1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) for the separation-enrichment and flame atomic absorption spectrometric detection of copper and lead in hair, water, and food samples

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ABSTRACT

A novel enrichment-separation procedure based on solid phase extraction of copper(II) and lead(II) at ultratrace levels on 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) has been established. The effective critical parameters like pH and eluent type etc. on the quantitative recoveries of the analyte elements were optimized. The matrix effects are also investigated. The procedure was validated by analysing water certified reference materials and addition-recovery tests. The relative standard deviation of the presented procedure was below 10%. The application of the presented solid phase extraction procedure was successfully performed for copper and lead determination in some food and water samples.

Keywords: Solid phase extraction; 1-nitroso-2-naphthol; Multiwalled carbon nanotubes; Impregnation; Environmental samples

1. Introduction

The main sources of the heavy metals at trace levels in the environment are industrial and traffic [1–3]. Humans, animals and plants are more likely to be exposed to heavy metal contamination from environment [4–7]. Trace metals in the environment play important roles in different biological processes in human and animal bodies as essential components and toxins [8–11]. Copper is one of the essential trace element for human, animals and plants. Copper at trace levels is closely bound up with many functions in human body [10,12,13]. The toxicity of lead at trace levels is a persistent public health problem throughout the world. Children are more susceptible to lead than adults because of hand to mouth activity [14–16]. Soil, air, and water pollutions by lead are of great concern because of its adverse effects to human health.

The accurate determination of trace elements in real samples is an important and challenging task in environmental analytical chemistry [17–21]. Inductively coupled plasma-mass spectrometry, inductively coupled plasma-optic emission spectrometry and atomic absorption spectrometry, etc. [22–26] are common modern instrumental detection techniques for the determination of elements at trace levels in the environmental and biological samples. In these determinations, lower levels of the elements than the limit of detection of the instrument [27–29] and negative and/or positive effects of the alkaline and earth alkaline elements on the determinations [30–33] are two critical problems. Separation-preconcentration methods have been used to prevent these problems [34–36]. Solid phase extraction with new improvements is still a very important place in the separation-preconcentration of traces analytes [37–40] due to its simplicity and rapidity. The selection of suitable adsorbent is an important factor to get quantitative recovery values for the analyte species in solid phase extraction studies [40,41]. Many kind of adsorbent have been used for that purposes. Carbon nanotubes are new generation materials for adsorption of metal ions at trace levels. They are very attractive solid phase extractor for the separation-pre-

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concentration of trace species from various real samples due to their stability and high surface areas [42–48]. To improve adsorption ratio on carbon nanotubes, analyte metal ions are converted to organometallic structure by using suitable chelating agents with different combinations like impregnation and/or chemical interactions [42–48]. 1-nitroso-2-naphthol was selected for this study as a chelating agent. Multiwalled carbon nanotubes was impregnated with 1-nitroso-2-naphthol. This combination is firstly used for the separation and preconcentration of traces of copper(II) and lead (II) from environmental samples.

The analytical potential of 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) as adsorbent for solid phase extraction of the separation-enrichment of copper(II) and lead(II) from various environmental and food samples was investigated in this work.

2. Experimental

2.1. Reagents and solutions

All of the solutions were made with water purified through reverse osmosis system. All chemicals used in the presented work were of analytical reagent grade. All the glassware were cleaned by soaking in 10% HNO_3 solution and then rinsed with reverse osmosis water. 1000 mg l^{-1} of standard solutions of Cu(II) and Pb(II) were prepared from high purity nitrate salts from Aldrich, Milwaukee, WI, USA. The working solutions for copper(II) and lead(II) were daily prepared by diluting stock solutions.

TMDA-53.3 Fortified environmental water and TMDA-64.2 Water certified reference materials from National Water Research Institute, Ontario, Canada were used. The buffer solutions used were prepared according to literature [4,7].

Multiwalled carbon nanotube (no.: 636614) was purchased from Aldrich, St. Louis, USA. A solution of 1-nitroso-2-naphtol (no: 6803) from E. Merck (Darmstadt, Germany) (% 0.1 m/v) was prepared by dissolving of 1-nitroso-2-naphtol in small amounts of ethanol and diluting to 50 mL with water.

