Preparation of a Chelating Resin and its Application as a Preconcentration System for Determination of Cadmium in River Water by Flow Injection Analysis

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ABSTRACT: A chelating resin of polystyrene divinylbenzene resin functionalized by 1-(2-pyridylazo) 2-naphtol (PSDVB-PAN) has been synthesized and its sorption properties have been investigated for pre-concentration and determination of cadmium at μg/L level by flame atomic absorption spectrometry. The procedure is based on the sorption of Cd(II) ions on a minicolumn of synthesized chelating resin. The retained cadmium ions can be quickly eluted from sorbent material, with the eluent stream consisting of nitric acid solution, directly to the nebulizer burner system of the flame atomic absorption spectrometer. The sorption capacity of PSDVB-PAN was found to be 7.5 mg/g at optimum pH and the chelating resin showed rapid kinetic sorption. The sorption equilibrium of Cd(II) on synthesized chelating resin was achieved just in 15 minutes. Parameters such as the pH effect on the cadmium sorption, sample volume, the sorption capacity of resin, the cadmium desorption from the resin and the analytical characteristics of the procedure were studied for the quantitative recoveries of the analyte ions. The developed system allowed a throughput rate of 15 samples h^{-1} with a detection limit of 1.5 μg/L. Relative standard deviation for 5 replicated injections of 50 μg/L was 1.8%. This procedure was applied for cadmium determination in river water samples collected from Citarum River, West Java, Indonesia.

Key words: Chelating Resin, PAN, Pre-concentration, Cadmium, Flow Injection Analysis

INTRODUCTION

Cadmium is a natural element from the earth's crust that is taken in by plants and then passed on to animals through the food chain. Its metabolism and toxicology are of great concern, since it has accumulation capabilities in living organisms besides its high toxic potential (Kristanto *et al.*, 2003; Ahmad *et al.*, 2010). Its wide use in technology brings about extensive contamination, making it important to determine this element in food, water and biological materials (Davis *et al.*, 2006; Viard *et al.*, 2004; Dhir and Khumar, 2010) However, the cadmium concentration level in such matrices is fairly low, and pre-concentration procedures are often required. Therefore, many procedures for cadmium determination at low level concentration have been developed (Ferreira *et al.*, 2007; Kaur and Gupta, 2008; Ensafi and Shiraz, 2008).

This explains the current interest in developing analytical procedures for the quantification of these elements. Although it is true that these elements can be directly determined in water using sensitive analytical techniques, such as electrothermal atomic absorption

spectrometry or ICP-MS, in many laboratories, particularly in developed countries, only Flame Atomic Absorption Spectrometry, FAAS, and Inductively Coupled Plasma Optical Emission Spectrometry ICPOES are available. The sensitivity obtained with FAAS or with ICP-OES is not sufficient to detect these elements in river water, since a pre-concentration method is required. To this end the use of supports loaded with chelating reagents is particularly convenient, because such resins containing various functionalized groups are easy to prepare and make these procedures highly selective. Therefore, pre-concentration and separation methods for trace metal ions have been developed by using various supports (Sharma, 2001; Pyrzyńska and Szeląg, 2001; Schubert *et al.*, 2003; Maltez *et al.*, 2004; Valdés *et al.*, 2006; Hakim e*t al.*, 2007). Amberlite XAD-16 is a polystyrene divinylbenzene (PSDVB) copolymer. It has no ionizable functional groups. It has been used for the pre-concentration and separation of trace heavy metal ions from various media including natural waters, urine, and dialysis concentrate. It is used as a solid

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matrix for synthesis of chelating resin and separation of organic materials which has hydrophobic properties. The preparation of new chelating resins by using PSDVB and some chelating agents have been performed by some researchers. Lee and co-workers (Lee *et al.*, 1999; 2001) synthesized a new chelating resin by using Amberlite XAD-16 and 4-(2-thiazolylazo) resorcinol and investigated the adsorption properties of the new resin. They synthesized two different chelating resins by using 4-(2-thiazolylazo) resorcinol and 1-(2-thiazolylazo)-2-naphthol as chelating agent and PSDVB as support for the pre-concentration of trace metal ions including uranium. 1-(2-pyridylazo) 2-naphtol (PAN) is a reagent for the spectrophotometric determination of lots of transition metal ions. It acts as a terdendate ligand complexing with metals through the hydroxyl oxygen atom, pyridine nitrogen atom and one of the azo group nitrogen atoms. This point is an important advantage of PAN. It has been also used for the separation and pre-concentration of trace heavy metals in various media (Lemos *et al.*, 2005; Toh *et al*., 2001; Pérez-Gramatges and Chatt, 2006). According to our knowledge, up to now, no systematic investigation on the preparation, retention characterization and application of chelating resin by combination of PSDVB and PAN for cadmium determination by flow injection analysis. In this research, the adsorption characteristics and its application in trace analysis have been performed. In the present work, a chelating resin was synthesized by immobilizing 1-(2-pyridylazo) 2-naphtol on PSDVB (PSDVB-PAN) through an azo (-N=N-) spacer and characterized. The synthesis of the chelating resin was followed by the study of its retention characteristics toward cadmium ions. Its application of pre-concentration of cadmium ions in

