Journal of Applied Chemistry

JAC
http://chemistry.journals.semnan.ac.ir

Solid phase extraction of heavy metal ions in environmental samples on chemically bonded single-walled carbon nanotubes with 2-((3-silylpropylimino) methyl) phenol

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Abstract

A new, simple method based on the use of chemically 2-((3-silylpropylimino) methyl) phenol (SPIMP) bonded single-walled carbon nanotubes (SPIMP-SWCNTs) as solid-phase extraction (SPE) stationary phase is proposed for simultaneous preconcentration of trace Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} ions prior to the measurement by flame atomic absorption spectrometry (FAAS). This new SPE method provides several advantages, such as high extraction efficiency, high breakthrough volumes, convenient extraction procedure, and short analysis times. The different experimental parameters for preconcentration of metal ions have been investigated on a column packed with SPIMP-SWCNTs. The optimum pH value for the separation of metal ions was 7.0. The metal ions retained on chemically modified SWCNTs efficiently were eluted using 6.0 mL of 4.0 mol L^{-1} HNO_3 solution. The detection limits of the method was found to be 2.10, 2.97, 1.55 and 3.03 µg L^{-1} for Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+}, respectively. The relative standard deviation (RSD) of the method was lower than 4.0% (n=8). The method has been successfully applied for analysis of the metal contents in different real samples including mineral water, sour cherry juice, pine apple juice and cabbage.

1.   Introduction

The determination of metal ions at trace level is very important in the content of environmental protection, food and agricultural chemistry as well as high purity materials [1-5]. Due to low concentrations of metal ions in environmental samples and matrix interferences [6-8], the determination of metal ions in complex matrices is limited and to overcome such limitation, generally caring out an efficient separation and preconcentration techniques is highly recommended

prior to their analysis to improve sensitivity and selectivity of their determination [9-11].

Solid-phase extraction (SPE) involves partitioning between a liquid (sample matrix or solvent with analytes) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent and purification of extract after extraction. The general procedure is to load a solution onto the solid phase, wash away undesired

components, and then wash off the desired analytes with another solvent into a collection tube [12]. This technique with unique advantages such as its flexibility, environmental friendly, absence of emulsion, simplicity, sampling in the field, safety and ease of automation, in the form of on-line or off-line mode with versatility of using various adsorbent modified with various chelating agent via physical or chemical pathway is suitable procedure for trace metal preconcentration prior to measurement [13-20]. The choice of selective sorbent should be based on analyte, sample matrix and technique for final detection, whereas higher preconcentration factors can be obtained using adequate experimental conditions [21]. Nanotechnology is one of the most important trends in science, perceived as one of the key technologies of the present century [22]. Nowadays, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for various inorganic and organic compounds/elements at trace levels [4, 23-25]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface having a strong interactions with other molecules as well as the large surface area make them a promising solid sorbent for preconcentration procedures [26-31]. The uniqueness of these materials is due to their mechanical, electrical, optical, catalytic, magnetic and photonic properties, and extremely large surface area, adsorption sites, reactive surface site [32, 33]. Recently, carbon nanotubes has shown surface was chemically modified for the tailored preparation of CNTs-based functional materials [34-36] by chemical reaction with carboxylic acid groups at the ends and side-walls of the CNTs with significantly improve their application as an efficient adsorbent for solid phase extraction procedure [37-46].

In the present investigation, single walled carbon nanotubes modified with 2-((3-silylpropylimino) methyl) phenol (SPIMP -SWCNT) has been used for the solid phase extraction of some metal ions in different samples and was synthesized and characterized by FTIR and SEM. The influences of the analytical parameters including pH, amounts of solid phase, eluting solution conditions (type and concentrations), sample volume and influence of interference of many ions on metal ions recoveries were investigated. These carbon nanoparticles are shown to provide a new pre-concentration or extraction tool/material for trace metal enrichment in different samples and efficiently was applied to separate and concentrate trace amount of some metal ions including Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} ions.

