"Gheorghe Asachi" Technical University of Iasi, Romania

REMOVAL AND PRECONCENTRATION OF CADMIUM ON POLYSTYRENE-*GRAFT*-ETHYLMETHACRYLATE COPOLYMER

Harun Ciftci[*]

Ahi Evran University, Faculty of Science and Arts, Department of Chemistry Kirsehir-Turkey,
e-mail: harunciftci@yahoo.com; Phone:+90 386 2114552, Fax:+90 386 2114525

Abstract

The removal and determination of toxic heavy metal ions in aqueous solutions has been given much more attention over the past few years. In this paper, a removal and separation/preconcentration method for cadmium species on Poly S_{15}-*g*-EMA_{100} (a kind of polystyrene-*graft*-ethyl methacrylate copolymer) in water samples was developed. Some experimental parameters, such as solution pH, sample flow rate, type and concentration of eluent, amount of adsorbent and effect of common matrix ions were investigated. Under the optimum conditions, adsorption isotherms and adsorption capacities have been examined. Langmuir model had been shown to fit the experimental data well, with the correlation coefficient (R^2) of 0.997. The Langmuir monolayer adsorption capacity (q_{max}) and constant of the adsorption energy (K_L) were estimated as 9.7 mg/g and 0.15 L/g, respectively. The method was applied to different water samples such as wastewater, tap water and dam water.

1. Introduction

Heavy metal ions exist in environmental samples from various sources such as plating facilities, mining process, batteries, electrodes, ceramics, oil refinery, metal based paints, alloy industries and agricultural activities, iec. (Ciftci, 2010a; Jang et al., 2008; Vasudevan et al., 2010;). Epidemiologic studies have shown that a high toxic metal accumulation is associated with increased risk of chronic degenerative disease, such as prostate, renal and lung cancers, gastrointestinal and cardiovascular disease (Hayes, 1997; Drasch et al., 2005; Stayner et al., 1993).

Cadmium and other heavy metals taken into organism bind to various blood proteins and are transported to all tissues. Cadmium concentration in drinking water recommended by The World Health Organization (WHO) is smaller than 5 µg L^{-1} (WHO, 1988). Therefore, the removal and determination of heavy metal content of water because of their toxic effects on living organisms is extremely important.

The levels of metal ions in natural samples are usually lower than the detection limit of most instruments, and metals usually exist in very complex matrix environments.

Therefore, various sample preparation techniques are required for separation and preconcentration of metal ions. Separation and removal of toxic metals from waters such as dam water, groundwater and sea water have been widely applied to purification of these samples.

The main purpose of such studies is to remove toxic metal ions from the sample and purification of samples (Mesci, 2013; Turker, 2012).

Many technologies have been developed for removal and the preconcentration of heavy metals from aqueous solution such as precipitation and co-precipitation, cloud point extraction, ion-exchange, electro-deposition, membrane filtration, dispersive

liquid–liquid micro extraction, flotation and solid phase extraction (SPE) (Zhu et al., 2006; Kalidhasan et al., 2009; Karatepe et al., 2010; Divrikli et al., 2007; Naseri et al., 2008; Undeva et al., 2000; Baytak et al., 2011).

Among those techniques, SPE has been widely used for separation and sensitive determination of metal ions, mainly in water samples. SPE has some advantages such as rapidity, simplicity, low solvent usage and lower extraction time, sensitivity and economy (Camel, 2003).

Different solid phases, such as chloromethylated polystyrene functionalized with N,N-bis(naphthylideneimino)diethylenetriamine, coir pith, maghemite nanoparticles, nano-scale diboron trioxide/titanium dioxide composite material, poly(ethylene glycol dimethacrylate-co-vinylimidazole, 1,6-bis (2-carboxy aldehyde phenoxy) butane functionalized

Amberlite XAD-16, thiouresulfonamide resin, poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric resin, Nb_2O_5/Al_2O_3 mixed oxide dispersed on silica matrix, clinoptilolite, Duolite XAD-761, multiwalled carbon nanotubes and TiO_2 nanotubes have been used as solid-phase extractants for the removal and preconcentration of cadmium ions (Chamjangali et al., 2010; Ciftci, 2010[b]; Colar et al., 2012; Kalfa et al., 2009; Segatelli et al., 2010; Matei et al., 2011; Ramesh et al., 2011; Oral et al., 2011; Senkal et al., 2007; Anthemidis et al., 2011; Costa et al., 2011; Tuzen et al., 2008; Zhoua et al., 2009).

