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An Alternative Method of Extracting Cu^{2+} From Aqueous Solution Using Modified Multiwall Carbon Nanotubes

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ABSTRACT

modified Multiwall carbon nanotubes that has a ultrahigh specific surface space with variety of chemically reactive functionalities, such as epoxy and hydroxyl groups on the basal plane and carboxylic acid groups along the area edge, which can be use different groups for fictionalization, consequently it has a great promise for use as sorbent materials. On the other hand silica is well-known one of the best sorbent for adsorption that we use it as substance for coated on the modified Multiwall carbon nanotubes for produce an ultra-sensitive sorbent. A new technique using a solid phase extraction (SPE) cartridge with modified Multiwall carbon nanotubes by silica as sorbent was developed for the pre concentration of trace amounts of copper and was determined by flame atomic absorption spectrometry (FAAS). Some of the important parameters were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ) were 0.235, 0.765 and the proposed method has a good reproducibility 2.05% (RSD %). The enrichment factor was 200 and the percentage of recovery was in the range of 97-100% .The method was successfully applied to the recovery of Cu^{2+} *in different type of water samples. Modified Multiwall carbon nanotubes and its derivates such as* $MCNT@SiO_2$ *in this study is full of potential to use as an excellent adsorbent in the extraction method like solid phase extraction (SPE).*

Keywords: *Multiwall carbon nanotubes; Silica; SPE; Preconcentration; FAAS; Copper*

INTRODUCTION

Though copper (II) ions are really important for several biological processes, its levels in some states are representation of a problem or illness in many living systems or environments. Although trace copper ions promote rancidity and off-flavors in nutrients, copper accumulation in the liver is a feature of Wilson's illness, producing neurological and psychiatric defects. Hence copper is both vital and toxic for many biological systems [1]. Consequently, determination of trace amounts of copper has received considerable attention in the battle against environmental pollution [2].

FAAS (flame atomic absorption spectroscopy) with its relative low cost and decent analytical performance is the significant instrument in the research laboratories for determination of a range of heavy metals. Accurate determination of trace heavy metals by FAAS is usually one of the important problems for the analytical chemist because of their low concentrations. Also other important problem in FAAS determinations of heavy metals are the effects of the matrix of the analyzed samples. In order hand, these problem analytical chemists mostly use separation and pre concentration methods such as co precipitation, liquid–liquid extraction (LLE), cloud point extraction (CPE), electro deposition, solid phase extraction (SPE), solid phase micro extraction (SPME), etc. [3, 4, 5] .

In recent years, SPE method have been well used for determination of copper ions in numerous environmental samples [6,7] because of its simplicity, rapidity, negligible cost, low consumption of reagents and its ability to combine with different detection techniques either in on-line or off-line mode [8] . The main part of the SPE is the sorbent material that determines the selectivity and sensitivity of the method. Though, the commonly used SPE sorbents, such as $C_{18,}$ silica and graphitic carbon, are often the only suitable option for a limited number of analytes. Reusability of the SPE column is also a problem. Thus, developing new SPE sorbent material is important [9]. Carbon derivates are well-known for their high adsorption capacity. They have been established to possess excessive potential as adsorbents for removing many types of environmental pollutants such as heavy metals [10, 11], Multi wall Carbon nanotubes (CNTs) [12,13] ,Fullerenes can be used as chromatographic stationary phases to offer high selectivity for specific compounds [14,15] or as sorbent materials for on-line clear up and preconcentration [16,17].

Recently, CNTs have been shown to be excellent classes of sorbent materials for SPE [18]. Since the first application of CNTs in SPE by Cai et al that he use multi-walled carbon nanotubes (MWCNTs) [18], In recent years many reports have been distributed focusing on progress of use CNTs-based SPE methods for a great variety of analytes, including phenolic compounds [19], insecticides [20], pharmaceuticals [21,22], inorganic ions [23], organ metallic compounds [24].

Different methods, especially Liquid- Liquid extraction of copper in the presence of various classical [15-19] and macrocylic [20, 21] co-extractant ligands have attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time-consuming, labor-intensive and requires large amounts of high purity solvents for extraction. Never the less, several other techniques for the pre concentration and separation of copper have been proposed including liquid chromatography [22] super critical fluid extraction [23], flotation [24], aggregate film formation [25], liquid membrane [26], column adsorption of pyrocatechol violet-copper complexes on activated carbon [27], ion pairing [28], ion pairing [29], pre concentration with yeast [30], and solid phase extraction using C_{18} cartridges and disks [31].