2. Experimental

2.1. Instruments

A Shimadzu 680- AA atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The pH of solution measured by PHS-3BW Bench top pH/mV Meter (BEL, Italy) with a combined glass-Ag/AgCl electrode calibrated against three standard buffer solutions at pH 4.0, 7.0 and 9.0 was employed for measuring pH values in the aqueous phase. A self-made plastic column was prepared to study the metal ion sorption on the chelating matrix in column SPE procedure by placing sorbent into an empty conical tip using the dry packing method. The column has an internal diameter of 10 mm and 5.0 cm length. To avoid filling losses when the sample solution passed through the conical column, a small amount of glass wool was placed at both the ends. The column was then connected to a LAMBDA CZs.ro multi flow peristaltic pump (LAMBDA, Switzerland) to form the preconcentration system.

2.2. Materials and reagents

Reagents of analytical grade and spectral purity were used for all experiments and doubly distilled water was used throughout. Standard solutions of Cu(II), Zn(II), Ni(II) and Fe(III) (1000 mg L^{-1}) were prepared by dissolving spectral pure grade chemicals $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ in double distilled water and further diluted daily prior to use according to requirements. Stock solutions of diverse elements were prepared from high purity compounds. Standard labware and glassware used were repeatedly cleaned with dilute

HNO_3 and rinsed with distilled water prior to use according to a published procedure. Acetate buffer solutions (CH_3COO^-/CH_3COOH) were prepared by mixing of appropriate volumes of 0.1 mol L^{-1} acetic acid and 0.1 mol L^{-1} sodium acetate solutions for pH 7.0. Single- walled carbon nanotubes (SWCNTs) with the highest purity available are purchased from Merck (Darmstadt, Germany) and used as received without any further purification.

2.3. Preparation of 2-((3-silylpropylimino) methyl) phenol (SPIMP) bonded to single walled carbon nanotube (SPIMP -SWCNT)

In the first, impurity of SWCNTs powder was removed by addition of 10% (v/v) hydrochloric acid solution while stirring the mixture for 2 h. Then, treated SWCNTs was filtered and washed with distilled deionized water and dried at 80 °C for 5 h. 1.0 g of this treated SWCNT was suspended in 250 mL of 32.5% (W/W) nitric acid solution and stirred for 36 hours at room temperature. Then the mixture was filtered and thoroughly rinsed with distilled deionized water till neutral pH and dried at 80 °C for 2 hours and chemically was modified by a new Schiff base according to following procedure. SWCNT -supported silylaminopropyl was synthesized by refluxing 0.1 g of functionalized SWCNT with 1.8 mL of trimethoxysilylpropylamine (TMSPA) in dry dichloromethane (20 mL) for 24 h and the solid was filtered and dried at room temperature. Then 0.9 mL of 2-hydroxybenzaldehyde (2-HBA) was added to a suspension of SWCNT -supported silyl-aminopropyl in methanol (20 mL) and the reaction mixture was refluxed for 24 h. Finally the mixture was filtered, washed with distilled water and dried at room temperature to obtain a greenish black precipitate as a chemically modified SWCNT -2-((3-silylpropylimino) methyl) phenol (SPIMP –SWCNT). The schematic diagram of preparation of this new sorbent is presented in Fig. 1.
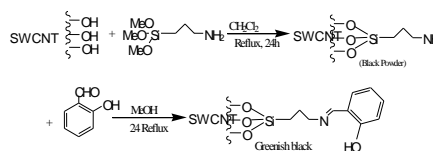

Fig. 1. Schematic diagram of the synthesis of proposed sorbent.

2.4. Preconcentration procedure

The procedure was examined using model test solutions as following. A self-made plastic column packed with 0.3 g of SPIMP -SWCNT sorbent (height of packing being about 10 mm) was used as the operational column. Before use, methanol and doubly distilled deionized water were successively passed through the column in order to equilibrate, clean and neutralize it. Then, 50 mL of the solution containing 0.2 μg mL^{-1} of Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} ions adjusted to the desired pH value with buffer solutions of acetate–acetic acid was passed through the column at a flow rate of 2.0 mL min^{-1} by using a peristaltic pump. Finally, the retained metal ions due to their chelation by this new sorbent was efficiently eluted with 6.0 mL of 4.0 mol L^{-1} nitric acid with a flow rate of 0.5 mL min^{-1} and the metal ions content in the eluent were determined by flame atomic absorption spectrometer using a standard calibration curve prepared daily. The column could be used repeatedly after washing with distilled water.

