Selective Solid-Phase Extraction of Cd(II) by an Ion-Imprinted Polymer from Environmental Samples

YUNSONG GE, ZHANGJIE HUANG* and ZHONGBO ZHU

Department of Chemistry, Yunnan University, Kunming 650091, P.R. China

*Corresponding author: Fax: +86 871 5032180; E-mail: zhjhuang2010@163.com

A new ion-imprinted polymers material was synthesized by copolymerization of 4-vinyl pyridine as monomer, ethylene glycol dimethacrylate as crosslinking agent and 2,2'-azobisisobutyronitrile as initiator in the presence of cadmium(II)-octyl benzothiazolyl sulfide complex. The ion-imprinted polymers was used as sorbent in a solid-phase extraction column. The effects of sampling volume, elution conditions, sample pH and sample flow rate on the extraction of cadmium ions form environmental samples were studied. The obtained ion-imprinted polymers particles exhibited excellent selectivity for target ion. The distribution ratio (D) values of Cd(II)-ion-imprinted polymers for Cd(II) were greatly larger than that for Cu(II) and Zn(II). The relative selective factor (AR) values of Cd(II)/Cu(II) and Cd(II)/Zn(II) were 246.9 and 238.4. The maximum adsorption capacity was calculated. The detection limit for 250 mL of sample was 0.2 μg L^{-1} using flame atomic absorption spectrometry. The analytical results for the certified reference samples (GBW08301) were in a good agreement with the certified value. The relative standard deviation for eleven replicate sample of 5.0 μg L^{-1} level is 3.2 %. The developed method was successfully applied to the determination of trace cadmium in environmental samples with satisfactory results.

Key Words: Ion-imprinted polymers, Solid-phase extraction, Cadmium ion, Flame atomic absorption spectrometry.

INTRODUCTION

Cadmium is a highly toxic element for animals and human, even at low concentrations. Through the food chain system of soil-plant-animal-human, Cd(II) is transferred into animals and human beings, causing severe contamination[1]. Due to its toxicity both to humans and animals cadmium concentration in the environment should be monitored.

For many years flame atomic absorption spectrometry (FAAS) has been a standard analytical tool for determination of metals in various matrices owing to its wide application range, simplicity in operation and low cost of analysis. However, cadmium content in many environmental samples is frequently below the quantification limit achieved with this technique, therefore introducing a preconcentration step prior to flame atomic absorption spectrometry determination is required[2-6].

Nowadays, molecular imprinting technology has become a powerful method for high selective adsorption of target molecules. For metal ions, molecular imprinting can be interpreted as ionic imprinting exactly. In recent years, a lot of ion-imprinted polymers (IIPs) have been prepared and used for selective solid-phase extraction (SPE) and preconcentration of metal ions[7-15].

In this study, an ion-imprinted polymer used for selective extraction and preconcentration of cadmium ions was synthesized using 4-vinyl pyridine (4-VP) as monomer, ethylene glycol dimethacrylate (EGDMA) as crosslinker and 2,2'- azobisisobutyronitrile as initiator in the presence of cadmium(II)-octyl benzothiazolyl sulfide (OBTS) complex. After removal of cadmium ions, Cd-imprinted polymer was used for solid-phase extraction and determination of cadmium ions in environmental samples. The proposed method presented high selectivity and possessed simple, convenient and accurate characteristics for cadmium determination.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of metal ions (Cd, Zn and Cu) in aqueous solution. The instrumental parameters were those recommended by the manufacturer. Hollow cathode lamps were used as the radiation sources. The wavelengths selected were as follows: Cd 228.8 nm, Cu 324.8 nm and Zn 213.9 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China). A peristaltic pump mode FIA-3110 (Titan Instruments Co., Ltd. Beijing, China) was used in the solid-phase extraction process.

Octyl benzothiazolyl sulfide was synthesized in our laboratory[16]. 4-Vinyl pyridine (4-VP), azobisisobutyronitrile

(AIBN) and ethylene glycol dimethacrylate were obtained from Alfa Aesar.

