Activated Carbon Cloth (ACC) as Efficient Adsorbent for Trace Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) as O-O-diethylphosphorodithioic Acid Chelates for the Enrichment From Water and Soil Samples

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INTRODUCTION

The exposure of trace chemicals and heavy elements to humans in today's urban and industrial society has risen dramatically in the last 50 years (1-3). Trace elements such as Cu, Fe, Zn, and Mn are necessary elements for the human body and lack of these elements can cause various diseases (4, 5), while elements such as As, Cd, Hg, and are toxic (6-8). The concentrations of trace elements are generally lower than the detection limits of some of the detection techniques, such as atomic absorption spectrometry (9-14). In addition, matrix effects from concomitant ions can cause problems for these analyses (15-18). Thus, preconcentration-separation methods are generally used prior to the determination of analyte elements (19-22).

Solid phase extraction is considered superior to other preconcentration-separation techniques due to its simplicity, consumption of small volumes of organic solvent, and the ability to obtain a high preconcentration factor and high analytical speed (23-27). In addition, novel solid phases for acid and bases, high surface area and high adsorption capacities have also been reported (28-35). Activated carbon cloth (ACC) is one of the adsorbents for solid phase extraction of trace analytes from environmental samples (36-40). It has mechanical strength, high surface

ABSTRACT

A preconcentration procedure based on the adsorption of Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) as their O-O-diethylphosphorodithioic acid chelates on activated carbon cloth (ACC) is presented. The analytical parameters including pH of the working media, amount of O-O-diethylphosphorodithioic acid, and eluent type, etc., were optimized. The effects of matrix components were also investigated. The analyte elements were quantitatively recovered at pH 6.0 with 0.5 mg O-O-diethylphosphorodithioic acid and 10 mL 3M HNO₃ was used as the eluent. Addition recovery tests were also performed for real samples. The relative standard deviations were generally lower than 5%. The validation of the proposed procedure was checked by the analysis of SPS-WW2 Wastewater certified reference material. The solid phase extraction method was applied to the separation-preconcentration of the analyte elements from environmental samples, including natural water and soil samples from Kayseri, Turkey.

area, stability for acids and bases, and the possibility for regeneration.

In the present work, a solid phase extraction procedure for trace Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) as their O-O-diethylphosphorodithioic acid on activated carbon cloth (ACC) has been established. The analytical parameters for the quantitative recovery of the analyte elements

were optimized and applied to the determination of these analytes in water and soil samples from Kayseri, Turkey.

Experimental

Instrumentation

A PerkinElmer[®] Model 3110 flame atomic absorption spectrometer (FAAS) (PerkinElmer, Inc., Shelton, CT, USA) was used for the determination of the analyte elements. All instrumental settings used were as recommended by the manufacturer. All measurements were carried out with an air/acetylene flame. A centrifuge ALC PK 120 Model (Buckinghamshire, England) was used for centrifuging. All pH measurements were carried out using a Sartorius PT-10 digital pH meter (Germany), equipped with a combined glass electrode.

Standard Solutions and Reagents

All solutions were prepared with reverse osmosis purified Milli-Q[®] water (18.2 MΩ·cm, Millipore Corporation, Milford, MA, USA). All reagents and solvents were of analytical reagent grade and used as received. The stock solutions (1000 mg/L) of the analyte elements and other cations were prepared by dissolving the appropriate amounts of nitrate salts of the analyte elements in reverse osmosis purified water.

O-O-diethylphosphorodithioic acid ammonium salt was purchased from Alfa Aesar, Heysham, England (CAS No: 1068-22-0). 0.1% (m/v) O-O-diethylphosphorodithioic acid ammonium salt was prepared daily

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in an ethanol-water mixture. Activated carbon cloth was purchased from Norm Company, Turkey (Code: Norm/AW1105). Activated carbon cloth has a surface area and thickness of $1000 \text{ m}^2 \text{ g}^{-1}$ and $0.4 \pm 0.1 \text{ mm}$, respectively. The buffer solutions as listed in the literature (41, 42) were used for all studies. Certified reference material (CRM) SPS-WW2 Wastewater (Spectrapure Standards AS, Oslo, Norway) was used for verification of the results.