Solid phase extraction (SPE) or liquid-solid extraction is poplar and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid-liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for Sample separation and concentration purposed [32].

In this study the aim was to develop fast and efficient method for selective extraction, concentration and determination of copper with a novel SPE method using modified Multiwall carbon nanotubes and reduced by mesoporous silica via direct reaction as adsorbent in a SPE column combined with FAAS. The silica used for SPE extraction columns is essentially porous and noncrystal-line, with the general formula $SiO_2 \times H_2O$. The silanol groups are the polar groups through which other organic moieties are bonded which we used it on the surface of modified Multiwall carbon nanotubes for the higher ability of modified Multiwall carbon nanotubes in adsorption Cu (Π) ions.

EXPERIMENTAL

Apparatus

The concentration of the Cu (Π) ions solutions was determined by using the Varian model spectra AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420. The size and morphology of modified Multiwall carbon nanotubes was observed by scanning electron microscopy (SEM model LEO 440i), before taken image with SEM the surface of sample was coated with gold. X-ray diffraction (XRD) measurements were carried out with Cu Kα radiation (40 kV, 60 mA, 2ϴ from 5 -115). Fourier transform-infrared (FT-IR) spectra were taken in KBr pressed pellets on a FT-IR Thermo Nicolet (USA).

Materials and reagents

All the materials and reagents were of analytical grade and were purchased Merck, Aldrich and Sigma Company. All the dilutions were prepared by deionized water.

Synthesis of Mesoporous Sio_2 on Modified Multiwall Carbon Nanotubes

A simple and feasible synthesis method for silica coating of modified Multiwall carbon nanotubes was modified according to the literature [1]. In a typical synthesis, 100 mg MWCNT and (0.1– 3g) CTAB were dispersed into 30 mL deionized water, and the mixture was sonicated for one hour. Then, the above mixture was added to 80 mL anhydrous ethanol and further sonicated for 0.5 h to form a stable dispersion. Instantly, 2 mL $NH_3.H_2O$ was added into the as-prepared MWCNT dispersion.

Subsequently, a TEOS solution (1mL TEOS in 40mL ethanol) was dropped in under mechanical stirring, and the reaction mixture was stirred for another 12 h without sonication. Finally, the MWCNT solution was centrifuged and washed with ethanol. The process results in the formation of a uniform and thick layer of silica on every individual MWCNT.

The surfactants were removed by a fast and efficient ion exchange method (1.2 g of

NH_4NO_3 in 60 mL of ethanol) to obtain SiO_2-coated MWCNT with mesoporous structure.

Column Preparation and Suggested Procedures

The adsorption of copper by the adsorbents was studied by the SPE technique. The SPE mode adsorption was selected because of its simplicity, fast and economic for the pre concentration and determination of trace amounts of cooper in diverse samples. MWCNT @SiO_2 (0.1 g) was placed in a 2mL SPE column using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the column was conditioned with 10mL of MeOH and 10mL of deionized water, respectively. The sample solution (50mL) was passed through the column at a flow rate of 2mL/min. Then, the column was washed with 5mL of 10% (v/v) Me OH aqueous solution to remove the co-adsorbed matrix materials from the column. The analytes retained on the column were eluted with 5mL of 4M HNO_3 aqueous solution that flow rate of eluent was 2ml/min.

Finally, the analyte ions in the eluent were determined by FAAS at 324.7 nm for Cu^{2+}. The effects of several parameters, such effect of pH, eluent type and its volume, effect of flow rates of sample and eluent solution and amount of adsorbent, effect of interfering ions and break through volume were also studied. The results of these studies were used to obtain the optimum conditions for adsorption capacity measurements. Using the procedure described above, the percent of recovery was calculated from the following equation) Eq. (1)):

$$R\% = \frac{(\mathrm{Cs.Vs})\mathrm{x}(\frac{\mathrm{Vw}}{\mathrm{Vs}})}{\mathrm{Vw.Cw}} \qquad (1)$$

Where Cs is analyte concentration in eluent (found by FAAS) (mg/L), and Cw is analyte concentration in sample solution (known) (mg/L), Vs is volume of eluent (mL) and Vw is volume of sample solution (mL).

