Coal Cinder Separation/Preconcentration of Trace Cu, Pb, and Cd in Environmental Water Samples and Determination by Flame Atomic Absorption Spectrometry

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INTRODUCTION

Water is a vital element for the survival of all living organisms, and its quality has a direct influence on their development. Water pollution caused by heavy metals, such as copper, lead, and cadmium, is of particular concern due to their toxicity to humans and other biological systems (1-4). Lead is one of many harmful elements to human health, usually causing fatigue, abdominal pain, joint pain, reproductive disorders, and anemia. Cadmium is listed as the sixth most poisonous substance jeopardizing human health and can result in renal disturbances, cancer, and hypertension. Although copper is an essential micronutrient for normal growth and development of humans and livestock, at high levels it can cause nausea, vomiting, diarrhea, liver damage, or even death. Many researchers have also reported heavy metal pollution of surface waters in different parts of the world (5-7). Hence, evaluation and removal of Cu, Pb, and Cd from environmental waters is of extreme importance.

A separation and preconcentration step is usually necessary prior to the determination of these metals owing to their low levels and the complex matrix. The most widely used techniques for separation and preconcentration of Cu, Pb, and Cd include ion exchange (8), coprecipitation (9,10), electrodeposition (11), membrane

ABSTRACT

Coal cinder was employed as a solid phase sorbent for the preconcentration and separation of trace Cu, Pb, and Cd ions in environmental water samples, followed by flame atomic absorption spectrometry determination.

The three analytes were adsorbed quantitatively by coal cinder at pH 5.0–5.5 for Cu and Pb, and 7.2 for Cd, then eluted completely with 0.5–1.0 mol L⁻¹ HNO₃. Using optimum conditions, the limits of detection were 0.6 µg L⁻¹ Cu, 4.9 µg L⁻¹ Pb, and 1.6 µg L⁻¹ Cd, with enrichment factors of 20–33.3, respectively. The relative standard deviations (RSD) were 0.72% Cu (n=9, C=0.05 µg mL⁻¹), 5.0% Pb (n=9, C=0.1 µg mL⁻¹), and 3.4% Cd (n=9, C=0.2 µg mL⁻¹).

The proposed method was applied to the determination of Cu, Pb, and Cd in environmental water samples with satisfactory results. In order to validate the developed procedure, a GSB 07-1182-2000 certified reference environmental water sample was analyzed, and the results were in good agreement with the certified values.

filtration (12), flotation (13), dispersive liquid-liquid microextraction (14), cloud point extraction (15), and solid-phase extraction (SPE) (16,17). Among these techniques, SPE has been frequently used for pharmaceutical (18), fine chemicals (19), biological medicine (20,21),

food and environmental analyses (22-24) due to its high efficiency, high reliability, high degree of automation, and low consumption characteristics. Materials used and derived from natural resources, such as nettle ash (25), palm shell (26), peanut shells (27), wood ash (28), and other natural materials (29-31), have been employed for the removal of heavy metals from environmental samples.

Coal cinder is a solid waste resulting from the coal burning process in all kinds of industrial and private boilers and furnaces. Since coal cinder has a porous structure, air penetrates into the coal during the burning process and escapes after cooling (32). In recent years, coal cinder has been used in wastewater treatment facilities and for industrial practices (33-35). Wang et al. (36) successfully used coal cinder for pre-processing and depth processing of industrial wastewater in place of active carbon. These facts reveal that coal cinder may be used as an inexpensive and good adsorption medium for extraction of heavy metals. However, to our knowledge no reports have been published on its application as an adsorbent for heavy metal ion extraction.

The aim of this work was to explore the possibility of using coal cinder as an adsorbent for the extraction of Cu, Pb, and Cd from environmental water samples, followed by flame atomic absorption spectrophotometry detection.

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EXPERIMENTAL

Instrumentation

Analyte determination was performed using a Model Shimadzu 6200 atomic absorption spectrometer (Kyoto, Japan) with deuterium lamp background correction. The operating conditions for Cu, Pb, and Cd are given in Table I.

A Model HL-2 peristaltic pump (Shanghai Qingpu Instrument Factory, P.R. China) and a self-made PTFE microcolumn (20 mm $\times$ 3.0 mm i.d.) were used for the separation and preconcentration process. A minimum length of PTFE tubing (i.d. 0.5 mm) was used for flow injection (FI).

The pH values were carefully measured with a PHS-3C pH meter (Shanghai Precision & Scientific Instrumental, Shanghai, P.R. China), supplied with a combined electrode.

