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Dispersive Solid Phase Extraction of trace Cu(II) in water samples by synthesis modify Multi walled carbon nanotubes carboxylate

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ABSTRACT: A flame atomic absorption spectrophotometric (FAAS) method for the determination of trace Cu(II) after adsorption of synthesis modify Multi walled carbon nanotubes carboxylate has been developed. The as synthesis modify Multi walled carbon nanotubes carboxylate have a good capacity to retain Cu^{2+}, but the raw and purified as synthesis modify Multi walled carbon nanotubes carboxylate are found not to adsorb Cu^{2+} ions. flame atomic absorption spectrometry (FAAS) was utilized for determination of Cu^{2+}. The effects of solution pH solution, elution conditions on pre-concentration of trace Cu^{2+} were studied and the effect of interfering ions was also investigated. Preconcentration factor was 100 .The method was successfully applied to the recovery of Cu^{2+} in different type of water samples. synthesis modify Multi walled carbon nanotubes carboxylate in this studyis full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction (SPE) and solid phase micro extraction (SPME). Analytical parameters such as the concentration factor, the limit of detection (LOD) of the technique, and relative standard deviation (RSD %) were achieved as 20, 9.0 μg L^{-1}, and 2.9%, respectively.

Keywords: *Cu(II) ion; Flame atomic absorption spectrometry; Heavy metal ions; Modify Multi walled carbon nanotubes carboxylate; Preconcentration of heavy metals; SPE;*

INTRODUCTION

The properties of nano magnetic particles have attracted many studies on their functionality as magnetic carrier. This characteristic make these elements a fit candidate in a wide range of heavy metal ions application in biology and water samples [1, 2], also in medical imaging uses such as magnetic resonance imaging (MRI) [3, 4], in isolating substances and materials in anions– cations pre-concentration [5]. The US Environment Protection Agency (US-EPA) has classified it as one of the group B1 carcinogenic elements [4]. The maximum allowable total cadmium in drinking water has been set at a concentration of 0.03 mg.L^{-1} by the World Health Organization (WHO) [5]. The direct determination of cadmium in water samples by flame atomic absorption spectrometry (FAAS) is very difficult due to the low concentration of cadmium ions and also interfering be-

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cause of influences of the components of the matrix. Therefore, separation and preconcentration steps are often required to achieve accurate, sensitive and reliable results by FAAS. Several techniques including precipitation/co-precipitation [6], liquid-liquid extraction [7] cloud point extraction [8] and solid-phase extraction [9] (SPE) have been developed for the separation and preconcentration of trace cadmium. Among all of methods, solid-phase extraction is the most common technique used for preconcentration of an analyte in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [9, 10]. In recent years a new kind of SPE, magnetic solid-phase extraction (MSPE), has attracted so much attention. The MSPE is based on magnetic materials as sorbent, which can be isolated from the matrix quickly by using a magnet. Compared with other isolation methods, MSPE can improve the extraction efficiency and simplify the process of preprocessing. In recent year, the application of nanomaterial's such as activated carbon [11-15], Different methods, co-extractant ligands has attracted considerable attention [16]. However, the use of classical extraction methods for this purpose is usually for the extraction and separation of Cu ions have been suggested including liquid chromatography [17-22] supercritical fluid extraction, flotation, aggregate film formation, liquid membrane, column adsorption of pyrocatechol violet-Cu complexes on activated carbon, ion pairing, ion pairing, preconcentration with yeast, and solid phase extraction using C18 cartridges and disks [23-33]. Consequently, in the current investigation, the researchers focused on the first application of MWCNTs-COOH as a novel adsorbent for dispersive solid-phase and extraction of Cu^{2+} wastewater samples before the flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation

The determination of Cu^{2+} by PG-990flame atomic absorption spectrometer is equipped with HI-HCl which was done according to the recommendations of the manufacturers. Accordingly, the pH measurements were used by Sartorius model PB-11.

Materials

In the current investigation, the following materials have been applied for the experiments; functionalized carbon nanotubes with carboxyl, hexahydrate Cu(II) nitrate, thio-semi-carbazide ligand, buffer, and nitric acid. Additionally, ethylenediamine, thio-semi-carbazide ligand (CH_5N_3S) was prepared from Darmstadt, Germany of Merck.

