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Separation and pre concentration of Cd(II) from water samples with impregnated resin containing mixed ligands; 1,4-diaminoantraquinone and 1,4-dihydroxyantraquinone

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Key words: Amberlite resin XAD-16, impregnation, 1, 4-diaminoantraquinone, 1,4-dihydroxy antraquinone, flame atomic absorption spectrometer, separation.

Abstract

A new study for separation and pre concentration of Cd(II) in water samples was done using adsorbant solid phase containing amberlit resin XAD-16 that impregnated with mixed ligands; 1,4-diamino antraquinone and 1,4-dihydroxy antraquinone with ratio 1:1. The solid phase was packed into mini column (10cm length and 5mm diameter) and water sample containing Cd(II) was passed through the column. Then, adsorbed ions were eluted using HCl (2M) as eluent and subsequent determination was done with flame atomic absorption spectrometer (FAAS).For access to the highest recovery, various parameters such as PH, ionic strength,type of eluent, sample flow rate and eluent flow rate were optimized. In this maner, the recovery obtained was quantitative (95%) and LOD (3Sb/m), RSD were obtained 1.2 $\times 10^{-9}$ M, 3.2% respectively.

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Introduction

Heavy metals are widely distributed in the environment as a result of numerous industrial process and cause toxic effects to human beings (Manzoori *et al.*, 2007).

Cadmium is known to be highly toxic for animals, plants and human even at low concentrations and can be accumulated in several organs. Low levels of exposure to this element over prolonged periods cause high blood pressure, sterility among males, kidney damage. Therefore, extraction of this ion from water and wastewater, before its discharge into the environment, is very important (Liu *et al.*, 2005).

Several methods such as UV-Vis spectrophotometry (Di *et al.*, 2005), atomic absorption spectrometry (Yaman and Akdeniz, 2004), ICP-AES (Cabon, 2002), ICP-MS (Karami *et al.*, 2004), striping voltametry (Li and Jiang, 2003), ion chromatography (Brainina *et al.*, 2004), potentiometry , spectrofluorometry (Abbas and Zahran, 2005) and polarography have been used. However, some of these methods are time consuming, require complicated and expensive instruments, have complex operational conditions, encounter various types of interference or have maintenance cost (Hassani *et al.*, 1999).

Liquid-liquid extraction (LLE) and solid phase extraction are two methods that used for pre concentration of metal ions from initial samples. Nowadays application of LLE is limited due to time consuming and need to using of large amount of organic solvents, that these solvents are toxic and expensive (Chayama and Sekido, 1991).

Unlike LLE, solid phase extraction is used frequently. Because of it has many advantages over LLE such as availability, easy recovery of solid phase and large pre concentration factors .In conventional solid phase methods, a polymeric matrix used to bind the chelating reagents treatment in wide range and need to long time for chemical binding of chelating agent to polymeric support (Daorattanachai *et al.*, 2005) and (Zhang *et al.*, 2005).

Alternatively, solvent impregnated resins (SIRs) don't have the problems of conventional adsorbent resins and benefit from advantages of LLE and SPE. Furthermore, high capacity and metal binding strength are the other important characteristics of the SIRs (Anjoys *et al.*, 2007) and (Kim *et al.*, 2005).

For these reasons, impregnated resins are used in two last decades for separation and pre concentration of metal ions. At the present study, mixed chelating agents with ratio of 1:1 from 1,4-diaminoantraquinone and 1,4-dihydroxyantraquinone is used for impregnation in/on Amberlit XAD-16 granules.

Experimental

Material and apparatus

All the materials used, were of analytical grad and supplied by E.Merk, Darmstadt, Germany. Stock solution of Cd (II) ion was prepared at concentration of 1.0×10^{-3}M by dissolving the appropriate amounts of its nitrate salt in 1M HNO_3 solution and diluting to the mark(100 mL) with distilled water.

