



RESEARCH PAPER

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**Removal of Pb(II) from aqueous solutions using solvent impregnated resin containing 1,4-diaminoantraquinone before the determination by flame atomic absorption spectrometry**

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**Key words:** Amberlite resin XAD-16, impregnation, 1, 4-diaminoantraquinone, flame atomic absorption spectrometry, separation.

**Abstract**

This study is a simultaneous separation and pre concentration of Pb (II) ion from water samples before determination with flame atomic absorption spectrometric. It is based on sorption of Pb(II) at the buffering pH of 8, on a mini column (10cm length and 5mm internal diameter) packed with 0.7 g Amberlite XAD-16 resin impregnated with chelating agent of 1,4-diaminoantraquinone (DAAQ). After passing of sample solution from the column, elution process was carried out with passing of 5 mL 2M HCl into column and then subjected to FAAS for the determination. The sample and eluent flow rate, eluent concentration and ionic strength effect were investigated and optimized. RSD, LOD (3sb/m), recovery were found to be 2.8%,  $1.8 \times 10^{-9}$  M, 92.95% respectively.

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## Introduction

Heavy metals are widely distributed in the environment as a result of numerous industrial processes and cause toxic effects to human beings. Pb(II) ion is one of the most toxic heavy ions with known negative impacts on both human health and ecological functions (Douglas, Wolfgang, 1995), (Du, B. *et al.*, 2002), (Dutta, S. & Das, A. K., 2007). Extraction of this ion from water and wastewater, before its discharge into the environment, is very important. Different techniques for lead ion extraction from the water and wastewater, such as chemical precipitation, complex formation, sorption, etc., have been extensively investigated. Among them, sorption has been found to be superior to other techniques for simplicity, ease of operation and reusability (Yavuz *et al.*, 2006), (Manohar *et al.*, 2002), (Feng *et al.*, 2004), (Song *et al.*, 2010), (Atia *et al.*, 2008). The determination of low concentration of metal ions by flame atomic absorption spectrometry (FAAS) usually needs separation and pre concentration steps due to insufficient sensitivity or matrix interference.

Solid phase extraction technique is used in the wide range for pre concentration and separation of ultra trace metal ions. In conventional solid phase methods, a polymeric matrix used to bind the chelating reagents on it through chemical reactions. But its application was limited for not having economic treatment in wide range and need to long time for chemical binding of chelating agent to polymeric support (Jain *et al.*, 2006), (Hennion, 1999), (Reis *et al.*, 2000), (Teixeira *et al.*, 2000), (Teixeira *et al.*, 1998), (Juang and Su, 2004).

Alternatively, solvent impregnated resins (SIRs) do not 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 (Prabhakaran and Subramanian, 2004), (Prabhakaran and Subramanian, 2003), (Hosseini and Hosseini-Bandegharari, 2009), (Hosseini *et al.*,

2009), (Hosseini-Bandegharari *et al.*, 2010), (Hosseini and Hosseini-Bandegharari, 2010), (Hosseini *et al.*, 2009). For these reasons, impregnated resins are used in two last decades for separation and pre concentration of metal ions. At the present study, chelating agent of 1, 4-diaminoantraquinone is used for impregnation in/on Amberlite XAD-16 granules. The prepared impregnated was used for separation and pre concentration of Pb(II) from co-existing ions in water samples.

## Materials and methods

### Material and apparatus

All the materials used, were of analytical grad and supplied by E.Merk, Darmstadt, Germany. Stock solution of Pb(II) ion was prepared at concentration of  $1.0 \times 10^{-3} \text{M}$  by dissolving the appropriate amounts of its nitrate salt in 1M  $\text{HNO}_3$  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.

FTIR spectra were obtained using AVATAR370-FTIR Thermo Nicolet in the  $4000\text{-}400 \text{ cm}^{-1}$  range using KBr discs

*Preparation of SIR*

2.0 g of the chelating agent (DAAQ) was located into a 50 mL stopper flask containing 30 mL 1, 2-dichloroethane and mixed for a few minutes to disperse into the solvent. After that, 3.0 g of the amberlit resin was added to the mixture and shaken for 48 h. After separation of impregnated resin beads with a porous filter, they were rinsed with aliquots of distilled water and 6M HCL until the filtrate solution did not show absorbance against distilled water.