Synthesis of carboxylic functionalized carbon nanotubes

A mixture of 4.0 g of nanotubes and 100 ml of HNO_3 was refluxed under stirring conditions at 120 °C. The product of (MWCNTs-COOH) was filtered with 1.2 mcm filter paper and then washed with deionized water to obtain the neutral pH. Finally, it was inserted in the oven at 60°C to dry off completely [30].

Synthesis of amine-functionalized carbon nanotubes

A certain amount of product produced in the previous step (MWCNTs-COOH) was added to 20 ml of ethylenediamine solution and then, it was placed in an ultrasonic bath for 5 h. In the last step, it was stirred for 24 h at 60 °C and finally, the product was collected by filtration and washed with methanol and dried in a vacuum oven [31].

The initial experiment of Cu^{2+} extraction for determining the suitable adsorbent

The procedure for extraction and recovery of copper ions by MWCNTs-COOH is as follows; in the first step, 0.2 g of thiosemicarbazone ligand and 0.3 g of MWCNTs (carboxylic and amine functions) and were dissolved in the little amount of acetone, and then it dried. Four 50-mL ballons were adopted, and then 0.05 g of MWCNT (amine function) was poured into one of the balloons. Afterward, 0.05 g MWCNT with carboxylic function, 0.05 g combination of ligand and amine MWCNT, and 0.05 g mixture of ligand and carboxylic MWCNT were added to each other balloons. Thereupon, a 1 ml buffer solution with a pH of 4.5 was added to balloons and a 2 ppm solution was prepared with an analyte. Four solutions were shaken at 25°C for 20 min, then these solutions for 15 min were centrifuged and the supernatant injected into an atomic absorption apparatus.

The effect of adsorbent amount for Cu^{2+} extraction

Seven 2.0 ppm solutions with 50 mL of Cu^{2+} were provided and poured into seven flasks. Seven solutions were adjusted at pH=10 (optimum pH) and different amounts of the adsorbent (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) added to flasks. The mixtures were shaken for 20 min, and then the mixtures were centrifuged and the top solution of the examine tube injected in flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was performed by the adsorbent, optimal conditions were achieved for it, and multiple real aqueous samples were investigated. The real samples were as follows; well and drinking water in Pishva Town were collected with temperatures of 20 and 22°C, pH=7.1, 7.3 in 23.8.95 at 9:45, 10:00, respectively. Finally, a fish farming sample was collected at, pH=6.20 in 23.8.95 at 11:20. First, these suitable bottles were provided for the sampling of samples. The bottles were washed first with ordinary and distilled water. The bottles dried completely, and the 'suitable' label was attached to each bottle. To collecting of water samples, the used containers sample dried and cleaned and they had already been washed. For the analysis of the samples in the first stage, colloidal and suspended particles were removed. To this aim, the water samples passed through 0.22 µm filters. Next, the volume of 100 mL of samples was poured into the sample container. The pH of samples was adjusted at 10 and then, nanotube and ligand were added to samples. They stirred for 20 min and the mixture was then centrifuged. Then, they were washed with HNO_3 0.1 M and were shaken again for 20 min. Finally, following the centrifugation of the mixture, absorption of Copper ion was identified from the filtered solution by flame atomic absorption spectrophotometry. In the first step, the sample itself was injected into the apparatus without any Copper ion, wherein water samples, the device displayed no absorption. To identify certain amounts of Copper of the samples, the method of standard elevation was used. This stage was accomplished like the first step, the only discrepancy was that 0.5 mL of 200 ppm solution with Cu^{2+} added to the water samples. Finally, the absorption of Copper ion was identified from the filtered solution by flame atomic absorption spectrophotometry.

RESULT AND DISCUSSION

This section deals with the results of the research experiments. The results achieved in the experimental chapter, calibration curve, and the factors influencing the extraction (e.g. pH, temperature effect, time, etc.) of Cu^{2+} ion by the MWCNTs are discussed which are followed in the presentation of scientific justification and overall conclusion of the study.

