometric Detection

Sureerat Sanguthai and Jintana Klamtet*

Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, Thailand, 65000

* Corresponding author. E-mail address: jintanaki@nu.ac.th

Abstract

A chelating polymeric sorbent was developed by functionalizing Amberlite XAD-4 resin with 4-(2-pyridylazo) resorcinol ligand for preconcentration of Cd(II) and quantitative analysis by flame atomic absorption spectrometry. The effect of several parameters such as pH, adsorption time, adsorption capacity, preconcentration factor, effect of interference and concentration of nitric acid were studied in a batch system. Optimized conditions with a pH of value 9.0, loading time of 30 min and nitric concentration of 0.5 mol l⁻¹ were selected. The detection limit of the method was found to be 0.26 mg l⁻¹. The chelating resin can be reused for sorption-desorption and is stable for up to 15 runs (recovery 85–91%) without appreciable loss of sorption capacity. The preconcentration factor achieved by this method is 5. The effects of interferences are reported. The precision of the method was evaluated with the relative standard deviations (R.S.D.) under optimum conditions being 1.78 and 0.29% (n=10) for 0.40 and 1.20 mg l⁻¹ of Cd(II), respectively. The proposed method has been applied for the determination of Cd (II) ions in water samples collected around Naresuan University, Phitsanulok Province.

Keywords: XAD-4 resin, Amberlite XAD-4/PAR resin, Solid phase extraction, Preconcentration, Cadmium

Introduction

Cadmium is one of the main elemental pollutants in the environment. Atmospheric emission of Cd may arise from such activities as mining and metallurgical processing, combustion of fossil fuel, textile printing, application of fertilizers and fungicides, recycling of ferrous scraps and motor oils, disposal and incineration of products containing Cd (e.g., plastics), and tobacco smoke (Landis, & Yu, 2005, p. 25). Pollutant cadmium in water may arise from industrial discharges and mining waste. Cadmium is widely used in metal plating. The effects of cadmium poisoning in humans are very serious, causing high blood pressure, kidney damage, destruction of testicular tissue and destruction of red blood cells (Manahan, 2001). It is, therefore, very important to

develop sensitive methods for the quantitative determination of trace cadmium.

In order to detect low cadmium concentrations in different samples, very sensitive techniques are required. Inductively coupled plasma mass spectrometry (Kuznetsov, Zemyatova, & Kornev, 2014, pp. 105 – 110) and electro thermal atomic absorption spectrometry (Jaing, Hu, Jaing, & Qin, 2006, pp. 7–13) have enough sensitivity to allow determination of cadmium at trace level. However, the disadvantages of the ICP-MS system include isobaric interference produced by polyatomic species arising from plasma gas and the atmosphere. The disadvantages of ETAAS analysis include interference from the matrix components and relatively long analysis times (Chamsaz, Akhounzadeh, & Abab-zavar, 2013, pp. 361–366). On the other hand, flame atomic absorption



spectrometry (FAAS) is an available technique in most laboratories and is one of the most extensively used techniques for various determinations of elements with significant precision and accuracy. However, the sensitivity obtained from this technique is not sufficient for detection of cadmium at low levels (Burham, 2009, pp. 1199-1205). Thus a preconcentration step is required before FAAS determination (Pahani, et al., 2009, pp. 49-54). A large number of such preconcentration techniques have been developed, including ion-exchange (Nakashima, 1963, pp. 54-60), co-precipitation (Kamjorova, & Blust, 2006, pp. 221-228), solvent extraction (Arain, et al., 2009, pp. 25 - 29) modified of sorbent (Burham, 2009, pp. 1199-1205) and solid phase extraction (Jain, Mandalia, Gupte, & Vyas, 2009, pp. 49 - 54).

This current paper reports on the preconcentration of cadmium using solid phase extraction. The solid phase extraction method was investigated because this method is one of the most effective, simplest and rapid methods, with the ability to achieve a high concentration factor. Many choices of sorption material have been used for separation and preconcentration of metal ions at trace levels. Previous materials researched include XAD resins (Jain, et al., 2009, pp. 49-54; Lemos, & Baliza, 2005, pp. 564-570; Tewari, & Singh, 2002, pp. 735-744), activated carbon (Strelko, Malik, & Sreat, 2005, pp. 1885-1905), silica gel (Liu, Liang, & Guo, 2005, pp. 25-30), ion-exchange resins (Hubicki, & Wolowicz, 2009, pp. 1414-1419), chelating resins (Narin, Surme, Bercin, & Soylak, 2007, pp. 113-119) and various polymers (Soylak, & Tuzen, 2006, pp. 1469- 1501; Erdogan, Merdivan, Hamamci, Akba, & Baysal, 2004, pp. 2565-2575). Amberlite-XAD is a type of resin widely used to develop several chelating materials due to its good physical and chemical properties such

as porosity, high surface area, durability and purity (Pahani, et al., 2009, p, 49 - 54).