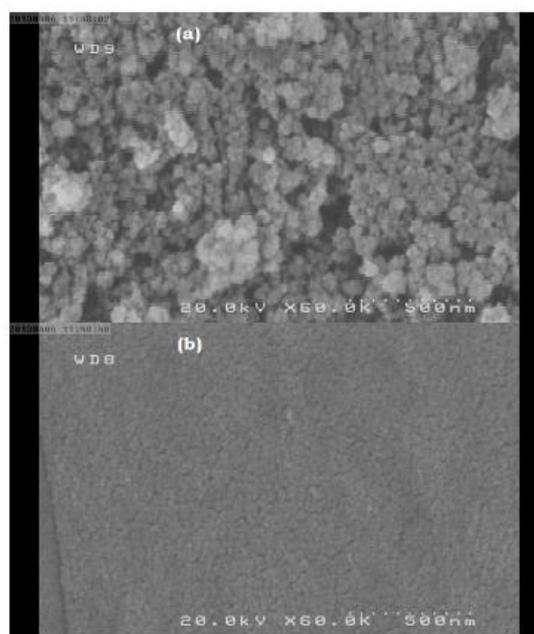
*The determination procedure*

100-mL of sample solution was passed through a short column packed with 0.7 g of the SIR at the optimum flow rate. Before passing the solutions, their pH and ionic strength were adjusted to desired value. after elution of column with 15 mL of distilled water for removing free concomitant, then the adsorbed Pb(II) content was desorbed by 5 mL 2M HCL. The elfluent was subjected to the FAAS for the Pb(II) determination.

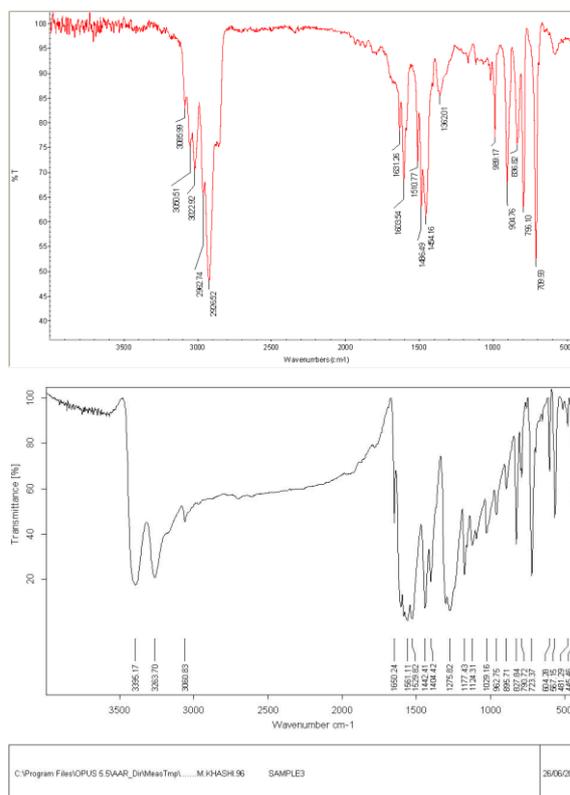
**Results and discussion**

*Characterization of the prepared SIR*

Amberlit XAD-16 resin is an adsorbent based on polystyrene divinyl benzene copolymer. It has excellent physical properties such as thermal and mechanical stability, hydraulic characteristic, high porosity, low polarity and it has the largest surface area (825m<sup>2</sup>g<sup>-1</sup>) among the XAD series of Amberlit resins. Thus, it was selected as an appropriate adsorbent for impregnation with DAAQ. 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 agent during the impregnation process. Furthermore, comparison of the FTIR spectra related to the resin before and after the impregnation reveals presence of -NH<sub>2</sub> and -C=O groups on the surface, which confirms adsorption of the chelating agent on the resin beads surface. (Fig.2)



**Fig. 1.** SEM micrographs of polymeric support samples; (a): Amberlite XAD-16, (b) conventional SIR containing DAAQ.



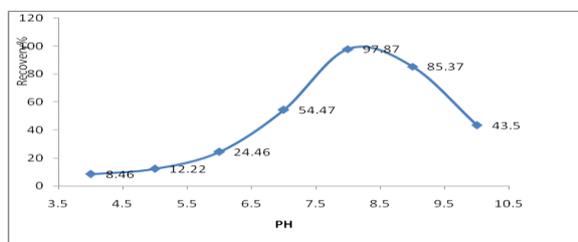
**Fig. 2.** IR spectra of polymeric support samples (a): Amberlite XAD-16, (b): conventional SIR containing DAAQ.