Polymeric resins have some advantages such as low cost, simple preparation, high porosity and thus highly available surface area, and stability in acidic or basic media (Chamjangali et al., 2010).

In the present work, a new solid phase extraction method was developed for the removal and preconcentration of trace cadmium from aqueous solutions. Some analytical parameters were investigated and optimized.

The developed method has been applied to water samples. Poly S_{15}-*g*-EMA_{100} was used as an adsorbent. Where, 15 and 100 are defined as *p*-chloromethyl styrene and monomer ratios, respectively.

2. Experimental

2.1. Apparatus

Metal determinations were carried out using an Analytik Jena Model ContrAA 300 High Resolution-Continuum Source Flame Atomic Absorption Spectrometer (GLE, Berlin, Germany) equipped with a xenon short-arc lamp as a continuum radiation source and a Neon background corrector in air–acetylene flame.

Working parameters of the equipment were established according to the manufacturer's guideline for each element.

The instrumental parameters for Cd^{2+} were as follows: wavelength 228.8018 nm, burner height 5 mm, evaluation Pixels 3 pm.

The air - acetylene flow rate was 50 L h^{-1}. Orion Star (Thermo Fisher, USA) pH meter was used to measure the pH of solutions.

2.2. Reagents and solutions

All reagents and solvents were of the analytical grade and used without further purification. All solutions were prepared using ultra pure water (specific resistance 18 MΩ cm) from a Milli-Q purification system (Millipore Corporation, Massachusetts, USA).

Standard solutions of cadmium were prepared by appropriate dilution of the stock standard solution (Merck, 1000 mg L^{-1}). Other chemical reagents were obtained from Merck (Darmstadt, Germany).

Poly S_{15}-*g*-EMA_{100} was prepared with polystyrene-*co*-*p*-chloromethyl styrene (PS-Cl) as macro initiator in the presence of CuCl/1,2-dipiperidinoethane and ethyl methacrylate (EMA) at 130b°C in *N,N*-dimethyl formamide according to literature (Coskun and Temuz, 2003). The reaction scheme of its synthesis is shown in Fig. 1.

2.3. Preparation of separation column

1.0-2.0 g of resin was treated with nitric acid (50 mL of 2 mol L^{-1}) for the removal of impurities in a beaker. It was filtrated and washed with deionized water until pH of the supernatant was neutral.

Then, it was dried in an oven at 80°C for 8 h. and 0.5 g of dried resin was packed into a glass column (100 mm×8 mm i.d.) plugged with small portion of glass wool at both ends. Before each use, the column was preconditioned by passing the blank solutions in working pH. The sample solution was permitted to flow through the column under gravity.

2.4. Separation/preconcentration procedure

The method was tested with model solutions before its application to the water samples. Preconcentrations were performed by using 50 mL test solution containing 0.1 mg L^{-1} of Cd^{2+} ions.

The model solutions were passed through the column after adjusting to the optimum experimental conditions.

The adsorbed ions on the resin in the column were eluted with 5 mL of 2 mol L^{-1} HNO_3 solution that had a flow rate of 5 mL min^{-1} and were determined by FAAS.

2.5. Analysis of water samples

Tap water and wastewater were collected from Kırşehir, Turkey. Dam water was collected from Hirfanlı dam lake (Kırşehir, Turkey).