Advantage factors in the chelating resin are high capacity and weak metal binding. While small amounts of high capacity resin can concentrate metal ion from a large sample volume, weak metal binding can be an advantage in the elution step. Selectivity is often related to the many ligands in the functional group of chelating resins (Nezhati, et al., 2009, pp. 1269-1274). These ligands include *m*-phenylenediamine, allyl phenol, phthalic acid, *o*-aminobenzoic acid and 1,6-bis(2-carboxy aldehyde phenoxy) butane which are covalently coupled with a polymer backbone through an azo (-N=N-), methylene (-CH₂-) or other groups (Pahani, et al., 2009, pp. 49-54; Nezhati, et al., 2009, pp. 1269-1274). There are many reports of functionalized Amberlite XAD series such as 2, 4, 7 and 16 (Pahani, et al., 2009, pp. 49 - 54; Jain, et al., 2009, pp. 49-54; Lemos, & Baliza, 2005, pp. 564-570; Tewari, & Singh, 2002, pp. 735-744; Strelko, et al., 2005, pp. 1885-1905). Some copolymer resins such as Amerlite XAD-7, prepared by being impregnated with Xylenol Orange (XO) for enrichment of Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II), under optimum conditions, have shown good characteristics for preconcentration of trace metal ions in pharmaceutical samples (Tewari, & Singh, 2002, pp. 735-744). Amerlite XAD-16 was modified with 1, 6-bis (2-carboxy aldehyde phenoxy) butane for preconcentration and determination of Cu(II) and Cd(II) in river water (Orala, Dolaka, Temel, & Zadanogullaria, 2011, pp. 724-730). These chelating resins show good potential for enrichment trace metals and their efficient separation is possible in the presence of various interfering ions (Oral, et al., 2011, pp. 724-730). The Amberlite XAD-4 (styrene-divinylbenzene copolymer) is widely supported and



used to develop several chelating resins for preconcentration procedures. These resins show good physical and chemical properties such as porosity, surface area, durability and purity (Kalal, Pahani, Hoveidi, Taghiof, & Menderjani, 2012, pp. 1-9). While a few reports on Amberlite XAD-4 functionalized with 4-(2-pyridylazo) resorcinol have been published, the resins modified by Amberlite XAD-4/PAR can be used for determining other trace metals in environmental or biological samples. This process of modifying or synthesizing resins can be applied to *modify* other sorbents.

Given this, Amberlite XAD-4/4-(2-pyridylazo) resorcinol was prepared through an azo (-N=N-) linkage, which was then used as an adsorbent. The procedures of adsorbing and stripping elements on a sorbent and the effect of the parameters for preconcentration of cadmium, including the amount of resin, pH, type and concentration of eluting agent, were investigated before flame atomic absorption detection, and the proposed method was also applied to the determination of cadmium in natural water samples.

Method and Materials

Instruments

The FAAS measurements of the metals analysed in this study were carried out using a Varian Spectra model AA 220 (Australia) equipped with an air-acetylene flame. The measurements were carried out in the absorbance mode at 228.8 nm, using a spectral bandwidth of 0.50. Background correction was used with a deuterium-lamp. The deuterium-lamp currents were set at 4 mA. The pH measurements were made with a pH-meter equipped with a glass electrode (Horiba model F 21, Japan).

Chemical

Amberlite XAD-4 (non-ionic divinyl polystyrene; surface area $750 \text{ m}^2 \text{ g}^{-1}$ and bead size, 20-60 mesh) was purchased from Alfa Aesar (USA). Standard solutions of Cd(II) were prepared by appropriate dilutions from standard atomic absorption solutions (1000 mg L^{-1} of Cd(II), Merck, Germany). All other chemicals used were of analytical grade. The 4-(2-pyridylazo) resorcinol monosodium salt hydrate (PAR) (Fluka, Switzerland) was prepared by dissolving the required amount of PAR in deionized water before use. A buffer solution was prepared by mixing appropriate amounts of citric acid (Ajax Finchem, Australia), di-sodium hydrogen phosphate (Merck, Germany), Sodium Tetraborate (Ajax Finchem, New Zealand) and sodium carbonate (Fluka, Switzerland).

Synthesis of chelating resin

The synthesis of chelating resin has been previously described (Pahani, et al., 2009, pp. 49-54; Lemos, & Baliza, 2005, pp. 564-570; Venkatesh, & Singh, 2005, pp. 187-194). 5.002 g of Amberlite XAD-4 was treated with a nitrating mixture containing 10 mL of concentrated nitric acid and 25.0 mL of concentrated sulfuric acid. The mixture was stirred at 60°C for 1 h using an oil bath. The nitrated mixture was poured into ice-cold water, filtered, washed repeatedly with deionized water until the acid was completely removed and then treated with a reducing mixture of 40.0 g of stannous chloride (Sigma-Aldrich, USA), 45.0 mL of concentrate hydrochloric (ACI labscan, Thailand) and 50.0 mL ethanol (Merck, Germany). The mixture was refluxed for 12 h at 90°C . The solid precipitate was filtered and washed with deionized water and 2.0 mol l⁻¹ Sodium hydroxide (Merck, Germany) to release the amino resin (R-NH₂) from (RNH₃)₂SnCl₆ (R=resin matrix). The amino resin was first washed in 2.0 mol



