

Preparation of L-cysteine Salicylaldehyde Schiff-base Modified Macroporous Polystyrene Resin and Its Application to Determination of Trace Cadmium and Lead in Environmental Water Samples

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(Received August 29, 2013; Revised January 16, 2014; Accepted July 18, 2014)

ABSTRACT

In this work, a new method that utilizes L-cysteine salicylaldehyde Schiff-base modified macroporous polystyrene resin (PS-CSC) as an effective sorbent has been developed for preconcentration of trace cadmium and lead in environmental water samples. The effect of pH, the contact time, the elution conditions, the flow rate, the initial concentration of target metal ions, and the effects of interfering ions on the preconcentration of the analytes were investigated. The maximum adsorption capacity of PS-CSC under optimum conditions for cadmium and lead were found to be 6.03 - 18.17 mg/g and 12.58 - 36.13 mg/g when the initial concentration of metal ions between 5.0 - 90 mg/L. The limits of detection for cadmium and lead were 2.46 ng/L and 0.52 µg/L, with a preconcentration factor of 200. The developed method has been validated by analyzing certified reference material and successfully applied for the enrichment and determination of trace cadmium and lead from environmental water samples.

Key words : L-cysteine salicylaldehyde Schiff-base, Macroporous polystyrene resin, Cadmium, Lead, Preconcentration

1. Introduction

Cadmium and lead have been well recognized for their negative effects on the environment. Both of these heavy metal ions can accumulate readily in living systems, and this accumulation can have adverse effects on metabolic processes.¹⁻²⁾ Flame atomic adsorption spectrometric (FAAS) analysis is one of the most popular techniques for determination of the presence of these heavy metal ions because of its high specificity and low cost. However, process sensitivity is usually insufficient for the determination of trace metal ions in environmental samples.³⁾ Due to the complexity of the sample matrix and low concentrations of cadmium and lead found in environmental water samples,³⁻⁵⁾ an efficient preconcentration step before level determination is required.⁶⁾ Several methods, such as co-precipitation,^{7,8)} liquid-liquid extraction,^{9,10)} cloud point extraction^{11,12)} and solid phase extraction^{6,13)} have been used for the enrichment of trace cadmium and lead from environmental samples before sample analysis using flame atomic absorption

spectrometry techniques. For its exhibited simplicity, its flexibility in allowing an analysis of the solid phase, its high preconcentration factor, and its low cost and extraction time for sample preparation, the solid phase extraction approach has gained rapid acceptance.³⁾ Macroporous polystyrene resin is a frequently used resin in such solid phase preconcentration procedures, due to its good physical and chemical properties such as porosity area, high surface area, durability, and easy modification.¹⁴⁾ In the present paper, a new chelating solid phase extractant on the base of a macroporous polystyrene resin chemically modified with L-cysteine salicylaldehyde Schiff-base (PS-CSC) was synthesized and a simple solid phase extraction procedure was developed for simultaneous preconcentration of trace cadmium and lead in environmental samples.

2 Experimental Procedure

2.1. Apparatus

A flame atomic absorption spectrometer from the Beijing Rayleigh Analytical Instrumentation Corporation (model WFX-1E2, Beijing, China), equipped with an air-acetylene flame and lead and cadmium hollow cathode lamps was used for metal ion analysis. The pH measurements were conducted using a PHS-2C pH-meter (Dazhong Instrumentation Corp., Limited, Shanghai, China). Infrared measurements were performed using a model WQF-300 spectrometer (Beijing, China) and KBr pellets.

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2.2. Reagents

The macroporous polystyrene resin was X-5 resin (Chemical Industrial Company affiliated with Nankai University, Tianjin, China). L-cysteine and salicylaldehyde was purchased from Shanghai Chemical Reagent Corporation, China. The stock solutions of metal ions (1.0 g/L) were prepared from analytical corresponding reagent grade metal salts in nitric acid, hydrochloric acid, or sulfuric acid by dissolving the appropriate amounts in distilled water. All working solutions were diluted according to experimental requirements. Dilute HNO_3 and NaOH were used for pH adjustment. All chemicals used were of analytical reagent grade.