Standard Solutions and Reagents

Stock standard solutions (1 mg mL⁻¹) of Cu, Pb, and Cd were prepared by dissolving CuSO₄·5H₂O, Pb(NO₃)₂, and CdCl₂·5H₂O (Beijing Hengyeyuan-zhong Chemical Reagent Corporation, Beijing, P.R. China) in 1% (v/v) H₂SO₄, 1% (v/v) HNO₃, and 1% (v/v) HNO₃, respectively. Working solutions were prepared by diluting the stock standards as necessary. All reagents used were of analytical reagent grade, and doubly distilled water was used throughout this study.

A series of Britton-Robison (B-R) buffer solutions containing phosphoric acid, acetic acid, and boric acid (Tianjin Kermel Chemical Reagents Development Center, Tianjin, P.R. China), each with a concentration of 0.04 mol L⁻¹, were used for pH adjustment.

TABLE I
FAAS Determination of Cu, Pb and Cd

Element	Wave-length	Lamp Current	Spectral Band Pass	Burner Height	Flow Rate of C ₂ H ₂	Flow Rate of Air
Cu	327.4 nm	6.0 mA	0.7 nm	8.0 mm	1.8 L/min	8.0 L/min
Pb	217.0 nm	5.0 mA	0.7 nm	8.0 mm	2.0 L/min	8.0 L/min
Cd	228.8 nm	5.0 mA	0.7 nm	8.0 mm	1.8 L/min	8.0 L/min

Pretreatment of Coal Cinder

The coal cinder of 130-160 mesh size (obtained from the boiler house of Hubei Normal University) was immersed in 4.0 mol L⁻¹ HCl and NaOH, each for 24 hours, respectively. Then it was filtered, washed with doubly distilled water until it became neutral, and dried prior to storage for later use.

Column Preparation

A total of 80.0 mg of coal cinder was filled into a PTFE micro-column (20 mm $\times$ 3.0 mm i.d.) and plugged with a small portion of skimmed cotton at both ends. The column was conditioned with B-R buffer solution.

Sample Preparation

Environmental water landfill leachate and pond water samples (Huangshi, P.R. China) were collected, filtered before analysis through a 0.45- μ m membrane filter (Shanghai Xingyajinghua Instrument Factory, Shanghai, P.R. China), and placed into polyethylene containers. Then the samples were acidified to the proper pH with 0.1 mol L⁻¹ HCl

and 0.1 mol L⁻¹ NaOH, then stored at 4 °C in a refrigerator for subsequent use.

General Procedure

Environmental water samples or standard solutions at the desired pH were passed through the coal cinder micro-column at a certain flow rate. The analyte trapped in the column was subsequently stripped with the optimum volume of the eluent, and analyzed by FAAS.

RESULTS AND DISCUSSION

Effect of pH

The pH value plays an important role with respect to extraction of Cu, Pb, and Cd by coal cinder. For this purpose, adsorption studies of Cu, Pb, and Cd were carried out at the pH range of 1.0–9.0. Figure 1 shows that quantitative adsorption ($\geq 90\%$) is obtained at the pH range of 5.0–9.0 for Cu, 4.0–5.5 for Pb, and 7.0–9.0 for Cd, respectively. Therefore, a pH of 5.2 for Cu and Pb, and 7.2 for Cd, was selected for this work.

Fig. 1. Effects of pH on the adsorption of 2.0 μ g mL⁻¹ Cu, Pb, and Cd on coal cinder.

Effect of Sample Flow Rate

Analyte retention on the adsorbent depends on the flow rate of the sample solution. In order to minimize the time required for sample processing, the effect of sample flow rate on coal cinder adsorption was examined at the range of 0.5–5.0 mL min⁻¹. The experimental results showed that quantitative adsorption of Cu, Pb, and Cd were always obtained at the flow rates of 0.5–5.0 mL min⁻¹. Hence, 2.5 mL min⁻¹ was employed as the optimum adsorption flow rate for the three analytes.

Effect of Elution Conditions

In order to quantitatively strip Cu, Pb, and Cd from coal cinder, HNO₃ was used as the eluent. Different concentrations of HNO₃ ranging from 0.1–2.0 mol L⁻¹ were studied. The experimental results indicated that quantitative recovery for the three analytes was obtained with 1.0–2.5 mol L⁻¹ HNO₃. Thus, 1.0 mol L⁻¹ HNO₃ was chosen for further experiments.

