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Three modified activated carbons by different ligands for the solid phase extraction of copper and lead

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Abstract

In the presented work, 5,5-diphenylimidazolidine-2,4-dione (phenytoin) (DFTD), 5,5-diphenylimidazolidine-2-thione-,4-one (thiophenytoin) (DFID) and 2-(4′-methoxy-benzylidenimine) thiophenole (MBIP) modified activated carbons have been used for the solid phase extraction of copper and lead ions prior to their flame atomic absorption spectrometric determinations. The influences of the various analytical parameters including pH, amounts of reagent, sample volume and eluent type, etc. on the recovery efficiencies of copper and lead ions were investigated. The influences of alkaline, earth alkaline and some transition metals on the adsorption of the analytes were also examined. The detection limits by three sigma for analyte ions were 0.65 and 0.42 $\mu g\,L^{-1}$ using activated carbon modified with DFID; 0.52 and 0.37 $\mu g\,L^{-1}$ using activated carbon modified with DFTD and 0.46 and 0.31 $\mu g\,L^{-1}$ using activated carbon modified with MBIP for Pb(II) and Cu(II), respectively. The procedure was applied to the determination of analytes in natural waters, soil, and blood samples with satisfactory results (recoveries greater than 95%, R.S.D.'s lower than 4%).
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1. Introduction

The atomic absorption spectrometry (AAS) offers fast elemental analysis and suffers from poor sensitivity in the determination of heavy metals in environmental samples. This draw back can be overcome by the combination of a suitable preconcentration-separation technique with subsequent AAS determination. Solid phase extraction (SPE) has been widely used for preconcentration of heavy metals due to advantages such as, high efficiency, simplicity, rapidity, low consumption of material especially toxic organic solvents [1–5], freedom from contamination and the possibility of combination with AAS.

The modified solid sorbents are then used and applied in the fields of normal or selective solid phase extraction of

the target species [6,7]. The selectivity of the modified solid phases toward certain metal ions is attributed to several well known factors such as the size of the organic modifier [8], the activity of the loaded surface groups [9,10], the type of the interacting donor atom and metal ion and the reported well known phenomenon of hard–soft acid–bases [11]. The reasons for widespread application of the activated carbon as a trace collector for metal ion preconcentration [12–26] are strong interaction and quantitative adsorption of molecules with π electrons on activated carbon. Activated carbon is a hydrophobic adsorbent which adsorbs non-polar or slightly polar substances in aqueous solutions, metal ions to be preconcentrated need to be transformed to corresponding metal chelates. Metal chelates could provide higher selectivity and high enrichment factor for such a separation and preconcentration techniques [26–34].

In the presented work, 5,5-diphenylimidazolidine-2,4-dione (phenytoin) (DFTD), 5,5-diphenylimidazolidine-2-thione-,
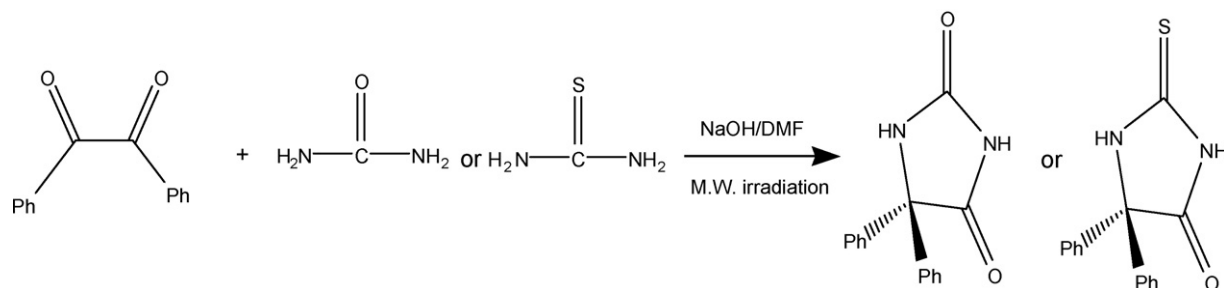
Scheme 1. Preparation of phenytoin and thiophenytoin.

4-one (thiophenytoin) (DFID) and 2-(4′-methoxybenzylide-nimine) thiophenole (MBIP) modified activated carbons have been used as solid phase materials for the preconcentration and separation of copper and lead ions in environmental samples. The analytical parameters for quantitative recoveries of analytes were investigated.

2. Experimental

2.1. Reagents and solutions

Acid and bases were of the highest purity obtained from Merck, Darmstadt and were used as received. Doubly distilled deionized water was used throughout. Stock solutions of copper(II) (1000 mg L^{-1}) and lead(II) was prepared by Cu(NO$_3$)$_2$ and Pb(NO$_3$)$_2$ (E. Merck, Darmstadt, Germany) in deionised doubly distilled water, respectively. Analytical grade nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium were of the highest purity purchased from Merck, Darmstadt and used without any further purification.