Sampling

The first Tap water sample were collected from a water tap in our lab (Tehran shargh (Ghiamdasht), Islamic Azad University, Tehran, Iran), and the second tab water sample were collected from a water tap in our location live (pakdasht, Tehran ,Iran) and the bottle of mineral water purchase from grocery store that the company name was Damavand .

Tap water samples used for development of the method were collected in glasses containers. Before the analysis, the organic content of the water samples was oxidized in the presence of 7% H_2O_2 and then concentrated nitric acid was added. These water samples were then filtered through a 0.45µm Millipore cellulose membrane to remove suspended particulate matter and stored in a refrigerator at 4 ˚C in the dark before analysis.

RESULTS AND DISCUSSION

Fig 2. Show the morphology and size of Multi walled carbon nanotubes (MWCNTs) modified by SiO_2 sorbent as shown in Fig. 1. Sorbent retained a homogenous distribution in the range of 156.0–10.0 nm. Fig.3. the formation of MWCNTs was followed by Raman Spectroscopy spectroscopy .the carbonyl vibration appears at 1580 cm^{-1}, while there are fingerprints at 160 cm^{-1} and 230 cm^{-1} due to the presence of hydroxyl species at the carbon nanotubes. [23].

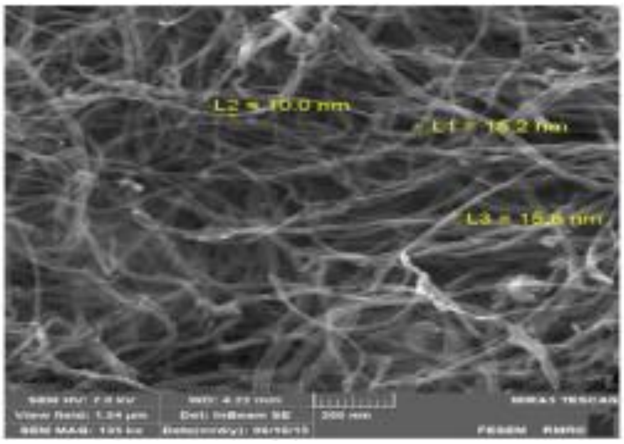

Fig2. *SEM image of Multi walled carbon nanotubes (SWCNTs)*

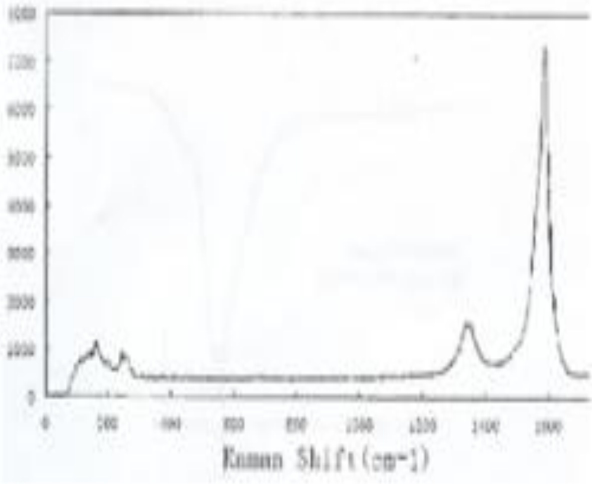

Fig3. *Raman Spectroscopy of Multi walled carbon nanotubes (MWCNTs)*

Characterization of MWCNT and MWCNT@SiO$_2$ Packed SPE Cartridges

IR Spectrum of MWCNT and MWCNT @ Sio$_2$

The FT-IR spectra of the MWCNT and MWCNT@SiO$_2$ shown in Fig. 4. In Fig. 4a shows the FT-IR patterns of MWCNT. The characteristic features were the absorption bands corresponding to O–H stretching at 3434.33 cm^{-1}, the peaks at 2922.01 and 2850.93cm^{-1} were designated as the asymmetric stretching and symmetric vibrations of CH$_2$, C=O stretching vibration of carboxyl appearance of a strong band at 1721.99cm^{-1}, the C–OH stretching at 1216cm^{-1}, O–H deformation at 1411cm^{-1} and C–O vibration at 1025.79cm^{-1}, the peak observed at 916cm^{-1} might be assigned to the C–H out of plane