Investigation of the influential factors on Cu^{2+} extraction

Study the effect of pH on Cu^{2+} extraction

The results of this study are provided in Fig. 1 As the results in Fig.1 indicate, at pH=6, Copper ion adsorption was maximized, while at lowest and highest pHs, the extent of adsorption declines, inferring that at pH<10 adsorptions of Cu^{2+} ions cannot occur completely. As revealed in Fig. 1, to determine the amount of MWCNTs-COOH required for effective removal of Cu^{2+}, different amounts of the MWCNTs-COOH (50 mg) for modification of MWCNTs-COOH with fixes amount (3 mg) and its effect for the removal of Cu^{2+} from 20 mL solutions of cobaltion (50 µg/L) were investigated.

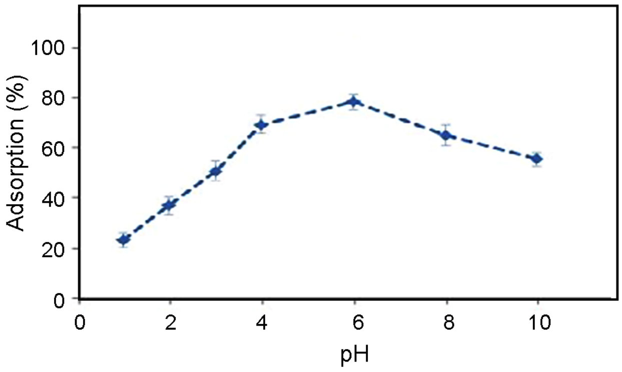

Fig. 1. The effect of pH in the Cu^{2+} adsorption

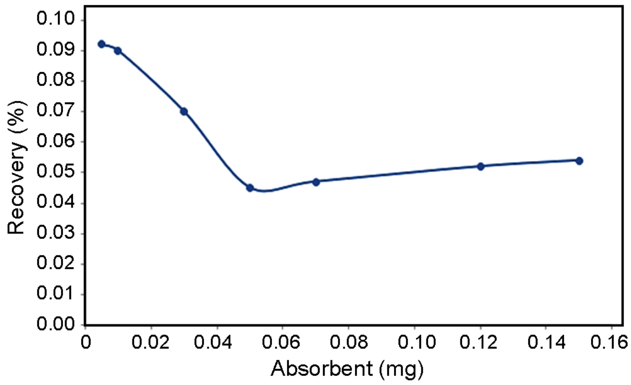

Fig. 2. The effect of adsorption Cu^{2+} of the adsorbent

Study the effect of MWCNTs-COOH level for Cu^{2+} extraction

The results of this study are shown in Fig. 2. As the results in the table ascertain, at 0.05 g of the MWCNTs-COOH, the adsorption percentage and recovery of Cu^{2+} have been maximized. As Fig. 2 shows, by increasing the adsorbent, the remaining quantity of Cu^{2+} decreases. Fig. 2 shows the amount of remaining Cu^{2+}.

Investigation of the effect of time on Cu^{2+} extraction

Based on the results, the extent of absorption increases, and the Copper ions present in the solution find more chance to be adsorbed in the adsorbent's sites. Therefore, the quantitative extraction of Copper ion is possible for a period of longer than 20 min, and within durations longer than 20 min and more, the reaction happens completely.

Survey of the effect of type of various desorption solvent for recovery of Cu^{2+}

Based on the results (Table 1), NaOH cannot be used as appropriate desorption and these bases do not possess a complete detergence power. Therefore, mineral acids with determined concentrations, H_2SO_4, and HNO_3 were applied. As shown in Table 1, the results of this table offer that all acids contain a good detergence power for Cu^{2+}, but the recovery percentage of HNO_3 is higher than that of other acids. In an acidic environment, the possible deposits dissolved and recovery of these ions increased. However, the results obtained from nitric acid were better than H_2SO_4, in that 0.1 M of solution washed 92.54% of the Cu^{2+} ion adsorbent. So, for the rest of the experiments, nitric acid 0.10 M was used as the desorption solution.