Test Procedure

An aliquot of stock solution containing 10–30 μg analyte ions was transferred into a beaker and 0.5 mg O-O-diethylphosphorodithioic acid ammonium salt solution and 5.0 mL buffer solution were added. The solution was left standing at room temperature for 2–3 minutes for complex formation. The sample solution was permitted to flow through the column containing 400 mg activated carbon cloth under gravity. Then, the column was washed with 2.0 mL of the blank solution. The analytes retained were eluted with 10 mL of 3M nitric acid. The eluent was evaporated at 60°C until it reached 2.5 mL volume. The metal concentrations in the final solution were determined by flame AAS.

Application to Real Samples and CRM

The method was also applied to soil samples from Kayseri, Turkey. A 1.0-g amount of soil was weighed into beakers and digested with 24 mL *aqua regia* at room temperature for 30 minutes, then dried at 95°C on a hot plate. After cooling, the residue was again digested with 24 mL of *aqua regia* following the same procedure as discussed above. The final residue in the beaker was dissolved with 15 mL distilled water and filtered to obtain a clear solution. Then the preconcentration procedure as provided in the “Test Procedure” section was applied to all samples.

The procedure was also applied to CRM SPS-WW2 Wastewater and bottled water samples from Kayseri, Turkey. The natural water samples were filtered through a $0.45 \mu\text{m}$ Millipore® cellulose nitrate membrane filter. Then the “Test Procedure” was applied to all samples.

RESULTS AND DISCUSSION

Effect of pH

In the solid phase extraction studies, the pH of the working media is an important and critical parameter for the quantitative

recovery of the analytes (43–47). The influence of pH of the working solution was investigated at the pH range of 3.0–7.0. The results are given in Figure 1. The pH of the solutions was adjusted by using buffer solutions. Quantitative recovery for Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) was obtained at pH 6.0 and thus selected for further studies.

Influence of Amount of O-O-diethylphosphorodithioic Acid

In the extraction studies for metal ions from the various media, the metal ions are generally converted to organometallic structures by using various chelating agents for their quantitative recovery (48–51). In the present work, the use of O-O-diethylphosphorodithioic acid ranging from 0.1–1.0 mg was investigated. The results in Figure 2 show that quantitative recoveries were obtained in the range of 0.1–0.5 mg. After 0.5 mg, the recovery of the analytes decreased. In further work, 0.5 mg of O-O-diethylphosphorodithioic acid was used.

Effect of Eluent Type

The influence of eluent type was also investigated. Ten mL of each eluent as listed in Table I was used

Fig. 1. Effects of pH on the recovery of the analyte elements (N=3).

Fig. 2. Effect of amount of ligand on the recovery of the analyte elements (N=3).

for this purpose. Quantitative recovery was only obtained for all analytes when 3M HNO₃ was used. Thus, all subsequent work was carried out using 10 mL of 3M HNO₃.

Influence of Sample and Eluent Flow Rate

Influence of the flow rate of the sample and eluent solutions was studied in the range from 1-3 mL/min. The recovery of Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) in the present work was quantitative at the sample and eluent flow rate of 2 mL/min and 3 mL/min, respectively. These values for the analyte ions were used for all further studies.

Sample Volume

Sample volume is a key factor that was optimized in the solid phase extraction studies to obtain

a high preconcentration factor. The effect of sample volume on the recovery of the analyte elements was investigated in the sample volume range of 10-300 mL. The recovery of the analytes was quantitative up to 100 mL sample volume. By analyzing 2.5 mL of the final volume after preconcentration of 100 mL of sample solution, a preconcentration factor of 25 was achieved for the analyte elements.

Effect of Concomitant Ions

As pointed out in the introduction section, the determination of metal ions at trace levels in environmental samples is problematic due to the influence of concomitant ions normally present at very high levels (52-61). Thus, the effect of concomitant ions on the recovery of the analytes on an activated carbon column was investigated.

Table II shows that the recovery results of Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) were not affected by the solution containing high concentrations of matrix ions. It was also found that some of the transition metals at mg L⁻¹ levels did not interfere in the recovery of the analyte elements. It can therefore be stated that the proposed preconcentration/separation method can be applied to saline samples that contain metal ions at the mg L⁻¹ level.

