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Separation and pre concentration of Co (II) from water samples with impregnated resin containing 1, 4-diaminoantraquinone

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Abstract

A new study for separation and pre concentration of Co(II) in water samples was done using adsorbant solid phase containing amberlit resin XAD-16 that impregnated with ligand; 1,4-diamino antraquinone. The solid phase was packed into mini column (10cm length and 5mm diameter) and water sample containing Co (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 manner, the recovery obtained was quantitative (95%) and LOD (3Sb/m), RSD were obtained 1.2×10^{-9} M, 3.2% respectively.

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Introduction

Cobalt is an essential trace element present in most body tissues, with the highest concentrations typically found in the liver. It is a component of vitamin B_{12} (cyanocobalamin), which is involved in the production of the blood red cells and the prevention of pernicious anemia (Underwood, 1977), (Seiler *et al.*, 1994). Cobalt toxicity is quite low compared to many other metals. However high exposure to this element can cause several health problems such as asthma and skin irritation (McKenzie and Smythe, 1988), (Belitz and Grosch, 1987). Therefore, quantitative determination of cobalt at low concentrations plays an important role in different fields such as environmental analysis, process control and medicine. Due to insufficient data, the allowed concentration level of cobalt in drink water has not been reported but in fresh water for aquatic life, the recommended maximum Concentration of total cobalt is 110 $\mu g\ L^{-1}$. The concentrations of cobalt in drinking water are generally in the range of 0.1–5.0 $\mu g\ L^{-1}$(Rojas *et al.*, 2012).

There are several methods for the determination of cobalt ions. The two most frequently used methods are flame atomic absorption spectrometry and electro thermal atomic absorption spectrometry (Cai *et al.*, 2002), (Cerutti *et al.*, 2003). However, to decrease the detection limit of these methods, usually pre-concentration methods, such as liquid and solid phase extraction (Praveen *et al.*, 2005), cloud point extraction (Citak and Tuzen, 2010), (Ghaedi *et al.*, 2008), adsorption (Agarwal and Mathur, 2001), *etc.*, are used.

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, 2011).

In this work we have used from amberlit resin XAD-16 impregnated with chelating agent 1,4-diaminoantraquinone as adsorbent solid phase that packed in mini column. Adsorbent process was done after passing analytical sample through the column and then elution done via Hcl as elution. Finally determination was done using atomic absorption spectrometer.

Experimental

Material and apparatus

All the materials used, were of analytical grad and supplied by E.Merk, Darmstadt, Germany. Stock solution of Co (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 (1,4-dihydroxy antra quinine) 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 $Co^{2+}$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 Co (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 ($825 m^2g^{-1}$) 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

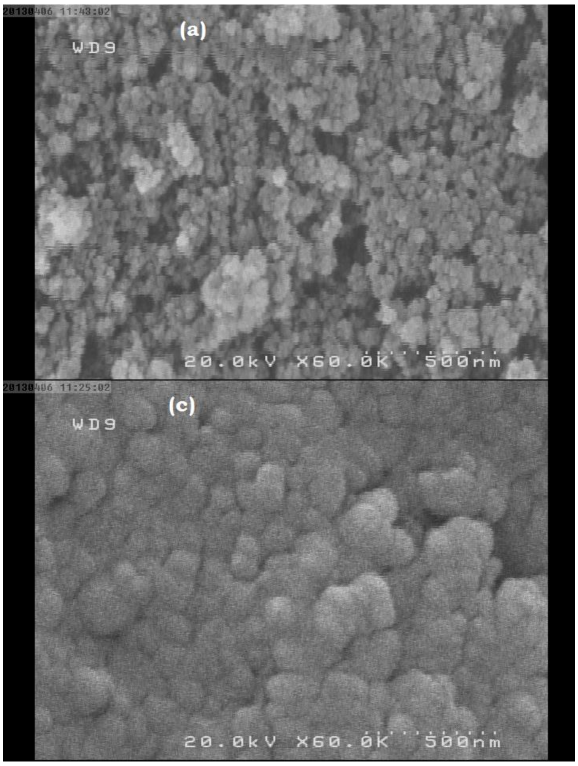

Fig. 1. SEM micrographs of polymeric support samples; (a): Amberlite XAD-16, (b): SIR containing DAAQ.