2.5. Analysis of the real samples

The cabbage sample was digested according to literatures. Leaves of cabbage were purchased from Semnan, Iran. Afterwards, they dried and were taken in small mesh. A 40 g leaves of cabbage was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3.0 mL 30% (W/W) H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 10.0 mL concentrated hydrochloric acid and 3.0 mL 70% (W/W) perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid

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residue was dissolved in water, filtered and its pH was kept at 7.0 by addition of KOH and diluted to mark in 250.0 mL volumetric flask. Also, before the analysis, the water and juice sample were filtered through a Millipore filter. Then, these samples was subjected to described procedure in above section (N=3) and the metal ions content was evaluated by standard addition method. The levels of analytes in the samples were determined by flame atomic absorption spectrometry.

3.   Results and discussion

To investigate the analytical potential of SWCNTs used as SPE sorbents, the experimental conditions affecting the enrichment efficiency such as sample pH, amount of SPIMP-SWCNT, eluent type, volume and concentration of eluting solution, sample volume, loading flow rate were studied in details since they determine both the purity of the final extract and the efficiency of the extraction.

3.1.   Characterization of adsorbent (SPIMHN – SWCNT)

Fourier transform infrared spectroscopy uses a fourier transform to convert raw data produced by the spectrometer in to a spectrum which is generally a plot of the absorbance or % transmittance of the sample versus the wave number. This is based on the vibrational excitation of molecular bonds by absorption of infrared light energy. FTIR spectroscopy has proven to be a versatile tool in analytical chemistry for quantitative and qualitative assessment of known and unknown chemical species [47, 48]. IR spectra of SWCNTs, surface supported aminopropylsilylate and SPIMP chemically modified SWCNTs are shown in Fig. 2a-c. IR spectrum of SWCNT shows some important characteristic vibrational frequencies at 3400-2500, 1627, 1155, 673, 592 (Fig. 2-A). After loading of trimethoxysilylpropylamine on SWCNT surface, some additional characteristic absorption bands at 2929, 3200-3350, 1563, 1405, 1300, 1121, 1031, 678, and 594 are appeared in IR spectrum of SWCNT- supported aminopropylsilylate that can be related to bending of NH-stretching, NH-bending, NH2 -scissoring, CH2-bending and CH2 rocking of

compound (Fig. 2-b). Finally 2-hydroxybenzaldehyde is bounded to supported aminopropylsilylate via iminic bound to obtain SWCNT chemically modified with 2-((3silylpropylimino) methyl) phenol (SPIMP) as extractor. IR spectrum well exhibits some characteristic peaks at 3500- 2500, 3020-3050, 2929, 2856, 1638, 1580, 1553, 1501, 1464, 1401, 1285, 1195, 1127, 1037, 757, 700, 678, 652, 615, 599 and 457 assigning to O-H phenolic, CH-aromatic, CH-aliphatic, CH-iminic, C=Niminic, C=C stretching and out of plain bending of phenolic OH and CH of aromatic ring(Fig. 2-c).

The scanning electron microscope (SEM) employs a beam of electrons that scans across the surface of the specimen in a raster pattern. This interaction emits radiation in the form of electrons and X-rays that are processed to form an image of the surface or to analyze the elemental composition of the sample. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample [49, 50]. SEM photograph of single walled carbon nanotube is given in Fig. 3. SEM images clearly evidence the presence of distributed nanodimensional tubular structures in the collected solid phase.
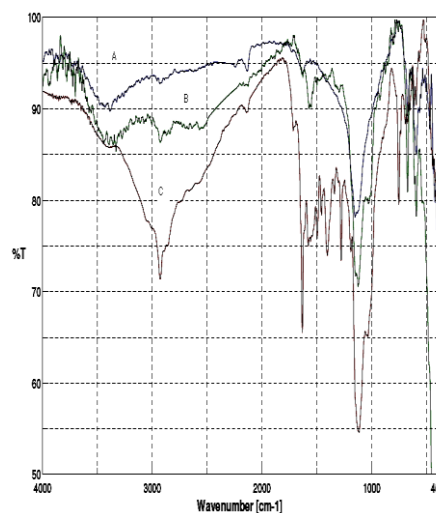