2.3. Preparation of PS-CSC

L-cysteine salicylaldehyde Schiff-base was synthesized according to the process detailed in the literature.¹⁵⁾ Macroporous polystyrene resin was nitrated, aminated, diazotized and then coupled with L-cysteine salicylaldehyde Schiff-base at 0 - 5°C to prepare the adsorbent.¹⁶⁾ The resulting reddish brown beads were filtered, water washed to neutral pH, and finally vacuum dried for further use.

2.4. Batch experiments

PS-CSC (0.1 g) was equilibrated with a suitable amount of metal ion solution at a certain pH in a glass stoppered bottle (250 mL) for a fixed period of time; the unextracted metal ion in the solution phase was measured using FAAS. This method was used to investigate the effect of shaking time and the maximum adsorption capacities of cadmium and lead on PS-CSC.

2.5. Column experiments

PS-CSC (2.0 g) was packed in a glass tube (200 mm × 10 mm i.d.) and a solution containing metal ions was adjusted to a suitable pH and percolated at a certain flow rate. The metal ions retained on the column were eluted with a suitable eluent and that determined using FAAS.

2.6. Samples and sample preparation

0.500 g of aquatic sediment reference material (GBW 07350) was added to a closed polytetrafluoroethylene beaker. Then, 7, 4, and 4 mL of concentrated HNO_3 , HClO_4 , and HF were added, respectively. The mixture was heated at 368 K for 12 h and evaporated nearly to dryness. After cooling, the residue was dissolved to 50 mL of 1.0 mol L⁻¹ HCl , and the solution was filtered. The environmental water samples were collected from Shiwuli River, Yi Lake, and Dongpu Reservoir (Hefei, Anhui, China), and then acidified with 2% HNO_3 and filtered with a 0.45 μm filter; the filtrate was stored in glass bottles. The samples were analyzed within 3 days of collection.

3. Results and Discussion

3.1. FTIR analysis of PS-CSC

The proposed structure of PS-CSC is shown in Fig. 1; it

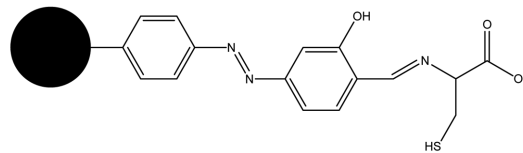


Fig. 1. Proposed structure of PS-CSC.

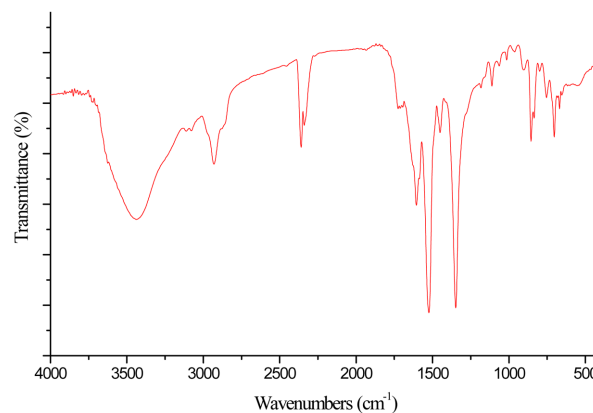


Fig. 2. FTIR of PS-CSC.

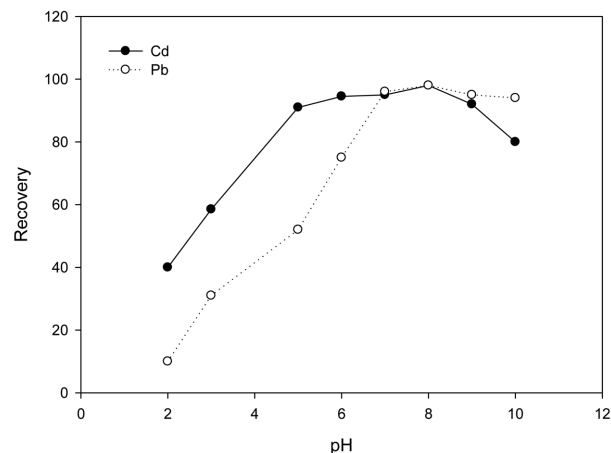


Fig. 3. Effect of pH.

was characterized by FTIR analysis. Fig. 2 shows the FTIR spectrum of PS-CSC. The broad spectral band at 3400 cm^{-1} was found to correspond to OH- and NH- vibrations. The strong band at 2926 cm^{-1} is CH-vibration. The bands that appeared at 1609 and 1449 cm^{-1} were contributed by C = N and -N = N- stretching, respectively. These results show that L-cysteine salicylaldehyde Schiff-base had been grafted onto the surface of macroporous polystyrene resin after modification.