The following buffer solutions with concentration of 1M were made and used to adjust the pH and strength of the working solutions: formic acid/sodium format for pH 2-4; acetic acid/sodium acetate for pH 4-6; ammonium nitrate/ ammonia for pH 6-9. The working solutions were adjusted at the pH 8 and ionic strength of 0. 1 M using ammonium/ammonia buffer solution. These solutions were prepared daily by diluting the stock solution.

A corning 130 model pH-meter was used for pH measurement. A flame atomic absorption spectrometer with Variant AA240 model was used for all absorbance measurements. Finally, for indicating of morphology difference between XAD-16 resin before and after impregnation, the scanning electron microscopic (SEM) micrographs were obtained using a VEGA/TESCAN instrument at an accelerating voltage of 25 kv.

Preparation of SIR

1.5000g of chelating agent DAAQ with same amount of AHAQ was located into a 100ml stopper flask and mixed manually. Then 30ml 1, 2-dichloro ethane was added to it and mixture was mixed for a few minutes to disperse chelating agents into solvent.

After that, 3.0000g of the Amberlit resin was added to the mixture and shaken to 48 h_s. After separation of impregnated resin beads with a porous filter, they were rinsed with aliquots of distilled water and HCl 6M until the filtrate solution didn't show absorbance against distilled water.

The determination procedure

100ml sample solution containing $Cd^{2+}$with concentration exactly 10^{-6}M was passed through a mini column (10cm length and 5mm diameter) packed with 1.0 g adsorbant SIR at flow rate 1ml/min. After that, the column was eluted with 20ml distilled water for removing free pollutants. Then elution process was done by 5ml HCl 2M at flow rate 0.5ml/min. The effluent was subjected to the FAAS for the Cd (II) determination.

For access to the highest recovery, various parameters such as PH, ionic strength, type of eluent, sample flow rate and eluent flow rate were optimized.

Results and discussion

Characterization of the SIR

Amberlit XAD-16 resin is an adsorbant based on poly styrene divinyl benzene copolymer. It has excellent physical properties such as thermal and mechanical stability, hydraulic characteristics, high porosity, low polarity and it has the largest surface area ($825m^2g^{-1}$) among the XAD series of amberlit resins[ ]. Thus , it was selected as an appropriate adsorbant for impregnation with chelating agents (DAAQ, DHAQ). To investigation of the surface morphology, SEM micrographs were used (Fig.1.). By comparing two images before and after impregnation, it is clear that the porous of the surface were filled with chelating agents during the impregnation process.

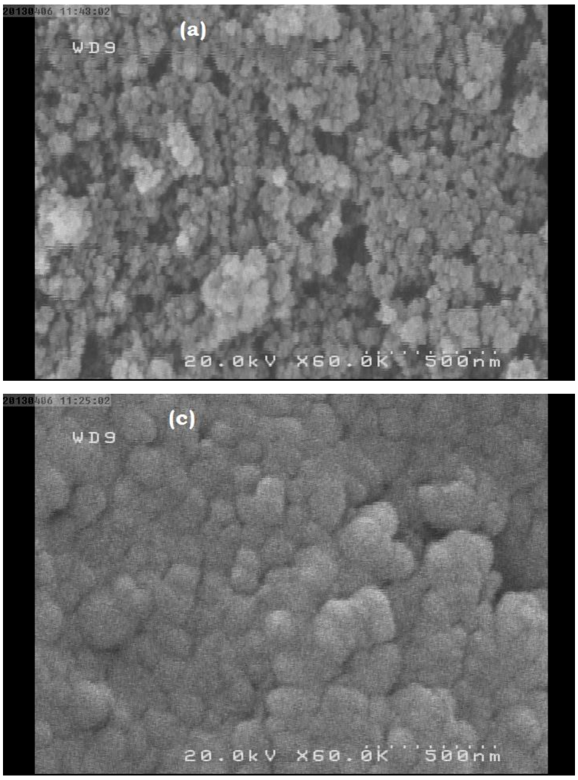

Fig. 1. SEM micrographs of polymeric support samples; (a): Amberlite XAD-16, (b): mixed-ligands SIR containing DAAQ+DHAQ.