Ultra-pure water of resistivity 18 MΩ cm obtained from a UPHW purification device (Ulupure Co. Shanghai, China) was used to prepare all the solutions. High purity hydrochloric acid and analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ were purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

All glass and plastic material were rigorously cleaned and kept into 10 % (m m^{-1}) nitric acid for at least 48 h. The material was then rinsed three times with ultra-pure water before being used. Standard stock solutions of Cd(II), Cu(II) and Zn(II) (1000 mg L^{-1}) were obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution.

Ion-imprinted polymers preparation: The Cd(II) ion-imprinted beads were prepared by bulk polymerization. An amount of 4 mmol of octyl benzothiazolyl sulfide, 4 mmol 4-vinyl pyridine (4-VP) and 2 mmol of $Cd(NO_3)_2 \cdot 4H_2O$ was dissolved in 30 mL of acetonitrile and stirred for 2 h. Then, 40 mmol ethylene glycol dimethacrylate and 50 mg azobisisobutyronitrile were added. The polymerization mixture was cooled to 0 ℃ and purged with N$_2$ for 15 min, sealed and heated at 70 ℃ with stirring for 10 h. After polymerization, the solid formed was ground into fine particles. The resulting polymer was treated with 2 M HCl solution by continuously stirring for 1 h to remove cadmium ions. The resultant polymer after filtration was dried at 80 ℃ for 24 h and sieved to get particles lower than 150 μm. In the same way, the non-imprinted polymer was also prepared without cadmium ions.

Solid-phase extraction of Cd(II): The stopcock of the glass column (100 mm in length and 10 mm in diameter) was covered with a fritted glass disc. A total of 500 mg of polymer (ion-imprinted polymers and non-imprinted polymers) was poured into the solid-phase extraction column. It was treated successively with 1 M HCl solution and water. The column was preconditioned by passing a blank solution and then a solution containing Cd(II) was passed through the column at flow rate of 5 mL min^{-1} (controlled by a peristaltic pump) after adjusting pH 6. The column was washed with 20 mL ultra-pure water and then eluted with 5 mL of 2 M HCl at a flow rate of 1 mL min^{-1}. The desorbed Cd(II) was measured by flame atomic absorption spectrometer.

General procedure of sample treatment: For river sediments reference material (GBW08301 China), 500 mg of the sediment sample was accurately weighed into a 100 mL beaker and aqua regia (30 mL concentrated hydrochloric acid and 10 mL of concentrated nitric acid) was added to the sample. The beaker was covered with a watch glass and the mixture was evaporated on a hot plate at 100 ℃ almost to dryness. Then 40.0 mL of aqua regia was added to the residue and the mixture was again evaporated to dryness. After cooling, resulting mixture was filtered using whatman No. 1 filter paper (pore size, 11 μm). The filtrate was diluted to 50 mL with ultra-pure water and was analyzed by the preconcentration procedure given above.

The river water samples were collected in pre-washed polyethylene bottles from a dirty region of Bao Xian River (Kumming, P.R. China). The bottles were cleaned with detergent, ultra-pure water, dilute nitric acid and ultra-pure water in sequence. The samples were immediately filtered through a Millipore cellulose nitrate membrane (pore size 0.45 μm), acidified to pH 2.0 with 2.0 M HNO$_3$ and stored in a pre-cleaned polyethylene bottle. Tap water sample was freshly collected from our laboratory. Tap water sample was immediately acidified by adding several drops of nitric acid and filtrated with 0.45 μm filter. Then the preconcentration procedure given above was applied to the samples.

