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Comparison of amounts of Cd (II) adsorbed in four vegetable species with using impregnated resin containing mixed ligands; 1,4-diaminoantraquinone and 1,4-dihydroxyantraquinone

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Abstract

In this study, initially four type vegetables were prepared with using acid digestion method. After that, preconcentration and separation of Cd(II) adsorbed was done with passing of prepared solutions from the column packed with 1g Amberlt resin XAD-16 impregnated with mixed ligands; 1,4-dihydroxyantraquinone and 1,4-diaminoantraquinone.Finally, determination process was done with flame atomic absorption spectrometer (FAAS).

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Introduction

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 (Lu *et al.*, 2003).

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).

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 (Yong-Liang *et al.*, 2007), (Atique Ullah *et al.*, 2014). 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 (Hongdeng Qiu *et al.*, 2011), (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.

Material and methods

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.

Acetic acid/sodium acetate buffer solution with concentration of 1M was made and used to adjust the pH and strength of the working solutions at 8 and 0.01M respectively. 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.

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. For indicating impregnation process, 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.

Acid digestion of vegetable samples

Applicability of the SIR in extracting Cd(II) from four vegetable species containing , , , and from areas of Neyshabur, a city in Iran, Razavi Khorasan Province

was studied. Exactly, 1 g of the fine powder sample was digested with 150 mL 12 M H_2SO_4 at 250 ºC for 4 h followed by 100 mL 65% HNO_3 at 100 ºC for 4 h again. The filtrate solution was gently heated till to obtain a moisture residue. The residue was transferred into a 100-mL volumetric flask and re dissolved in 25 mL 1 M HCl. After adjusting its pH using the buffering solution, it was diluted to the mark and subjected to the extraction/determination processes. The accuracy of the determinations was investigated by spiking Cd(II) ion to the water

solutions at various concentrations. The results are present in Table 1. As observed from the results, the recoveries for the spiked amounts were found to be > 95%, which confirmed the accuracy at the 95% confidence level for application of the proposed method. Moreover, in treatment with the references samples, the agreement between found and expected values demonstrated that the described method was accurate for trace analysis of Cd(II) in the complex matrices.

Table 1. Determination of Cd(II) in vegetable samples.

Sample	Spiked (mg.L⁻¹)	Found±SD (mg.L⁻¹)	Recovery (%)
Spinach	-	8.59± 0.04	-
	2.00	10.32± 0.04	97.45
Leek	-	9.49±0.06	-
	2.00	10.89±0.06	94.78
Parsley	-	18.94± 0.05	-
	2.00	20.51± 0.05	97.94
Coriander	-	19.29±0.05	-
	2.00	21.52±0.05	101.08

The determination procedure

100ml sample solution containing Cd^{2+} with pH 8 and strength ionic 0.01M, 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.
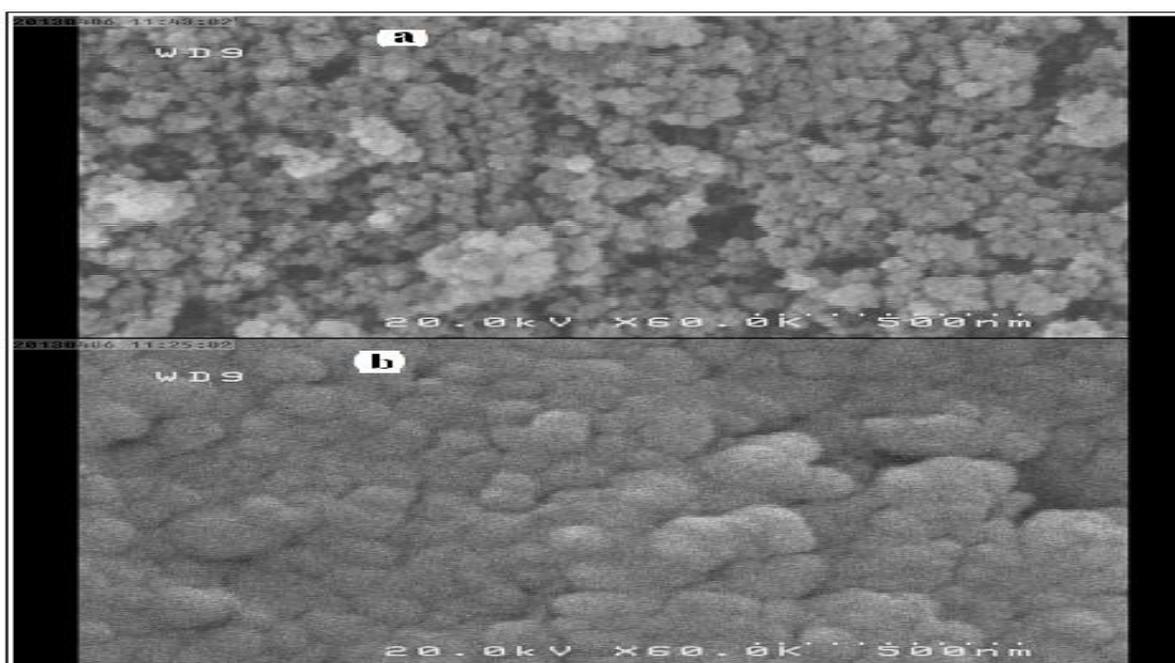

Fig. 1. SEM micrographs of polymeric support samples; (a): Amberlite XAD-16, (b): mixed-ligands SIR containing DAAQ+DHAQ.

Analytical application

In treatments with aliquots of 100 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 2.435×10^{-8} to 1.779×10^{-6} M.

Cd (II): A= $3.537C \times 10^{+6}$+ 0.0186 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 1.698×10^{-10} M.

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 vegetable samples with the recovery factor higher than 90%. plant hormones in plant defense responses. Plant Molecular Biology **69,** 473–488.

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