vibration. In Fig.3b we have pattern of MWCNT@SiO$_2$ that shows us a new weak band at 1637 cm^{-1} which may be contributed from the skeletal vibrations of the reduced MWCNT lattice [7, 8] or water. The band at 1077.23 cm^{-1} was assigned to the stretching vibrations of Si-O-Si bond [9]. In the meantime, it was clear to see that there was no characteristic bands for oxygen containing groups between 1300 and 1600 cm^{-1} and that the band at 1637.47 cm^{-1} (C=O) disappeared, which conformed that the oxygen containing groups were removed to a high extent based on this proposed method.

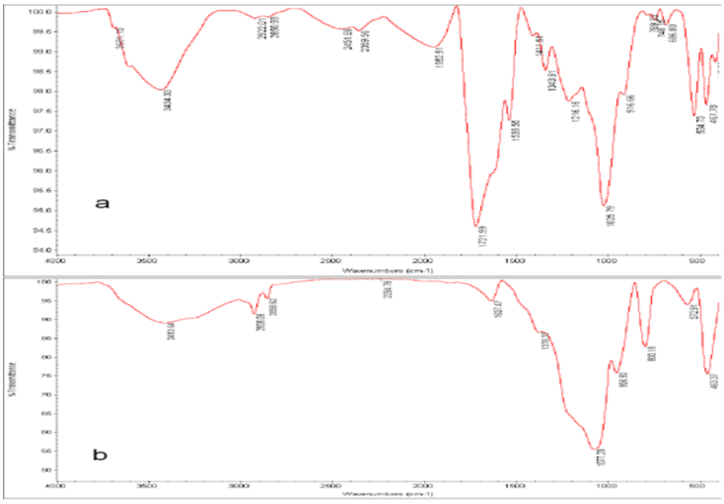

Fig4. *FTIR spectra of (a) MWCNT, (b) MWCNT@SiO$_2$.*

Optimization of SPE Procedures

Effect of pH

The metal chelate stability constant and its chemical stability considerably influence the SPE recovery. The pH shows a very important role on metal chelate formation and following extraction. Therefore, pH was the first optimized parameter. pH of the analyte solutions was adjusted to desired values with diluted hydrochloric acid (0.1 mol L^{-1}) and/or ammonia solution (0.1 mol L^{-1}) The variation in recovery of Cu(II) with pH is shown in Fig.5. . According to the results shown in Fig.4 up to pH 4.5-5.0, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of MWCNT@SiO_2 occurs and there is a weak tendency for retention between Cu (II) and MWCNT@SiO_2, whereas at higher values (pH>5), Cu (II) reacts with hydroxide ions to produce Cu $(OH)_2$. Therefore, pH 4.5 was selected for subsequent work and real sample analysis.

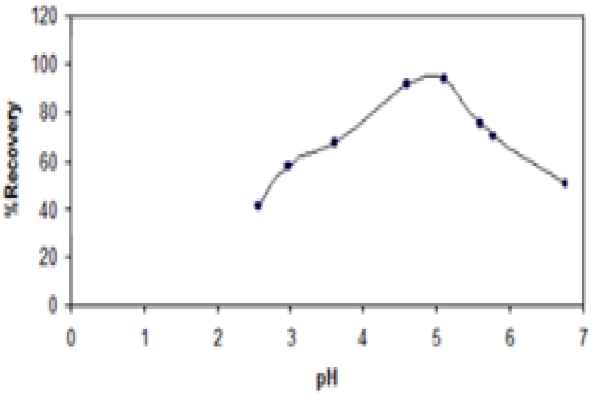

Fig5. *Influence of sample pH on the percentage recovery of Cu (II), conditions: 100 mg adsorbent, 50 ml of 5 mg/L of copper ions.*

Effect of Flow Rates of Sample and Eluent Solution

The effects of flow rates of sample solution and eluent solution on the recovery of Cu (II) was also examined between under the optimum conditions in the range of 1–10.0 mL min^{-1} by controlling the flow rate with peristaltic pump. The recovery of the ions were independent of flow rate in the range of 0.5–2.0 mL min^{-1} for eluent solution and range of 1–5.0 mL min^{-1} for sample solution.