2.2. Instruments

The lead and copper determinations were carried out on a Shimadzu 680 A atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector, at wavelengths of 217.0 and 324.8 nm for lead and copper, respectively, using an air–acetylene flame. The pH was determined with a Metrohm 691 pH/ion meter with a combined glass–calomel electrode.

2.3. Synthesis of 5,5-diphenylimidazolidine-2,4-dione (phenytoin) and 5,5-diphenylimidazolidine-2-thione-,4-one (thiophenytoin) under microwave irradiation

To a mixture of 5 mmol urea (0.3 g) or thiourea (0.38 g) and 5 mmol (1.261 g) 1,2-diphenylethanedione (bezil) in a beaker of 50 mL, 0.3 g sodium hydroxide and four drops dimethyl-formamide were added. The reaction mixture unsealed was irradiated under 20% microwave with alternatively of 1 min for 3–5 min. The progress of the reaction was monitored by TLC (*n*-hexane:ethyl acetate). After completion of the reaction, the mixture was poured into cold water and filtered. Then the filtrate was acidified by concentrated HCl to precipitate phenytoin or thiophenytoin as products rapidly (Scheme 1). The precipitate was filtered and washed twice with cold water. The pure products were obtained by recrystallization of them from the water/ethanol mixture solvent in 60–67% yield.

2.3.1. Spectral data of DFID

IR (KBr, cm^{-1}): 3201 (s), 3283 (s), 3080 (w), 1768 (s), 1736 (s), 1712 (vs), 1682 (sh), 1494 9 (m), 1442 (m), 1396 (m), 1224 (m), 1190 (m), 1070 (w), 1012 (m), 780 (s), 764 (s), 740 (s), 698 (s), 658 (m), 638 (s), 597 (w), 520 (w), 434 (w), 420 (s). ^{1}H NMR (DMSO, ppm): 11.12 (s, 1H), 9.32 (s, 1H), 7.3–7.42 (m, 10H). mp (290–296 °C).

2.3.2. Spectral data of DFTD

IR (KBr, cm^{-1}): 250 (s), 3160 (s), 3020 (w), 2890 (w), 2760 (w), 1740 (vs), 1720 (vs), 1580 (s), 1524 (vs), 1488 (m), 1440 (s), 1378 (vs), 1310 (m), 1278 (m), 1222 (m), 1194 (w), 1152 (vs), 1100 (w), 1024 (m), 996 (vs), 940 (s), 902 (s), 844 (w), 826 (w), 766 (s), 720 (vs), 692 (vs), 658 (vs), 645 (s), 622 (m), 584
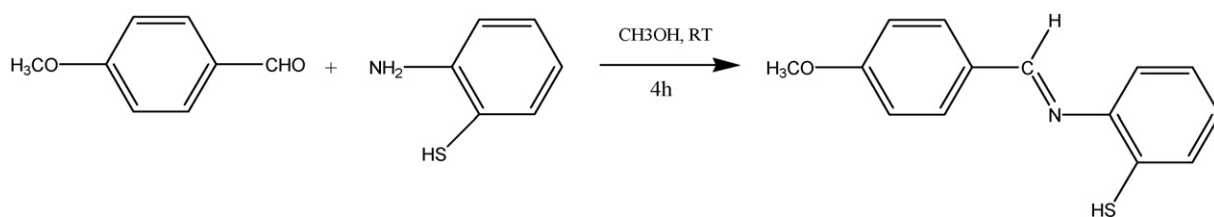
Scheme 2. Preparation of 2-(4′-methoxybenzylidenimine) thiophenole.

(m), 530 (s), 478 (s). ^{1}H NMR (DMSO, ppm): 12.22 (s, 1H), 11.38 (s, 1H), 7.3–7.42 (m, 10H). mp (220–225 °C).

2.4. Synthesis of 2-(4′-methoxybenzylidenimine) thiophenole

To 0.2 mmol (0.2501 g) 2-amino thiophenole in 10 mL methanol, 0.2 mmol (0.2724 g) of 4-methoxybenzaldehyde was added and reaction mixture was stirred at room temperature. The progress of reaction was monitored by thin layer chromatography. After 4 h the yellowish white precipitate (product) was produced by removing the solvent. The precipitate was dissolved in acetone and filtered. The filtrate was kept over night to give 0.340 g pure product (85%) (Scheme 2). The compound as recently synthesized compound was identified by IR, ^{1}H NMR.