Fig. 2. FT-IR spectra of SWCNT (a), surface supported aminopropylsilylate (b), modified SWCNT with 2-((3silylpropylimino) methyl) phenol (c).
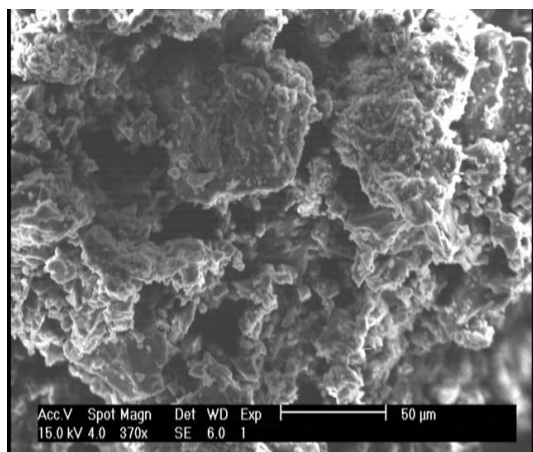
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Fig. 3. SEM image of modified SWCNT.

3.2.   Effect of pH on sorption

The oxidation of carbon nanotubes with nitric acid leads to the surface functionalization with more oxygen-containing groups such as hydroxyl, carbonyl and carboxyl. The surface charge depends on the pH of the surrounding electrolyte. The pH of the solution is considered to be the most important controlling parameter in the adsorption process. Therefore, solution pH value is the first parameter to be optimized. In order to evaluate the effect of pH on the sorption of metal ions on single walled carbon nanotubes, 50.0 ml of sample solution containing four metal ions, namely Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} at concentration of 0.2 μg mL^{-1} were adjusted to a pH range of 3.0–9.0 with adding 0.1 mol L^{-1} sodium hydroxide and/or 0.1 mol L^{-1} hydrocholorydryc acid and was passed through the column at a flow rate of 2.5 mL min^{-1}. Then the metal ions retained on column were eluted using 5.0 mL of 4.0 mol L^{-1} of HNO_3 solution at a flow rate of 1.0 mL min^{-1}. The analytes in the elution were determined by FAAS. The results are shown in Fig. 4. As it can be seen, maximum recoveries was obtained at pH 7.0. In acidic region due to competition of hydronium ion with metal ions for binding to the same sites recoveries significantly will be decreased. The SPIMP-SWCNT surface becomes more negative with increasing pH that which causes electrostatic interactions that lead to higher retention of metal ions species. At higher pH value probably due to the precipitation of ions as their related hydroxide the recoveries significantly will be decreased. Therefore, pH of 7.0 was selected for

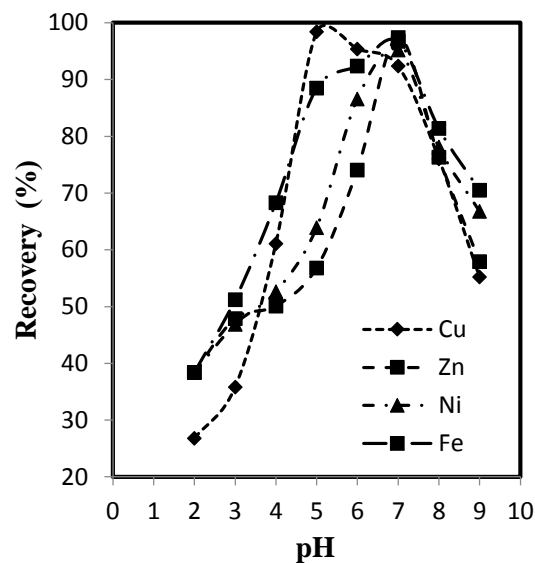throughout this work and optimization of other variables.