1-1 hydrochloric acid and then washed with deionized water to remove the excess of hydrochloric acid. Afterwards the amino resin was washed with 250 mL of ice-cold water, the amino resin was filtered and the reaction mixture was treated with 1.0 mol l-1 hydrochloric acid and 1.0 mol l-1 sodium nitrite (added in small aliquots of 1 mL) until the reaction mixture showed a permanent dark blue color with starch-iodide paper, this step the polymer was thus converted to the diazonium salt, washed polymeric resin with ice cold water and treated with 4-(2-pyridylazo)resorcinol (3.002 g in 250 cm³ of 2% sodium hydroxide solution) at

0-5°C for 24 h until the reaction was complete. The resulting brown colored beads were filtered, washed with deionized water and dried in air. The resin beads were let to swell in deionized water before usages. The procedure for modifying the XAD-4 resin/PAR is summarized in Figure. 1, the procedure modified of these resin is similar modified with many sorbents such as Amerlite XAD-16 modified with 1, 6-bis (2-carboxy aldehyde phenoxy) butane (Orala, et al., 2011, pp. 724-730) and Amberlite XAD-2 modified with 2-aminothiophenol (Lemos, & Baliza, 2005, pp. 564-570).

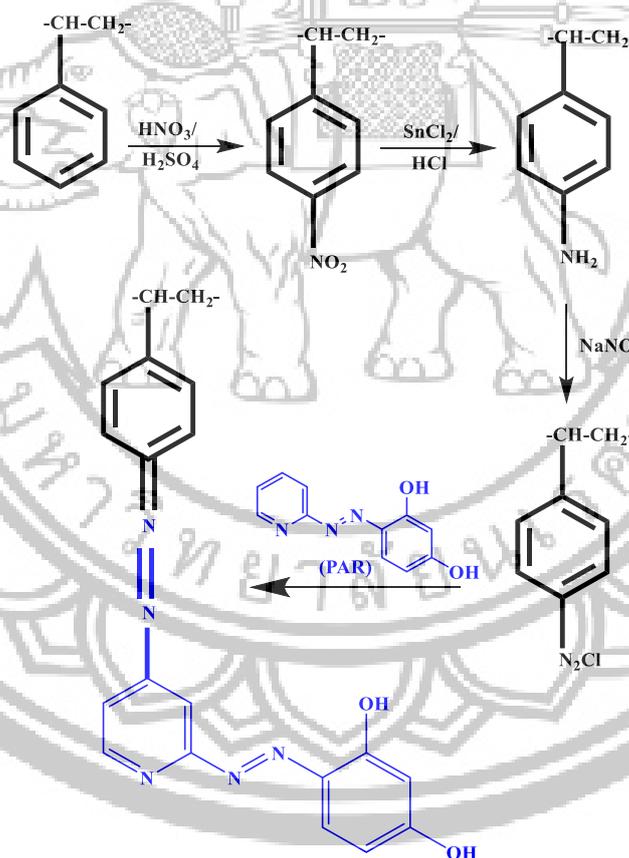


Figure 1 The methodology of the modified Amberlite XAD-4/PAR resin.



Sampling site

The samples used for the determination of Cd(II) contamination were gathered from various small lakes and ponds around the university campus. The map of the Naresuan University campus shown in Figure 2 indicates these sampling sites. Site A1 is the water

reservoir of Naresuan University, A2 is a pond near the Faculty of Engineering, A3 are irrigation canals and flumes on the border of the campus, A4 is a pond near the Faculty of Science and A5 is another canal.



Figure 2 Map of the sampling site locations of Naresuan University located in Phitsanulok province.

Batch Method

The solution containing 5.0 mg l^{-1} of Cd(II) was placed in a beaker. Amberlite XAD-4/ PAR resin was added to the sample solution to achieve a pH of 9. The mixture was stirred for 30 min and the modified resins were filtered off. The metal ions from the resin were desorbed by shaking the resin beads with 15.0 mL of 2.0 mol l^{-1} nitric acid for 20 min and again filtered. The final concentration of Cd (II) in the solution was measured by FAAS.

Results and discussion

Effect of pH

One of the most important parameters affecting the absorption of metal ions is the pH of the solution, because the formation of metal ions complex and maximal efficiency for a given preconcentration and separation can be established by optimization of the pH. The influence of pH in the range 7-11 on the absorption of Cd(II) in the Amberlite XAD-



4/PAR resin was studied. The results are graphically shown in Figure 3. It can be seen that the percentage of metal ions adsorbed at pH 7–8 was low, 40% and 50% only, peaked at pH of 9, and decreased gradually between pH 10– 11. This demonstrates

that increasing the pH level was effective in reducing the concentration of Cd(II) in the chelating resin, but a pH level above 9 did not improve the recovery rate. So, the pH of 9 was selected for the determination of Cd(II) content in the sample solutions.