2.4.1. Spectral data of product

IR (KBr, cm^{-1}): 2992 (w), 2972 (w), 2918 (w), 2841 (w), 2553 (w), 1615 (vs), 1605 (vs), 1567 (vs), 1518 (s), 1482 (s), 1467 (s), 1392 (m), 1315 (s), 1238 (vs), 1191 (s), 1165 (vs), 1110 (m), 1027 (s), 964 (m), 923 (w), 872 (m), 843 (vs), 812 (vs), 817 (vs), 867 (m), 718 (m), 541 (m), 559 (m). ^{1}H NMR (CDCl$_3$): (8.31 ppm, s, 1H), (7.82 ppm, d, 2H), (7–7.2 ppm, m, 4H), (6.89 ppm, d, 2H), (3.81 ppm, s, 3H), (3.2 ppm, s, 1H). mp (91–95 °C).

2.5. Preparation of modified activated carbons

Ligand loaded activated carbon was prepared by addition of each ligand solution to the activated carbon. After 18 h, the solutions were filtered through the filter paper and modified activated carbons were washed with distilled water. The mixtures were finally, dried at 70 °C overnight.

2.6. Preconcentration procedure

The pH of model solutions containing 0.08–2.50 µg mL^{-1} of lead and copper was adjusted to the desired pH value by adding 10 mL buffer solution. Before each operational cycle the solid phase was preconditioned with the buffer solution. The samples were passed through the column of modified activated carbon with the aid of a suction pump at a flow rate 5 mL min^{-1}, to effect the deposition of analyte. The adsorbed ions were then eluted with 5 mL of 3.0 mol L^{-1} nitric acid in acetone with a flow rate of 1.5 mL min^{-1}.

2.7. Applications

River and waste water samples were collected from Zohre River (Fahlian River), Iran and from Yasouj Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 µm. The organic content of the water samples were oxidized in the presence of 1% H$_2$O$_2$ and addition of concentrated nitric acid. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles. Then the procedure in Section 2.6 was applied.

Forty grams of spinach from Gachsaran, Iran or 50 g soil from Yasouj, Iran or 60 mL blood from a healthy person was put in a beaker. Twenty millilitres of distilled deionized water, 30 mL HNO$_3$ and 6 mL of H$_2$O$_2$ (30%) was added to solution, while stirring in heat until its volume decreased to half, then it was filtrated. It was transferred in 200 mL volumetric flask and completed to 200 mL with distilled water. For measurements these samples were adjusted to desired pH, and then the preconcentration procedure given was experimentally applied for the each modified activated carbon.

3. Results and discussion

For obtaining maximum accurate and precise signal for evaluation of lead and copper content, the effective parameter must be optimized. These parameters such as pH of sample, amount of ligand and solid phase, type of eluting agent and its concentration and flow rate must be optimized.

3.1. Effect of pH on recovery

In the solid phase extraction studies, the influence of pH of the aqueous solution is one of the main factors for quantitative recoveries of heavy metal ions [35–38]. Due to this important point, the influences of pH on the recoveries of copper and lead on three different modified activated carbons were investigated at the pH ranges 2–9 for sorbents with model solutions, keeping the other parameters constant. Analyte deposition depended on the sample pH, and as shown in Fig. 1, high recovery efficiency was achieved at a pH range of 5.0–6.0. To achieve high efficiency and good selectivity for three adsorbent, a pH of 5.5 was selected for subsequent work.

3.2. Effect of ligand amount

In order to determine the amounts of ligand required for quantitative recoveries for copper and lead ions, the proposed method was applied, changing ligands amounts at the range of 0–30 mg. The recoveries were not quantitative without ligands (<20%). The recovery values of the analyte metal ions
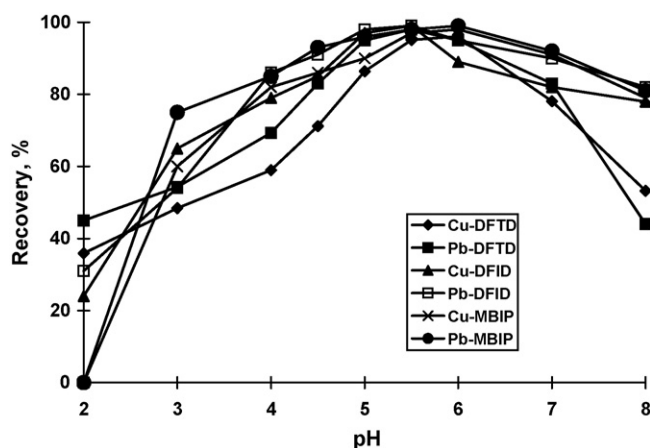

