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Solid-phase Extraction Using Modified Carbon Nanotube and Cupferron Ligand for Preconcentration and Determination of Trace Amounts of Copper in Real Samples

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Abstract

A solid phase extraction procedure for simultaneous separation and preconcentration of trace amounts of Cu^{+2} ion from various real samples prior to its determination by flame atomic absorption spectrometry has been developed. The proposed method is based on the utilization of multiwalled carbon nanotube in combination with Cupferron ligand as a solid phase extractant. The influences of the analytical parameters, including pH, amounts of ligand and adsorbent, sample volume, volume and concentration of eluent, flow rates of solution and , interference effects from the foreign metal ions were investigated for the optimum recoveries of the analyte ion. The optimum pH for the separation of Cu^{+2} ion on the new sorbent was 7.0. The relative standard deviation (RSDs) and the recoveries of standard addition for this method were lower than 5 % and 95-100 %, respectively. A sample volume of 200 mL resulted in a preconcentration factor of 100. The proposed procedure was successfully applied to the determination of copper in various real samples with satisfactory results.

Keywords: *Solid phase extraction, Flame atomic absorption spectrometry, Heavy metals, Multiwalled carbon nanotubes, Cupferron ligand, Preconcentration.*

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Introduction

Determination of trace metal ions is very important for monitoring environmental pollution. Some serious inorganic pollutants are which cannot be destroyed as Heavy metals (HMs). In generally, heavy metals are highly persistent environmental pollutants, and having a considerable Geo-accumulation index and *enrichment factor* and gradual removal rate. They have toxic and undesirable effects on organisms' health as humans, animals, plants and aquatic ecosystems [1-4]. The main pollution sources of heavy metals are waste residue, waste water from industries that could be infected food, air and fresh water [5]. Because of roles of HMs in the human body and environment, an important field in analytical and environmental chemistry and concerned science is the accurate and precise determination of metal ions at trace levels [6,7]. Determination of trace quantities of HMs requires the aplication of sensitive and selective techniques such as flame atomic absorption spectrometry (FAAS) [8], electrothermal atomic absorption spectrometry (ETAAS) [9], inductively coupled plasma mass spectrometry (ICP-MS) [10], inductively coupled plasma optical emission spectrometry (ICP-OES) [11], and X-ray fluorescence spectrometry (XRFS) [12]. In comparison with the other techniques, FAAS has the advantages of sensitivity, simplicity and cost-effective. However, direct determination of trace amounts metals in complex matrices by FAAS is limited due to low concentrations and matrix interferences [13]. Generally, in determination of trace metals, need to a pre-concentration and separation method to enhance and improve the selectivity and sensitivity of analysis that the widely used techniques for this purpose include liquid–liquid extraction [14, 15], ion-exchange [16, 17], coprecipitation [18-20], solid-phase extraction [21-26], flotation [27], electrochemical deposition [28, 29], and cloud point extraction [30]. Among various pre-concentrative separation techniques, solid phase extraction (SPE) has also emerged as a powerful tool for the separation/enrichment of metal ions, to its simplicity, rapidity, adaptability with different detection techniques, and the ability to attain a high pre-concentration factor [31]. Various solid phases including chelex 100 [32], silica gel [33,34], Amberlite XAD resins [35], polyurethane foam [36], and activated carbon [37] have been applied for the solid-phase extraction of traces HMs in environmental samples prior to analysis operation. The choice of the sorbent is a key factor to achieve the appropriate selectivity, the quantitative recovery and the high preconcentration factor in the SPE. Nanoparticle materials have been proven to possess great potential as adsorbents for removing many kinds of environmental pollutants.

Multiwalled carbon nanotubes (MWCNTs), one of the most commonly used building blocks of nanotechnology, are unique and one-dimensional macromolecules that possess outstanding thermal and chemical stability and unique physicochemical and electrical properties [38], MWCNTs, due to their high surface area and large micropore volume, are also considered to be extremely good adsorbents for the removal of many compounds. Recently CNTs have been shown to be excellent classes of sorbent materials for SPE [39].

This article describes the application of modified multi walled carbon nanotubes (MWCNTs) and Cupferron ligand for the separation and pre-concentration of copper from different aqueous matrices prior to determination by FAAS.

Experimental

Instrumentation

In this study, A Varian spectra AA 240 atomic absorption spectrometer was used as instrumental detection system. Air-acetylene burner was used for the determination of the metal ions. A pH meter, Sartorius PT-10 (Germany) was employed for measuring pH values in the aqueous phase. IR spectra were recorded on Broker FT-IR using KBr.

Reagents

All the chemicals used were of the analytical reagent grade from Merck (Darmstadt, Germany). Doubly distilled deionized water was used throughout the work.