river water samples was performed. The optimal analytical conditions including pH, resin amounts, flow rates of sample and elution solutions and matrix effects were also investigated. In this paper we also introduce an on-line method for pre-concentration of trace amounts of cadmium(II) in river water samples employing the synthesized chelating resin prior to their detection by flame atomic absorption spectrometry (FAAS).

MATERIALS & METHODS

The concentrations of metal ions were determined by a GBC-Avanta model atomic absorption spectrometer without background correction, equipped with an air-acetylene burner and hollow cathode lamps of the analytes. The operating conditions such as wavelength, bandwidth, and acetylene/air flow rates were adjusted according to the recommendations of manufacturer's. All pH measurements were made with an Orion 470 model digital pH meter equipped with a combined pH electrode. Functional groups of the chelating resin synthesized were identified with a Shimadzu-SpectraOne model FTIR spectrometer. The diagram of the on-line preconcentration system is shown in Fig. 1.

The manifold was adapted to the nebulizer system of the flame atomic absorption spectrometer (FAAS). The flow system was made up of a peristaltic pump (Ismatec) furnished with Tygon tubes to delivery all solutions, a two-position eight-way Teflon rotary valve and a PSDVB-PAN packed minicolumn for the on-line preconcentration of cadmium. All connections were made using fittings, unions and tees made of plastic materials. To minimize the dispersion, the length of the capillary PTFE tube between the end of the minicolumn
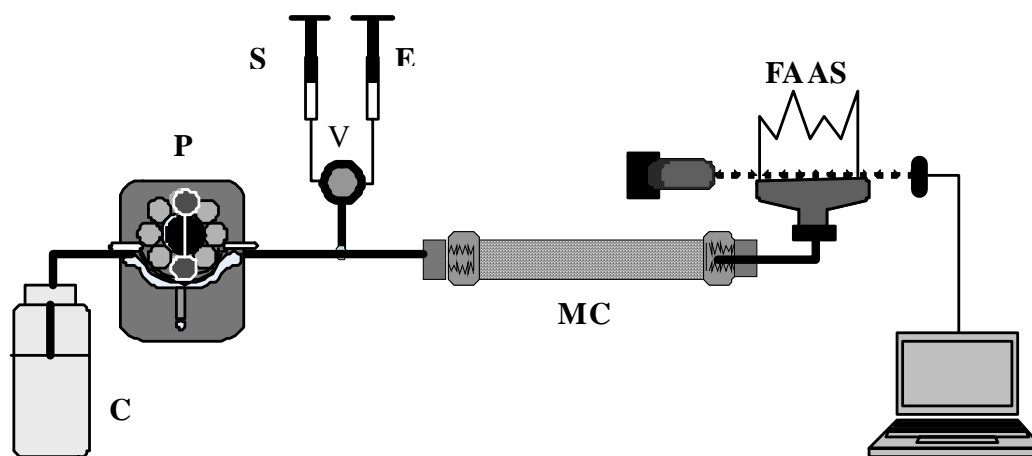

Fig. 1. Schematic diagram of the flow system used in the preconcentration and determination of cadmium by FAAS. S: sample; E: eluent; P: peristaltic pump; MC: PSDVB-PAN minicolumn; V: eight-port valve; and FAAS: flame atomic absorption spectrometer

and the nebulizer was as short as possible (about 5 cm). The laboratory-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm contains about 200 mg of PSDVB-PAN. The use of minicolumns packed with PSDVB-PAN in this flow system did not show any shrinkage nor swelling during the elution/ preconcentration steps.

Ultrapure water from an Easypure RF water purification system (Barnstead, Dubuque, USA) was used to prepare all solutions. All reagents were of analytical reagent grade. Cadmium(II) working solutions at µg/L level were prepared daily by diluting a 1000 µg mL^{-1} cadmium solution. Nitric acid solution was prepared by direct dilution with deionized water from the concentrated suprapur solution (Merck). The laboratory glassware was kept overnight in a 5% v/v nitric acid solution. Afterwards, it was rinsed thoroughly with ultrapure water and dried. Polystyrene divinylbenzene (Amberlite XAD-16, 20-60 mesh, Sigma Chem. Co.) and 1-(2-pyridylazo) 2-naphtol were used for synthesis of the sorbent.