2.2. Instrumentation

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) was used for metal analysis. The hollow cathode lamp of lead and copper were run under the conditions suggested by the manufacturer. Analysis of the analytes was carried out with air/acetylene flame with 100 mm long slot-burner head. Nel pH-900 pH meter (Ankara-Turkey) with glass-electrode was used for pH adjustments.

2.3. Preparation of 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes(NNMWCNTs)

To impregnation of 1-nitroso-2-naphtholon the surface of multiwalled carbon nanotubes, 1.0 g multiwalled carbon nanotubes was added to 2 ml of 1-nitroso-2-naphthol solution and diluted to 30 ml with reverse osmosis water. It was stirred for 30 min. Then, 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) was filtered

off. It was washed with water and dried overnight at 100°C and used at the experimental works.

2.4. Column Preparation

About 250 mg of 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) was loaded into a 1.0 cm × 1.5 cm column and then washed with reverse osmosis water and conditioned with working buffer solutions. The bed height was approximately 1.0 cm.

2.5. Test procedure

Twenty five mL of model solution containing 20 µg of Pb(II) and 10 µg of Cu(II) ions and 2.0 ml of phosphate buffer solution for pH 7 was passed on the column to allow adsorption at 3 mL min^{-1} under gravity, and then the glass column was washed with 10 ml water. Then the adsorbed Pb(II) and Cu(II) ions were eluted with 7 ml of 3 M acetic acid at 3 mL min^{-1} under gravity. The analytes contents in eluent were determined by flame FAAS.

2.6. Application to real samples

The proposed method was applied to TMDA-53.3 fortified environmental water and TMDA-64.2 Water certified reference materials (CRM) and a tap water and a waste water from a plant in Kayseri-Turkey. 25 ml of CRM was transferred to a beaker and 'test procedure' given above was applied to it. Copper and lead contents were determined by flame atomic absorption spectrometry.

The procedure was applied to different samples including a tobacco from Turkey, latency from Sudan, a cinnamon from India, a thalngan from India and a human hair from Turkey. To digest real samples, 1000 mg of sample was placed into a flask. Then 15 ml of concentrated nitric acid and 5 ml of concentrated hydrochloric acid were added and heated for 1 hour at 150°C. It was repeated twice. The digested sample was dissolved in reverse osmosis water. It was filtered through a filter paper. It was diluted up to 40 ml with reverse osmosis water. Then 'test procedure' given above was applied. Blank digestion was performed by using the same procedure.

3. Results and discussions

3.1. Characterization of the NNMWCNTs

The pristine multiwalled carbon nanotubes and 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes were characterized by using Fourier transform infrared spectrometer (Perkin Elmer Spectrum 400) (Fig. 1a,b).When compared with the FT-IR spectrums of the pristine MWCNT and NNMWCNTs, Significant differences and new peaks are seen. In the IR spectrum of (PAN-imp-ACC), peaks at 3234 cm^{-1}, 2970 cm^{-1}, 1602 cm^{-1}, 1303 cm^{-1}, and 1037 cm^{-1}, correspond to the stretching frequencies of OH (phenolic), CH, =CH, N=O, C–O, and C=C, respectively.

The SEM images of pristineMWCNT and NNMWCNTs was shown Fig. 2a,b. The morphology of the MWCNT and NNMWCNTs shows some differences. The coverage of the

surface of the pristineMWCNT with 1-nitroso-2-naphthol cause the some changes on the surface structure. The white areas on the carbon nanotube after the modification is an evident for impregnation.

Without ligand the recoveries of analyte ions on MWTCNTs were not quantitative (<90%) in our working conditions. After impregnation MWTCNTs with NN,
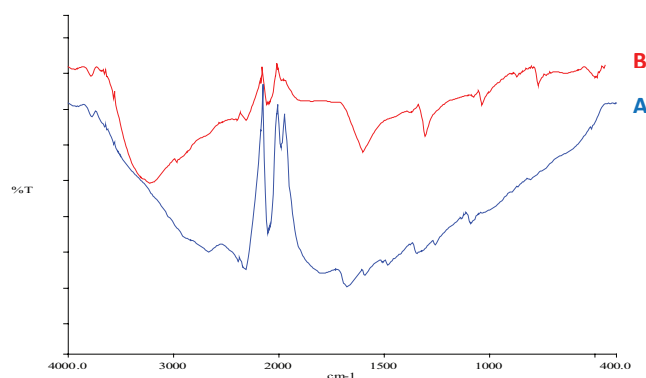