Effect of PH on the extraction of the Cd(II)

For study of this parameter, various buffer solutions of Cd (II) in the PH range of 2-11 was prepared. Then, these solutions were passed through the column at flow rate 1ml/min. Elution process was done using 5ml HCl 2M at flow rate 0.5ml/min. The results show that the best recovery is gained at PH=9. At PH upper this amount, absorbance is decreased that is probably related to precipitation or complex formation of Cd (II) with hydroxyl group (Fig.2.).

Effect of sample and eluent flow rate on extraction process

A series buffer solutions cd^{2+} at PH=9 were used for investigation of this factor. These solutions were passed through the column at different flow rates from 0.5 to 6ml/min while elution process was fixed at 0.5 ml/min. The results show that optimum sample flow rate is 1.5ml/min (Fig.3.). After optimization of sample flow rate, elution process was done in different eluent flow rates, while sample flow rate was located at 1.5 ml/min. as indicated in Fig.4; optimum eluent flow rate is 0.5ml.min^{-1}.

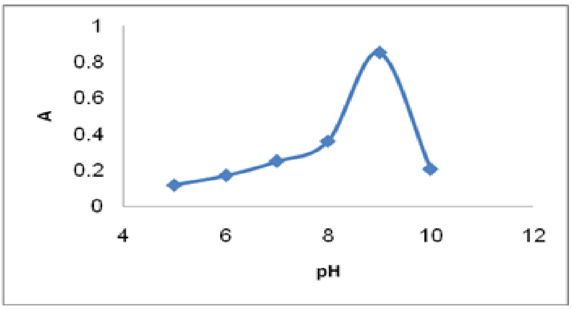

Fig.2. Effect of pH on the extraction of Cd(II).

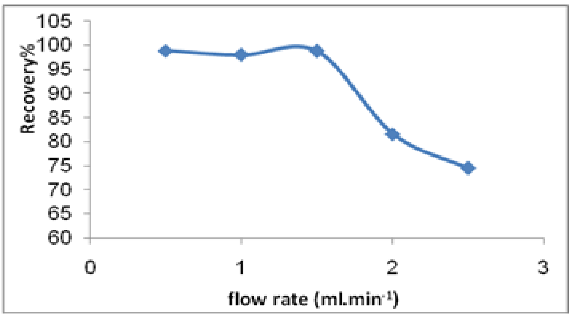

Fig.3. Effect of eluent flow rate on extraction of Cd(II).

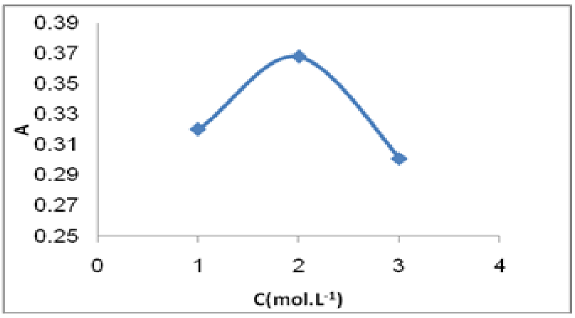

Fig. 4. Effect of eluent concentration on extraction of Cd(II).

Another factor that was evaluated and optimized was concentration of HcL as eluent. For this purpose, proposed method was done in different concentration of eluent. After elution and determination of eluted solutions, it was indicated that HcL 2M is the best concentration for elution of adsorbed Cd(II) ions on SIR surface. At upper concentration recovery factor was decreased. Thus this concentration was selected for next studied.