The procedure given by Saxena (Saxena *et al.,* 1997) with some little modifications was applied to the synthesis of the PSDVB-PAN chelating resin. 10.0 g of Amberlite PSDVB was treated with a nitrating mixture, containing 20mL of concentrated nitric acid and 50mL of concentrated sulfuric acid and stirred for 1 h at 60 ºC on a water-bath. The nitrated mixture was poured into ice-cold water. It was further filtered, washed repeatedly with distilled water until free from acid. Then it was reduced with SnCl$_2$ (40 g), concentrated hydrochloric acid (45 mL), and ethanol (60 mL), and refluxed for 12 h at 40 ºC. The amino polymer was filtered off and washed with mixture of HCl-ethanol, water, and 2M NaOH so as to get the free amino polymer. The amino polymer was treated with 100mL of 2M HCl for 30 min, washed with distilled water in order to remove excess of HCl, suspended in 250 mL of ice cold water and mixed with 1M HCl and 1M NaNO$_2$ in aliquots of 2.0 mL each time with constant stirring. The diazotized resin was filtered and washed with ice-cold water. It was reacted with 1-(2-pyridylazo) 2-naphtol (2.0 g taken in 100mL solution in water/ethanol mixture) at 4 ºC for 24 h. The resulting resin was filtered and washed with distilled water. The formula of XAD-16- PAN resin is given in Fig. 2.

The flow system was operated in a volume-based mode. A sample solution (S) containing cadmium was pumped at 2.0 mL min^{-1} and percolated through a minicolumn that retained the cation. Then, cadmium (II) ions were retained by chemical sorption, and the remaining solution was discharged. By switching the injection valve, a stream of 1.0 mol L^{-1} nitric acid (E) flows at 2.0 mL min^{-1} and displaces the cadmium (II) ions. This eluate was taken directly to the nebulizer-
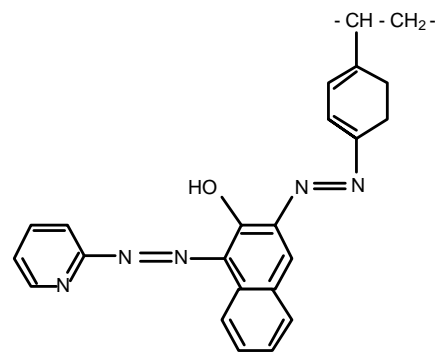
Fig. 2. Formula of chelating resin (polystyrene divinylbenzene resin functionalized by 1-(2-pyridylazo) 2-naphtol)

burner system of the spectrometer. Signals were measured as peak height by using instrument software. Signal was read five times and averaged.

RESULTS & DISCUSSION

Analytical data of the intermediates and synthesized resin were illustrated in Table 1. PSDVB-NO$_2$ shows two strong bands at 1527 (asymmetrical stretching) and 1348/cm (symmetrical stretching), which describe characteristic nitro groups. In the IR spectrum of PSDVB-NH$_2$, a band was observed at 1625/ cm owing to amine groups (N-H bending). The IR spectrum of PAN functionalized PSDVB was compared with that of pure PSDVB. As it can be seen in Table 1, there are additional bands at 3448/cm (O-H stretching) and 1630/cm$^-$(-N=N- stretching), which appear to originate due to modification of the resin by the ligand and are characteristics of O-H and -N=N- vibrations, respectively. The results obtained are in good agreement with information given in literature (Çekiç *et al.,* 2004; Lee *et al.,* 2001).

Table 1. Infrared absorption band data of the intermediates and synthesized resin

Intermediates and synthesized resin	IR spectrum of functional group/cm			
	νN-O	νN-H	νN=N	νO-H
PSDVB-NO$_2$	1527			
	1348			
PSDVB-NH$_2$		1625		
PSDVB-PAN			1630	3448

The retention of cadmium ions on chelating resin is dependent on the pH of a sample solution due to the competitive reaction between chelate forming groups and hydrogen ions in the solutions. For this purpose, the influence of pH on the retention of cadmium ions was evaluated by batch method. A 1 mg/L standard

solution of Cd(II) as model solution was contacted with 0.2 g of chelating resin. The pH of this solution was adjusted in the range of 3 to 9 using different buffer solutions.