The water samples for metal ion determination were collected in high density

polyethylene sample bottles including 2 mL of 1% (v/v) hydrogen peroxide solutions and 1 mL
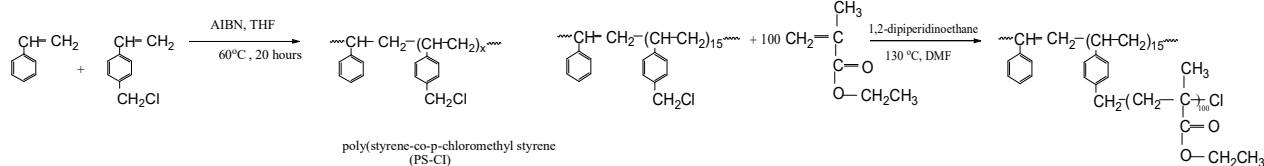
concentrated nitric acid.

poly(styrene-co-p-chloromethyl styrene)
(PS-Cl)

Fig. 1. Synthesis of Poly S_{15}-*g*-EMA$_{100}$

The samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm.

3. Results and Discussion

## 3.1. Effect of test solution pH on recovery of Cd^{+2}

The pH of the medium is of prime importance for efficient retention and recovery of the metal ions on the resin. Its influence strongly depends on the nature of the sorbent used. The recovery of the analyte was determined by applying the preconcentration procedure by changing the pH of model solution in the range of 4.0-9.0. The pH of each model solution was adjusted with different buffer solutions, such as sodium acetate-acetic acid, sodium mono hydrogen phosphate-potassium dihydrogen phosphate and ammonium chloride-ammonia.

Prepared solutions which had a working pH were passed through the column at an optimized flow rate. Effect of the pH on the recovery values are summarized in Fig. 1.

As shown in this Fig., optimum recoveries were found between the pH values of 5.5 - 7.0. In acidic medium (pH<5.5), adsorption was found to be considerably lower.

The possible explanation is that in acidic medium, hydrogen ions and hydronium ions compete with metal ions. As a result active negative sites become protonated, resulting in the prevention of metal ion adsorption on the surface of adsorbent.

Sorption was observed to increase as the solution pH was increased. Increasing pH decreases the concentration of H^+, therefore reducing the competition between metal ions and protons for adsorption sites on the resin surface (Anirudhan et al., 2012).
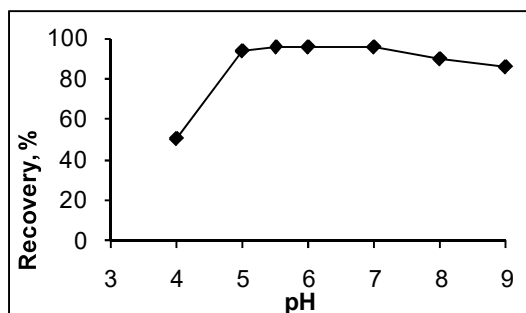
3.2. Choice of eluent agents

The type, amount, and concentration of eluent are other important parameters for this kind of studies. For the successful application of removal and preconcentration systems, inorganic acids such as HCl and HNO$_3$ are recommended in desorption of metal ions from polymeric materials. They rapidly decrease the pH of the medium and assist the proton exchange to replace the bounded metal ions in the solid phase. In this study, HCl and HNO$_3$ solutions in different concentrations were used for recovery of cadmium. The effect of various eluents on the recoveries of cadmium ion is given in Table 1.

Among different eluents used, 5 mL of 2 mol L^{-1} HNO$_3$ provided higher recovery of cadmium ions. It is likely that not only an acidic effect, but also oxidizing power of HNO$_3$ plays a role in elution. Therefore, this solution was chosen as an eluent for the metal ions from Poly S_{15}-*g*-EMA$_{100}$.

3.3. Effect of sample flow rate

The sample flow-rate should be optimized to ensure quantitative recovery along with decreasing the time required for sample processing. The flow rate of sample solution on the retention of metal ions was examined in the range of 0.5-6.0 mL min^{-1} under optimum conditions. The metal ions were desorbed from resin by using 5 mL of 2 mol L^{-1} HNO$_3$ solutions. Results are shown in Fig. 2. The recoveries of metal ions ranged between 95 % and 100 % at flow rates varying from 0.5 to 5 mL min^{-1}. If sample flow rate is higher than 5 mL min^{-1}, it is observed that recoveries decrease because of the insufficient interaction time between the metal ions and resin. Accordingly, the optimum flow rate was recommended as 5 mL min^{-1}.
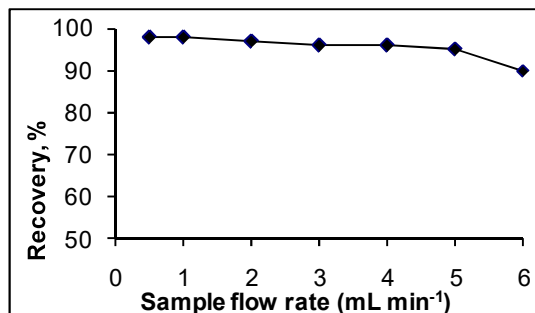
Fig. 1. The effect of pH on the recovery of Cd^{2+}

