



# Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid-phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture

S. Vellaichamy, K. Palanivelu\*

Centre for Environmental Studies, Anna University, Chennai 600 025, India

## ARTICLE INFO

### Article history:

Received 19 July 2010

Received in revised form 9 September 2010

Accepted 7 October 2010

Available online 14 October 2010

### Keywords:

Heavy metals

Multiwalled carbon nanotubes

FAAS

Solid phase extraction

D2EHPA

## ABSTRACT

A solid phase extraction method has been developed for the determination of copper, nickel and zinc ions in natural water samples. This method is based on the adsorption of copper, nickel and zinc on multiwalled carbon nanotubes (MWCNTs) impregnated with di-(2-ethyl hexyl phosphoric acid) (D2EHPA) and tri-n-octyl phosphine oxide (TOPO). The influence of parameters such as pH of the aqueous solution, amount of adsorbent, flow rates of the sample and eluent, matrix effects and D2EHPA-TOPO concentration have been investigated. Desorption studies have been carried out with 2 mol L<sup>-1</sup> HNO<sub>3</sub>. The copper, nickel and zinc concentrations were determined by flame atomic absorption spectrometry. The results indicated that the maximum adsorption of copper, nickel and zinc is at pH 5.0 with 500 mg of MWCNTs. The detection limits by three sigma were 50 μg L<sup>-1</sup> for copper, 40 μg L<sup>-1</sup> for nickel and 60 μg L<sup>-1</sup> zinc. The highest enrichment factors were found to be 25. The adsorption capacity of MWCNTs-D2EHPA-TOPO was found to be 4.90 mg g<sup>-1</sup> for copper, 4.78 mg g<sup>-1</sup> for nickel and 4.82 mg g<sup>-1</sup> for zinc. The developed method was applied for the determination of copper, nickel and zinc in electroplating wastewater and real water sample with satisfactory results (R.S.D.'s <10%).

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Heavy metals are major pollutants in marine, ground and industrial wastewater [1]. Heavy metals like mercury, lead, cadmium, nickel, chromium, copper and zinc are toxic even in extremely minute quantities present in air, water and food [2]. Among these heavy metals, copper, nickel and zinc ingestion beyond the permissible limits causes various chronic disorders in human beings. Therefore, a systematic study on the preconcentration and separation of copper, nickel and zinc ions from natural water is of considerable significance from an environmental point of view [3].

Several analytical techniques including inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry are available for the determination of trace metals with sufficient sensitivity for most of the environmental applications. But the required instruments are expensive, day-to-day maintenance cost is high and various types of inherent interferences appear. In order to achieve concentration of target metals in excess of detection limits of flame atomic absorption

spectrometry (FAAS), initial pre-concentration and separation procedures have been carried out [4,5].

A number of classical methods such as co precipitation [6], flotation [7], ion exchange [8], biosorption [9], cloud point extraction [10], solid phase extraction (SPE) [11] and solvent extraction [12] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples including food and natural water, by researchers around the world [13,14]. Among these, solid phase extraction is an attractive separation-pre-concentration technique for heavy metal ions. The main advantages of solid phase extraction system are: high enrichment factor, lower consumption of reagents, no problem with the miscibility of solvent and environment friendly [15].

Various solid phase adsorbent materials like activated carbon [16], Amberlite XAD resins [17], Chromosorb resins [18] and Amberlite-572 [19] have been successfully used for the preconcentration and separation of heavy metal ions at trace level. However, the development of new SPE pre-concentration and separation systems has been growing [20]. In this context, multiwalled carbon nanotubes (MWCNTs) have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels. In addition, large surface area and hexagonal arrays of carbon atom suggest a good characteristic of adsorbing processes [21,22]. As of now, only a few publications are found on the use of MWCNTs

\* Corresponding author. Tel.: +91 44 22359014; fax: +91 44 22354717.

E-mail addresses: [kpvelu@annauniv.edu](mailto:kpvelu@annauniv.edu), [kpvelu@hotmail.com](mailto:kpvelu@hotmail.com) (K. Palanivelu).

for metal ions pre-concentration and separation of copper, zinc and nickel and its determination by using FAAS [23].