The effect of desorption flow rate ranging from 0.1–5.0 mL min⁻¹ was also examined. Figure 2 shows that quantitative recoveries were obtained at less than 3.5 mL min⁻¹ for Pb and Cd; however, for Cu at

0.3 mL min⁻¹. Therefore, the desorption flow rate of 2.5 mL min⁻¹ was employed for Pb and Cd, and 0.3 mL min⁻¹ for Cu.

The effect of elution volume for the quantitative elution of the studied ions was investigated. The results showed that 3.0, 4.0, and 5.0 mL of 1.0 mol L⁻¹ HNO₃ was sufficient to quantitatively recover Cu, Pb, and Cd, respectively.

Effect of Sample Volume

In order to assess the possibility of enriching low concentrations of analytes from large volumes, the maximum applicable sample volume was studied. Sample solutions of 10.0, 25.0, 50.0, and 100.0 mL, containing 10.0 µg each of Cu, Pb and Cd, respectively, were examined under the optimum conditions. Figure 3 shows that for up to a 100-mL volume, the recoveries of the three analytes were still over 95%. Therefore, 100 mL of sample solution was adopted for the pre-concentration of the analytes from the sample solution. As mentioned previously, 3.0, 4.0, and 5.0 mL of 1.0 mol L⁻¹ HNO₃ was enough to elute Cu, Pb, and Cd from coal cinder, respectively. Thus, enrichment factors of 33.3, 25, and 20 were obtained for Cu, Pb and Cd, respectively.

Adsorption Capacity

Adsorption capacity determines how much coal cinder is required to quantitatively concentrate the analytes from a given solution. Using optimum conditions, a series of Cu, Pb, and Cd concentrations were investigated. The results showed that the adsorption capacity of the coal cinder micro-column for Cu, Pb, and Cd was 0.47, 1.31, and 0.57 mg g⁻¹, respectively.

Interferences

In order to evaluate the anti-interference capability of the proposed method, the effects of common coexisting cations and anions in the present system were investigated. Different typical potential interfering ions were added to 2.0 µg mL⁻¹ of Cu, Pb, and Cd solution, respectively, then subjected to the recommended procedure. The results in Table II list the recoveries obtained in the presence of foreign ions relative to the interference-free response. It can be seen that the influence of most of the common ions is very weak, indicating that the developed method has great potential application for different sample matrices.

Fig. 2. Effects of desorption flow rate on the recoveries of 2.0 µg mL⁻¹ Cu, Pb, and Cd.

Fig. 3. Effects of sample volume on the recoveries of 2.0 µg mL⁻¹ Cu, Pb, and Cd.

Analytical Performance

Using optimum conditions, the analytical performance of the method was evaluated following the general procedure. The relative standard deviations (RSD) were 0.72% Cu (n=9, C=0.05 $\mu\text{g mL}^{-1}$), 5.0% Pb (n=9, C=0.1 $\mu\text{g mL}^{-1}$), and 3.4% Cd (n=9, C=0.2 $\mu\text{g mL}^{-1}$),

respectively. This shows that the method has good precision for the analysis of trace Cu, Pb, and Cd. With enrichment factors of 20–33.3, the detection limits of the method, based on three times the standard deviation of 9 runs of the blank solution, were 0.6, 4.9, and 1.6 $\mu\text{g L}^{-1}$ for Cu, Pb and Cd, respectively.

A comparison of the characteristic data of the present method with those reported previously (18,23, 37-39) is provided in Table III. As can be seen, the detection limits of the present method are much lower than those previously published. Compared to the adsorbents of alizarin violet functionalized silica gel for Pb (37); 2-aminothiophenol, β -nitroso- α -naphthol, and Tiron functionalized amberlite XAD-2 for Cu (23,38-39); and SP70- α -benzoin oxime chelating resin for Pb and Cd (18), the results obtained in our study using inexpensive and easily obtainable coal cinder is superior to all of these materials.

TABLE II

Effects of Interfering Ions on Determining 2.0 $\mu\text{g mL}^{-1}$ Cu, Pb, and Cd

Interfering Ions	Cu(II)		Pb(II)		Cd(II)	
	Permit ratio ^a	Recovery ^b (%)	Permit ratio ^a	Recovery ^b (%)	Permit ratio ^a	Recovery ^b (%)
K ⁺	7500	95.36	2500	88.90	7500	98.50
Na ⁺	7500	91.55	7500	100	5000	88.75
Ca ²⁺	1000	90.68	1500	90.65	100	88.20
Mg ²⁺	1500	90.28	2500	91.74	1000	86.20
Cl ⁻	11600	91.55	11600	100	7735	88.75
NO ₃ ⁻	11925	95.36	3975	88.90	11925	98.50
SO ₄ ²⁻	6000	90.28	10000	91.74	4000	86.20
CO ₃ ²⁻	1500	90.68	2250	90.65	150	88.20

^a Concentration ratio of the interfering species to analytes.