RESULTS AND DISCUSSION

Adsorption capacity of the imprinted polymers for Cd(II): 100 mg of imprinted or non-imprinted sorbent was equilibrated with 50 mL of various concentrations of Cd(II) solutions at pH 6 for 4 h. The concentrations of Cd(II) in solution were measured by flame atomic absorption spectrometry and the adsorption capacity of imprinted or non-imprinted polymers for Cd(II) ions were calculated by following equation:

$$Q = \frac{(C_0 - C_e)V}{W}$$

where, Q is the loading capacity of the polymer (mg g^{-1}) C_0 and C_e are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mg L^{-1}); V is the volume of the aqueous phase (mL); and W is the amount of polymer (g).

As can be seen in Fig. 1, the amount of Cd(II) adsorbed per unit mass of the imprinted polymer increased with the initial concentration of Cd(II). The average maximum adsorption capacity was 5.1 mg g^{-1} for Cd(II)-imprinted polymers.
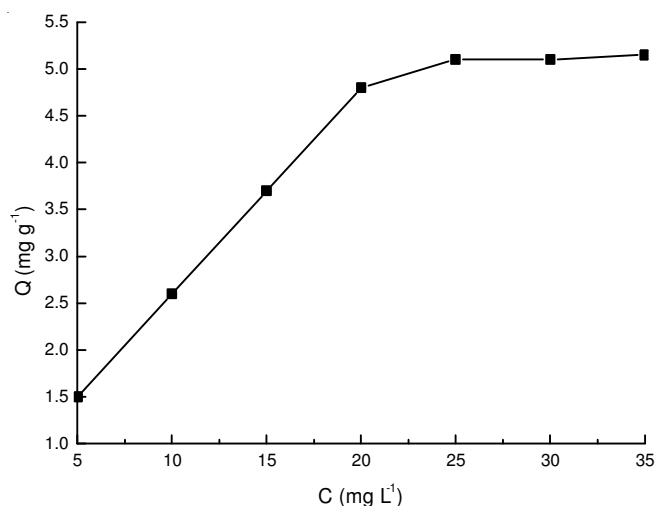

Fig. 1. Effect of initial concentration on the adsorption capacity of Cd(II)-imprinted polymers (1). 100 mg of the imprinted polymers; pH 6.0; V 50 mL; temperature 25 ℃

Effect of pH: The effects of the sample pH on the retention of Cd(II) ions on the ion-imprinted polymers were studied at different pH values from 1 to 7. In consideration of hydrolysis, pH above 7 was not tested. The pH was adjusted

to the desired value with aqueous ammonia and diluted HNO_3. A volume of 50 mL of the sample containing 100 μg L^{-1} of cadmium ions were passed through the ion-imprinted polymers column at a flow rate of 5 mL min^{-1}, then the solid-phase extraction column was eluted with 5 mL of 2 M HCl at a flow rate of 1 mL min^{-1}. The cadmium content of the eluate was measured by flame atomic absorption spectrometry. The extraction curve of cadmium as a function of the pH is shown in Fig. 2.
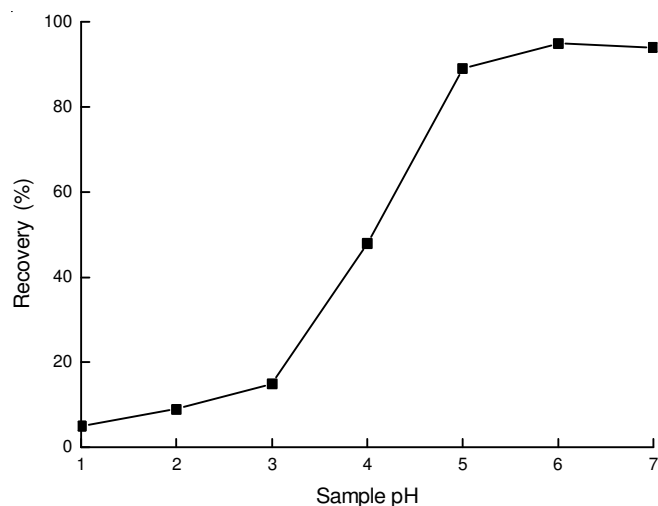