Fig. 1. Effect of pH on copper and lead ion recoveries (N = 3).
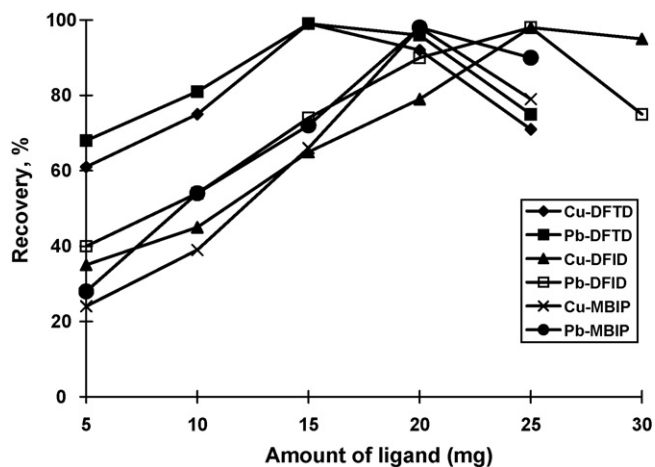
Fig. 2. The effect of amount of ligands on copper and lead ion recoveries.

Fig. 3. Effect of amount of activated carbon on copper and lead ion recoveries, sample flow rate 5 mL min^{-1}, eluent: 5 mL of 3.0 mol L^{-1} HNO$_3$ in acetone.

(Fig. 2) increased with increasing amounts of ligand added and reached quantitative values (95%) with 15, 20 and 25 mg of DFTD, MBIP and DFID, respectively. Therefore, these values were recommended as optimum ligand value for quantitative recoveries.

3.3. Amounts of activated carbon

The influences of the amounts of activated carbon filled to the column were also investigated. The results were given in Fig. 3. Quantitative recovery values for analytes were obtained for AC-DDFD solid phase in the range of 0.6–0.8 g of activated carbon, for AC-DFID solid phase in the range of 0.8–1.0 g of activated carbon and for AC-MBIP solid phase in the range of 0.5–0.6 g of activated carbon. In further studies, 0.6 g of activated carbon for AC-DDFD, 0.8 g of activated carbon for AC-DFID and 0.5 g of activated carbon for AC-MBIP were used.

3.4. Effect of eluent

The nature and concentration of eluent were found to have a significant effect on the desorption process of lead from
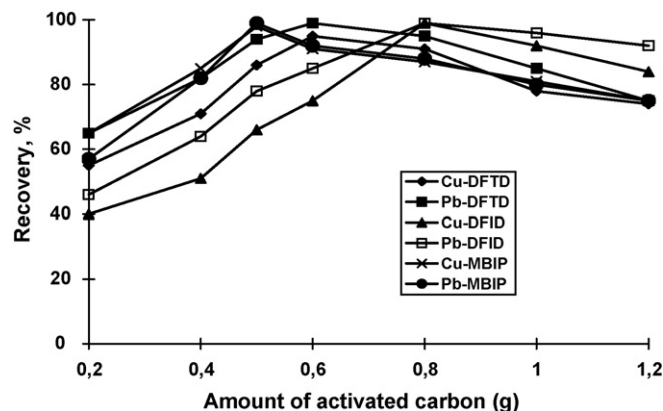
the column. Different eluents, such as HCl, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$ and CH$_3$COOH at various concentrations, were examined. The results are shown in Table 1. It is obvious that 5 mL of 3.0 mol L^{-1} nitric acid in acetone were sufficient for quantitative recovery of absorbed analytes from modified activated carbon.

3.5. Flow rate of sample solutions

The effect of flow rate of the sample solution on the recoveries of metal ions on modified activated carbon was examined in the range of 1.0–10 mL min^{-1}. It was found that, under

Table 2
Effect of interference of some ions (all prepared from nitrate salts)

Ion	Tolerance limit (ion)/(Cu(II) or Pb(II))	
	DFTD and DFID	MBIP
Al^{3+}, Sn^{2+}, Mn^{2+}, Ca^{2+}, Ag$^+$, Ni^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}, Na$^+$, K$^+$, Li$^+$	1000	1500
Cd^{2+}, Zn^{2+}	500	800
Fe^{2+}, Fe^{3+}	200	350
Hg^{2+}	100	150

Table 1
Effect of eluting solution condition on copper and lead ion recoveries (eluent volume: 5 mL)