Effect of Sample Solution Volume

Another parameter studied to find the best experimental conditions is the volume of sample solution and/or analyte concentration. For this determination, 50.0–1100.0 mL of sample solutions containing 5ppmCu (II) was processed according to the suggested procedure. The recovery of Cu(II) was quantitative (>98%) obtained up to a sample volume of 1000.0 mL and the adsorbed Cu(II) can be eluted with 5 mL eluent. Therefore, an enrichment factor of 200 was achieved by this method. Finally In our suggested procedure, a sample volume of 50.0 mL was chosen for pre concentration method.

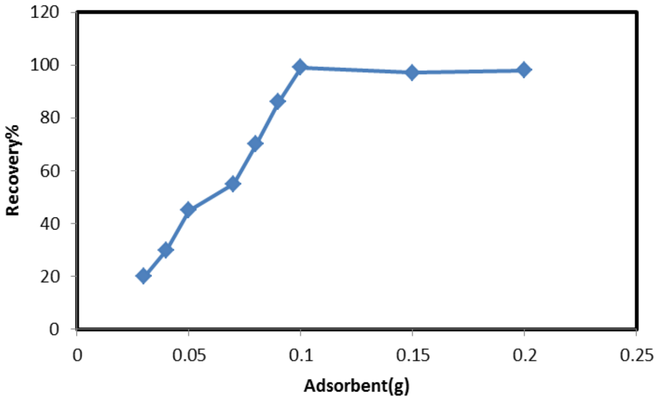

Fig6. *Removal percentages of cooper ions at different amounts of adsorbent, conditions: 50 ml of 5 mg/L of copper ions, pH= 4.5.*

Effect of Amount of Sorbent

To reach a high extraction recovery, different amounts of MWCNT@SiO_2 ranging from 50 to 300 mg were applied to extract the target compounds from the sample solutions. The results are shown in Fig.5 from which it can be seen that the extraction recovery achieved by 100 mg, but almost the same as obtained with

300 mg or more than of the adsorbent. Based on the above results, 100 mg of MWCNT@SiO_2 was selected for the following experiments.

ELUENT TYPE AND ITS VOLUME

Other important factors which affect the percent of recovery are the type, volume, and concentration of the eluent solution used for the removal of metal ions from the sorbent. For this determination, various types of eluents were examined according to the suggested procedure. The results for this study are listed in Table 1. 4.0 mol L^{-1} HNO_3 was found to be adequate for quantitative elution (≥95%).The effect of eluent volume on the recovery of Cu (II) was also studied and listed in table.2. the results show the best quantitative recovery is 5.0 mL of 4.0 mol $L^{-1}HNO_{3.}$ As a result 5.0 mL of 4.0 mol L^{-1} HNO_3 was nominated in the subsequent pre concentration method.

Table1. *Effect of type and concentration of various eluent on the recovery of Cu.*

	%Recovery			
Eluent concentration (M)	1	2	3	4
NaOH	9	11	12	22
NH_3	12.5	12.5	18	19
HCl	12.5	16.5	30	35
H_2SO_4	25	28	28.5	36
$HClO_4$	21	33	38	39
HNO_3	65	77	98	98.5

Table2. *Effect of eluent volume on the recovery of Cu.*

Volume of eluent	**%Recovery**
HNO_3 (4M) 2 ml	44
HNO_3 (4M) 4 ml	79.5
HNO_3 (4M) 5 ml	98.5
HNO_3 (4M) 8 ml	98.5
HNO_3 (4M)10ml	99

Reusability of Column

The stability and potential regeneration of the column were studied. After each time extraction, the column was washed with 10 mL of MeOH and 10mL of deionized water. Therefore, the column was available for a next extraction immediately at least 50 adsorption elution cycles without significant decrease in the recovery of Cu (II) ions.