Table 1. Selection of the appropriate desorption for recovery of Cu^{2+}

Solvent	Recovery (%)
HNO_3 0.1M	95.20(2.8)[a]
HNO_3 1M	85.32(2.7)
HNO_3 3M	76.75(2.8)
H_2SO_4 0.1M	75.64(2.5)
H_2SO_4 1M	74.50(2.8)
NaOH 0.1M	67.66(2.9)

a) measurement RSD after three replications

Survey of optimization of the volume effect of desorption solvent for Cu^{2+} recovery

After the investigation and choice of optimal desorption, the volume of solvent was investigated, with the results which are shown in Table 2. The volume of 12 mL for HNO_3 was selected as the optimal volume for washing.

Investigation the effect of breakthrough volume

Following the optimization of the pH of the desorption solvent and sample solution, etc., to elute the Cu^{2+} in the adsorbents, the maximum volume of the aqueous solution containing Cu^{2+} should be measured. If the volume of the test solution to be less than the breakthrough volume, and passaging of that volume, all analytes are kept in the solid phase. The results in (Table 3) verify that up to 250 mL of ions are adsorbed by the nano adsorbents and if the sample volume is greater than this value, some of the Cu^{2+} is not kept on the ad-

Table 2. The optimum volume of the desorption solvent

Solvent volume	Recovery (%)
5 ml	49.65(2.3)[a]
7ml	50.44(2.5)
9 ml	70.46(2.6)
12 ml	90.55(2.7)
14 ml	89.65(2.7)
16ml	89.64(2.6)
18ml	88.69(2.5)

a) Measurement RSD following three replications

Table 3. investigations of the effect of solution volume in the sample

V (ml)	Recovery (%)
50	89.7(2.9) [a]
100	77.2(2.8)
150	78.7(2.7)
250	78.5(2.5)
350	63(2.9)
500	41(2.9)

a) Measurement RSD following three replications

sorbent and pass over the adsorbent with no inhibition. Also with definition by the concept of breakthrough volume, it can be reported that the breakthrough volume in the current study is 250 mL and if the sample solution volumes which includes Cu^{2+} is over 250 mL, adsorption does not occur completely and hence if 250 mL of sample volume is passed over the adsorbent and then with 12 ml of the desorption solvent washed, the concentration factor could not be achieved as 30. This concept that the concentration of Cu^{2+} in 7 mL of desorption solvent which was passed over the adsorbent grows by 20 times. Based on the related results (Table 3), the breakthrough volume calculations are as follows:

Concentration factor = breakthrough volume/the desorption solvent volume =100

Determination of the blank standard deviation (S_b)

The accuracy or replicability of any method is the main factor to recognize its validity and reliability. To inquire about the method's replicability, the results data of the study of four blank solutions (deionized water) deposited in Table 4.

Table 4. measurement RSD following three replications

Sample	Device response
1	0.021(2.8) [a]
2	0.020(2.9)
3	0.020(2.5)
4	0.023(2.8)

a) Measurement RSD following three replications

Based on the results achieved in Table 4, the blank standard deviation was obtained as follows; Sb=0.0004

Determination of the accuracy and RSD% of the method

This parameter was used to investigate the accuracy and proximity of the examined data. As shown in 2.9% standard deviation has been calculated for three tests and the relative standard deviation (RSD) achieved for three replications.

The linear range and a calibration curve of the method

To assess the linear range in the analysis method, a calibration curve should be plotted. This curve is not linear across all concentrations and different factors cause the calibration curve to the situation in the linear range and follow from Beyer Law. the calibration curve of the method is as conform and the line equa-

Table 5. The effect of interfering ions on the recovery of Cu^{2+}

Ions	Added value(ppm)	Recovery percentage Cu(II)
Na^+	200	88.92(2.5) [a]
Zn^{2+}	5.0	97.84(2.1)
K^+	200	88.88(2.7)
Mg^{2+}	100	88.78(2.7)
Cu^{2+}	5.0	89.79(2.7)
Cl^-	308.7	89.18(2.4)
NO_3^-	317	90.29(2.8)
SO_4^{2-}	400	90.94(2.8)

a) Measurement RSD after three replications tion is y=0.005x+0.056 and R^2=0.997.