Fig. 4. Effect of pH on metal ions recoveries, sorbent: 0.2 g, eluent: nitric acid, 4.0 mol L^{-1}, 5.0 mL, flow rate (sample): 2.5 mL min^{-1}, flow rate (eluent): 1.0 mL min^{-1}.

3.3.   Effect of the amount of sorbent on metal ions recovery

In the adsorption step, an appropriate amount of solid phase filled to column should be used in order to obtain quantitative retention of metals. Also it determines the adsorption capacity of an adsorbent for given initial concentration of the adsorbate. To test the effect of the amount of sorbent filled to the column on quantitative retention of analyte, different amounts of sorbent in range from 0.1 to 0.35 g were passed through the column with a peristaltic pump following the column procedure. It was seen that by increasing solid phase amount till 0.3 g recoveries increased and further addition lead to decrease in metal ions recoveries. Quantitative adsorption was not obtained when the mass of sorbent was smaller than 0.3 g. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. So, 0.3 g of SPIMP-SWCNT was selected for further studies (Fig. 5).

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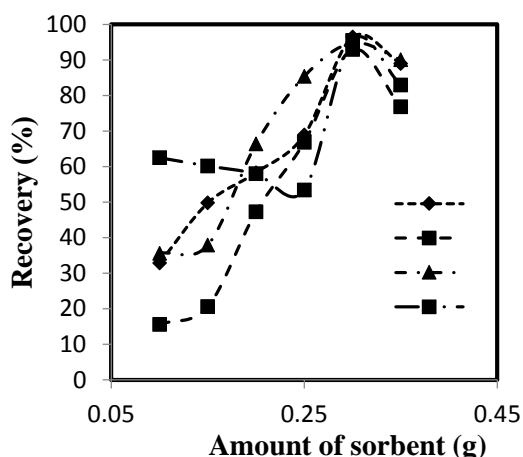
Fig. 5. Effect of amount of solid phase on metal ions recoveries, pH: 7.0, eluent: nitric acid, 4.0 mol L^{-1}, 5.0 mL, flow rate (sample): 2.5 mL min^{-1}, flow rate (eluent): 1.0 mL min^{-1}.

3.4. Effect of the type, concentration and volume of eluent

The type and condition of elution solvent are vital for the extraction efficiency. So the choice of elution solvent and its optimum conditions should be carefully taken into account. In order to select the best eluent suitable for quantitative stripping of the understudy metal ions, various acidic eluting solutions such as, HCl, HNO_3 in water, HNO_3 in acetone, H_2SO_4, H_3PO_4 and CH_3COOH, were used in order to identify the best eluent for desorption of metal- SPIMP chelates on single walled carbon nanotubes. The results were summarized in Table 1. As it can be seen, HNO_3 in water was used as eluent in further experiments, while using other acids lead to inefficient elution of metal ions. It was probed that nitric acid can cause a reversible change in the structure of SPIMP chelates providing efficient and rapid release of metals from the binding cavity. Other eluents such as HCl were tested and no significant differences were obtained.

Subsequently, it is required that the influence of the concentration of nitric acid solution on metal ions recoveries must be optimized. In this regard a set of similar experiments at was conducted using various the concentration of nitric acid solution in the range of 2.0-6.0 mol L^{-1} and the results are presented in Table 1. It was found that maximum recoveries were obtained

using 4.0 mol L^{-1} of HNO_3 that was selected for subsequent work.

The effect of the eluent volume on the recovery of metal ions was also evaluated when 6.0 mL HNO_3 was selected. Finally, 6.0 mL of 4.0 mol L^{-1} HNO_3 in water was specified as the eluent for desorption of metal chelates from chemically bonded SWCNT and was used for the optimization of the other parameters.