Effect of Foreign Ions

The influence of common foreign ions on the adsorption of Cu (II) on MWCNT@SiO_2 was studied. In this work, 50.0 ml solutions containing 5ppm of Cu and various amounts of interfering ions were treated according to the suggested procedure. The tolerance level was defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than 5%, when compared with the signal of 5ppm copper alone. The results, listed in Table 3, demonstration that the presence of major cations and anions in natural water has no important influence on the adsorption of Cu (II) ions under the designated conditions.

Table3. *Effect of foreign ions on the percent recovery of 5 ppm Cu in water samples.*

Diverse ion	**Amounts taken(mg)**	**% Found**	**%Recovery of Cu^{2+}ion**
Na^+	92.5	$1.15(2.4)^b$	98.3(2.6)
K^+	92.6	1.32(2.3)	98.6(2.5)
Mg^{2+}	14.7	0.3(1.2)	98.9(1.4)
Ca^{2+}	26.8	2.26(2.0)	98.6(1.5)
Sr^{2+}	2.43	2.86(2.6)	98.4(1.8)
Ba^{2+}	2.64	3.16(2.1)	98.3(1.3)
Mn^{2+}	2.66	1.36(2.5)	93.3(2.8)
Co^{2+}	2.16	1.43(2.1)	99.5(2.9)
Ni^{2+}	1.66	3.04(2.3)	98.44(2.6)
Zn^{2+}	2.38	1.95(2.3)	98.56(2.2)
Cd^{2+}	2.66	1.96(2.4)	98.27(2.8)
Pb^{2+}	0.64	2.3(1.5)	93.21(2.3)
Hg^{2+}	0.44	2.87(2.6)	93.3(2.2)

Ag^+	2.63	3.46(2.9)	96.6(2.2)
Cr^{3+}	1.33	2.92(2.30	93.3(2.3)
UO^{2+}	2.84	2.8(2.1)	98.3(2.3)
[a] Initial samples contained 10µg Cu^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).[b] Values in parentheses are RSDs based on five individual replicate analysis.			

Analytical Figures of Merits

Under optimized conditions, a calibration curve for Cu (II) was found by preconcentrating a series of Cu (II) standards according to the procedure mentioned. The curve was linear from 1.0 mg/l to 7.0 mg/l for Cu. As analytical figures of merit, limit of detection (LOD), limit of quantification (LOQ) defined as $3S_B/m$ and $10S_B/m$, relative standard deviation (RSD) for the proposed preconcentration and speciation method have been determined and listed in table 4.

Table4. *Analytical figures of merits for Cu.*

Parameters	
RSD% n=10	2.05%
LOD(µm/L)	0.235
LOQ(µm/L)	0.765
Enrichment factor	200
flow rates of sample (mL/min)	5
calibration equation	Y=0.067X+0.0239
correlation coefficient	0.9966

Determination of Copper in Real Water Samples

Three type of water samples (information described in section 2.7 sampling) were used for the determination of copper. The analytical results are given in Table 5. The percent of recoveries for the addition of different concentrations of Cu (II) to water samples were 97.5 and 99%.

These satisfactory percent of recoveries indicate no significant effects from the matrix composition of the real water samples.

Table5. *Determination of copper in real water samples.*

sample	**Taken amount (µg)**	**Flame atomic absorption (µg)**	**%Recovery**
Tap water (Tehran, Iran)	0	3.3(2.56)[a]	-
	30	34.2(1.2)	95.6
Tap water (pakdasht,Tehran, Iran)	0	4.3(2.4)	-
	30	36.3(1.60)	96.5
Mineral water (Damavand company)	0	N.D[b]	-
	30	30.3(2.67)	94

a) Values in parentheses are RSD based on four replicated analyses.

b) No adsorption, passes through column

CONCLUSION

In conclusion, the projected SPE possesses the following advantages: the technique is rapid when compared with the previously reported procedures for the separation and determination of copper; the time taken for the separation and determination of copper in a 500 mL sample is at the most 30 min. Furthermore, it is a simple, very sensitive, selective and reproducible method for the separation of Cu^{2+} and in this work the recovery yields obtained with $MWCNT@SiO_2$ were about 95-100% then it show MWCNT and its derivation e.g. in this work $MWCNT@SiO_2$ is full of potential for use as a adsorbent in the extraction method like SPE and SPME .

This composite may find applications in the development of sensor, super capacitor device, or as support for catalysts, and others.

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