Preparation of modified MWCNTs and preconcentration procedure

Raw MWCNTs were refluxed with concentrated HNO_3 for 1 h at 100 °C in order to oxidize the surface of them. Then, the oxidized MWCNTs were washed with distilled water until neutral pH of solution and dried at room temperature [40]. 30 mg of oxidized MWCNTs , 5.0 mL of 0.05 % (w/v) Cupferron in water, and Cu^{+2} solution (0.6 µg.L^{-1}) with pH=7 were stirred for 6 h. Afterward, modified MWCNTs were transferred onto a filter paper, washed with distilled water and dried at room temperature. In this step, copper was adsorbed on modified MWCNTs. The adsorbed copper was eluted from sorbent with 10 mL of HNO_3 (4.0 M) at a flow rate of 0.5 mL.min^{-1}. Finally, eluted solution was determined by FAAS and then the absorbance of copper was measured compared with a blank [39].

Preparation of samples

The proposed methods was applied to different real samples including tap and mineral water samples, and gold-plating wastewater and were collected from Tehran City and Eshtehrad industrial town respectively and stored in polyethylene bottles. The samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size and acidified with 1.0% nitric acid and were subsequently stored at 4.0°C in a refrigerator. The organic content of the water samples were oxidized in the presence of 1.0% H_2O_2 and by addition of concentrated nitric acid. The pH of the samples was adjusted to 7.0 with buffer solution. Then the preconcentration procedure given above was applied to understudy water samples [13, 17-19].

Results and discussion

The morphology and composition of the sorbent were characterized by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Figures 1-3 display the FT-IR spectra of raw MWCNTs and oxidized MWCNTs and modified MWCNTs with Coppferron, respectively. The peaks at 1718 cm^{-1} and 1458 cm^{-1} in the spectrum of oxidized MWCNTs can be assigned to C=O stretch and O-H bend, respectively. The peaks at 2360 cm^{-1} and 2343 cm^{-1} due to asymmetrical and symmetrical C–H stretching vibrations [13-15, 18,19]. The great peak at 3447 cm^{-1} can be attributed to OH group. The SEM images at various magnifications revealed that the sorbent has a porous structure (Figure 4).

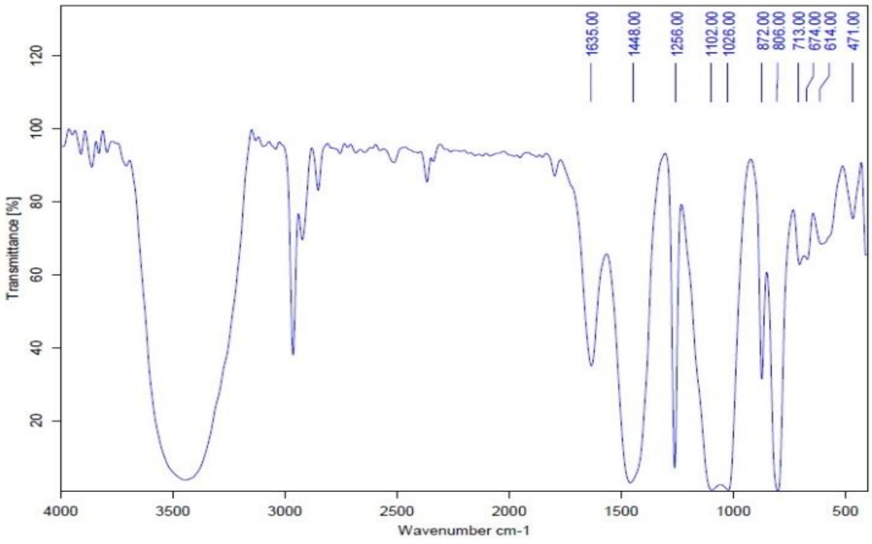

Figure 1. FT-IR spectra of raw MWCNTs.

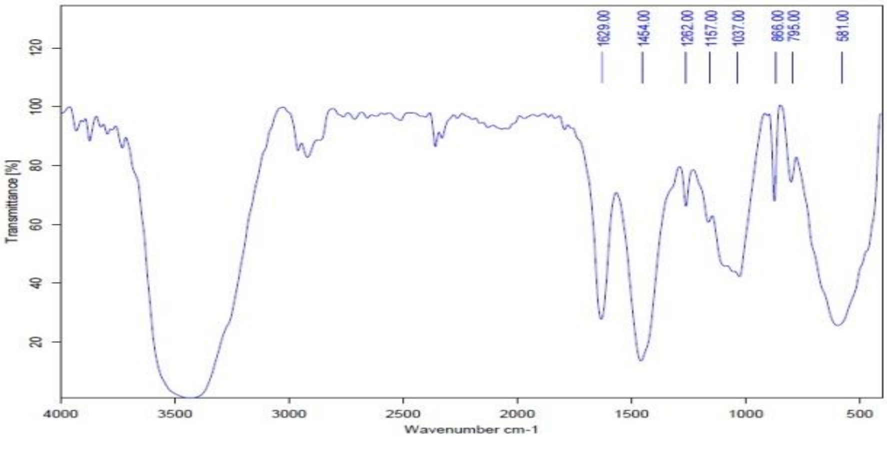

Figure 2. FT-IR spectra of oxidized MWCNTs.