Table 1: Effects of eluent conditions on metal ions recoveries

Condition of eluent	Metal ions recovery (%)			
	Cu^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}
5.0 mL of HNO_3 in water (4.0 mol L^{-1})	95.7	92.3	94.5	97.0
5.0 mL of HNO_3 in acetone (4.0 mol L^{-1})	87.2	96.5	85.1	74.3
5.0 mL of HCL (4.0 mol L^{-1})	27.2	45.1	68.7	36.5
5.0 mL of H_2SO_4 (4.0 mol L^{-1})	34.2	58.7	29.7	51.6
5.0 mL of H_3PO_4 (4.0 mol L^{-1})	45.5	51.0	73.4	47.2
5.0 mL of CH_3COOH (4.0 mol L^{-1})	20.05	85.3	24.6	59.1
5.0 mL of HNO_3 in water (2.0 mol L^{-1})	67.2	87.4	79.5	80.6
5.0 mL of HNO_3 in water (4.0 mol L^{-1})	96.0	95.1	93.5	94.0
5.0 mL of HNO_3 in water (5.0 mol L^{-1})	97.2	86.4	88.3	91.5
5.0 mL of HNO_3 in water (6.0 mol L^{-1})	98.7	78.5	75.2	96.0
2.0 mL of HNO_3 in water (4.0 mol L^{-1})	58.4	60.5	71.2	60.2
4.0 mL of HNO_3 in water (4.0 mol L^{-1})	77.2	75.9	84.0	81.4
6.0 mL of HNO_3 in water (4.0 mol L^{-1})	95.4	93.9	92.3	97.6
8.0 mL of HNO_3 in water (4.0 mol L^{-1})	91.1	85.8	88.7	87.1

3.5. Effect of flow rate on metal ions recoveries

In the column SPE system, the sample flow rate is another factor, which not only affects the recoveries of analytes, but also controls the analyses time. Loading flow rate through the sorbent format should be suitable. Generally, sample loading time can be saved at a high flow rate while the possible analytes loss happens owing to an incomplete adsorption of metal ions by the sorbents; complete adsorption can be achieved at a low flow rate but it is time consuming. Therefore, a suitable flow rate for loading sample should be investigated to achieve high recovery and short loading time. The flow rates were adjusted in a range of 1-4 mL min^{-1}. The recoveries of the metal ions are shown in Fig. 6. The

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recoveries of the analytes decrease obviously when the flow rate is over 2.0 mL min⁻¹. Thus, a flow rate of 2.0 mL min⁻¹ is employed in this work. The flow rates of eluent solution were investigated in the ranges of 0.5-3.0 mL min⁻¹. After eluent flow rate of 2.0 mL min⁻¹, the recovery values of the analytes were not quantitative. For the all experiments, 0.5 mL min⁻¹ was selected as eluent flow rate.
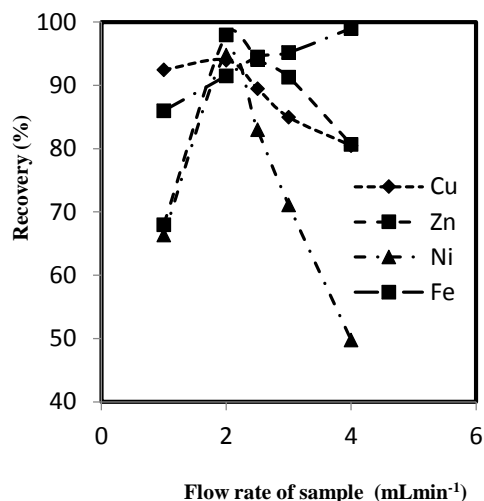
Fig. 6. Effect of flow rate of sample on metal ions recoveries, pH: 7, sorbent: 0.3 g, eluent: nitric acid 4.0 mol L⁻¹, 6.0 mL, flow rate (eluent): 1.0 mL min⁻¹.
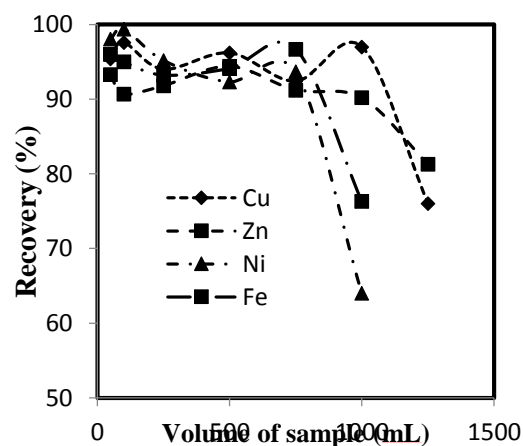
3.6. Sample volume and preconcentration factor