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

For study of this parameter, various buffer solutions of Co (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 Co (II) with hydroxyl group (Fig.2.).

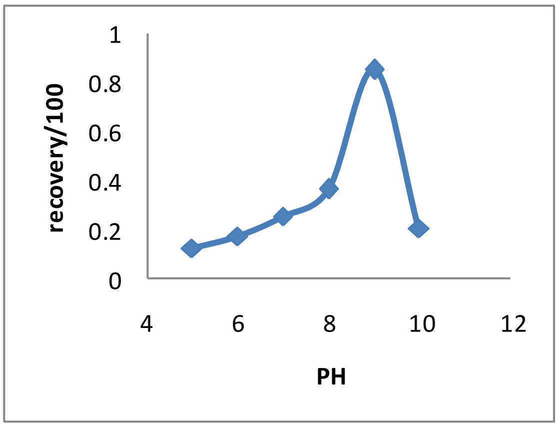

Fig. 2. effect of PH on Co (II) extraction.

Effect of sample flow rate on extraction process

A series buffer solutions co^{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 4ml/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.).

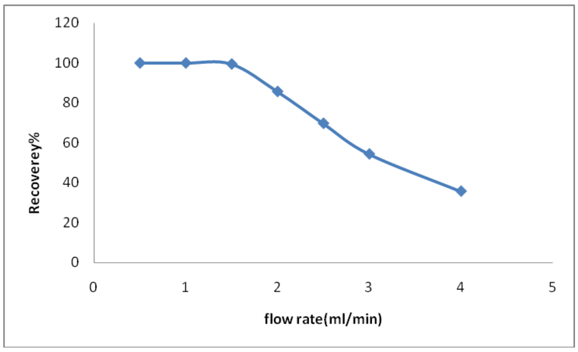

Fig. 3. Effect of sample flow rate on extraction process.

Effect of ionic strength on extraction of Co (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 0.05-0.5mol/L. Absorbance data show that with increasing of NH_4NO_3 concentration to 0.05M, recovery increases. After that, decreasing in recovery factor is probably due to salting effect (Fig. 4).

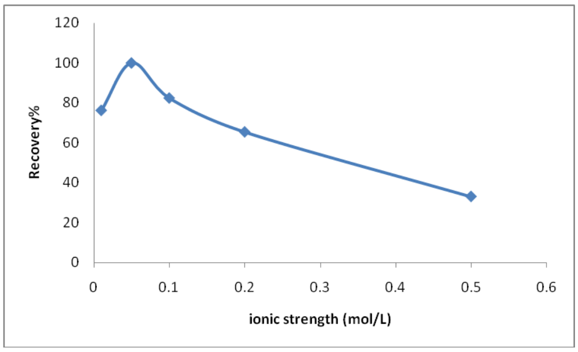

Fig. 4. effect of ionic strength on Co (II) extraction.

Effect of sample volume on the recovery

To evaluate the effect of sample volume on the sorption procedure, various samples of Co(II) that bufferized at PH=9 and were containing 0.05 M NH_4NO_3 , prepared that in all of them, mmol of Co(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.

Analytical application

In treatments with aliquots of 250 ml of the solutions, Co (II) contents was extracted with the SIR with chelating agents (i.e. 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 .

Co (II): $A= 3.537C\times 10^{+6}+ 0.0186$ $R^2=0.9899$

Where A is the absorbance, C is the molar concentration of Co (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 Co (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 Co (II) ions to the water samples at several concentrations.

The obtained results are summarized in Table 1. As observed from the results, the recoveries for the spiked sample solutions were in the range 97.76%–103.16%, which confirmed satisfactorily applicability of the proposed method for complicated environmental samples.

Table 1. Determination of Co (II) in water samples.

concentration of Co (II), ng.ml^{-1}		
added (ml)	**found**	**recovery%**
0	18	-
20	39.2	103.16
40	56.7	97.76
60	77.8	98.82
80	99.1	101.12

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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