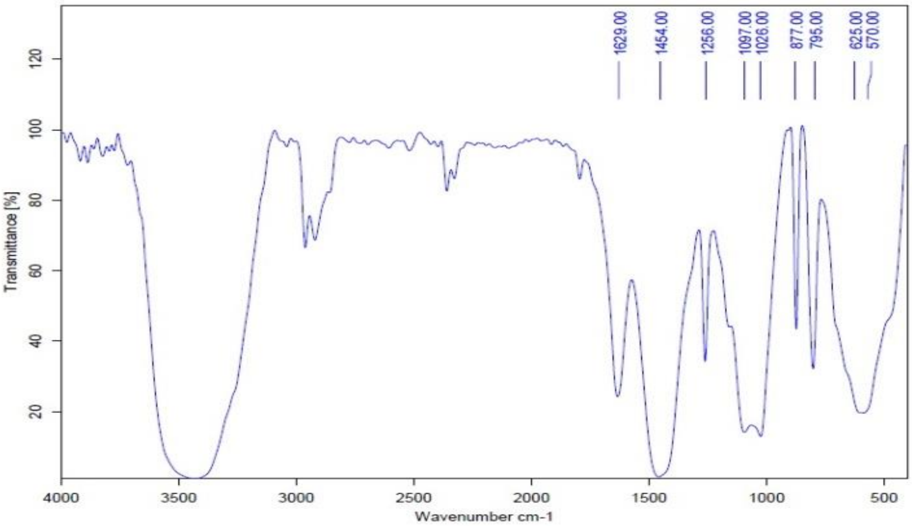

Figure 3. FT-IR spectra of modified MWCNTs with Coppferron.

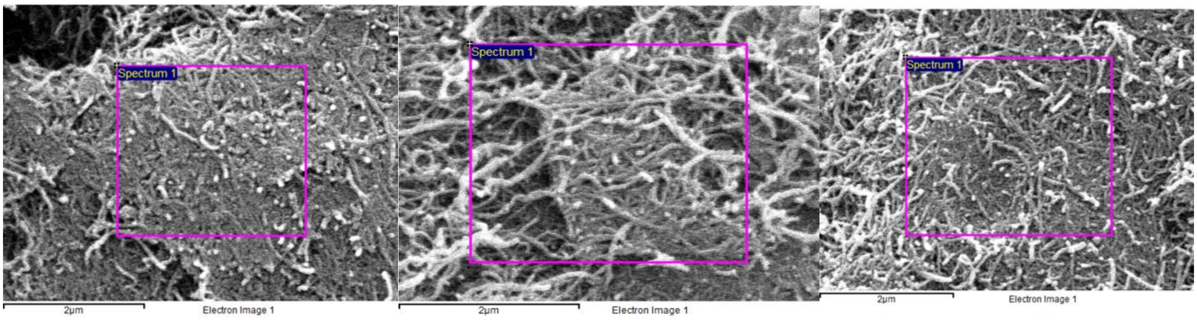

Figure 4. SEM image of Multi walled carbon nanotubes (MWCNTs).

To compare the tendency of oxidized MWCNTs and modified MWCNTs for the adsorption of copper, the experiments were carried out by the preconcentration procedure and showed that although, oxidized MWCNTs have a low tendency for the adsorption of copper (less than 60 %), they are not selective for the separation of copper in contamination matrices. Therefore, the oxidized MWCNTs are not a suitable sorbent for the separation of copper. On the other hand, copper percent recoveries for modified MWCNTs are higher than 98 %. Moreover, modified MWCNTs are selective for the separation of copper and were chosen as sorbent [25,26, 39].

To find out the analytical potential of MWCNTs as a solid-phase extraction sorbent, experimental parameters affecting the preconcentration of copper such as, type and volume of eluent solution, sample pH, flow rates of sample and eluent, sorption capacity and breakthrough volume were studied and optimized.

Type and volume of eluent

To desorption copper ions from modified MWCNTs, several solvents such as, hydrochloric acid, ethanol, acetone, and nitric acid were examined. The results showed that the best recovery was achieved when nitric acid and then hydrochloric acid was used as eluent. Then, various concentration and volume of nitric acid were checked. By increasing the eluent volume, desorption was increased but enrichment factor was decreased. Finally, it was found that 13.0 mL of HNO_3 (0.1 M).