Eluent	DFTD		DFID		MBIP	
	Cu, R (%)	Pb, R (%)	Cu, R (%)	Pb, R (%)	Cu, R (%)	Pb, R (%)
1 mol L^{-1} HCl	<5	<5	<5	<5	9.1 ± 0.8	18.3 ± 0.8
2 mol L^{-1} HCl	55.9 ± 1.1	63.4 ± 0.9	<5	<5	<5	<5
3 mol L^{-1} HCl	81.3 ± 1.1	89.4 ± 1.0	71.4 ± 1.1	78.5 ± 1.1	<5	<5
3 mol L^{-1} HCl in acetone	97.5 ± 1.0	99.7 ± 0.9	89.4 ± 0.8	94.6 ± 0.9	96.8 ± 0.8	97.3 ± 0.8
1.0 mol L^{-1} HNO$_3$ in acetone	59.6 ± 0.9	62.3 ± 0.9	63.4 ± 0.8	66.2 ± 0.7	53.3 ± 0.6	73.7 ± 0.7
2.0 mol L^{-1} HNO$_3$ in acetone	75.4 ± 0.9	84.3 ± 0.8	87.4 ± 0.8	84.6 ± 0.8	76.4 ± 0.8	81.0 ± 0.9
2.5 mol L^{-1} HNO$_3$ in acetone	93.9 ± 0.9	95.7 ± 0.8	93.4 ± 0.8	92.6 ± 0.8	96.4 ± 0.8	98.9 ± 0.8
3.0 mol L^{-1} HNO$_3$ in acetone	98.6 ± 0.9	99.3 ± 0.8	98.4 ± 0.9	98.6 ± 0.8	98.3 ± 0.9	98.4 ± 0.8
3 mol L^{-1} H$_2$SO$_4$ in acetone	34.3 ± 1.1	41.5 ± 1.0	<5	<5	25.2 ± 1.1	45.3 ± 1.1
4 mol L^{-1} H$_2$SO$_4$	54.9 ± 1.1	64.1 ± 1.1	55.9 ± 1.1	49.4 ± 1.1	<5	<5
3 mol L^{-1} acetic acid	<5	<5	59.3 ± 1.0	69.4 ± 1.1	<5	<5
4 mol L^{-1} H$_3$PO$_4$	53.3 ± 1.1	64.6 ± 1.0	64.5 ± 1.1	63.9 ± 1.1	<5	<5

Table 3
Specification of presented method at optimum conditions for each element

Parameters	Pb			Cu		
	DFID	DFTD	MBIP	DFID	DFTD	MBIP
Linear range ($mg\,L^{-1}$)	0.25–76	0.15–90	0.14–85	0.20–80	0.15–90	0.10–83
Detection limit ($\mu g\,L^{-1}$)	0.42	0.37	0.31	0.65	0.52	0.46
Loading capacity ($mg\,g^{-1}$)	80	87	89	80	87	89
R.S.D. (%)	0.9	1.0	0.9	0.8	0.9	1.0
Recovery (%)	98.3	98.4	98.7	98.6	98.7	98.5

optimum conditions, the flow rate of the sample solution was lower than $5\,mL\,min^{-1}$ and elution solution flow rate was lower than $1\,mL\,min^{-1}$ and had no noticeable influence on the quantitative and reproducible recoveries of metal ions. Analyte ions were quantitatively recovered with eluent flow rates in the range of 0.5–$1.5\,mL\,min^{-1}$. Thus, a flow rate of 5 and $1.5\,mL\,min^{-1}$ was employed both for the sample solution and eluent.

3.6. Interferences

In order to examine the effect of the various tested metal ions in the optimum conditions, extraction of these metal ions in the presence of some selected metal ions by and have been carried out which prompted us to perform an intensive selectivity study to evaluate the possible interference of some metal ions in the process of selective solid phase extraction of Pb(II) and Cu(II). Interferences that may be concomitant with this ion were investigated. The effect of calcium, magnesium and other alkali and alkaline earth ions were presented in Table 2. Table 2 display that these ions up to 1000-fold are negligi-

ble and this high selectivity enable the method for accurate and precise determination of Cu(II) and Pb(II) ions in real samples.

3.7. Enrichment factor and loading capacity

For investigation of enrichment factor and break through volume various volumes of Pb(II) and Cu(II) ion were passed through activated carbon columns modified with or then the effluent was sent to AAS for evaluating these ion content. The results indicate that ions content in $1200\,mL$ of $0.05\,\mu g\,mL^{-1}$ ions were quantitatively sorbed on three solid phases and reversibly were eluted using $5\,mL$ $3.0\,mol\,L^{-1}$ nitric acid in acetone. The enrichment factor was 240.

3.8. Calibration graphs and precisions

The calibration curve were obtained by using $250\,mL$ solutions at pH 5.5 at the optimum condition. The results are shown in Table 3, which indicate wide linear range and applicability of method for trace metal enrichment.

Table 4
Recovery studies of trace metal ions in spinach and blood samples

Modified solid phase	Ion	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	R.S.D. (%)	Recovery (%)
AC-DFTD	Cu[a]	0	65.1	1	–
		75	142.3	0.9	103
	Pb[a]	0	55.1	1	–
		75	132.1	1	102.7
AC-DFID	Cu[a]	0	64.1	1	–
		75	140.6	0.8	102
	Pb[a]	0	52.1	1	–
		75	128.4	0.8	101.7
AC-MBIP	Cu[a]	62.4	1	1	–
		138.9	0.7	0.7	102
	Pb[a]	0	53.6	1.1	–
		75	129.8	0.7	101.6
AC-DFTD	Cu[b]	0	66.3	1.1	–
		50	118.2	0.9	103.8
	Pb[b]	0	43.9	1.6	–
		50	95.2	1.2	102.6
AC-DFID	Cu[b]	0	68.3	1	–
		50	119.7	0.8	102.8

[a] Spinach.
[b] Blood.