Analytical Features

The detection limits (LODs) of the present method for the determination of the analyte elements were studied. The detection limits, defined as the concentration equivalent to 3 times the standard deviation of the blank solution ($n=11$, $XL=3s/PF$, XL : limit of detection, PF : preconcentration factor), are listed in Table III. The precision of the present method was calculated as the relative standard deviation of the measurements carried out with the sample solutions ($N=9$), also listed in Table III.

Application of Present Method to CRM and Real Samples

For validation, the present method was applied to CRM SPS-WW2 Wastewater (Spectrapure

TABLE I
Effect of Eluent Type on the Recovery of the Analyte Elements (N=3)

Eluent	Ni	Co	Recovery, %			
			Cu	Mn	Pb	Cd
2M HNO ₃	93±2	88±3	61±2	89±5	73±1	80
3M HNO ₃	95±3	96±4	95±1	96±3	95±3	97±2
2M HCl	96±2	89±3	23±5	82±8	26±1	12
3M HCl	99±1	98±2	42±1	90±3	89±1	21±1
2M CH ₃ COOH	56±3	46±3	0	89±4	0	18±3
3M CH ₃ COOH	44±2	39±1	0	85±3	0	23±1

TABLE II
Matrix Effects (N=3)

Ion	Added	Conc. (µg/mL)	Mn	Recovery (%)			Ni	Co	Cu
				Cd	Pb				
K ⁺	KCl	1125	93±2	98±1	92±3		93±1	95±1	87±2
Mg ²⁺	Mg(NO ₃) ₂ ·4H ₂ O	1125	90±2	99±1	95±5		93±2	93±2	99±4
Na ⁺	NaNO ₃	375	90±1	98±1	91±3		93±2	92±2	88±3
Ca ²⁺	Ca(NO ₃) ₂ ·4H ₂ O	375	92±1	97±1	90±5		90±2	90±2	85±5
SO ₄ ²⁻	Na ₂ SO ₄	375	97±3	90±2	93±5		93±4	98±1	97±1
Mn ²⁺	Mn(NO ₃) ₂ ·4H ₂ O	1	-	95±1	90±3		97±2	98±2	96±4
Co ²⁺	Co(NO ₃) ₂ ·6H ₂ O	1	90±1	92±1	90±3		98±3	-	85±5
Cu ²⁺	Cu(NO ₃) ₂ ·3H ₂ O	1	98±1	90±2	93±3		92±3	96±2	-
Zn ²⁺	Zn(NO ₃) ₂ ·6H ₂ O	1	94±3	96±1	96±3		94±2	97±2	95±4

Standards AS, Oslo, Norway) after the optimization stage. The results in Table IV list the quantitative recoveries obtained for all analyte

elements. It can be seen that the results agree with the certified values of the analyte elements in SPS-WW2 Wastewater.

TABLE III
Detection Limit and Relative Standard Deviation for Analyte Elements

	Analyte Elements					
	Pb	Cu	Cd	Ni	Co	Mn
Detection limit (µg/L)	31.3	10.5	11.4	15.4	12.9	2.6
Relative Standard Deviation (%)	6.4	4.3	1.8	3.3	2.5	2.6

TABLE IV
Application of Solid Phase Extraction to CRM SPS-WW2 Wastewater

	Analytes					
	Pb	Cu	Cd	Ni	Co	Mn
Certificated Value (µg/L)	500	2000	100	5000	300	2000
Found (µg/L)	525±2	1805±3	101±1	4526 ±2	301±0	2029 ±2
Recovery (%)	105	90	101	90	100	101

TABLE V
Application of Activated Carbon Cloth for Solid Phase Extraction Procedure to Soil Samples From Kayseri, Turkey