Fig. 2.   Effect of sample pH on the adsorption of Cd(II) on the Cd(II)-imprinted polymers. Sample volume: 50 mL, Cd(II) concentration: 100 μg L^{-1}. Sample flow rate: 5 mL min^{-1}, HCl concentration: 2 M, HCl flow rate: 1 mL min^{-1}, elution volume: 5 mL

The per cent recovery of cadmium ions is very low owing to the protonation of poly-Cd(II)-OBTS-VP below pH 3, but the per cent recovery of cadmium ions increases rapidly; after pH 5, the increase in the per cent recovery is relatively very low, the per cent recovery of cadmium ions near the maximum at pH 6. So pH 6 was chosen as optimum for further experiments.

Selectivity of the imprinted polymers: The distribution ratio, the selectivity factor of Cd(II) with respect to other ions and the relative selectivity factor were calculated as the following equations :

$$D = \frac{Q}{C_e}$$

$$\alpha_{Cd/M} = \frac{D_{Cd}}{D_M}$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n}$$

where, Q represents the adsorption capacity (mg g^{-1}), C_e the equilibrium concentration of metal ions (μg mL^{-1}), D_{Cd} and D_M represent the distribution ratios of Cd(II) and other ions (mL g^{-1}). α_i and α_n represent the selectivity factor of imprinted sorbent and non-imprinted sorbent, respectively.

In order to determine the selectivity of the method, competitive adsorption of Cd(II)/Zn(II) and Cd(II)/Cu(II) from their binary mixture was also investigated by batch procedure. These ions have the same charge and similar ionic radius. In their binary mixture the two metal ions had the same concentration

of 10 μg mL^{-1} and the sorbent was 50 mg. As can be seen in the Table-1, the imprinting effect was clearly observed. The D values of the present ion-imprinted polymers for Cd(II) was large, while decreased significantly for Zn(II) and Cu(II). The relative selectivity factor(s) values of Cd(II)/Zn(II) and Cd(II)/Cu(II) were 238.4 and 246.9, respectively, which are greater than 1 (Table-1). This means that Cd(II)-imprinted sorbent had higher selectivity for Cd(II). And the results indicated that Cd(II) could be determined even in the presence of Zn(II) and Cu(II) interferences.

TABLE-1
SELECTIVITY PARAMETERS OF IMPRINTED POLYMERS
AND NON-IMPRINTED POLYMERS

Metal ions	E (%) (IIPs)	E (%) (NIPs)	D_i (mL g^{-1})	D_n (mL g^{-1})	α_i	α_n	α_r
Cd	99.2	26.1	24800	70.6	-	-	-
Zn	32.5	24.7	96.3	65.6	257.5	1.08	238.4
Cu	21.8	16.4	55.8	39.2	444.4	1.80	246.9

The effect of different foreign ions *e.g.*, NaCl, KBr, $MgSO_4$, $CaCl_2$, Na_2SO_4, KNO_3 and Na_3PO_4, on the adsorption of Cd(II) was studied using the batch procedure. The results showed that 60-250-fold electrolytes did not interfere with adsorption and desorption of Cd(II), indicating that the present imprinted polymers can be suitably used as sorbents for Cd(II) in high electrolytes. The reported tolerance limit is defined as the ion concentration causing a relative error $< \pm 5$ %.

Effect of flow rate of sample solution and eluent: Effect of the sample flow rate on the adsorption of cadmium ions was examined under the optimum conditions (pH, eluent, *etc.*). A volume of 50 mL of the sample containing 100 μg L^{-1} of cadmium ions was passed through the ion-imprinted polymers column. The flow rate was adjusted in the range of 1-8 mL min^{-1} using a peristaltic pump. In the test, the quantitative recoveries of the metal ions will decrease with the further increasing of the flow rate that is over 5 mL min^{-1}. Thus, a flow rate of 5 mL min^{-1} was selected in this work.