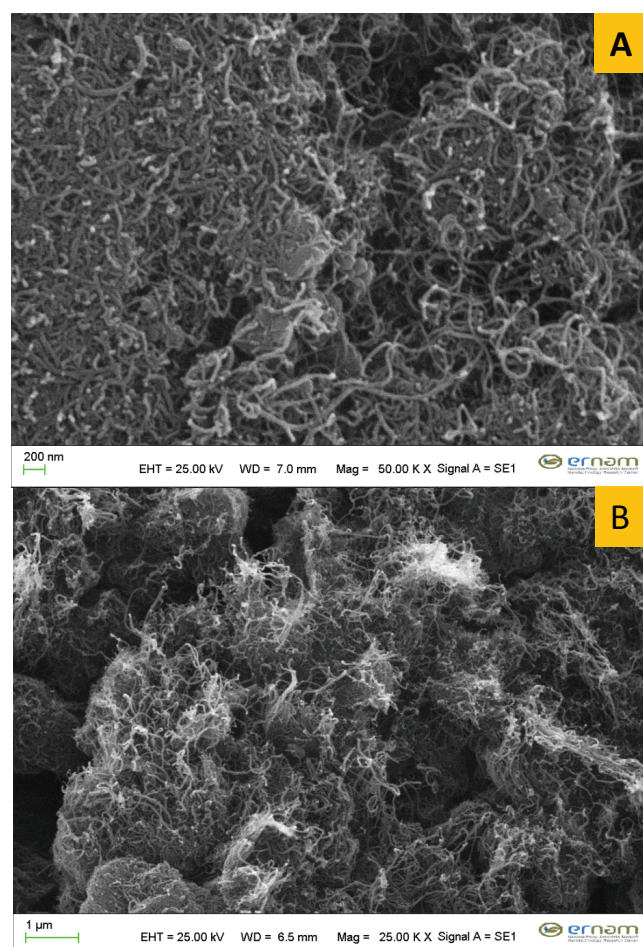Fig. 1. FTIR spectrum of pristine MWCNT (A) and NNMWCNTs (B).

Fig. 2. SEM images of pristine MWCNT (A) and NNMWCNTs (B).

the recovery values reached to quantitative values under the experimental conditions given in experimental. This point showed that the necessity of the impregnation of MWTCNTs with NN.

3.2. Influences of pH of the working media

pH is a critical and important parameter for the quantitative recoveries of metal ions in the separation-enrichment studies [49–54]. The effect of pH on the recoveries of Cu(II) and Pb(II) on 1-nitroso-2-naphthol impregnated multi-walled carbon nanotubes (NNMWCNTs) were investigated in thepH range of 2.0–7.0. The results are depicted in Fig. 3. The quantitative recoveries (>95%) were obtained at the pH 7.0. All further works were performed at pH 7.0 by using phosphate buffer solution.

3.3. Influences of type ofeluent

The elution of copper(II) and lead(II) from 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) was also studied by using different eluent solutions by working at the optimal conditions. The results are depicted in Fig. 4. The recoveries for lead(II) and copper(II) were found quantitative only with 3 mol l^{-1} acetic acid. Experimental results showed that to broke the interaction between 1-nitroso-2-naphthol impregnated multi-walled carbon nanotubes (NNMWCNTs) and Pb(II) and
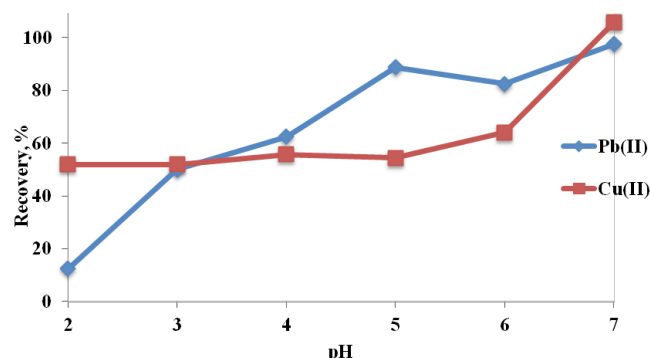