To explore the possibility of adsorbing low concentrations analytes from large volumes of sample solution and also to obtain reliable and reproducible analytical results and high concentration factors, it was very important to get satisfactory recoveries for all analytes as possible. The sample volume is an important parameter, which reflects the analyte retaining ability of the sorbent. Therefore it was necessary to obtain the breakthrough volumes in the SPE process.   For this purpose, various sample volumes (range from 50.0 to 1250.0 mL) containing each Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} of 10.0 μg were passed through the column under the optimum condition. The recoveries of the metal ions from different volumes of aqueous solutions containing the same amounts of the metal ions are shown in Fig.7. Hence, the loaded sample volume of Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} was chosen 1000, 1000, 750 and 750 mL as the final volume for the

enrichment due to proposed method's sensitivity and reliability. At the higher volumes, the recoveries for analytes were not quantitative.

The preconcentration factor for simultaneous preconcentration is calculated by the ratio of the highest sample volume for each analytes and the lowest eluent volume. The preconcentration factor was 166.6 for Cu^{2+} and Zn^{2+} and 125 for Ni^{2+} and Fe^{3+}, respectively.

Interference ions	Tolerance Limit (mgL⁻¹)			
	$C_{ion}/C_{Cu^{2+}}$	$C_{ion}/C_{Zn^{2+}}$	$C_{ion}/C_{Ni^{2+}}$	$C_{ion}/C_{Fe^{3+}}$
Cl⁻ ,NO₃⁻	1000	1000	1000	1000
Na⁺, K⁺, Ba²⁺, Ca²⁺, Li⁺	1000	1000	1000	1000
Cr³⁺	250	100	100	500
Mg²⁺	250	250	500	1000
F⁻	500	250	500	1000
NH₄⁺	250	250	250	1000
I⁻	250	750	250	1000
Br⁻	500	250	250	1000
CH₃COO⁻	1000	750	750	1000
SO₄²⁻	750	250	750	750
SCN⁻	250	100	250	750
Co²⁺	100	100	500	1000
Cu²⁺	-	750	1000	1000
Zn²⁺	500	-	1000	1000
Ni²⁺	1000	500	-	1000
Fe³⁺	1000	500	500	-

Fig. 7. Effect of sample volume on metal ions recoveries, pH: 7, sorbent: 0.3 g, eluent: nitric acid 4.0 mol L⁻¹, 6.0 mL, flow rate (sample): 2.0 mL min⁻¹.

3.7. Matrix effects

The retention of metal ions onto SWCNTs, as it was already mentioned, exhibits a typical electrostatic interactions. Thus, even though their high surface area

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as well as a high volume of pores, the presence of some foreign ions such as alkaline and alkaline earth and some transition metal and some anions still could provoke competition for those sorption sites of sorbent. In order to assess the possible analytical application of the recommended speciation-preconcentration procedure, the effect of some foreign ions which interfere with the determination of trace of these ions or/ and often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 95%.

The results summarized in Table 2, clearly indicate that the major species which could be present in natural water do not interfere with the determination of metal ions under the selected conditions.

Table 2: Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

3.8. Investigation of method Performances

The calibration curve were obtained by using 250.0 mL solution at the optimum conditions. The results are shown in Table 3, which indicate wide linear range and applicability of method for trace metal enrichment. Under the selected conditions, eight portions of standard solutions were enriched and analyzed simultaneously following the general procedure. The detection limits of this method, evaluated as the concentration corresponding to three times the standard deviation of eight replicate measurements of blank solution using the preconcentration method, were found to be 2.1, 2.97, 1.55 and 3.03 μgL^{-1} for Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+}, respectively. The relative standard deviation (R.S.D.) of the method for Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} was 2.81%, 2.5%, 3.25% and 1.72% respectively. The characteristic performances of method which presented in Table 3 show good linear range, low detection limits, high reproducibility and low relative standard deviation for all elements.