Table 5
Recovery of trace copper and lead ions from spiked samples ($N = 3$)

Modified solid phase	Ion	Added ($\mu g \, L^{-1}$)	Found ($\mu g \, L^{-1}$)	R.S.D. (%)	Recovery (%)
AC-DFTD	Cu[a]	0	28.9	1.1	–
		50	80.8	0.9	103.8
	Pb[a]	0	25.6	1	–
		50	76.4	0.8	101.6
AC-DFID	Cu[a]	0	26.7	1.2	–
		50	77.9	0.9	102.4
	Pb[a]	0	24.9	1.3	–
		50	74.3	1	98.8
AC-MBIP	Cu[a]	0	27.6	1.1	–
		50	78.3	0.9	101.4
	Pb[a]	0	25.2	1.2	–
		50	75.9	0.9	101.4
AC-DFTD	Cu[b]	0	70.3	1	–
		100	172.3	0.8	102
	Pb[b]	0	66.4	1.2	–
		100	168.3	0.9	101.9
AC-DFID	Cu[b]	0	68.9	1.2	–
		100	170.8	0.9	101.9
	Pb[b]	0	68.2	1.1	–
		100	170.1	0.8	101.9
AC-MBIP	Cu[b]	0	71.4	1.1	–
		100	172.4	0.9	101
	Pb[b]	0	69.7	1.2	–
		100	170.8	0.9	101.1
AC-DFTD	Cu[c]	0	23.2	1.3	–
		50	74.1	1	101.8
	Pb[c]	0	19.2	1.3	–
		50	70.1	0.9	101.8
	Cu[c]	0	20.8	1.2	–
		50	71.3	0.9	101
	Pb[c]	0	20.6	–	–
		50	71.7	1	102.2
AC-MBIP	Cu[c]	0	22.1	1.3	–
		50	73.2	0.8	102.2
	Pb[c]	0	18.9	1.3	–
		50	70.1	0.8	102.4

[a] Soil.
[b] Waste water.
[c] River water.

3.9. Accuracy and applications

The reproducibility of methods was studied at optimum condition with six experiments. The efficiency for lead and copper ions based on modified activated carbon were more than 98% for Pb(II) and Cu(II) using three modified activated carbon that indicate repeatable results (Table 3).

The procedure was applied to the determination of lead and copper in different samples, including natural water and food samples. The reliability was checked by spiking experiments and independent analysis to real samples. The results are presented in Tables 4 and 5. The recovery of spiked samples is satisfactorily reasonable and was confirmed using standard addition method, which indicate the capabil-

ity of the system in the determination of analytes in different samples.

4. Conclusion

The ligands loaded on activated carbon are sensitive and accurate methods for determination of trace amounts of copper and lead ions in low concentrations. The results presented have confirmed the applicability of the separation and preconcentration of metals. This method is simple and there is no necessity for elaborate cleanup procedure. Each column can be used for at least 10 successive analyses without considerable change in metal ions recovery. The detection limits of analytes are superior to those of preconcentration techniques for analyses [38–46]. The good features of the proposed method showed that it's a convenient

and low cost one. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of analytes.

References

[1] M. Angelova, B. Schentov, V. Nedkova, G. Nikoloff, A. Alexiev, Ch. Petrova, Serum zinc in children with enterocolitis, chronic diarrhoea with malabsorption syndrome and type 1 diabetes, Trakia J. Sci. 4 (2006) 11–17.

[2] Y. Dogan, N. Durkan, S. Baslar, Trace element pollution biomonitoring using the bark of *Pinus brutia* (Turkish red pine) in the Western Anatolian part of Turkey, Trace Elements Electrol. 24 (2007) 146–150.

[3] A. Abbaspour, A. Izadyar, Carbon nanotube composite coated platinum electrode for detection of Cr(III) in real samples, Talanta 71 (2007) 887–892.

[4] A.M. Alvarez, J.R.E. Alvarez, R.P. Alvarez, Heavy metal analysis of rainwaters: a comparison of TXRF and ASV analytical capabilities, J. Radioanal. Nucl. Chem. 273 (2007) 427–433.

[5] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration and determination of copper, nickel, cobalt, lead and iron content using a surfactant coated alumina, Bull. Chem. Soc. Jpn. 79 (2006) 432–436.

[6] J. Vukovic, S. Matsuoka, K. Yoshimura, V. Grdinica, R.J. Grubesic, O. Zupanic, Simultaneous determination of traces of heavy metals by solid-phase spectrophotometry, Talanta 71 (2007) 2085–2091.