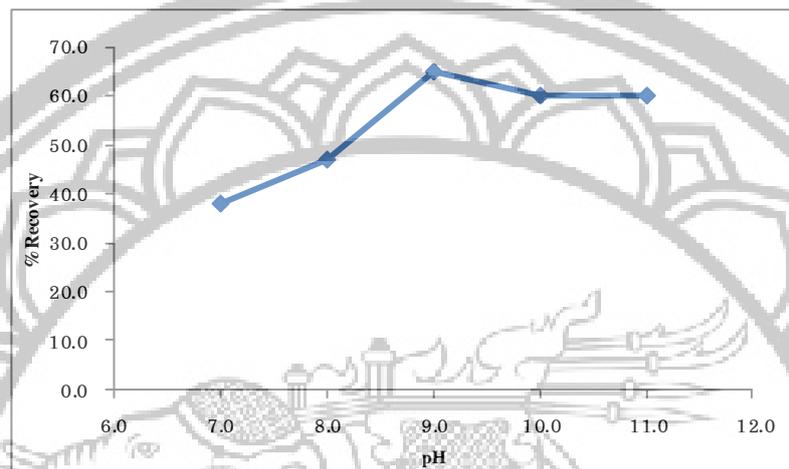


Figure 3 Effect of pH on sorption of Cd(II) on to Amberlite XAD-4/4-(2-pyridylazo)resorcinol

Effect of loading time

The 0.50 g resins were stirred with 250 mL of sample solution containing 5 mg l^{-1} Cd(II) at room temperature for different time ranges between 5–60 min. With the optimum pH value of 9 (as identified and discussed above), the desorption process was carried out using 0.50 mol l^{-1} nitric acid. The quantitative elution was determined with FAAS. The loading time results are depicted in Figure 4 As

can be seen from the results, at 10 min the percentage of recovery increased and became stable at 30–40 min (62– 64%). The results show the percentage of recovery stabilises to an equilibrium state of adsorption of heavy metals by the XAD-4/PAR resin over time; specifically at about 30 min, which was shown to be the suitable loading time for adsorption of the heavy metals and therefore used in the subsequent experiments.

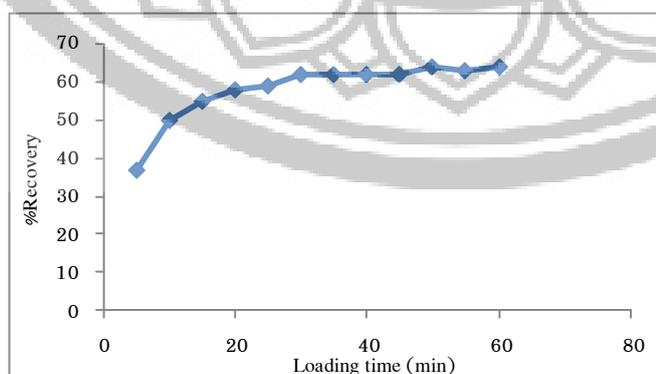


Figure 4 Effect of loading time on the adsorption of Cd(II) on to Amberlite XAD-4/4-(2-pyridylazo)resorcinol



Effect of eluent concentration and eluent volume

250 mL of sample solution containing 5.0 mg l^{-1} of Cd(II) was placed in a beaker. The matrix was stirred for 30 min under optimum conditions of 0.50, 1.00, 1.50, 2.00, 2.50 and 3.00 nitric acid solution which were tested as the eluent. The sample volumes of eluent for the desorption of the analytes from the sorbent were 5.0, 10.00, 15.00 and 20.00 mL of nitric acid. The results demonstrated that 15.0 mL of 0.50 mol l^{-1} nitric acid was sufficient for quantitative elution, giving the highest recovery (70%) and complete elution with the metal ions forming on the modified resins. Thus, the concentration and volume of 15.0 mL 0.50 mol l^{-1} nitric acid were used in the following experiments.

Effect of desorption time

The effect of different times on the elution of the Cd(II) on Amberlite XAD-4/PAR resin was examined. The time intervals studied were from 5 to 60 min, at pH 9, using 250.0 mL of 5.0 mg l^{-1} Cd(II) solution and 0.50 g of sorbent. The desorption as a function of time is related to the stripping of the metal ions from the chelating resins. Under these experimental conditions,

the desorption reaction was fast, and the Cd(II) desorption rate was little changed with the delay of desorption time. The quantity of Cd(II) recovered with the increase of desorption times was 69–73%. Therefore, 30 min was chosen as the desorption time in these experiment.

