Activated carbons modified as a tool for separation and pre-concentration in heavy metals analysis

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ABSTRACT

A sensitive, simple and relatively fast methods has been developed to selectively separate and concentrate trace amounts of heavy metal ions from aqueous samples for the measurement by flame atomic absorption spectrometry. The method is based on the adsorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+} on 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) loaded on activated carbon. The metals content on the complexes are eluted using 6 ml 4M HNO_3. The detection limits by three sigma for analyte ions were $1.6\mu g\, l^{-1}$, $1.8\mu g\, l^{-1}$, $1.3\mu g\, l^{-1}$, $1.7\mu g\, l^{-1}$, $1.6\mu g\, l^{-1}$ and $1.7\mu g\, l^{-1}$ using AMTD for Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}, respectively. The presented procedure was applied to the determination of analytes in vegetable samples and different water samples with successfully results (recoveries greater than 97%, R.S.D.'s lower than 1.8 % for n=3).
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INTRODUCTION

Important positive and negative roles of trace heavy metal ions in human health are known[1].Considering biological research, the role of some trace and ultra-trace elements in the body is very rich and varied. Since these heavy elements are taken in mostly by human diet, the determination of their concentration in food and waters is very important. Considering biological research, the role of some trace and ultra-trace elements in our body is very rich and varied. Some of them are essential to life while others are toxic even at very low concentrations.

For the determination of low contents of trace elements in geological and technological samples, pre-concentration procedure is required. Of all pre-concentration and separation procedures sorption possesses several advantages: large pre-concentration factors that can be obtained in a short time, simplicity of phase separation and suitability for automation [2-6]. Solid phase extraction combines the benefits of solvent extraction and solid phase pre-concentration, eliminating some of their drawbacks. It consists of the recovery of hydrophobic metal species on solid support of hydrophobic functionality. Desorption of metals is simply achieved by the change in solvent polarity. It does not require the use of concentrated acids or other aggressive reagents, and provides the opportunities of online combination of pre-concentration and determination steps.

Various solid phase extraction materials including Diaion HP-20[7], cellulose[8], activated carbon[9], Lewatit S 100[10], SDS coated alumina[11] polyurethane foam[12], Chelex 100[13], microcrystalline naphthalene[14], modified silica[15] and diaion HP-2MG[16].

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Among which activated carbon has been widely applied. The reasons for widespread application of the activated carbon as a trace collector for metal ion pre-concentration are strong interaction and quantitative adsorption of molecules with π electrons on activated carbon. Because activated carbon is a type of hydro-phobic adsorbent which adsorbs non-polar or little polar substances in aqueous solutions, metal ions to be pre-concentrate need to be transformed corresponding metal chelates[17-33]. Metal chelates could provide higher se-lectivity and high enrichment factor for such a separa-tion and pre-concentration techniques.

It was assumed that the sorption is quantitative when the chelate contains systems of π-electrons in the mol-ecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbital do not have a substantial influence[34]. The major advantage of these models is their simplicity; how-ever, the models fail to describe accurately the adsorp-tion equilibrium under varying conditions, such as pH and ionic strength. The adsorption equilibrium studies have revealed that pH is the dominant parameter con-trolling the adsorption[35].

The purpose of this work is pre-concentration-separation of Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+} on activated carbon modified 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD). The influences of the some ana-lytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investi-gated.

EXPERIMENTAL

Instruments

The measurements of metal ions were performed with a 680 AA shimadzu spectrometer equipped with a hollow cathode lamp and a deuterium background cor-rector, at respective wavelengths (resonance line) using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solu-tion pH.

Reagents

Acids and bases were of the highest purity avail-able from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate lead, cadmium, mercury, iron, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, so-dium and potassium(all from Merck) were of the high-est purity available and used without any further purifi-cation. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate so-lution for preparing the desired pH buffer solution. Ac-tivated Carbon(AC)(gas chromatographic grade, 40-60 mesh from Merck), were soaked in hydrochloric acid for 1 d, it was then washed with deionized water and dried at 110^0C for 1d. The ligand 2-amino-5-mercapto-1,3,4-thiadiazole (AMTD) was purchased from Merck Company and used as received.

Preparation of AMTD coated activated carbon

Ligand loaded activated carbon was prepared by dissolving a weighed amount of AMTD in water to the required amount of activated carbon. After 48 h, the solutions were filtered through the filter paper and acti-vated carbons were washed with distilled water until the filter out was no longer alkaline. Finally, the mix-tures were dried at 70^0C overnight. The solid phase columns were initially preconditioned with solution with desired pH. For the final optimum experiments the solid phase was prepared as follow: 25mg AMTD per 800mg of AC.