Fig. 2. The effect of solution flow rate on the recovery of Cd^{2+}

3.4. Effect of sample volume

The maximal preconcentration factor can be obtained by increasing the sample to eluent volume ratio by either decreasing the eluent volume or increasing the sample volume. For this purpose, the maximum volume of sample solution was investigated by increasing the volume of cadmium ion solution with a constant amount of ions (2.5 μg of cadmium ions) at pH 5.5. Samples solution volumes of 50, 100, 200, 400, 600, 800 and 1000 mL containing cadmium was passed through the column. The results are shown in Fig. 3. It was observed that if the sample volume ranged between 50 mL to 600 mL for cadmium, recoveries of metal ions were higher than 95%. The preconcentration factor is calculated as the ratio of the highest sample volume (600mL) to the lowest eluent volume (5.0 mL). The preconcentration factor (PF) was obtained 120.

3.5. Influence of interfering species

One of the important problems in removal and separation of the heavy metal ions is interference from matrix. To investigate the effect of other constituent on the recovery of the analyt, the possible interfering elements were added to 50 mL of model solutions containing 10 μg Cd^{2+} ions with their nitrate or chloride salts at pH 5.5. The recovery values for different amounts of foreign ions are given in Table 2. As can be seen, added ions have no significant effect on the recovery of cadmium ions.

3.6. Adsorption capacity of resin

The sorption rate of Cd^{2+} by Poly S_{15}-*g*-EMA_{100} was high (Fig. 4). The sorption equilibrium was also achieved within a short period of 20 min.

Table 1. Effect of type and concentration of eluting agent on the recovery of Cd^{2+}

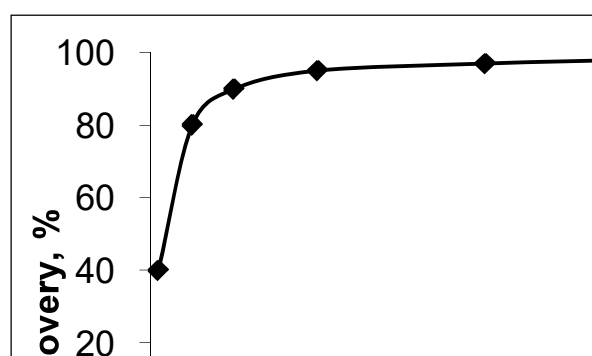| Eluent	Recovery (%) *
1 mol L^{-1} HCl, 5 mL	74±2
2 mol L^{-1} HCl, 5 mL	82±2
3 mol L^{-1} HCl, 5 mL	88±2
1 mol L^{-1} HNO_3, 5 mL	92±1
2 mol L^{-1} HNO_3, 5 mL	100±2
3 mol L^{-1} HNO_3, 5 mL	97±2

*Results are mean ± standard deviation of three replicate analyses.

Table 2. Effects of the matrix ions on the recovery of Cd^{2+}

Interfering ions	Concentration (mg L^{-1})	Recovery * (%)
K^+	1000	99±2
Na^+	1000	101±2
Ca^{2+}	1000	95±2
Mg^{2+}	500	96±1
Zn^{2+}	5	96±2
Cu^{2+}	5	100±2
Co^{2+}	5	96±2
Ni^{2+}	5	98±3
Pb^{2+}	5	95±2
Cr^{3+}	5	96±1
Al^{3+}	5	98±2
Fe^{3+}	5	96±2