A literature review covering most of the research work dealing with the fundamental aspects of pre-concentration and separation of the above metals reveals that D2EHPA is member of organophosphorous acids is often chosen as extractant [24]. During the selection of partner for D2EHPA, from the various mixtures of organophosphorous extractants, it was found that the neutral organophosphorous extractant such as tri-*n*-octyl phosphine oxide (TOPO) is most frequently used. This kind of synergistic system consisting of a mixture of acidic plus neutral extractants have been used in SPE processes [25]. The pre-concentration and separation of Co, Cu, Ni, Zn and Pb from a mixture of metals based on the commercial extractants like D2EHPA and D2EHPA-TOPO comparative studies have been reported [26]. In this paper, a simple methodology is proposed for the solid phase extraction of mixed metal ions namely Cu, Ni and Zn. The adsorption is based on the MWCNTs impregnated with D2EHPA-TOPO. The effect of variables such as pH, sample volume, eluent flow rate, matrix effect, D2EHPA-TOPO concentration, column height and amount of adsorbents were studied by column method. The validity of the proposed method was applied to the determination of the above mentioned metal ions in spiked water samples and electroplating wastewater. Characterization of adsorbents before and after pre-concentration has also been done using Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM).

## 2. Materials and methods

### 2.1. Instruments

The measurements of analyte ions were performed with Analytic jena vario 6 flame atomic absorption spectrometer. All measurements were carried out in air/acetylene flame. A 10 cm long slot-burner head equipped with a hollow cathode lamp and a deuterium background corrector has been used for this study. The operating parameters for working elements were set as recommended by the manufacturer. The instrumental and operating conditions were as follows: wavelength, 234.7, 232.0 and 213.9 nm; band pass 1 nm; lamp current 5, 10 and 3 mA; fuel flow rate 2 mL min<sup>-1</sup>, for copper, nickel and zinc. All pH measurements were performed with WTW pH meter. The IR spectrum of copper, nickel and zinc–D2EHPA-TOPO complex was performed using a Perkin Elmer FT-IR RX1 spectrum. SEM images were obtained from JEOL/EQ JSM Instruments 6360.

### 2.2. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Laboratory glassware were kept overnight in a 10% (v/v) HNO<sub>3</sub> solution and then rinsed with double-distilled water.

The standard stock solutions (1000 mg L<sup>-1</sup>) of copper, nickel, and zinc ions were prepared from NiSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O and ZnSO<sub>4</sub>·7H<sub>2</sub>O (Merck Chemicals, Mumbai, India) and the working solutions were prepared by appropriate dilution with double-distilled water. The calibration curve was established using the standard metal ion solutions prepared in 1 mol L<sup>-1</sup> HNO<sub>3</sub> by dilution from the stock solutions. The calibration ranges of copper, nickel and zinc ions were follows: 0, 0.5, 1.0, 2.0 and 3.0 mg L<sup>-1</sup>, 0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg L<sup>-1</sup> and 0, 0.5, 1.0, 1.5 and 2.0 mg L<sup>-1</sup>. The pH of the aqueous sample solution was adjusted using dilute nitric acid or sodium hydroxide.

MWCNTs (outer diameter 60–80 nm, inner diameter 30–50 nm and length fewer than 20 μm) were obtained from Nanokarbon Co.

Ltd. (South Korea). D2EHPA and TOPO were supplied by Merck chemicals, Darmstadt, Germany and were dissolved in hexane (CDH, New Delhi, India).

### 2.3. Adsorbent preparation

MWCNTs material was oxidized with concentrated HNO<sub>3</sub> according to the literature [27] with minor modification, in order to create binding sites onto MWCNTs surface. Before impregnation, MWCNTs were washed with 1 mol L<sup>-1</sup> NaOH, 1 mol L<sup>-1</sup> HNO<sub>3</sub>, and acetone sequentially, in order to eliminate the trace metal ions, other inorganic and organic impurities. Afterwards, the material was washed with ultra pure water to remove the excess impurities (neutral pH of solution). Bulk of MWCNTs was poured into 500 mL of solution containing a mixture of D2EHPA-TOPO in hexane with constant stirring for 30 min at room temperature. Then the solvent was evaporated for 24 h and dried in a hot air oven at 75 °C. After the carbon was dried, it was stored for future experimental studies.

### 2.4. Column preparation

A glass column (100 mm length and 10 mm i.d.) with a glass wool over its stopcock was used as a mini column for the study. A total of 500 mg of MWCNTs impregnated with D2EHPA-TOPO was slurried in water and then placed into the column. A small amount of glass wool was placed on top to avoid disturbance of the adsorbent during the sample passage. The column bed height was approximately 1.2 cm. The column was preconditioned by the blank solution having same pH with the sample solution prior to use. After the elution in each case, the adsorbent in the column was washed with 15–20 mL of the eluting solution and water subsequently.