3.2. Effect of pH

The adsorption levels of cadmium and lead on PS-CSC in aqueous solutions with different pH values were examined by column experiment. Sorption and desorption flow rate was fixed at 2.0 mL/min. The extracted metal ions were eluted using 15 mL of HCl (6.0 mol/L) and determination by

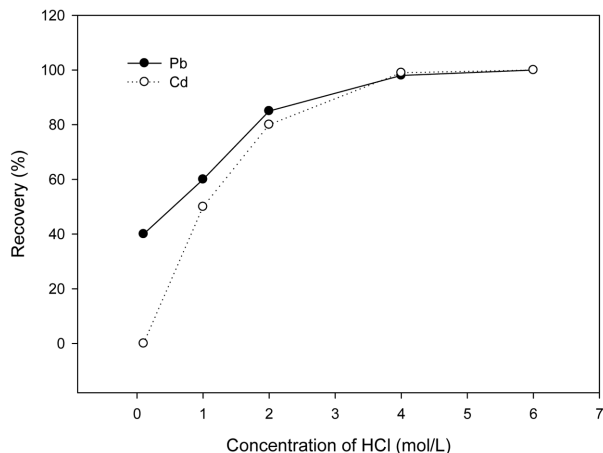


Fig. 4. Effect of concentration of HCl on the recovery of cadmium and lead.

FAAS gave the percentages of recovery of the eluted metal ions at various pH values (Fig. 3). Retention experiments were carried out in triplicate to determine the precision of the method. It was found that the retention behavior for both metal ions varies significantly with the changes of pH. The optimum adsorption pH ranges are 5.0 - 8.0 and 7.0 - 10.0 for cadmium and lead (Recovery > 95%), respectively. The adsorbed metal ions cannot be desorbed by distilled water, and therefore the chelating process can be seen to contribute predominantly to the retention of these heavy metal ions. Therefore, pH 7.0 was chosen for the preconcentration of cadmium and lead in the following experiments.

3.3. Effect of eluent

The effects of different organic and inorganic acids, such as HCl, HNO₃, EDTA, and citric acid, on the desorption of cadmium and lead from the column were determined at different concentrations using 15 mL volumes of various eluents. The results show that the use of an organic acid such as EDTA or citric acid does not give quantitative results (Recovery > 95%). It was possible to quantitatively desorb the analyte with HCl and HNO₃. The different concentrations of HCl for the recovery of both metal ions (Fig. 4) revealed that at least 4 mol/L HCl can lead to quantitative desorption. The more concentrated HCl solutions did not change the elution yield or elution kinetics.

3.4. Effect of flow rate

Figure 5 shows the effect of flow rate on the retention of cadmium and lead on PS-CSC. The optimum flow rates (Recovery > 95%) for cadmium and lead extraction were less than 2.0 and 4.0 mL/min, respectively. To avoid a tedious extraction process, the flow rate of less than 1.0 mL/min was not employed. For the desorption process, both metal ions can be desorbed quantitatively at a flow rate of 1.0 - 2.0 mL/min. Above 2.0 mL/min, the recovery levels for both heavy metal ions were less than 90%. The flow rate was maintained at 2.0 mL/min throughout the column experiment.