For the elution of Cd(II) from the column, three parameters, *i.e.* elution volume, eluent (HCl) flow rate and eluent concentration were investigated and optimized. Flow rate of HCl solution was the first parameter to be optimized. A volume of 50 mL of the sample containing 100 μg L^{-1} of cadmium ions was passed through the ion-imprinted polymers column at 5 mL min^{-1}. Elution of the solid-phase extraction column was performed with 5 mL of 2 M HCl at different flow rates between 0.5 and 2.5 mL min^{-1}. The results showed that 5 mL of 2 M HCl at a flow rates of 1 mL min^{-1} was sufficient for 95 % recovery. In order to find optimum volume of the elution solvent, different volumes of HCl from 2 to 8 mL were investigated. Quantitative elution was attained using volumes $\geq$ 5 mL. The influence of HCl concentration on the elution of cadmium ions from the sorbent was also examined and the results are shown in Fig. 3. Cadmium ions were quantitatively eluted from the column with 2 M HCl solution.

The capacity of imprinted polymers had no considerable decrease after 30 cycles of repeated experiments. The Cd(II)-ion-imprinted polymers showed good reusability and stability towards Cd(II).
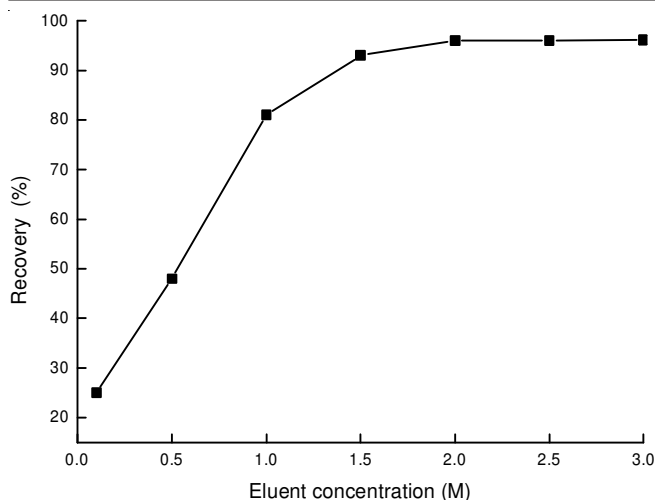
Fig. 3. Influence of HCl concentration on the elution of Cd(II) from the Cd(II)-ion-imprinted polymers. Sample volume: 50 mL, sample pH 6, Cd(II) concentration: 100 μg L^{-1}, HCl flow rate: 1.0 mL min^{-1}, elution volume: 5 mL

Maximum sample volume and enrichment factor: The enrichment factor was studied following recommended column procedure by increasing volume of Cd(II) solution and keeping the total amount of loaded Cd(II) constant to 5 μg. For this purpose, 50, 100, 150, 200 and 250 mL of sample solutions containing 5 μg Cd(II) were passed through the column at the optimum flow rate. The results showed that the maximum sample volume could be up to 250 mL with the recovery > 95 %. Therefore, 250 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. And a high enrichment factor of 50 was obtained.

Analytical accuracy and precision of ion-imprinted polymers-solid-phase extraction: Under the selected conditions, eleven portions of 5 μg L^{-1} Cd(II) standard solutions (250 mL) were treated and analyzed simultaneously following the column procedure. The relative standard deviations of the method was 3.2 %, indicating that the method had good precision for the analysis of trace Cd(II) in solution samples. The limit of detection given by LOD = $(3 \times SD)/m$, where SD is the standard deviation of eleven procedural blanks and m is the slope of the external 2 M hydrochloric acid calibration graph[17], was calculated to be 0.2 μg L^{-1} for a pre-concentration factor of 50.

The method has been applied to the determination of Cd(II) in environmental standard reference materials (GBW08301, river sediments). The results are given in Table-2.