Effect of the sample volume

In order to explore the possibility of enriching low concentrations of analyte from a large volume by the batch procedure, the effect of sample volume on the recovery of Cd(II) was also investigated. For this purpose, the volume of sample solution containing 5.0 mg l^{-1} of Cd(II) was varied from 50.0 to 500.0 mL. The metal amounts were held constant while increasing the sample volume and the experimental procedure previously outlined was followed. The results are presented in Figure 5. A recovery of 91% of Cd (II) was obtained up to 250.0 mL. When the sample volume exceeded 250.0 mL, the recovery percentage decreased, possibly due to the lowering of the concentration of metal ions in the solution when the sample volume was increased. Therefore for this experiment, 250 mL of model solution was adopted for the preconcentration of analyte from water samples.

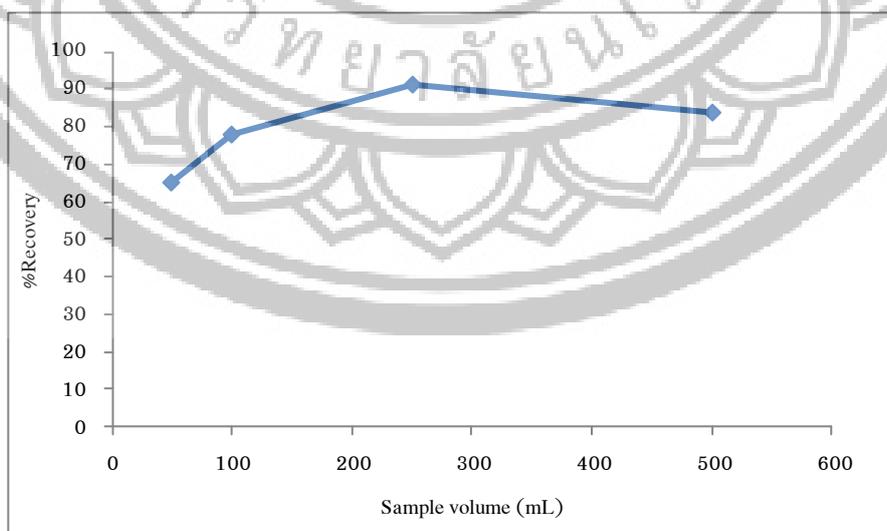


Figure 5 Effects of sample volume on the recoveries of analytes ($n = 3$).

Effect of the amount of adsorbent

The retention of Cd(II) ion was examined in relation to the amount of adsorbent. The amount of adsorbent was varied from 0.20 to 1.50 g. The procedure was applied to the model solutions according to the procedure given above by use of these batch methods. The results indicated that the best recovery quantities of Cd(II) were achieved between 0.20–0.50 g of chelating resin. When adding more than 0.50 g of the chelating resin, the quantity recovered decreased, which may be due to having a constant amount of resins with higher amounts of sorbent being used. This indicates that a higher volume of eluent should be used. Therefore, the optimum amount of adsorbent used was 0.50 g of chelating resin which was used in the subsequent experiments.

Reusability of the resin

The metal ions were absorbed and desorbed on 0.5 g of the Amberlite XAD-4/PAR resin several times by using a solution (250.0 mL) having a concentration of 5.0 mg l^{-1} Cd(II) under optimum

experimental conditions. The chelating resins was reused after regeneration with 2.0 mol^{-1} nitric acid and deionized water, respectively, and were stable up to 15 runs (recovery 85–91%) without appreciable loss of sorption capacity.

Adsorption capacity of resin

The sorption capacity of the resin for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The adsorption capacities of Amberlite XAD-4/PAR resin were determined by the batch method, with the adsorption capacity varied from 0.20 to 20.0 mg L^{-1} of Cd(II) solution, which was adjusted to the pH 9.00, then preconcentrated and eluted according to the parameters as shown in Table 1. The results are shown in Figure 6. The maximum adsorption capacity was reached between 8.0 to 20 mg L^{-1} . The saturated adsorption capacity of immobilized adsorbance for Cd(II) was found to be about 10 mg L^{-1} ($0.044 \text{ mmol g}^{-1}$).