Fig. 3. Influences of pH on the recoveries of copper(II) and lead(II) on 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) (N = 3).
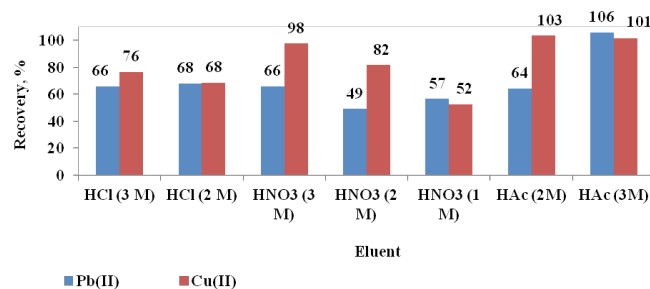

Fig. 4. Effects of the different eluent solutions on the recoveries of the analyte elements from 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) (N = 3).

Cu(II), 7.0 ml of 3 mol l^{-1} acetic acid is necessary. These interactions could not broke quantitatively by using other eluents given in Fig. 4. Therefore, 7.0 ml of 3 mol l^{-1} acetic acid was selected as eluent solution in the following experiments.

The recoveries of analyte ions were quantitative till ten usage of the 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs), due to loss of 1-nitroso-2-naphthol from the surface of multiwalled carbon nanotubes by using 3 mol l^{-1} acetic acid. After 10 usage of adsorbent, it was reimpregnated with 1-nitroso-2-naphthol for next experiments.

3.4. Sample flow rate

The effect of the sample flow rate was tested over a range of 2–5 mL min^{-1}, with all other conditions kept constant. Pb(II) and Cu(II) ions were quantitatively recovered (≥95%) within a sample flow rate of 2–5 mL min^{-1}. For further works, 3 mL min^{-1} was selected as optimal sample flow rate.

3.5. Sample volume

The influences of sample volume on the recovery of copper(II) and lead(II) were also investigated by passing 25–100 ml of model solutions under the optimal conditions. The results are depicted in Fig. 5. At the higher volumes then 750 ml, the recoveries for analytes were not quantitative. The preconcentration factor was calculated by the ratio of the highest sample volume (750 ml) for copper(II) and lead(II) and the lowest final eluent volume (7 ml) and was found as 107.
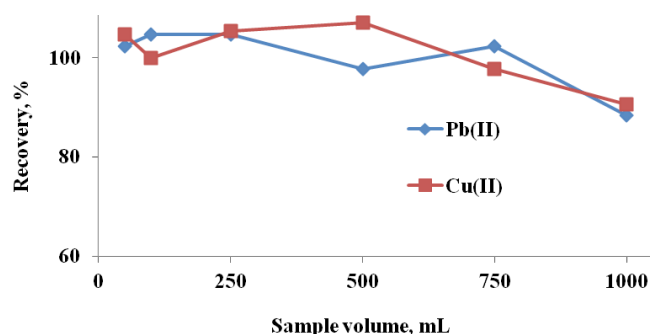

Fig. 5. The influences of the sample volume on the recovery values of copper(II) and lead(II) from 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) (N = 3).

3.6. Effect of Matrix ions

As pointed in the extraction section, the matrix effects are one of the main important problem in the instrumental detection of metals at trace levels [55–63], to solve these problems a powerful separation procedure is necessary. The influences of some cations and anions on the solid phase extraction of copper(II) and lead(II) on 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs)were investigated. The experimental results are summarized in Table 1. It was observed that the presence of ions normally present in real environmental samples. Also, cobalt(II), manganese(II), and zinc(II) were not affected the quantitative recoveries of the analyte ions till 10 mg L^{-1} of Co(II), Mn(II) and Zn(II).

3.7. Analytical features of the presented method

The limits of detection for analyte elements, defined as the concentration equivalent to three times the standard deviation (N = 10) of the blank solutions for Cu and Pb were 22 and 19 μg l^{-1}, respectively.