Preconcentration procedure

The pH of model solutions containing $0.05\mu g/mL^{-1}$ of ions metal was adjusted to the desired pH value by adding nitric acid and NaOH 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 $3mL/min^{-1}$, to effect the deposition of analyte. The adsorbed ions by adding 6mL of 4.0M nitric acid at column for 5min then were passed through the column with a flow rate of $2.0mL/min^{-1}$. The analyte ions in the eluent were deter-mined by flame atomic absorption spectrometer.

Analysis of the real samples

Spinach(mixture of 4 food vegetable) was pur-chased from Gachsaran Iran. A 40g of spinach was heated in silica crucible for 3h on a hot plate and the

charred material was transferred to furnace for overnight heating at 650^0C. The residue was cooled, treated with 10.0mL concentrated nitric acid and 3mL 30% H_2O_2 again kept in furnace for 2h. The final residue was treated with 3mL concentrated hydrochloric acid and 2-4 mL 70% perchloric acid and evaporated to fumes. The solid residue was dissolved in water, filtered and by keeping the pH at 5.5 by adding nitric acid and NaOH solution. The pre-concentration procedure given above was applied to these solutions.

River and waste water samples were collected from river Iran. Before the analysis, the samples were filtered through a cellulose membrane filter(Millipore) of pore size 0.45mm. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid. The water samples were filtered through a filter paper. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles.

For the pre-concentration procedure, pH of the 250ml of water samples was adjusted to 5.5 using phosphate buffer and the sample passed through the column at flow rate of 3ml/min^{-1}. The analyte ions retained on column were eluted with 6mL of 4mol L^{-1} HNO$_3$. The effluent was sent to flame atomic absorption spectrometry for evaluation of their metal content evaluation[2].

RESULTS AND DISCUSSION

The purpose of this work is to investigate the feasibility of absorption of these ions on activated carbon modified with AMTD. For obtaining maximum signal for evaluation of these ion contents, the effective parameters viz. pH of sample, amount of ligand and solid phase, type and concentration of eluting agent and flow rate must be optimized.

Effect of pH on recovery

In the solid phase extraction studies for heavy metal ions based on chelation, the influence of pH of the aqueous solution one of the main factor for quantitative recoveries of the analytes. Due to this important point, the influences of pH were investigated at the pH ranges 2-8 for both sorbents with model solutions, keeping the other parameters constant. Analyte deposition depended on the sample pH, and as shown in figure 1,
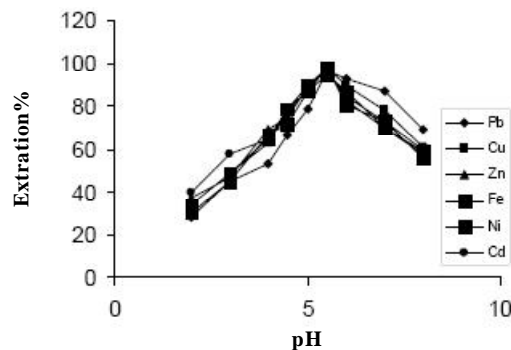

Figure 1: Effect of pH on recovery of metal ions(N=3), 250mL of 0.05μg/mL^{-1} of each ions at various pH with flow rate of 3mL/min^{-1}, 25mg AMTD; eluting solution, 6mL 4.0M HNO$_3$ with flow rate 2.0mL/min^{-1}
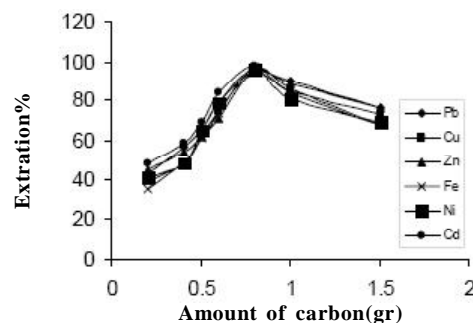

Figure 2: Effect of amount of AC on recovery of metal ions (N=3), 250mL of 0.05μg/mL^{-1} of each ions pH=5.5 with flow rate of 3mL/min^{-1}, 25mg AMTD , 6mL 4.0M HNO$_3$ with flow rate 2.0mL/min^{-1}

high deposition efficiency was achieved at a pH of 2.0-8.0. The progressive decrease in the retention of lead at a low pH is due to the competition of the hydrogen ion with the lead for reaction with AMTD. The decrease in absorption at pH>5.5 is probably due to the precipitation of lead as lead hydroxide and formation of a negative charge on the activated carbon, which results in the reduction of AC adsorption. To achieve high efficiency and good selectivity, a pH of ~5.5 was selected for subsequent work.