Results are mean ± standart deviation of three replicate analyses.
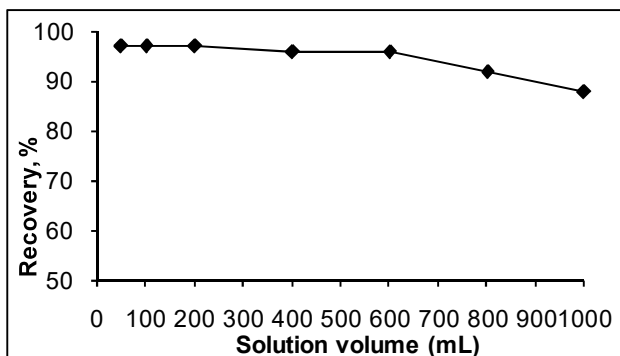
Fig. 3. The effect of sample volume on the recovery of Cd^{2+}

Fig. 4. Time course of Cd^{2+} recovery by Poly S_{15}-*g*-EMA_{100}

Adsorption capacity of resin was obtained by batch experiments. 0.2 g of resin was added into a 250 mL flask which contained 100 mL of Cd^{2+} solution of various concentrations (1-100 mg L^{-1}) in optimum pH. The mixture was stirred with a magnetic stirrer at 150 rpm for 60 min at 25 ±2°C. Mixture was passed through a paper filter. Adsorbed metal ions on the resin were determined by using FAAS after eluted with 5 mL of 2 mol L^{-1} HNO$_3$ solutions. The Langmuir adsorption model was applied to describe the equilibrium isotherm. The adsorption capacity of Cd^{2+} ions adsorbed per gram adsorbent (mg/g) was calculated using the Eq. (1):

$$q_e = (C_0 - C_e)V/m \qquad (1)$$

where: q_e is the equilibrium concentration of Cd^{2+} ions on the adsorbent (mg/g); C_0 and C_e are the initial and final metal concentration (mg/L), respectively; m is the mass of adsorbent (g); V is the volume of Cd^{2+} solution (L).

The adsorption isotherm indicates how the adsorption species spread between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. There are several isotherm equations available for analyzing experimental adsorption equilibrium data. In this study, the linearized equation form of the Langmuir model used to evaluate maximum metal uptake is expressed as Eq. (2).

$$C_e/q_e = C_e/q_{max} + 1/K_L q_{max} \qquad (2)$$

where: K_L (L/g) is a constant related to the energy of adsorption/desorption and q_{max} (mg/g) is the maximum uptake (Bunluesin et al., 2007; Ciftci et al., 2011 Ciftci et al., 2013;.

Langmuir model had been shown to fit the experimental data well, with the correlation coefficient (R^2) of 0.997. The Langmuir monolayer adsorption capacity (q_{max}) and K$_L$ were estimated as 9.7 mg/g and 0.15 L/g, respectively (Fig. 5).

Langmuir adsorption isotherm is an example of a favorable isotherm and is applicable under the following hypothesis: a uniform surface of the solid, uniform energies of adsorption on the surface, the absence of interaction between adsorbed species and adsorption in a single layer. The q_{max} parameter gives the theoretical monolayer saturation capacity and is a measure of the amount of metal adsorbed when the monolayer is completed (Ulmanu et al., 2008).

3.7. Analytical features and applications of method

Under the optimum experimental conditions, analytical parameters of the proposed procedure, such as linear range, calibration curve, equation of calibration curve, correlation coefficient, limit of detection (LOD) and precision were examined.

The linear range of calibration graph was found to be 0.1 to 3.0 mg L^{-1} with a correlation coefficient of 0.9986 for standard cadmium solutions. The limits of detection, defined as LOD= [3σ/(m.PF)], where σ is standard deviation of 10 replicate blank signals, m is slope of the calibration curve and PF is preconcentration factor for proposed procedure (Yalçınkaya et al., 2011). LOD for cadmium ions was found to be 0.40 μg L^{-1}. In order to determine the precision of the proposed method, the standard model solution containing 0.1 mg L^{-1} metal ions was used as the sample. The relative standard deviation (RSD) for seven replicate analyses of Cd^{2+} ions was obtained 1.8 %. The capacity of the adsorbent was checked again after being used approximately fifty times. It was found that sorbent capacity did not significantly change.