As it can be seen in Fig. 3. quantitative recoveries (e" 95%) were obtained for cadmium ions at pH above 7. The progressive decrease in the retention of lead at pH > 7 is probably due to the precipitation of lead as lead hydroxide. Therefore, the working pH was chosen as 7 for the following experiments.

Retention Capacity of PSDVB-PAN Resin
In order to study the retention capacity of PSDVB-PAN resin, the batch method was used. To 250 mg resin was added 25 mL of solution containing 2.5 mg of analyte ion at pH 7. After shaking for 1 h, the mixture was filtered. The concentration of cadmium in the supernatant solution was determined by flame atomic absorption spectrometry. The capacity of sorbent for cadmium ions was found 7.5 mg metal/g PSDVB-PAN as it can be seen in Fig. 4.
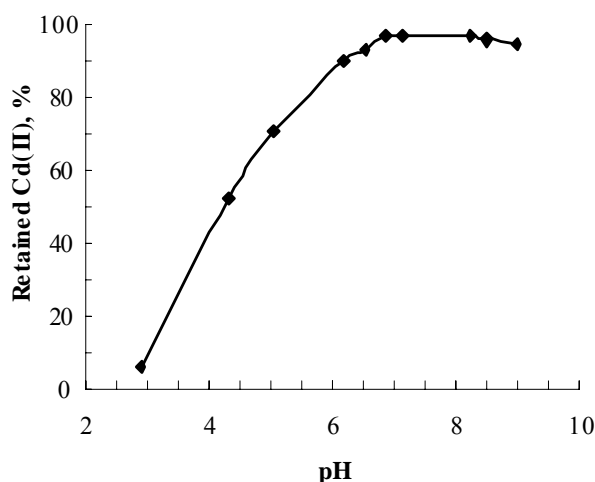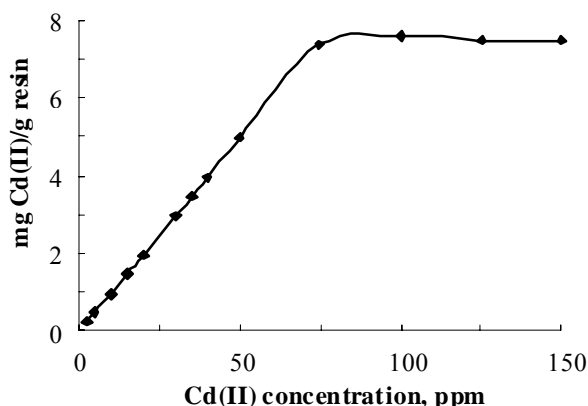
In order to optimize the conditions of the eluent, 1 mL of metal solutions containing 50 g/L of Cd(II) at their respective pH, were at 2.0 mLmin^{-1} passed through the minicolumn packed with the chelating resin and eluted with 1 mL of nitric acid with various concentration (0.1 – 3 M). Fig. 5. shows the results for cadmium metal ions. As shown in this figure, higher recovery was obtained when 1M or more concentrated HNO_3 was used as an eluent.The influence of the eluent volume in the step of cadmium desorption from the minicolumn was also investigated. Results showed that the analytical signal is constant at eluent volume within the range of 1 to 1.5 mL. At volume less than 1 mL, the analytical signal considerably decreased, resulting in broader peaks. Fig. 6. shows the influence of the eluent volume on the degree of recovery for the metal ions, 1 mL were sufficient to achieve recoveries close to 100% in all cases.
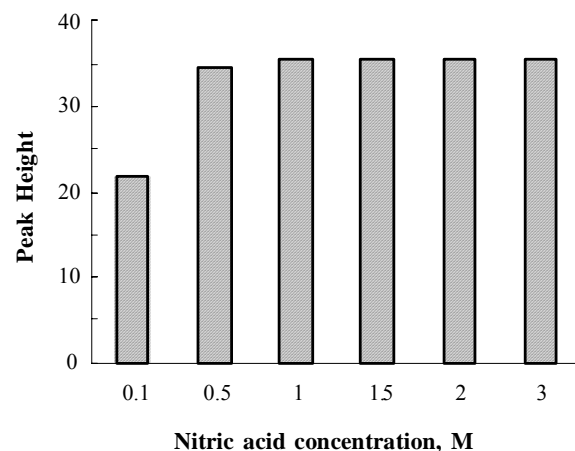