Analyte	Soil from Koca Hacı			Soil from Yahyali		Soil from Kirazlı Dere	
	Added (µg)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Co	0	BDL	-	BDL	-	BDL	-
	10	10.1±2	101	10.6±1	106	9.3±2	93
	20	19±1	95	18.5±2	92	19±1	95
Cu	0	BDL	-	BDL	-	BDL	-
	10	10.2±2	102	10.1±1	101	9.0±0	90
	20	18.9±1	94	20±1	100	19.6±2	98
Cd	0	BDL	-	BDL	-	BDL	-
	5	5±1	100	3±2	60	5.4±2	108
	10	8.5±1	85	5.8±2	58	7.0±2	70
Mn	0	BDL	-	BDL	-	BDL	-
	5	4.9±0	98	3.8±0	76	5.1±1	102
	10	8.6±2	86	6.8±2	68	7.5±1	75
Ni	0	BDL	-	BDL	-	BDL	-
	10	9.5±0	95	9.2±0	92	10.1±1	101
	20	20.4±3	102	20.2±2	101	19.2±2	96
Pb	0	BDL	-	BDL	-	BDL	-
	20	17±2	85	19.3±1	96	14±1	70
	40	30.9±1	77	38.8±0	97	30±1	75

BDL: Below the detection limit.

The solid phase extraction of the analyte elements was also performed for the soil samples and bottled water samples obtained from Kayseri, Turkey, by using the method of addition recovery tests. The results listed in Table V for the soil samples and in Table VI for the bottled water samples show that, generally, quantitative recovery values were obtained for the analyte elements.

CONCLUSION

The analytical potential of activated carbon cloth ACC) as an efficient adsorbent for the separation/preconcentration of Cu(II), Co(II), Cd(II), Pb(II), Mn(II), and Ni(II) as their O-O-diethylphosphorodithioic acid chelates was investigated using real soil and water samples. The analytes were quantitatively recovered at pH 6.0 and the preconcentration factor was calculated as 25. The detection limits were in the range of 2.6–31.3 µg L⁻¹ and the relative standard deviation of the determinations was < 7%. Thus, the proposed method can successfully be used for the determination of lead, nickel, and cobalt in soil and water samples. The proposed method was verified by analyzing CRM SPW-WW2 Wastewater with good results.

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TABLE VI
Application of Activated Carbon Cloth for Solid Phase Extraction
Procedure to Bottled Water Samples From Kayseri, Turkey

Analyte	Added (μg)	Bottled Water 1 Found (μg)	Recovery (%)	Bottled Water 2 Found (μg)	Recovery (%)	Bottled Water 3 Found (μg)	Recovery (%)
Co	0	BDL	-	BDL	-	BDL	-
	10	9.8 $\pm$ 2	98	10.0 $\pm$ 1	100	10.1 $\pm$ 2	101
	20	19.8 $\pm$ 3	99	20.2 $\pm$ 2	101	18.4 $\pm$ 1	92
Cu	0	BDL	-	BDL	-	BDL	-
	10	10.6 $\pm$ 2	106	9.2 $\pm$ 2	92	9.6 $\pm$ 0	96
	20	20.6 $\pm$ 1	103	21 $\pm$ 1	105	20 $\pm$ 2	100
Cd	0	BDL	-	BDL	-	BDL	-
	5	5.1 $\pm$ 2	102	5.2 $\pm$ 2	104	4.8 $\pm$ 2	96
	10	10.5 $\pm$ 1	105	10.5 $\pm$ 2	105	10.4 $\pm$ 2	104
Mn	0	BDL	-	BDL	-	BDL	-
	5	5.2 $\pm$ 2	104	5.2 $\pm$ 0	104	5.1 $\pm$ 1	102
	10	10.5 $\pm$ 1	105	10.5 $\pm$ 2	105	10.3 $\pm$ 1	103
Ni	0	BDL	-	BDL	-	BDL	-
	10	9.9 $\pm$ 0	99	10.3 $\pm$ 0	103	10.3 $\pm$ 1	103
	20	20 $\pm$ 3	100	20.2 $\pm$ 2	101	19.6 $\pm$ 2	98
Pb	0	BDL	-	BDL	-	BDL	-
	20	18.4 $\pm$ 2	92	19.6 $\pm$ 2	98	19.6 $\pm$ 1	98
	40	40.5 $\pm$ 2	101	38.4 $\pm$ 0	96	40.4 $\pm$ 1	101

BDL: Below the detection limit

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