The improved method was applied to 600 mL water samples. The validity of the proposed method was further proven by analyzing spiked analyte ion samples. Experimental results are given in Table 3.

3.8. Comparison to Other Procedure

A comparison of the proposed procedure with other reported preconcentration procedures is given in Table 4. Analytical characteristics obtained for this study are comparable to many procedures in the table. The LOD of proposed procedure is lower than studies of Elif et al. (2011) and Yalçınkaya et al. (2011). The enrichment factor is 120 and is higher than those published in the literature (Chamjangali et al., 2010; Elif et al., 2011; Yalçınkaya et al., 2011). The adsorption capacity of resin is higher than studies of Chamjangali et al. (2010), Parham et al. (2009), Shabani et al. (2010) and Elif et al. (2011).
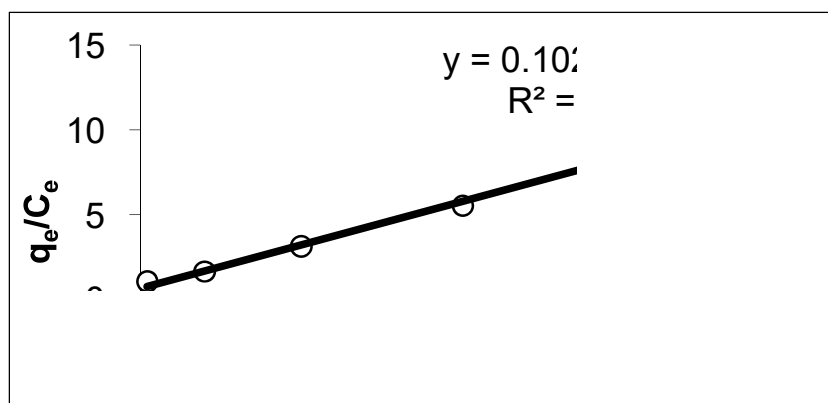
Fig. 5. Linearized Langmuir adsorption isotherm of Cd^{2+} for Poly S_{15}-g-EMA_{100}
Table 3. Levels of cadmium in different water samples

Sample	Added ($\mu g\ L^{-1}$)	Found* ($\mu g\ L^{-1}$)	Recovery %
Wastewater	0	16.4±1.2	
	20.0	35.8 ±2.4	98.3
Tap water	0	1.8±0.4	
	5.0	6.5±0.5	104.6
Dam water	0	2.4±0.3	
	5.0	7.6±0.4	102.7

Mean ± ts/√N with 95% confidence level

Table 4. Comparison of present method for preconcentration of Cd^{2+} ions with other methods in literature

Adsorbent	Preconcentration factor	LOD ($\mu g\ L^{-1}$)	Adsorption capacity($mg\ g^{-1}$)	References
Chloromethylated polystyrene functionalized with (NAPdein)	50	0.25	1.0	Chamjangali et al. (2010)
Solid sulfur	250	0.2	0.0034	Parham et al. (2009)
Alumina modified with (SDS) and 1,10-phenanthroline	160	0.14	1.13	Shabani et al. (2010)
1,6-*bis*(2-carboxy aldehyde phenoxy) butane with the Amberlite XAD-16	100	1.19	4.43	Elif et al. (2011)
Nano hybrid material (ZrO_2/B_2O_3)	15	3.1	109.9	Yalçinkaya et al. (2011)
Poly S_{15}-g-EMA_{100}	120	0.40	9.7	Present paper

4. Conclusions

This study showed that Poly S_{15}-g-EMA_{100} could be used as selective, economical and efficient sorbent material for removing and separation/preconcentration of trace cadmium.

There is no need for loading of any chelating and/or complexing agent onto the sorbent.

The sorbent can be used fifty times without a marked loss in sorption capacity.

Hence, the polymeric adsorbent was found to be very stable when the adsorption–desorption processes did not alter the physical and chemical characteristics of the adsorbent.

In addition, the purposed method is simple, accurate and an alternative procedure for removing and preconcentration of cadmium in water samples.

Acknowledgements

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