Effect of amounts of activated carbon on recovery

The AMTD-AC can retain all of the mention metal ions while the untreated AC cannot quantitatively retain Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}. Evidently; the pre-concentration of the metals with the untreated AC is not suitable for Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}. Therefore, AMTD -AC seems to be a better sorbent in simultaneous sorption of the studied elements. The ef-

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fects of the amount of activated carbon at fix value of AMTD on the sorption of metal ions at pH =5.5 were examined in the range of 0.2-1.5g. The results demonstrated that, quantitative recoveries(>95%) of the working elements were observed in the range of 0.8 g. Above 800mg, the recoveries were below 95% with 6mL of the eluent. In the proposed procedure, 800mg of activated carbon is recommended (Figure 2). In preparing the ligand-impregnated adsorbents, some properties are required for ligand: they should be chemically stable, their solubility in aqueous solutions should be sufficiently low and they should be strongly adsorbed onto the substrates. In addition, we preferred ligands capable to form complexes with as many metals as possible at the natural pH of the sample solution.

Effect of ligand amount on recovery

The effects of the ligand amount on the retention of the analyte ions on AMTD were also examined and are depicted in figure 3. The recoveries of analytes were quantitative till by the addition of 25mg ligand. After that, the recovery values decreased, probably due to the formation of charged complex which could not been completely retained on solid phase.

Sample flow rate

Two important factors for the quantitative recoveries and desorption of metal chelates on the solid-phase extraction studies are flow rates of the sample and eluent solutions. The influences of the flow rates of the sample and eluent solution for the recoveries of analytes were investigated in the flow rate ranges of 1-12mL/min. The recovery values for analyte ions were quantitative in all the working range of sample flow rates. The quantitative recovery values for eluent solution were obtained at the flow rate range of 2-4mL/min. All further studies were performed at the sample and eluent flow rates of 2.0mL/min.

Type and volume of the 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_2SO_4 and H_3PO_4 at various concentrations, were examined and results are shown in figure 4 and TABLE 1. From result of figure 4 and TABLE1, it is obvious that 6mL of nitric acid with a concentration of
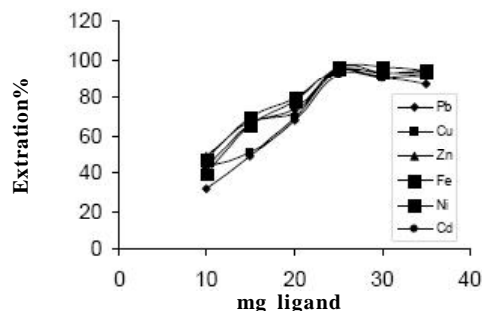

Figure 3: Effect of amount of ligand loaded on 0.8g AC on recovery of metal ions (N=3), 250mL of 0.05μg mL^{-1} of each ions pH=5.5 with flow rate of 3mL/min^{-1}, 25mg 6mL 4.0M HNO$_3$ with flow rate 2.0mL/min^{-1}
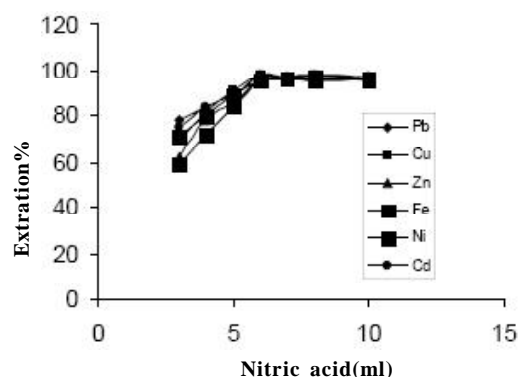

Figure 4: Effect of volume of HNO$_3$ 4M on trace metal ion recovery, 250mL of 0.05μg/mL^{-1} of each ions pH=5.5 with flow rate of 3mL/min^{-1}, 25mg AMTD

TABLE 1: Effect of eluent condition on ion recoveries efficiency

Acid	Pb%	Cu%	Zn%	Fe%	Ni%	Cd %
H_2SO_4 3M	43	33	37	45	37	32
H_2SO_4 4M	59	56	62	69	68	61
HCl 3M	83	78	79	71	80	82
HCl 4 M	92	90	89	87	91	91
HNO_3 3M	84	88	82	83	77	72
HNO_3 4M	99	98	96	97	98	96
H_3PO_4 3M	54	35	43	54	48	42
H_3PO_4 4M	64	49	68	69	79	69