Fig. 3. Effect of pH on the recovery of cadmium

Fig. 5. Signal peak height obtained as a function of concentration of eluent
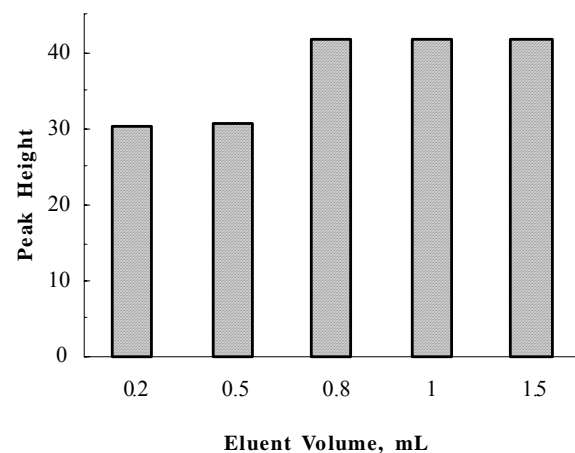

Fig. 4. Retention Capacity of PSDVB-PAN Resin

Fig. 6. Signal peak height obtained as a function of volume of eluent

The repeatability of the method was examined under the optimum experimental conditions described above by using the model solutions. The precision of the procedure calculated by five measurements., determined as the relative standard deviation in standard solutions containing 50 μg/L of cadmium, was 1.8 %. The signal profiles obtained for cadmium standard solution of 50 μg/L and 100 μg/L are shown in Fig. 7.

$100 \ \mu g \ L^{-1}$
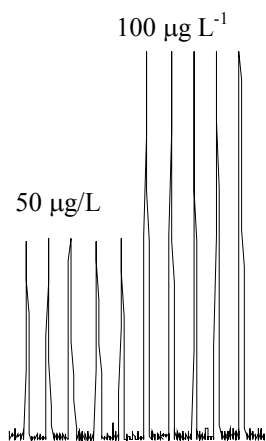
50 μg/L

Fig. 7. Signal reproducibility for 50 μg/L and 100 μg/L of cadmium standard solution

The on-line flow system using PSDVB-PAN as chelating resin for pre-concentration allowed the determination of cadmium in the concentration range of 10 to 150 μg/L for 1 mL of injection volume. The calibration graph under the optimum chemical and flow conditions with the manifold depicted in figure 1 was given as $H = 3.528 + 0.217C$, where H is the peak height of analytical signal and C is the cadmium concentration in solution (μg/L). By using direct aspiration in FAAS without the pre-concentration system, the linear range for cadmium determination was between 1 and 5 μg/L $(A = 0.0045 + 0.2655C)$. The experimental pre-concentration factor, calculated as the ratio of the slopes of the calibration graphs with and without pre-concentration (Fang, 1993), was 800 for 1 mL of sample injection volume. The detection limit (DL), defined as the cadmium concentration that gives a response equivalent to three times the standard deviation (s) of the blank (n=11), was found to be 1.5 μg/L for 1 mL injection of sample solution. The detection limits of the analyte ions can be decreased by one order of magnitude by increasing the sample volume. In order to estimate the accuracy of the procedure, different amounts of cadmium ions were added to 500 mL of river water samples and the resulting solutions were submitted to the preconcentration procedure given in Experimental. A good agreement was obtained between the added and measured analyte amounts (Table 2).

The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed method.

Application to River Water Samples

The Amberlite XAD-16-PAN method has been employed for the preconcentration and analysis of cadmium ions in river water samples. For that purpose, the procedure given was applied. The results, which are shown in Table 2, have been calculated on the assumption of 100% recovery of cadmium ions.

Table 2. Results of determination of cadmium ions in river water samples

River Water Samples	Cd (II), μg/L		Recovery (%)
	add	found	
R-01	0	21.80	-
	20	40.90	97.85
R-02	0	15.89	-
	20	35.23	97.91

CONCLUSION

Based on these results found in the present study, it can be concluded that PSDVB-PAN resin is an effective material for the preconcentration of cadmium ions in the river water samples. The proposed flow injection system with on-line preconcentration using a minicolumn packed with PSDVB-PAN provides quite good sensitivity, accuracy and precision for the determination of cadmium. The combination of flow injection systems with FAAS using polymeric resins functionalized with complexing reagents can be a promising way in the preconcentration and determination of cations in a wide range of samples. The enrichment factor and the detection limit of the procedure can be further improved by increasing preconcentration time without degradation in the efficiency due to the favorable kinetics and low hydrodynamic impedance of the present system. The combination of FAAS with a flow injection system resulted in a simple, sensitive and robust analytical procedure. Such characteristics are very important and of practical interest for routine laboratories equipped just with FAAS for element analysis. The simplicity of the manifold is a great advantage of this procedure if compared to many methods existing for cadmium preconcentration.

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