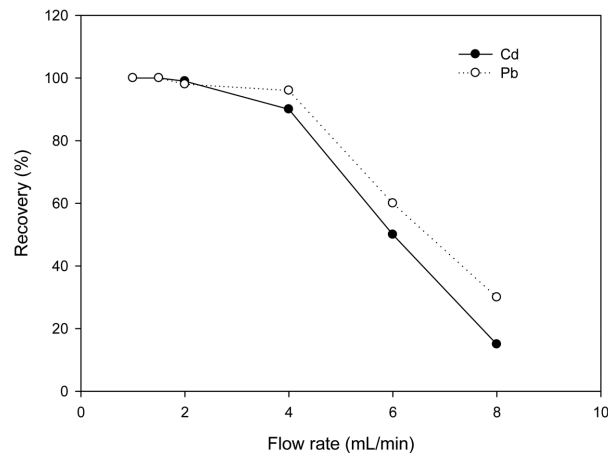


Fig. 5. Effect of retention flow rate on the recovery of cadmium and lead.

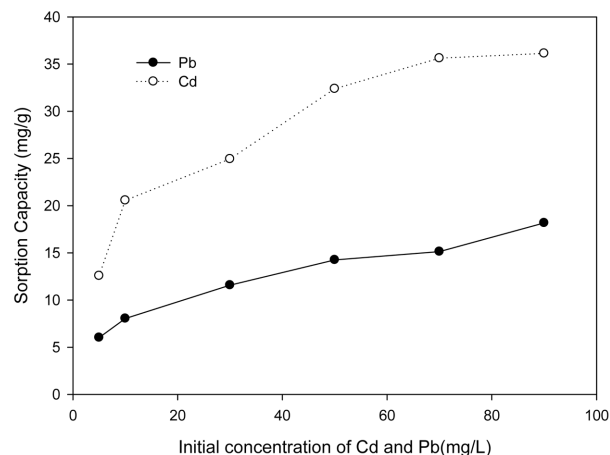


Fig. 6. Effect of initial concentration of cadmium and lead.

3.5. Effect of initial concentration

The adsorption levels of cadmium and lead on PS-CSC in aqueous solutions with different initial concentrations were examined using a batch experiment. It was found that the adsorption of cadmium and lead onto PS-CSC was strongly dependent on initial metal ion concentration (Fig. 6). The adsorption capacity of cadmium and lead on PS-CSC was found to increase dramatically with increasing of the initial concentration (5 - 50 mg/L), and then to increase slowly at high concentrations (50 - 90 mg/L). This can be explained by the saturation of the surface sites of PS-CSC. The sorption capacity values for cadmium and lead were found to be 6.03-18.17 mg/g and 12.58 - 36.13 mg/g when the initial concentration was between 5.0 - 90 mg/L under the optimum conditions. This is satisfactory for the trace analysis of both heavy metals in aqueous solutions.

3.6. Sorption kinetics

PS-CSC (0.1 g) was equilibrated by shaking with 200 mL of a solution containing 50 mg/L of cadmium and lead for different time intervals (2, 7, 10, 20, 30, 40, 50, 60, and 100 min) and the recommended batch experiment was

applied. The profile of sorption capacity for both heavy metal ions as a function of time is shown in Fig. 7. It is notable that the recovery levels of cadmium and lead can reach 80% in 15 min. The fast extraction rate indicates that PS-CSC is a reliable adsorbent for the preconcentration of trace cadmium and lead from aqueous solutions.

3.7. Interference studies

The effects of coexisting ions, such as K(I), Na(I), Ca(II), and Mg(II) on the preconcentration of cadmium and lead were studied using a column experiment. The tolerance limits of the coexisting ions were defined as the maximum concentration of the foreign substances that could cause an approximately $\pm 5\%$ relative error in the determination. The tolerance limits for the heavy metal ions were found to be 2.0 mol/L for Na(I) and K(I), and 0.8 mol/L for Ca(II) and Mg(II). These results show that the presence of a solid phase matrix might be used to enrich cadmium and lead from environmental water samples, as the common constituents at normal levels do not adversely affect the adsorption efficiency of the matrix. The reusability of the present