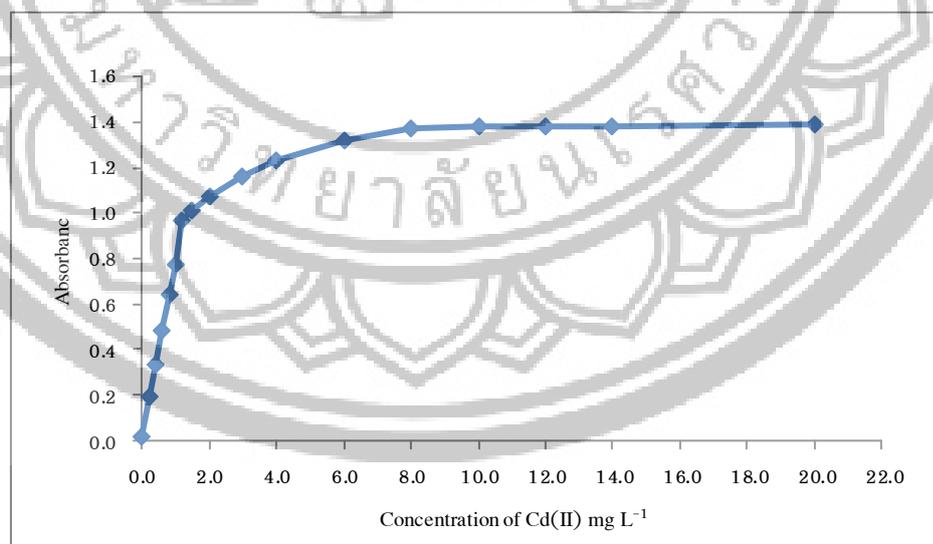


Figure 6 Adsorption capacity of Amerlite XAD-4/4-(2-pyridylazo) resorcinol.



Analytical performance

Under the optimal experimental conditions (Table 1), the detection limits were calculated to be 0.26 mg l^{-1} (evaluated as the concentration corresponding to three times the standard deviation of 20 runs of the blank solution). The precision of the method was evaluated as the RSD, obtained after analyzing a series of ten replicates with the preconcentration step. The precision was found to be 1.78 and 0.29% at 0.4 and 1.20 mg l^{-1} of

Cd(II), respectively. The linear response range for Cd (II) was found to be $0.20\text{--}1.00 \text{ mg l}^{-1}$ and the preconcentration factor achieved by this method was 5.0. The calibration curves were constructed at the optimum conditions according to the procedure, with the regression equation $y = 0.7349x + 0.0447$ (where y = the absorbance and x = the metal concentration in solution: mg l^{-1}), and the correlation coefficient (R^2) was 0.9994, showing good linearity for the calibration curve.

Table 1 Optimum conditions for determination and preconcentration of Cd(II) using Amberlite XAD-4/ PAR

Parameters	Studied parameter	Optimum parameter
pH	7-11	9.00
Loading time (min)	5-60	30.0
HNO ₃ concentration (mol L ⁻¹)	0.50-2.0	0.50
eluent volume (mL)	5.0-20.0	15.0
desorption time (min)	5-40	30.0
sample volume (mL)	50.0-500.0	250
amount of adsorbent (g)	0.20-1.50	0.50

Effect of interference

The effect of diverse ions on the adsorption of Cd(II) on Amberlite XAD-4/PAR were investigated. Pb(II), Zn(II), Fe(II) and Fe(III) are the main interferences present in the water samples which were studied in the concentration range 0.10 , 0.20 and 1.00 mg L^{-1} . The effect of each species was considered to be interference when the signal in the presence of the species resulted in an absorbance deviation of more than $\pm 5\%$. The results showed that 0.10 , 0.20 and 1.00 mg l^{-1} of Pb(II), Zn(II), Fe(II) and Fe(II) cause interference in the determination of Cd(II). This problem demonstrates that the stationary phases were efficient at retaining the analytes, whilst effectively separating potentially interfering matrix components which have little affinity with the chelating resins. For the future, the cause of interference in the determination of

Cd(II) in water samples can be adapted by masking with EDTA and cyanate at low concentrations. As has been reported, a masking agent is used to prevent detection by completely masking the interference with diverse ions. Masking agents such as citrate, phosphate, fluoride and thiocyanate are generally useful to overcome interference due to cations. (Karthikegan, Parameshwan, & Shetty, 2008, pp. 493-496; Shar, & Soomro, 2004, pp. 77-82).

Determination of Cadmium in water samples

The proposed method was applied for determination of cadmium in water samples which were collected around Naresuan University. The results achieved using this method were compared with the results from the wet digestion



method, which is these method demonstrated by (Belay, 2014, pp. 1-5). The results are shown in Table 2. Under these conditions, the concentration of Cd(II) in the water samples was found to be 0.07-1.16 mg l⁻¹. Most of these values exceed the Cd(II) limit values suggested by WHO, which states the maximum acceptable level of 0.20 mg L⁻¹.

The concentrations found in the study were in good agreement with those given by the standard reference method mentioned above, according to the t-test ($t_{table} = 2.776$, $t_{cal} = 0.60$) for a 95% confidence level. This indicates that there are no statistically significant differences between the two methods for cadmium determination in water samples.