Study of the effect of disturbances on the measurement of Cu^{2+}

A disturbing ion is an ion that causes a certain variation of over ±5% in the adsorption and recovery of Cu^{2+}. To study the effect of disturbance of other ions on Cu^{2+} extraction, a certain quantity of interfering factors added to the initial solution, and the experiment was performed at breakthrough volume. Absorption of the recovered solution is analyzed with flame atomic absorption and then compared versus the solution absorption resulting from the sample recovery which lacks the interfering ion. As can be shown in Table 6, in the presence of external ions, Cu recovery occurred with ±5% variations and the external ions had no particular effects on the analysis and cause no disturbance.

Determining the method's limit of detection

The lowest Cu^{2+} concentration or weight in a sample that could be determined with a certain confidence level is called the limit of detection (LOD), which is defined as follows. The LOD of a method is a concentration of an analysis sample where the device response to concentration (which is significantly different from the response of the control sample) is defined as follows; the limit of detection is the lowest amount of Cu^{2+}, where the presented method can detect it. Based on the presented definition, LOD can be calculated by the following relation:

$$\mathrm{LOD} = \frac{3S_b}{m} \tag{1}$$

Where S_b and m are the standard deviations of the blank signal and the slope of the calibration curve, respectively. Based on the experimented, S_b=0.0009 and the slope of the calibration curve is 0.0008. Therefore, LOD can be calculated at 20.0 ppb.

Investigation of the obtained results on real sample

The proposed method has been successfully applied to the determination of Copper ion in three real drinking water samples tap water of Tehran, pure water (TWT Corporation of Varamin) and industrial wastewater sample of Charmshar Varamin. The results were shown in Table 6, together with results of a recovery test by added known amounts of silver in water sample. The results of this analysis are shown in Table 6, the level of Cu(II) ions was measured across different water and biological samples at 250 mL.As can be seen, in the water samples, in the Tap water sample of Pishva–Varamin, on 27 Jan 2022, and industrial wastewater sample of Charmshar Varamin on 30 Jan 2022, there is a larger amount of Cu^{2+} than in the experimented water samples. Although, in other samples, there is less Cu(II) ions. Based on this, the performance and power of preconcentration and Cu(II) ions measurement could be deduced.

A comparison between the current method and other methods

A comparison of this method with other methods verified that the current method is more accurate, easiest, and faster as it had smaller relative standard deviation values in comparison with other methods [34-53]. The current method is one of the foremost systems for determining the very trace amounts of heavy metal ions including Cu in aqueous samples. Another point in the usage of nanotube adsorbent is that instead of using the proposed ligand, one can put other ligands on the adsorbent which to adsorb mineral ions, thereby measuring trace amounts of metal ions. A wide variety of ligands can be used given their properties, which act selective towards one or several ions and applying this set, preconcentration, and determination of cations

Table 6. Determination of Cu in the real sample

Recovery	R.S.D.% (n=5)	This method (μg.g $^{-1}$)*	Reference method (μg.l $^{-1}$)*	Samples
89	3.3	10.9	11.9	Tap water
93	2.9	6.09	5.20	Pure water
95	3.1	19.8	18.0	Industrial wastewater

*Average of five determinations.

can be carried out. Using flame atomic absorption and solid drop microextraction, single-drop liquid-liquid extraction, and homogeneous liquid-liquid extraction with other devices, one can determine trace amounts of Cu^{2+} by this adsorbent and achieve a smaller limit of detection value.

CONCLUSIONS

In comparison with other procedures reported for measurement of Cu(II), this method has considerable advantages that are easy and inexpensive and can be applied quickly for environmental aqueous samples. Furthermore, it minimizes the utilization of organic, toxic, and costly solvents. Moreover, the design and development of this procedure for separation, measurement, and preconcentration of Cu^{2+} are essential considering its importance in various industries and the little concentration of Cu^{2+} ion in most samples. Therefore, this research aims to present an effective, selective, cost-effective, and simple method for measurement of the level of Cu(II) across different environmental aqueous samples (in this research, the limit of detection, the value of breakthrough volume, and RSD has been obtained). This research indicated that the measurement of Cu^{2+} occurs at an appropriate level without the interference of any other interfering factor and thus the current method can be applied easily in the measurement of the quantity of Cu(II) in aqueous samples.

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