The method was applied to the determination of analytes in TMDA-53.3 Fortified environmental water and TMDA-64.2 water certified reference materials to establish the validity of the proposed solid phase extraction method. The results are presented in Table 2. The results are in good agreement with reference values.

3.8. Application of the presented method to real samples

The method was applied to the determination of copper and lead in a tap water from Kayseri-Turkey. The recovery-the analytes from spiked samples of were also studied. The results are given in Table 3. Quantitative recoveries were obtained for copper(II) and lead(II) ions.

The proposed solid phase extraction procedure was also applied to determination of copper and lead contents of a tobacco from Turkey, latency from Sudan, a cinnamon from India, a thalngan from India and a human hair sample from Turkey. The results are given in Table 4.

4. Conclusions

A simple and rapid solidphase extraction method based on the adsorption of traces copper(II) and lead(II) on 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes

Table 1
Effect of matrix on the recoveries of Pb(II) and Cu(II) from 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) (N = 3)

Coexisting ion		Na$^+$	K^{+-}	Co^{2+}	Mn^{+2}	Zn^{+2}	Mg^{+2}	Ca^{+2}	SO$_4^{-2}$	Cl$^-$	PO$_4^{-3}$
Added as		NaNO$_3$	KCl	Co(NO$_3$)$_2$·6H$_2$O	Mn(NO$_3$)^2	Zn(NO$_3$)^2	Mg(NO$_3$)$_2$·6H$_2$O	CaCl$_2$	Na$_2$SO$_4$	KCl	Na$_3$PO$_4$
Concentration (mg/L)		10,000	1000	10	10	10	400	200	400	1000	800
Recovery, %	Pb(II)	104 ± 5	104 ± 5	93 ± 10	104 ± 5	100 ± 10	104 ± 5	93 ± 10	104 ± 5	104 ± 5	93 ± 10
	Cu(II)	96 ± 2	95 ± 1	94 ± 0	100 ± 2	96 ± 0	95 ± 2	98 ± 2	95 ± 1	95 ± 1	94 ± 0

Table 2
Evaluation of Pb(II) and Cu(II) concentrations in water certified reference materials (N = 3)

Analytes	TMDA-53.3 Fortified environmental water			TMDA-64.2 Water		
	Certified value ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)	Certified value ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Pb(II)	350	331 ± 10	95	286	298 ± 10	104
Cu(II)	312	312 ± 10	100	270	267 ± 15	99

Table 3
Addition and recovery of analytes on 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs) from a tap water from Kayseri-Turkey (N = 3)

Analytes	Added (μg)	Found (μg)	Recovery (%)
Pb(II)	0	0	–
	2.5	2.5 ± 0.1	100
	4.0	3.8 ± 0.1	95
Cu(II)	0	0	–
	0.6	0.6 ± 0.1	98
	1.4	1.4 ± 0.1	100

Table 4
Determination of analyte elements in water, smoke, food and hair samples by using presented solid phase extraction method (N = 3)

	Wastewater ($\mu g\ L^{-1}$)	Tobacco ($\mu g\ g^{-1}$)	Sudan Latency ($\mu g\ g^{-1}$)	Indian Cinnamer ($\mu g\ g^{-1}$)	India Thalngan ($\mu g\ g^{-1}$)	Human Hair ($\mu g\ g^{-1}$)
Pb(II)	3.0 ± 0.7	1.2 ± 0.1	1.0 ± 0.4	0.6 ± 0.1	1.5 ± 0.3	0.6 ± 0.1
Cu(II)	0.15 ± 0.02	0.03 ± 0.01	0.13 ± 0.02	0.11 ± 0.05	0.15 ± 0.04	0.10 ± 0.05

(NNMWCNTs) has been established prior to their flame atomic absorption spectrometric determinations. The method was applied to determination of copper and lead at environmental samples. The presented method is simple, fast and preconcentration factor is relatively higher than the methods in literature. The adsorbent was used for 10 subsequent preconcentration cycles without any loss on the adsorption properties of 1-nitroso-2-naphthol impregnated multiwalled carbon nanotubes (NNMWCNTs). The presented technique could be applicable to the separation and preconcentration of the other metal ions with some modifications in environmental samples. The next studies will be focused on this point.

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