Note**Pre-concentration Study of Pb(II) and Cd(II) from Aqueous Solution Using Silica Gel Loaded with Dithizone**

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Abstract

Pre-concentration of Pb(II) and Cd(II) from aqueous solution on silica gel loaded with dithizone has been studied. Several parameters influencing the desorption of the adsorbed Pb(II) and Cd(II) on the surface of adsorbent were optimized and the calibration curve was constructed for the determination of Pb(II) and Cd(II) in synthetic samples using AAS. Results show that the adsorbent can effectively pre-concentrate the two metals with the recovery $\geq 90\%$ using HCl of 5 M as eluent.

Key words: pre-concentration, lead, cadmium, silica gel, dithizone

1 Introduction

Increasing environmental pollution by lead (Pb), cadmium (Cd), mercury (Hg) and other toxic metals has increased the demand for sensitive and precise quantitative analysis for heavy metals in various samples[1]. Due to the low level found in many various samples, direct determination of these metals requires mostly an initial and efficient pre-concentration step. This step can be performed simply in many ways including liquid and solid phase extraction techniques [2]. The selective solid-phase extractors are those derived from the immobilization of the organic ligand such as dithizone on the surface of solid supports. Silica gel is the most widely used solid support due to the well documented thermal, chemical, and mechanical stability compared to other organic and inorganic solid supports [3]. This paper describes briefly the application of silica gel loaded with dithizone for solid phase pre-concentration of Pb(II) and Cd(II) from aqueous and natural water samples.

2 Experimental

Cd(II) ($3 \mu\text{g mL}^{-1}$) and Pb(II) ($6 \mu\text{g mL}^{-1}$) solutions of 20 mL was passed over the column packed with dithizone-loaded silica gel prepared analog to previous report [3]. The flow rate was adjusted to 0.5 mL/min for Cd(II) and 1.0 mL/min for Pb(II). The adsorbed Cd(II) and Pb(II) ions were desorbed using strong acids. The filtrate (from adsorption process) and eluents (from desorption step) were collected and then subjected to AAS for metal analysis. To obtain optimum condition, some parameters including weight of adsorbent and type, concentration and volume of eluent were optimized. For pre-concentration study, 80 mL of tap water spiked with various concentration of corresponding metal were passed over the column and treated as described above.

3 Results and Discussion

This study was conducted in order to evaluate the potential application of silica gel loaded with dithizone for pre-concentration of trace level of Pb(II) and Cd(II). Some parameters influencing pre-concentration

efficiency such as adsorbent weight, type, concentration and volume of eluent (for desorption process) were examined and the results are presented in Fig. 1 and 2 as well as Table 1.

Fig. 1 Effect of adsorbent weight on extraction efficiency

Fig. 2 Effect of type and concentration of eluent on the extraction efficiency of Cd(II) ions

It is clearly observed that optimum pre-concentration efficiency is obtained when 0.3 g and 0.2 g adsorbents are respectively used. Increasing adsorbent weight results in the decrease in pre-concentration efficiency, probably due to the longer column which must be used, causing the desorbed metals are re-adsorbed by the lower column packing. Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions including HCl and H₂SO₄. Figure 2 gives the effect of type and concentration of eluent on the efficiency of Cd(II) pre-concentration. The same trend is also observed for Pb(II) ion (Figure is not shown). In general, HCl gives better efficiency than H₂SO₄ does. This probably due to the solubility of the salts formed during the desorption process, i.e. CdSO₄ and PbSO₄ versus CdCl₂ and PbCl₂. The sulfate salts of Pb(II) and Cd(II) are less soluble in water than their corresponding chloride salts [4]. When H₂SO₄ is used as eluent some of the desorbed metals are precipitated in the column packing as sulfate salts and can not be eluted.

Calibration curves for both metals after pre-concentration processes are linear in the range concentration of 0-1 $\mu\text{g mL}^{-1}$ for Cd(II) and 0-6 $\mu\text{g mL}^{-1}$ for Pb(II) with correlation coefficient (r) of 0.9908 and 0.9951, respectively. Table 1 collects the results of pre-concentration of 80 mL synthetic samples of tap water spiked with various concentrations of Pb(II) or Cd(II) on silica gel loaded with dithizone and eluted using 10 ml of HCl 5M. It is obvious that the pre-concentration results for both metal ions are satisfactory as indicated by high recovery percentage ($\geq 90\%$), which are comparable to those previously reported using dithizone-achored poly(EGDMA-HEMA) microbeads, e.g. in the range 89-98% [5]. Moreover, the pre-concentration factor can be further increased by simply increasing the sample volume, suggesting that the sensitivity of the method can be enhanced in accordance with Cd(II) and Pb(II) levels in the environment.

Table 1 Pre-concentration of Pb(II) and Cd(II) from synthetic samples of tap water spiked with both metals

Pb(II) spiked/ $\mu\text{g mL}^{-1}$	Pb(II) found / $\mu\text{g mL}^{-1}$ (%)	Cd(II) added / $\mu\text{g mL}^{-1}$	Cd(II) found / $\mu\text{g mL}^{-1}$ (%)
0.5	0.52 (104)	0.05	0.049 (98)
0.7	0.66 (94)	0.10	0.098 (98)
1.0	0.96 (96)	0.15	0.132 (88)
1.5	1.38 (92)	0.20	0.193 (97)

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