Table 3: Specification of presented method at optimum conditions for each element (N=8)

Parameters	Cu^{2+}	Zn^{2+}	Ni^{2+}	Fe^{3+}
Linear range (μgmL^{-1})	5-600	5-600	5-800	5-800
Detection Limit (μgL^{-1}) (3σ, n=8)	2.1	2.97	1.55	3.03
R.S.D. (%)	2.81	2.5	3.25	1.72
Preconcentration factor (PF)	166.6	166.6	125	125

3.9. Accuracy and applications of the method

In order to study the accuracy and the applicability and reliability of the proposed method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the determination of analytes from different matrices. For the analysis of various analytes, the standard addition method was used. The results were given in Table 4. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The presented method could be applied successfully for the separation, preconcentration and determination of trace amounts of Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} ions in both spiked and various samples.

4. Conclusions

This new sorbent with high efficiency has been applied for the preconcentration and subsequent determination of metal ions such as Cu^{2+}, Zn^{2+} , Ni^{2+} and Fe^{3+} ions. The presence of the active sites on the surface, inner cavities and inter-nanotube space contributes to the high metal preconcentration capability of SWCNTs. The developed method is simple, rapid, precise, accurate and reliable offering a higher preconcentration factor and lower detection limit can be applied for the determination of analytes in environmental samples. The method is economical due to the possibility of multiple uses of the sorbent without a marked loss in sorption capacity. The system showed reproducibility and reliability in analytical data, with an R.S.D. value of lower than 4%. A comparison with some of the previous works is also given in Table 5. The detection

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limits (LOD) and preconcentration factors (PF) for metal ions are better than or comparable to some of the previously reported values.

5.　Acknowledgment

Table 4: Recovery ions in different sample

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Metal ion	Immobilized ligand	Solid phase material	Sample volume (mL)	PF	LOD (µg L^{-1})	References
Cu, Pb, Fe	1-PTSC	Dowex Optipore L-493 resin	250	62.5	0.64, 0.55, 0.82	[51]
Co, Cu, Cd, Pb, Mn, Ni	TAN	Amberlite XAD-1180 resin	250, 500, 500, 1000, 1500, 1500	50, 100, 100, 200, 300, 300	3.6, 0.8, 0.3, 1.1, 0.1, 0.2	[52]
Pb	Dithizone	Graphen	250	125	0.61	[53]
Bi	[BMIM]PF$_6$	MWCNT	500	333	2.3	[54]
Pb	ABT	MWCNT	200	100	0.27	[55]
Cu, Mn, Zn	PBHCD	Amberlite XAD-16	500	50	5.6, 4.5, 1.8	[56]
Cu, Zn, Ni, Fe	SPIMP	SWCNT	1000, 1000, 750, 750	166.6, 166.6, 125, 125	2.1, 2.97, 1.55, 3.03	Present work

Table 5: Comparative data for SPE preconcentration procedures for analyte ions in conjugation with FAAS

Sample	Added (µgL^{-1})	Cu		Zn		Ni		Fe	
		Found (µgL^{-1})[a]	Recovery (%)	Found (µgL^{-1})	Recovery (%)	Found (µgL^{-1})	Recovery (%)	Found (µgL^{-1})	Recovery (%)
Mineral water[b]	0	7.70±0.10	-	10.50±0.02	-	8.85±0.50	-	3.72±0.03	-
	20	26.90±0.1	6.0	29.70±0.03	96.0	27.90±0.3	99.2	24.65±0.40	104.6
Sour cherry juice[c]	0	5.20±0.23	-	31.10±0.70	-	10.44±0.66	-	6.05±0.33	-
	20	24.30±0.36	95.5	51.70±0.47	103.0	29.85±0.52	97.1	25.65±0.40	98.0
Pine apple juice[d]	0	4.90±0.10	-	12.20±0.09	-	3.70±0.34	-	3.72±0.20	-
	20	24.50±0.32	98.0	32.50±0.60	101.5	22.80±0.76	95.5	23.12±0.38	97.0
Cabbage[e]	0	10.80±0.14	-	25.60±0.43	-	17.90±0.45	-	23.30±0.47	-
	20	29.90±0.55	95.5	44.60±0.66	95.0	37.80±0.50	99.5	44.20±0.72	104.5

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