Effect of pH

The pH value plays an important role for the quantitative recoveries of the metal ions during the solid phase extraction procedure. In order to evaluate the effect of pH values on the recovery of Cu(II) as Cupferron chelates adsorb on multiwalled carbon nanotubes, from sample solutions, were adjusted to a pH range of 1.0-8.0 by either diluted hydrochloric acid or sodium hydroxide solution. The results in Fig. 5 show that the absorbance was nearly constant in the pH range of 4.0-8.0. Accordingly, a pH=7 was selected for subsequent optimization studies and real sample analysis.

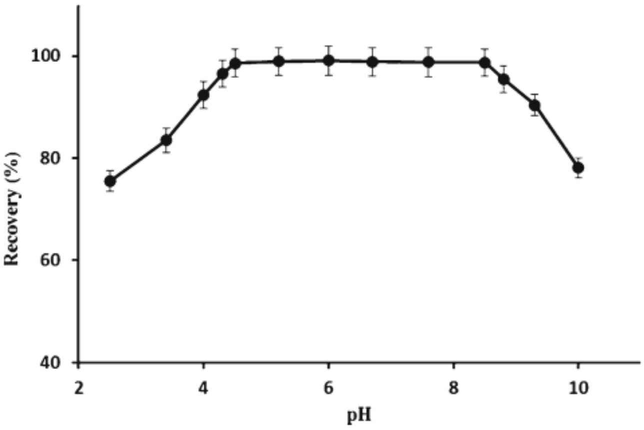

Figure 5. Effect of pH on the extraction efficiency of Copper. Experimental conditions were the following: 10 ml of 0.1 $\mu g.ml^{-1}$ Cu^{+2} solution; the sample flow rate, and amount of sorbent 50 mg; (N=3).

Sorption capacity and breakthrough volume

The sorption capacity is the maximum copper quantity taken up by 100 mg of modified MWCNTs. To find out the influence of sample`s volume, 20 mg of modified MWCNTs sorbent were subjected to several loadings with 15 mL sample solution and then, followed by the determination of retained Cu(II) using FAAS. The maximum capacity was 5 mg Cu(II) per gram of modified MWCNT sorbent. Under optimum conditions, the breakthrough volume of the method was studied by 50.0-1200.0 mL of sample solutions containing 5 ppm Cu(II). Consequently, by considering the final elution volume of 5.0 mL of eluent, and a breakthrough volume of 200 mL, an enrichment factor of 100 was achievable.

Interferences

In order to evaluate the selectivity of this method, the effects of various foreign ions on the recovery of copper were investigated. The interference was due to the competition of other metal ions for co-extraction with copper ion. In these experiments, A 50 mL portion of sample solution containing analytes and a given amounts of foreign ions were concentrated and were treated according to the recommended procedure. The tolerance limit was defined as the largest amount of the foreign ion which causes ±5% error on the recovery. Table 1 indicates that most of the tested ions do not influence the copper determination. It was observed that the presence of ions normally in samples do not interfere under the experimental conditions applied.

Table 1. Effect of coexisting ions.

Foreign ion	Foreign ion/Cu ratio	Recovery (%)
K^+	2000	97.6±3.7
Mg^{+2}	800	96.3±3.4
Na+	900	101.5±5.9
Ni^{+2}	1000	103.6±6.0
Mn^{+2}	800	96.8±4.5
Zn^{+2}	700	102.7±4.9
Co^{+2}	600	100.7±4.5

Analytical figures of merit

Precision, linearity and limits of detection (LOD) were investigated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. With the use of 200 mL sample solution, the calibration graph exhibits the linearity over the range of 0.4 to18.0 mg.L^{-1} of Cu with the correlation coefficient of 0.9997. The limit of detection, defined as the concentration equivalent to three times the standard deviation of a reagent blank solution (N=10) which was 0.11 ng.mL^{-1}for Cu. The relative standard deviation (RSD) values over the range studied are obtained for ten determinations. Results show that LOD of the presented preconcentration study were found as: 2.1% for 5.0 mg.L^{-1} of Cu.

Application

The proposed method was applied to the determination of Cu in real samples. The reliability of the method for the analysis of the real samples was investigated through the recovery experiments and comparing the results with the data obtained by flame atomic absorption spectrometry.

Conclusion

In this work, the adsorption behavior of gold on modified multi-walled carbon nanotubes was studied. As a sorbent, oxidized CNTs modified with Copferron exhibits low detection limit and high enrichment factor for preconcentration of Cu(II) in different matrices with acceptable accuracy and precision. The preparation of this sorbent is simple which can be used several times, thus this method is economical. The obtained results show that this method is suitable to determine copper ion by FAAS in different real samples including tap and mineral water samples, and gold-plating wastewater.

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