Table 2 Results obtained for metal determination of Cd(II) water samples (n=3)

Sample	Proposed method			Wet digestion		
	Add(mg l ⁻¹)	Found (mg l ⁻¹)	Recovery	Add(mg l ⁻¹)	Found (mg l ⁻¹)	Recovery
Sample1	-	0.09±0.012	-	-	0.13±0.04	-
	1.0	0.80±0.040	71±0.02	1.0	1.16±0.01	103±0.01
Sample2	-	0.18±0.003	-	-	0.03±0.01	-
	1.0	1.16±0.011	98±0.01	1.0	1.10±0.02	107±0.03
Sample3	-	0.13±0.110	-	-	0.16±0.01	-
	1.0	1.27±0.009	114±0.01	1.0	1.12±0.09	96±0.01
Sample4	-	0.07±0.025	-	-	0.26±0.11	-
	1.0	1.09±0.008	102±0.01	1.0	1.32±0.03	106±0.01
Sample5	-	0.15±0.020	-	-	0.16±0.02	-
	1.0	1.15±0.005	100±0.01	1.0	1.13±0.05	97±0.03

Comparison with other chelating matrices

Comparison of preconcentration/enrichment factors and capacities by differential ligands with Amberlite XAD resin for preconcentration of Cd (II) by various methods for the figure of merits, is given in Table 3, The sorption capacity of the present

sorbent corresponds with XAD-16/1, 6-bis (2-carboxy aldehyde phenoxy) butane (Oral, et al., 2011, pp. 724-730). This method developed in the current research has been successfully applied to the analysis of trace metal ions in natural water samples.

Table 3 Comparison of, preconcentration/enrichment factor and capacities of Cd(II) ions using functionalized with XAD resin differential ligands.

Sorbent	PF/EF	Capacity(mmol g ⁻¹)	Reference
Amberlite XAD-2/ pyrocatechol	200	40.90	Kumar, et. al, 2001.
Amberlite XAD-2 / 2amino-thiophenol	28	3.70	Lemos, et. al,2005.
Amberlite XAD-4/ o-diethylthiophosphate	20	-	Santos, et. al,2005
XAD-16/1,6-bis(2-carboxy aldehyde phenoxy)butane	100	0.040	Oral, et. al,2011
Amberlite XAD-4/PAR	5	0.044	This work

EF: enrichment factor; PF: preconcentration factors; DL: detection limit



Conclusion

The results of the present investigation showed that Amberlite XAD-4/PAR resin can be used as a support material for preconcentration and determination of Cd(II) in water samples. The capacity of the chelating resin, Amberlite XAD-4/PAR, was found to be 10.0 mg l^{-1} ($0.044 \text{ mmol g}^{-1}$) and it was shown that this resin can be used for preconcentration with good precision and quantitative recovery up to 15 cycles without any loss in its sorption behavior, demonstrating high quantitative recoveries (98%), with a preconcentration factor of 5. The method used in the study was also successful in preconcentrating metal ions from large volume samples.

Acknowledgement

The authors are grateful for the financial support of the office of National Research Council of Thailand (NRCT) (Project, 2013) and Center of Excellence for Innovation in Chemistry (PERCH-CIC) for financial support in the form of research project. Many thanks to Mr. Roy Morien of the Naresuan University Language Centre for his editing assistance and advice on English expression in this document.

References

- Arain, M. A., Wattoo, F. H., Wattoo M. H. S., Bux, A., Ghanghro, & Ahmad, S., et al. (2009). Simultaneous determination of metal ions as complexes of pentamethylene dithiocarbamate in Indus river water. *Arabian Journal of Chemistry*, 2, 25–29.
- Belay, K. (2014). Analysis of lead (Pb), cadmium (Cd) and chromium (Cr) in Ethiopian spices after wet (acid) digestion using atomic absorption Spectroscopy. *Global Journal of Science Frontier Research: B Chemistry*, 14, 1–5.
- Burham, N. (2009). Separation and preconcentration system for lead and cadmium determination in natural samples using 2-aminoacetylthiophenol modified polyurethane foam. *Desalination*, 249, 1199–1205.
- Chamsaz, M., Akhoundzadeh, J., & Arbab-zavar, M. H. (2013). Preconcentration of lead using solidification of floating organic drop and its determination by electrothermal atomic absorption spectrometry ". *J Adv Res*, 4(4), 361–366.
- Depecker, G., Branger, C., Margailan, A., Pigot, T., Blanc, S., Peillard, F.R., Coulom, B., & Boudenne, J. (2009). Synthesis and applications of XAD-4-DAN chelate resin for the separation and determination of Se(IV). *Reactive & Functional Polymers*, 69, 877–883.
- Erdogan, S., Merdivan, M., Hamamci, C., Akba, O., & Baysal, A. (2004). Polymer supported humic acid for separation and preconcentration of thorium (VI). *Anal. Lett.*, 37(12), 2565–2575.
- Hubicki, Z., & Wolowicz, A. (2009). A comparative study of chelating and cationic ion exchange resins for the removal of palladium (II) complexes from acidic chloride media. *J. Hazardous Mater*, 164, 1414–1419.