*Effect of pH on the sorption process*

For study the effect of pH on adsorption of Pb(II) ions by the resin beads, different solutions within the pH range of 2-10 was prepared while the other factors were fixed.

*The experiment was carried out as follows*

Aliquots of 100 mL solution containing  $10^{-6}$  M Pb(II) were passed through the column with sample flow rate of 1ml/min. the elution was carried out using 5 mL 2M HCl. As shown in Fig.3, the extraction efficiency increases by addition of pH from 2-8. Low efficiency at the upper pH is probably related to either precipitation or complexation of the metal ion as hydroxyl compounds.



**Fig. 3.** Effect of pH on the extraction of Pb(II).

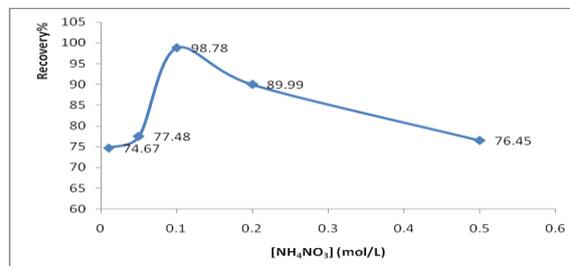
*Effect of ionic strength of solution on the sorption process*

For investigation of this factor, addition of ammonium nitrate to the solution up to the concentration of 1M was carried out. Fig.4 indicates that the recovery factor decreases at the ionic strength value greater than 0.1M. Thus, 0.1 M concentration of  $NH_4NO_3$  was selected for the future experiments. This phenomenon is corresponding to salting in and out effects.

*Desorption studies and stability tests*

From the reusability point of view, the solvent impregnated resin must be stable in various cycle of usage and the adsorbed metal ion should be easily desorbed without destroying the SIR under the operation conditions. To find the convenient eluent for desorption of Pb(II) ion from the SIR, various types of acid solutions including nitric, and hydrochloric acid were examined at different concentration values. The results showed that using

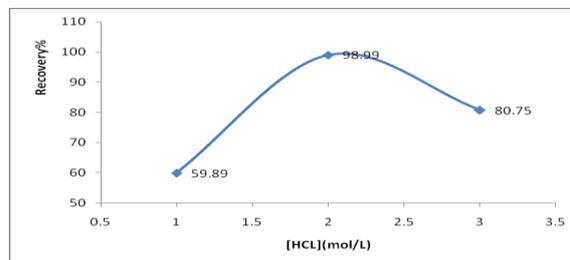
of concentrated nitric acids (more than 4M) as eluent, caused the SIR to be slowly oxidized and diminish the reusability. But, SIR showed a considerable stability in wide concentration range of HCl at a 40-50 cycle usage. Thus hydrochloric acid was selected as eluent.



**Fig. 4.** Effect of ionic strength on the extraction of Pb(II).

*Effect of eluent concentration on the sorption process*

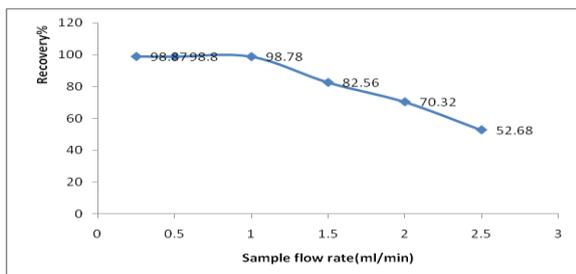
This factor was investigated using HCl within the concentration range 1-3M. The results are present in Fig. 5. As it is shown, by increasing of eluent concentration, efficiency increases. But at concentration greater than 2M, the recovery is decreased, which is probably related to the formation of chloride precipitant.