[7] G. Alberti, M. Pesavento, R. Biesuz, A chelating resin as a probe for the copper(II) distribution in grape wines, React. Funct. Polym., in press.

[8] M.L. Bruening, D.M. Mitchell, J.S. Bradshaw, R.M. Izatt, R.L. Bruening, Effect of organic solvent and anion type on cation binding constants with silica gel bound macrocycles and their use in designing selective concentrator columns, Anal. Chem. 63 (1991) 21–24.

[9] M.E. Mahmoud, E.M. Soliman, Silica-immobilized formylsalicylic acid as a selective phase for the extraction of iron(III), Talanta 44 (1997) 15–22.

[10] C. Sivani, G. Ramakrishna, J. Naidu, D. Narasimhulu, J.D. Rekha, P. Kumar, P. Chiranjeevi, Determination of Co (II) in water and soil samples using spectrophotometry coupled with preconcentration on 4-amino methyl pyridine anchored silica gel column, J. Hazard. Mater. 146 (2007) 137–141.

[11] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533–3539.

[12] B.F. Senkal, M. Ince, E. Yavuz, M. Yaman, The synthesis of new polymeric sorbent and its application in preconcentration of cadmium and lead in water samples, Talanta 72 (2007) 962–967.

[13] M. Soylak, Y. Akkaya, Separation/preconcentration of Xylenol Orange metal complexes on Amberlite XAD-16 column for their determination by flame atomic absorption spectrometry, J. Trace Microprobe Techn. 21 (2003) 455–466.

[14] R.E. Santelli, M. Gallego, M. Valcarcel, Preconcentration and atomic absorption determination of copper traces in waters by on-line adsorption elution on an activated carbon minicolumn, Talanta 41 (1994) 817–823.

[15] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb^{2+}, Chem. Anal. 51 (2006) 593–603.

[16] D. Pozebon, V.L. Dressler, A.J. Curtius, Determination of copper, cadmium, lead, bismuth and selenium (IV) in sea water by electrothermal vaporization and inductively coupled plasma mass spectrometry after online separation, J. Anal. Atom. Spectr. 13 (1998) 363–369.

[17] J. Shiowatana, K. Benyatianb, A. Siripinyanond, Determination of Cd, Co, Hg and Ni in seawater after enrichment on activated carbon by slurry sampling electrothermal AAS, Atom. Spectr. 21 (2000) 179–186.

[18] M. Soylak, M. Dogan, Column preconcentration of trace amounts of copper on activated carbon from natural water samples, Anal. Lett. 29 (1996) 635–643.

[19] M. Soylak, M. Dogan, I. Narin, L. Elci, Atomic absorption spectrometric determination of copper, cobalt, cadmium, lead, nickel and chromium in table salt samples after preconcentration on activated carbon, Kuwait J. Sci. Eng. 28 (2001) 361–370.

[20] H. Koshima, H. Onishi, Adsorption of metal ions on activated carbon from aqueous solutions at pH 1–13, Talanta 33 (1986) 391–395.

[21] M.B. Gholivand, F. Ahmadi, E. Rafiee, Solid phase extraction and determination of ultra trace amounts of copper using activated carbon modified by *N,N'*-bis(salicylidene)-1,2-phenylenediamine, Sep. Sci. Technol. 42 (2007) 897–910.

[22] J.P. Chen, M. Lin, Surface charge and metal ion adsorption on an H-type activated carbon: experimental observation and modeling simulation by the surface complex formation approach, Carbon 39 (2001) 491–1504.

[23] M. Ghaedi, F. Ahmadi, M. Soylak, Preconcentration and separation of nickel, copper and cobalt using solid phase extraction and their determination in some real samples, J. Hazard. Mater. 147 (2007) 226–231.

[24] M. Ghaedi, F. Ahmadi, M. Soylak, Simultaneous preconcentration of copper, nickel, cobalt and lead ions prior to their flame atomic absorption spectrometric determination, Ann. Chim. 97 (2007) 277–278.

[25] S. Cerutti, M.F. Silva, J.A. Gasquez, R.A. Olsina, L.D. Martinez, On-line preconcentration determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, Spectrochim. Acta B 58 (2003) 43–50.

[26] E.A. Takara, S.D. Pasini-Cabello, S. Cerutti, J.A. Gasquez, L.D. Martinez, On-line preconcentration/determination of copper in parenteral solutions using activated carbon by inductively coupled plasma optical emission spectrometry, J. Pharmaceut. Biomed. Anal. 39 (2005) 735–739.

[27] M. Soylak, Determination of trace amounts of copper in metallic aluminium samples after separation and preconcentration on an activated carbon column, Fresen. Environ. Bull. 7 (1998) 383–387.