^b Recoveries of the analytes.

TABLE III

Comparison of Proposed Method with Earlier Reported Methods

Matrix	Analytes	Extraction Solvents	Technique	LODs	EF ^a	Ref.
Wastewater	Pb	Alizarin violet functionalized silica gel	Sequential injection spectrophotometry	0.02 $\mu\text{g mL}^{-1}$	10	37
Water	Cu	Amberlite XAD-2 functionalized with 2-aminothiophenol	FAAS	1.31 $\mu\text{g L}^{-1}$	14	38
River Water	Cu, Cd, Co, Ni, Pb, Zn, Mn, Fe	Amberlite XAD-2 functionalized with Tiron	FAAS	Cu 2.0 $\mu\text{g L}^{-1}$ Pb 24 $\mu\text{g L}^{-1}$ Cd 1.3 $\mu\text{g L}^{-1}$	Cu 200 Pb 25 Cd 50	39
Food	Cu	Amberlite XAD-2 functionalized with β -nitroso- α -naphthol	FAAS	1.1 $\mu\text{g L}^{-1}$	29	23
Food	Pb, Cd, Co, Cr	SP70- α -benzoin oxime chelating resin	FAAS	Pb 16 $\mu\text{g L}^{-1}$ Cd 4.2 $\mu\text{g L}^{-1}$	Pb 75 Cd 100	18
Water	Cu, Pb, Cd	Coal cinder	FAAS	Cu 0.6 $\mu\text{g L}^{-1}$ Pb 4.9 $\mu\text{g L}^{-1}$ Cd 1.6 $\mu\text{g L}^{-1}$	Cu 33.3 Pb 25 Cd 20	This work

^a EF = Enrichment Factor.

TABLE IV
Analytical Results of Cu, Pb, and Cd in Environmental Water by Coal Cinder Micro-column SPE-FAAS

Samples		Concentrations ($\mu\text{g mL}^{-1}$)		
		Added	Found ^a	Recovery (%)
Pond Water	Cu(II)	0	ND	-
		2.0	2.18 $\pm$ 0.02	109.00
	Pb(II)	0	ND	-
		2.0	1.86 $\pm$ 0.07	93.04
	Cd(II)	0	ND	-
		2.0	1.82 $\pm$ 0.008	90.95
Landfill Leachate	Cu(II)	0	0.55 $\pm$ 0.01	-
		2.0	2.52 $\pm$ 0.01	98.50
	Pb(II)	0	0.88 $\pm$ 0.08	-
		2.0	2.78 $\pm$ 0.09	95.03
	Cd(II)	0	ND	-
		2.0	1.83 $\pm$ 0.007	91.25

ND = not detected.

^a For five determinations.

TABLE V
Analytical Results for Certified Reference GSB 07-1182-2000 Environmental Water (mean $\pm$ S.D., n=3)

Elements	Certified ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)
Cu	1.04 $\pm$ 0.04	1.03 $\pm$ 0.003
Pb	1.356 $\pm$ 0.030	1.317 $\pm$ 0.024

Analytical Applications

The proposed method was applied to the determination of Cu, Pb, and Cd in pond water and landfill leachate samples. The spike recoveries of the analytes were also investigated. The analytical results in Table IV for the spiked water samples show that the proposed method has fairly good recoveries (91.0–109.0%) for the three analytes.

In order to evaluate the accuracy of the developed method, Cu and Pb in certified reference environmental water (GSB 07-1182-2000) were analyzed. The analytical results in Table V show that they are well within the standard values.

CONCLUSION

A simple, sensitive, and accurate method based on coal cinder solid phase extraction-flame atomic absorption spectrometry (SPE-FAAS) for the determination of Cu, Pb and Cd in environmental water samples has been developed and resulted in satisfactory recoveries (91.0–109.0%). Coal cinder micro-column extraction, with enrichment factors of 20.0–33.3, was utilized for improving the sensitivity of FAAS analysis. Coal cinder is a useful, effective, reliable, and inexpensive adsorbent in comparison to other adsorbents applied for the removal of heavy metals in environmental water samples. The strong anti-interference capability indicates the method's potential for heavy metals determination in different sample matrices.

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