**Fig. 5.** Effect of eluent concentration on the extraction of Pb(II).

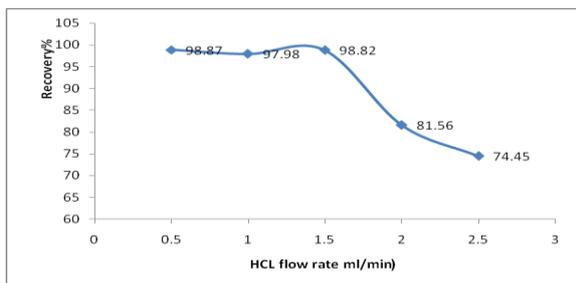
*Sample and eluent flow rates and volumes*

This study was carried out with change of sample and eluent flow rates in the range of 0.3 – 3 and 1– 3 mL  $min^{-1}$  respectively and determination of recovery factor using 100 mL of solutions containing  $1.0 \times 10^{-6}$  M Pb(II). When the influences of flow rates of sample were examined, the eluent flow rate was kept constant at 0.5 mL  $min^{-1}$  and also the flow rate of sample was kept at 1 mL  $min^{-1}$ , when the effects of flow rates of the eluent were examined. As shown in Fig. 6, the recovery factor for extraction of Pb(II) is decreased at flow rates above 1 mL  $min^{-1}$ .



**Fig. 6.** Effect of sample flow rate on the extraction of Pb(II).

According to the previous investigation, HCl is the most suitable agent for the quantitative elution of metal ions [16]. Hence, HCl at various concentrations, volumes and flow rates was examined. The experiments showed that Pb(II) ions can be thoroughly eluted from the columns using 5 mL of 2 M HCl. As detailed in Fig. 6, the optimized elution of Pb(II) could be carried out at the flow rates of 1.5 mL min<sup>-1</sup> in treatment with this SIR (Fig. 7).



**Fig. 7.** Effect of eluent flow rate on the extraction of Pb(II).

The effect of sample volume was investigated as follows

The experiment was carried out similarly with different volumes of the sample solution in the range of 50-700 ml, while amount of Pb(II) ions were fixed (1×10<sup>-7</sup> mol). It was found that the reproducibility was improved by increasing the volumes up to 500 ml and diminished afterward. Hence, to obtain an appropriate preconcentration factor, the process was carried out using aliquots of 500-mL of water sample. With regards of the eluent volume, a preconcentration factor of 100 was obtained through the extraction process.

*Effect of matrix ions interference*

For the investigation of interfering effects of some foreign cations and anions that there were in the sample, determination process was carried out as follows:

100 ml solution of Pb (II) ion with concentration 10<sup>-6</sup>M was prepared while different amounts of foreign ions was added to it and then the recommended procedure was followed. The tolerance limit was defined as the highest amount of foreign ion that produced an error not exceeding 5% in the determination of metal ion of interest. The results are summarized in Table 1. As it is shown, no one of the examined ions is interfered.

**Table 1.** Tolerance ratio of foreign ions on the determination of 10<sup>-6</sup>M pb(II) in aliquots of 500ml of the solution.

Co-existing ions	tolerance ratio (molmol <sup>-1</sup> )
K <sup>+</sup> , Na <sup>+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup> , Cl <sup>-</sup> , I <sup>-</sup> , CrO <sub>4</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup>	5000
Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Mn <sup>2+</sup> , NO <sub>3</sub> <sup>-</sup>	500
Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup>	100

*Analytical figures of merit*

Considering the extraction process, the following linear regression equation was obtained for the

determination of the Pb(II) ions over the dynamic range of 0.2-10ppm under the optimum conditions: A= 2.5682 ×10<sup>+6</sup> C+ 0.0026; r<sup>2</sup>= 0.9985 ; where A is

the absorbance, C is the molar concentration and  $r^2$  is the correlation coefficient. The RSD obtained for  $1 \times 10^{-6}$  M of Pb(II) was 2.3% (n=7) and The limits of detection (LOD) corresponding to three times of the standard deviation of the blank divided to the slop of calibration curve (n=5) was found to be  $1.8 \times 10^{-9}$  M.

*Analysis of real samples*

For investigation of reliability of method, the proposed method was applied to determine Pb(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 500-mL aliquots of the samples analyzed with proposed method. The accuracy of the measurements was investigated using the spiked amounts of Pb(II) ions to the water samples at several concentrations.

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.

**Table 2.** Determination of Pb(II) in natural water samples at the conditions that 250 mL of the sample was examined according to the proposed method.

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

**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 40-50 cycle without any lowering its sorption capacity. It is very useful in the measurement amount of Pb(II) at neutral water samples with the recovery factor higher than 90%.

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