- Jain, V. K., Mandalia, H. C., Gupte, H. S., & Vyas, D. J. (2009). Amberlite XAD-4 functionalized with m-phenyldiamine: Synthesis, characterization and applications as extractant for preconcentration and determination of rhodium (III) in water samples by Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES). *Microchemical. J*, 93, 49-54.
- Jiang, H., Hu, B., Jiang, Z., & Qin Y., (2006). Microcolumn packed with YPA4 chelating resin on-line separation/preconcentration combined with graphite furnace atomic absorption spectrometry using Pd as a permanent modifier for the determination of trace mercury in water samples. *Talanta*, 70(1), 7-13.
- Kalal, H. S., Panahi, H. A., Hoveid, H., Taghiof, M., & Menderjani, M. T. (2012). Synthesis and application of Amberlite xad-4 functionalized with alizarin red-s for preconcentration and adsorption of rhodium (III)". *Iranian J Environ Health Sci Eng*, 9(1), 1-9.
- Karthikegan, J., Parameshwan, P., & Shett, A. N. (2008). Indirect complexometric determination of mercury (II) using 3-acetyl-2-thiohydantion as a selective masking agent. *Indian J. Chem. Tec*, 15, 493-496.
- Komjarova, I., & Blust, R. (2006). Comparison of liquid-liquid extraction, solid-phase extraction and co-precipitation preconcentration methods for the determination of cadmium, copper, nickel, lead and zinc in seawater. *Anal. Chim. Act*, 576, 221-228.
- Kuznetsov, V. V., Zemyatova, S. V., & Kornev, K. A. (2014). Automated determination of uranium (VI) in seawater using on-line preconcentration by coprecipitation. *J. Anal. Chem*, 69(2), 105 - 110.
- Landis, W. G., & Yu, M. H. (2005). *Introduction to Environmental Toxicology*. Lewis Publishers: New-York.
- Lemos, V. A., & Baliza, P. X. (2005). Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper. *Talanta*, 67, 564-570.
- Liu, Y., Liang, P., & Gu, L. (2005). Nanometer titanium dioxide immobilized on silica gel sorbent for preconcentration of metal ions prior to their determination by inductively coupled plasma atomic emission spectrometry. *Talanta*, 68, 25-30.
- Manahan, S. E. (2011). *Fundamentals of Environmental Chemistry*. Boca Raton: CRC Press LLC.
- Nakashima, F. (1963). Determination of cadmium in uranium by ion exchange and square-wave Polarography. *Anal. Chim. Acta*, 28, 54-60.
- Narin, I., Surme, Y., Bercin, E., & Soylak, M. (2007). SP70- α -benzoin oxime chelating resin for preconcentration-separation of Pb(II), Cd(II), Co(II) and Cr(III) in environmental samples. *J. Hazard. Mater*, 145, 113-119.



- Nezhati, M. N., Panahi, H. A., Moniri, E., Kelahrodi, S., Assadian, F., & Karimi, M. (2009). Synthesis, characterization and application of allyl phenol modified amberlite XAD-4 resin for preconcentration and determination of copper in water samples. *Korean J. Chem. Eng*, 27, 1269–1274.
- Orala, E. V., Dolaka, I., Temel, H., & Zadanogullari, B. (2011). Preconcentration and determination of copper and cadmium ions with 1,6-bis (2-carboxy aldehyde phenoxy) butane functionalized Amberlite XAD-16 by flame atomic absorption spectrometry. *J. Hazardous. Mater*, 186, 724–730.
- Panahi, H. A., Kalal, H. S., Moniri, E., Nezhati, M. N., Menderjani, M. T., & Kelahrodi, S. R., et al. (2009). Amberlite XAD-4 functionalized with m-phenyldiamine: Synthesis, characterization and applications as extractant for preconcentration and determination of rhodium (III) in water samples by Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES). *Microchemical Journal*, 93, 49–54.
- Shar, G. A. & Soomro, G. A. (2004). Spectrophotometric determination of Cobalt(II), Nickel(II) and Copper With 1-(2-pyridylazo)-2-naphthal in micelle medium. *The Nucleus*, 41, 77–82.
- Soylak, M., & Tuzen, M. D. (2006). SP-850 resin as a new solid phase extractor for preconcentration–separation of trace metal ions in environmental samples. *J.Hazard. Mater*, 137, 1496–1501.
- Strelko, V., Malik, D. J., & Streat, M. (2005). Interpretation of transition metal sorption behavior by oxidized active carbons and other adsorbents. *Sep. Sci, Technol*, 39, 1885–1905.
- Tewari, P. K., & Singh A. K. (2002). Preconcentration of lead with Amberlite XAD-2 and amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry. *Talanta*, 56, 735–744.
- Venkatesh, G., & Singh, A. K. (2005). 2-[[1-(3,4-Dihydroxyphenyl) methylidene] amino] benzoic acid immobilized Amberlite XAD-16 as metal extractant. *Talanta*, 67, 187–194.
- Ziyadanogullari, R., Dolak, I., Tegin, I., & Guzel, R. (2009). Synthesis and preconcentration of Amberlite XAD-4 resin modified by dithioethylenediamine. *Asian J. Chem*, 21, 165–175.