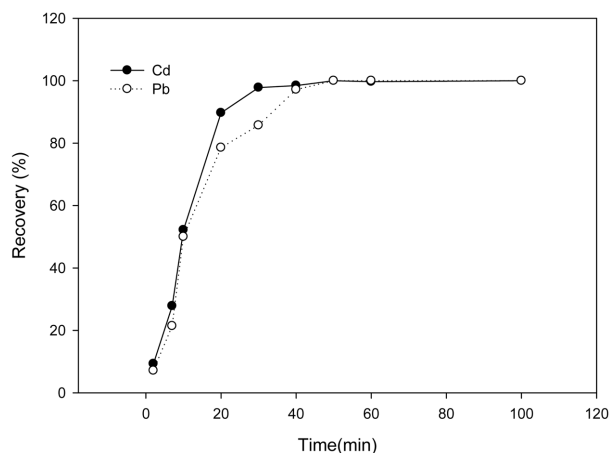


Fig. 7. Effect of contact time.

matrix was examined after several loading and elution cycles. Trace amounts of cadmium and lead in environmental water samples can be quantitatively retained after 20 repeated uses and the sorption recovery can reach 96.80%.

3.8. Analytical performance

The analytical performance of the method was examined by column experiment. The limits of detection (LODs) of cadmium and lead were below 2.46 ng/L and 0.52 $\mu\text{g/L}$, respectively (calculated as 3 times the standard deviation of 11 replicate runs of procedure blanks). The relative standard deviation of the methods for cadmium and lead were 3.55% and 5.27%, demonstrating good method precision. The maximum preconcentration factor for both heavy metal ions was 200.

To confirm the reliability of the method for the analysis of trace cadmium and lead in environmental samples, an aquatic Sediment reference material (GBW 07350, China) was used for method validation. Under optimum experimental conditions, the determined concentrations of cadmium and lead were $0.40 \pm 0.10 \mu\text{g/g}$ and $28.2 \pm 3.5 \mu\text{g/g}$, respectively (certified value: Cd $0.46 \pm 0.05 \mu\text{g/g}$; Pb $28.5 \pm 2.9 \mu\text{g/g}$). Good agreement was obtained between the content estimated using the proposed method and the certified values for both metal ions. The results also indicate that the developed enrichment method for cadmium and lead are not affected by potential interference factors in real environmental samples.

3.9. Analysis of environmental water samples

Under optimum conditions, natural water samples (1000 mL) were passed through the column for preconcentration and direct determination of both the target metal ions. Satisfactory results are shown in Table 1. The method developed in the present paper for preconcentration and determination of trace amounts of cadmium and lead in environmental water samples has been proved to be reliable.

Table 1. Determination of Cadmium and Lead in Environmental Water Samples

Samples	Metal ions	Added ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)	Recovery (%)	
Shiwuli River	Cd	0.00	3.76	-	
		5.00	8.60	96.80	
	Pb	0.00	10.08	-	
		5.00	14.82	94.80	
Dongpu Reservoir	Cd	0.00	2.19	-	
		5.00	7.64	109.00	
	Pb	0.00	8.33	-	
		5.00	13.18	97.00	
	Yi Lake	Cd	0.00	14.96	-
			5.00	19.74	95.60
Pb		0	35.30	-	
		5.00	40.65	107.00	

4. Conclusion

The present study focused on the development of a new method to enrich trace cadmium and lead in environmental water samples using a novel PS-CSC adsorbent. The results demonstrate the feasibility of using PS-CSC adsorbent for preconcentration of cadmium and lead from aqueous solutions. The adsorption efficiency of cadmium and lead are pH, time, and elution condition dependent. This enrichment method shows fast metal sorption kinetics and high adsorption efficiency. The maximum adsorption capacities of cadmium and lead on PS-CSC sorbent are 6.03-18.17 mg/g and 12.58 - 36.13 mg/g when the initial concentration of metal ions is between 5.0 - 90 mg/L; the optimal pH values for quantitative sorption were 5.0 - 8.0 and 7.0 - 10.0 for cadmium and lead, respectively. These results indicate that the present method is accurate and precise. On the basis of the results obtained in this study, we believe that PS-CSC sorbent can be used for sorption of trace amounts of cadmium and lead from environmental water samples.

Acknowledgment

This work was jointly supported by the National Natural Science Foundation of China (21107001), the National Science and Technology Support Project of China (2011BAJ03B04), The China Postdoctoral Science Foundation (2013M541842), the Natural Science Fund of Education Department of Anhui Province (KJ2013Z034), and the Doctor Foundation of Anhui Jianzhu University (2012).

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