TABLE-2
DETERMINATION OF CADMIUM (μg g^{-1}) IN THE CERTIFIED
REFERENCE MATERIALS AFTER APPLICATION OF THE
PRESENTED PROCEDURE (n = 5)

Sample	Certified value (μg g^{-1})	Present value (μg g^{-1})
River sediments (GBW08301)	2.45 ± 0.15	2.40 ± 0.20

In order to check for possible matrix effects and investigate the applicability of the method to real sample analysis. The results are listed in Table-3. Recoveries of cadmium were

in the range of 96.0-105.0 %. These results indicated the suitability of the Cd(II)-IIP for selective solid-phase extraction and determination of trace Cd(II) from environmental samples.

TABLE-3
DETERMINATION OF CADMIUM (μg L^{-1})
IN WATER SAMPLES (n = 5)

Sample	Added (μg L^{-1})	Found[*] by present method (μg L^{-1})	Recovery (%)
River water	0	5.5 ± 0.1	-
	10	15.2 ± 0.2	97
	20	26.5 ± 0.3	105
Tap water	0	BDL	-
	10	9.6 ± 0.2	96
	20	20.8 ± 0.4	104

- not determined. BDL: below the detection limit. [*]Mean ± SD

Conclusion

A new Cd-imprinted sorbent based on octyl benzothiazolyl sulfide ligand was developed as solid-phase extraction material for selective preconcentration of cadmium ions from environmental samples. The imprinted polymer has obvious imprinting effect on the imprinting ion. The relative selective factor (AR) values of Cd(II)/Cu(II) and Cd(II)/Zn(II) were 246.9 and 238.4. The method shows good linearity and reproducibility. The proposed procedure was applied for the determination of cadmium in environmental samples.

REFERENCES

1. Y.W. Liu, X.J. Chang, S. Wang, Y. Guo, B.J. Din and S.M. Meng, *Anal. Chim. Acta*, **519**, 173 (2004).
2. M. Gawin, J. Konefal, B. Trzewik, S. Walas and A. Tobiasz, *Talanta*, **80**, 1305 (2010).
3. Z.C. Li, H.T. Fan, Y. Zhang, M.X. Chen, Z.Y. Yu, X.Q. Cao and T. Sun, *Chem. Eng. J.*, **171**, 703 (2011).
4. H. Ciftci, *Desalination*, **263**, 18 (2010).
5. H. Parham, N. Pourreza and N. Rahbar, *J. Hazard. Mater.*, **163**, 588 (2009).
6. A. Malekpour, S. Hajialigol and M.A. Taher, *J. Hazard. Mater.*, **172**, 229 (2009).
7. S. Daniel, J.M. Gladis and T.P. Rao, *Anal. Chim. Acta*, **488**, 173 (2003).
8. Y.H. Zhai, Y.W. Liu, X.J. Chang, S.B. Chen and X.P. Huang, *Anal. Chim. Acta*, **593**, 123 (2007).
9. D.K. Singh and S. Mishra, *J. Hazard. Mater.*, **164**, 1547 (2009).
10. S. Daniel, P.E.J. Babu and T.P. Rao, *Talanta*, **65**, 441 (2005).
11. J.C. Zhao, B. Han, Y.F. Zhang and D.D. Wang, *Anal. Chim. Acta*, **603**, 87 (2007).
12. I. Dakova, I. Karadjova, V. Georgieva and G. Georgiev, *Talanta*, **78**, 523 (2009).
13. S. Daniel, P.P. Rao and T.P. Rao, *Anal. Chim. Acta*, **536**, 197 (2005).
14. S.J. Ahmadi, O. Noori-kalkhoran and S. Shirvani-Arani, *J. Hazard. Mater.*, **175**, 193 (2010).
15. S. Daniel, R.S. Praveen and T.P. Rao, *Anal. Chim. Acta*, **570**, 79 (2006).
16. J. Chang, Z.J. Huang and M.S. Xi, *Asian J. Chem.*, **23**, 2669 (2011).
17. J. Otero-Romani, A. Moreda-Pineiro, P. Bermejo-Barrera and A. Martin-Esteban, *Anal. Chim. Acta*, **630**, 1 (2008).