[28] K. Jankowski, J. Yao, K. Kasiura, A. Jackowska, A. Sieradzka, Multi-element determination of heavy metals in water samples by continuous powder introduction microwave-induced plasma atomic emission spectrometry after preconcentration on activated carbon, Spectrochim. Acta 60B (2005) 369–375.

[29] P. Daorattanachai, F. Unob, A. Imyim, Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon, Talanta 67 (2005) 59–64.

[30] I. Narin, M. Soylak, M. Dogan, Trace enrichment and atomic absorption spectrometric determination of lead, copper, cadmium and nickel in drinking water samples by use of an activated carbon column, Anal. Lett. 30 (1997) 2801–2810.

[31] G. Chakrapani, D.S.R. Murty, P.L. Mohanta, R. Rangaswamy, Sorption of PAR-metal complexes on activated carbon as a rapid preconcentration method for the determination of Cu, Co, Cd, Cr, Ni, Pb and V in ground water, J. Geochem. Explor. 63 (1998) 145–152.

[32] M. Ghaedi, F. Ahmadi, A. Shokrollahi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, J. Hazard. Mater. 142 (2007) 272–276.

[33] L.H.N. Arakaki, M.G. da Fonseca, E.C. da Silva, A.P.D. Alves, K.S. de Sousa, A.L.P. Silva, Extraction of Pb(II), Cd(II), and Hg(II) from aqueous solution by nitrogen and thiol functionality grafted to silica gel measured by calorimetry, Thermochim. Acta 450 (2006) 12–15.

[34] H. Refiker, Preconcentration of some precious metals using DEBT impregnated resin, Master Thesis, Middle East Technical University, 2005.

[35] M. Alan, D. Kara, A. Fisher, Preconcentration of heavy metals and matrix elimination using silica gel chemically modified with 2,3-dihydroxybenzaldehyde, Sep. Sci. Technol. 42 (2007) 879–895.

[36] M. Yavuz, F. Gode, E. Pehlivan, S. Ozmert, Y.C. Sharma, An economic removal of Cu^{2+} and Cr^{3+} on the new adsorbents: pumice and polyacrylonitrile/pumice composite, Chem. Eng. J., in press.

[37] C. Huang, B. Hu, Z. Jiang, Simultaneous speciation of inorganic arsenic and antimony in natural waters by dimercaptosuccinic acid modified mesoporous titanium dioxide micro-column on line separation and inductively coupled plasma optical emission spectrometry determination, Spectrochim. Acta B 62 (2007) 454–460.

[38] N. Rajesh, B.G. Mishra, P.K. Pareek, Solid phase extraction of chromium (VI) from aqueous solutions by adsorption of its diphenylcarbazide complex on a mixed bed adsorbent (acid activated montmorillonite-silica gel) column, Spectrochim. Acta A, in press.

[39] J.A. Priya, P.S. Rao, Y. Vijaya, A.S. Reddy, A. Krishnaiah, Biosorption of chromium(VI), nickel(II) and copper(II) ions from aqueous solutions using *Pithophora algae*, Toxicol. Environ. Chem. 89 (2007) 421–442.

[40] X. Kong, Q. Jia, W. Zhou, Coupling on-line preconcentration by ion-exchange with microwave plasma torch-atomic emission spectrometry for the determination of cobalt and nickel, Microchem. J., in press.

[41] R. Liu, P. Liang, Determination of trace lead in water samples by graphite furnace atomic absorption spectrometry after preconcentration with nanometer titanium dioxide immobilized on silica gel, J. Hazard. Mater., in press.

[42] K. Kiran, K.S. Kumar, K. Suvardhan, K. Janardhanam, P. Chiranjeevi, Preconcentration and solid phase extraction method for the determination of Co, Cu, Ni, Zn and Cd in environmental and biological samples using activated carbon by FAAS, J. Hazard. Mater., in press.

[43] M. Ghaedi, M.R. Fathi, F. Marahel, F. Ahmadi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, Fresen. Environ. Bull. 14 (2005) 1158–1163.

[44] D. Rekha, K. Suvardhan, J.D. Kumar, P. Subramanyam, R.P. Prasad, Y. Lingappa, P. Chiranjeevi, Solid phase extraction method for the determination of lead, nickel, copper and manganese by flame atomic absorption spectrometry using sodium bispiperdine-1,1′-carbotetrathioate(Na-BPCTT) in water, J. Hazard. Mater. 146 (2007) 131–136.

[45] D. Rekha, P.R. Prasad, P. Chiranjeevi, Platinum determination in environmental samples using preconcentration cloud-point extraction with flame atomic absorption spectrometry, Environ. Monit. Assess., in press.

[46] I. Narin, Y. Surme, E. Bercin, M. Soylak, SP70-α-Benzoin oxime chelating resin for preconcentration-separation of Pb(II), Cd(II), Co(II) and Cr(III) in environmental samples, J. Hazard. Mater. 145 (2007) 113–119.