4.0 M were sufficient for quantitative recovery of absorbed lead.

Calibration graphs and precisions

The calibration curve were obtained by using 250mL 0.02-2.0μgmL^{-1} ions solutions at pH=5.5 at the optimum condition. The eluting solution was sent to AAS for evaluating ion content and results are shown in TABLE 2. The results indicate that calibration curve was linear for Lead, copper, zinc, iron, nikel and cad-

TABLE 2 : Specification of presented method at optimum conditions for each element

Parameters	Zn	Cd	Ni	Pb	Fe	Cu
Linear Range ($\mu g\ mL^{-1}$)	0.05-1.6	0.03-1.7	0.04-1.6	0.05-1.3	0.02-1.1	0.04-1.2
Detection Limit ($ng\ mL^{-1}$)	1.3	1.7	1.6	1.6	1.7	1.8
RSD %	1.6%	1.7%	1.3	1.8%	1.7%	2.2%
Recovery %	98%	99%	98%	97%	99%	98%

TABLE 3 : Effects of the matrix ions on the recoveries of the examined metal ions(N=3)

Ion	Tolerance limit ion mg L^{-1}
Na^+, K^+, Cl^-, SO_4^{2-}, Al^{3+}, Mn^{2+},	1000
Sn^{2+}, Mg^{2+}, HCO_3^-, $PO_4^{3-}Ba^{2+}$, Ca^{2+}	750
Zr^{2+}, Pd^{2+}, Cr^{3+}, Co^{2+}	400
Ag^+, Hg^{2+}	100

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^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}.

TABLE 4: Recovery of trace elements from waste water and river water sample after preconcentration on activated carbon modified with AMTD (N=3)

Ions[a]	Waste water				River water			
	Added	Founded	RSD %	Recovery %	Added	Founded	RSD %	Recovery %
Pb^{2+}	0	65.4	1.3	---	0	64.3	1.3	----
	50	116.4	1.6	102.2	100	165.8	1.7	101.5
Cu^{2+}	0	86.4	1.5	---	0	83.9	1.4	---
	50	137.6	1.7	102.4	100	185.6	1.7	101.7
Zn^{2+}	0	55.9	1.7	---	0	46.8	1.6	-----
	50	104.2	1.7	97.8	100	145.3	1.2	98.5
Fe^{3+}	0	94.6	1.4	---	0	164.3	1.8	--
	50	145.8	1.9	102.4	100	267.4	1.4	103.1
Ni^{2+}	0	63.8	1.5	---	0	43.9	1.6	---
	50	114.3	1.0	101	100	94.2	1.2	100.6
Cd^{2+}	0	56.9	1.5	---	0	37.7	1.4	---
	50	105.6	1.7	97.4	100	136.5	1.8	98.8

mium ion in the range of 0.05-1.3, 0.04-1.2, 0.05-1.6, 0.02-1.1, 0.04-1.6, 0.03-1.7μgmL^{-1} using AMTD relative standard deviation of measurement was found for lead, copper, zinc, iron, nikel and cadmium 1.8%, 2.2% ,1.6% , 1.7%,1.3 and 1.7%. Detection limits for this ion is 1.6$\mu g\ l^{-1}$, 1.8$\mu g\ l^{-1}$, 1.3$\mu g\ l^{-1}$, 1.7$\mu g\ l^{-1}$, 1.6 $\mu g\ l^{-1}$ and 1.7g l^{-1} for Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}.

Examination of reproducibility

In order to investigate reproducibility of method at optimum condition six experiments for pre-concentration of these ions on activated carbon modified with or and results are brought in TABLE 3. The results show that efficiency for lead ion based on modified AC are 98.5 , 98.8 , 97.8 , 98.1 , 97.6 and 98.9 % for Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}that indicate repeatable results.

Interferences

In order to examine the effect of the various tested

Interferences that may be concomitant with this ion were investigated. The interference effect of calcium, magnesium and other alkali and alkaline earth ions were presented in TABLE 3 display that these ions up to 1000 fold are negligible and this high selectivity able the method for accurate and precise determination Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Cd^{2+}ion content in real samples.

Analytical performance of the method

The correctness of results was verified by analyzing the concentration after the addition of known amounts of analytes into a river , waste water samples and vegetable sample. The results were summarized in TABLES 4,5. Satisfactory recoveries were obtained for spiked analyte ions. The recoveries were higher than 97%, thus confirming the accuracy of the presented procedure.

CONCLUSION

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The ligands loaded on activated carbon are sensitive and accurate method for determination of trace amounts of copper and lead ions in low concentrations. The results presented in this paper 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. After the use by passing simple solution of ligand the column could be used for at least 100 times.

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