Effect of ionic strength on extraction of Cd (II)

The used buffer for preparation of sample solutions is ammonium nitrate/ammonia pair. Thus for investigation of ionic strength on extraction process, water samples were prepared at different concentration of ammonium nitrate in the range 0.05-2mol/L. Absorbance data show that with increasing of NH_4NO_3 concentration to 0.1M, recovery increases. After that, decreasing in recovery factor is probably due to salting effect.

Effect of sample volume on the recovery

To evaluate the effect of sample volume on the sorption procedure, various samples of Cd(II) that bufferized at PH=8 and were containing 0.05 M NH4NO3 , prepared that in all of them, mmol of Cd(II) was constant while volumes of the sample varied from 100 to 1000 ml. These solutions were analyzed according to recommended method in above. The results show that with addition of volume to 250ml, recovery is convenient (> 90%) but at volumes upper than 250ml, decreasing in recovery is obvious.

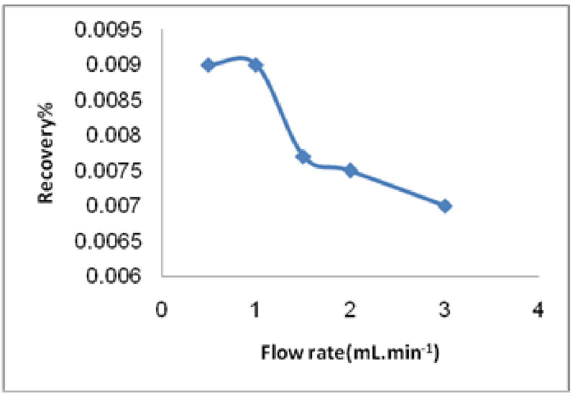

Fig. 5. Effect of sample flow rate on extraction of Cd(II).

Analytical application

In treatments with aliquots of 250 ml of the solutions, Cd (II) contents was extracted with the SIR with mixed chelating agents (i.e. DHAQ, DAAQ) and then subjected to the determination procedure. The calibration curve was linear in the range of 2.435 $\times 10^{-8}$ to 1.779 $\times 10^{-6}$ ppm.

$$\text{Cd (II): } A= 3.537C\times10^{+6}+ 0.0186 \qquad R^2=0.9899$$

Where A is the absorbance, C is the molar concentration of Cd(II) and R^2 is the correlation coefficient.

The limit of detection (LOD) was defined as three times of the standard deviation of blank (n=7) divided to the slop of calibration curve ($3S_b/m$), was found to be 1.698 $\times 10^{-10}$ M.

Analysis of real sample

For investigation of reliability of method, the proposed method was applied to determine Cd(II) metal ion in several natural water samples collected from water sources of Neyshabur, a city in Khorassan Razavi. Before the usage of water samples, they were filtered through a membrane filter with a pore size of 0.45 mm and then 250-mL aliquots of the samples analyzed with proposed method. The accuracy of the measurements was investigated using the spiked amounts of Cd (II) ions to the water samples at several concentrations.

Table 1. Determination of Cd(II) in natural water samples.

Sample	**Spiked (µg)**	**Found±SD (µg)**	**Recovery (%)**
Spring water	-	0.80± 0.04	-
	2.81	3.32± 0.04	91.96
Tap water	-	-	-
	2.81	2.79±0.06	99.29
Well water	-	0.73± 0.05	-
	2.81	3.51± 0.05	99.15

The obtained results are summarized in Table 2. As observed from the results, the recoveries for the spiked sample solutions were in the range 91.96%–99.29%, which confirmed satisfactorily applicability of the proposed method for complicated environmental samples.

Conclusion

Using of solvent impregnated resin (SIR) as adsorbent Solid phase in the extraction of metal ions exhibits some advantages such as faster rate of equilibrium, high capacity and sorption rate to some extent. It could be used for 90-100 cycle without any lowering its sorption capacity. It is very useful in the measurement amount of Cd (II) at neutral water samples with the recovery factor higher than 90%.

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