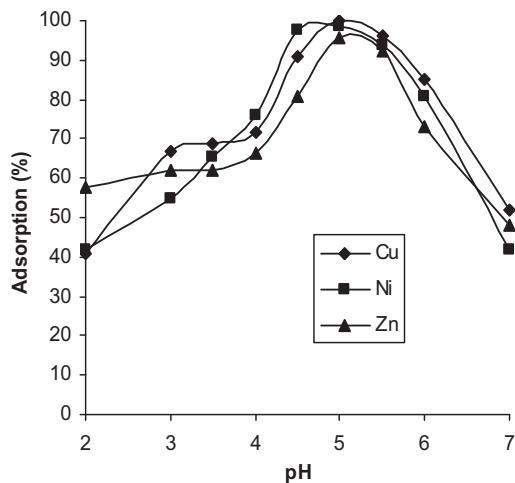
### 2.5. Test procedure

A 100 mL of synthetic aqueous sample solution containing 500 μg L<sup>-1</sup> each of copper, nickel and zinc was taken for this study. The pH of the synthetic aqueous sample was adjusted by dilute sulphuric acid or sodium hydroxide. The resulting solution was passed through the preconditioned column containing MWCNTs impregnated with D2EHPA-TOPO. The flow rate was adjusted to the optimum value determined experimentally (1–2 mL min<sup>-1</sup>). The retained metal ions were then eluted from the solid phase with 10 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub> solution. This solution was aspirated into air-acetylene flame for the determination of copper, nickel and zinc. The adsorbent (MWCNTs) was used repeatedly (up to 25 cycles) after and subsequent washing with 2 mol L<sup>-1</sup> HNO<sub>3</sub> solution and distilled water. The quantitative adsorption of copper, nickel and zinc adsorbed on the column was calculated from the difference between the starting amount of metal (*N<sub>s</sub>* in mg) and the amount of metal ion present in the aqueous solution after passing through the column (*N<sub>f</sub>* in mg) according to Eq. (1). All the experiments were conducted in triplicate.

$$\text{Adsorption (\%)} = \frac{N_s - N_f}{N_s} \times 100 \quad (1)$$

## 3. Results and discussion

Preliminary studies were conducted to evaluate the adsorption of heavy metal ions namely copper, nickel and zinc onto MWCNTs impregnated with equimolar concentration of D2EHPA-TOPO is 0.3 mol L<sup>-1</sup>. The pH, flow rate and metal ion concentrations were maintained as 5.0, 2 mL min<sup>-1</sup> and 500 μg L<sup>-1</sup>. The results clearly indicated that MWCNTs can retain all the above metal ions, while the untreated MWCNTs cannot quantitatively (<20%) retain copper, nickel and zinc. Evidently, the pre-concentration of the metals

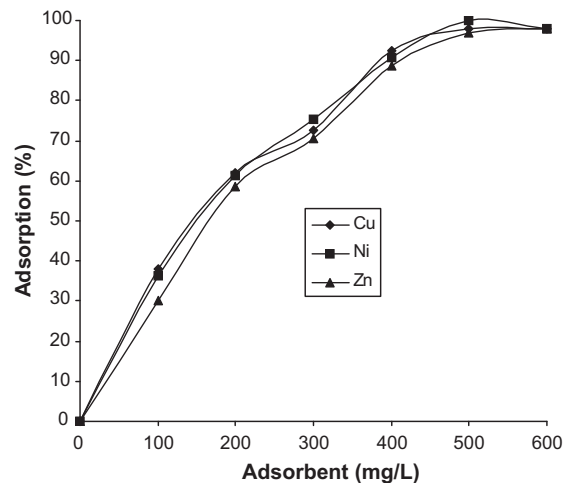


**Fig. 1.** Effect of pH on the MWCNTs impregnated with D2EPHA-TOPO (conditions: concentration of copper, nickel and zinc metal ions:  $500 \mu\text{g L}^{-1}$ , flow rate  $2 \text{ mL min}^{-1}$ ).

with the untreated MWCNTs is not suitable for Cu, Ni and Zn by column technique for all the metal ions. The adsorption of metal ion (<30%) was less in the case of MWCNTs impregnated with TOPO alone and D2EHPA showed better adsorption for copper, nickel and zinc (>70%) than TOPO. The quantitative adsorption (>95%) of the above mentioned elements were observed in the case of the mixture of two extractants (D2EHPA-TOPO). Cortina et al. observed that the experimental metal distribution coefficient of (>95%) metal ion adsorption obtained with the mixture of two extractants (D2EHPA-TOPO) with metal ion distribution coefficient due to the acidic organophosphorous extractant (D2EHPA) which defines the synergistic behavior of the mixture. The results show that the calculated metal ion distribution value is less in the case of MWCNTs impregnated with neutral organophosphorous extractant (TOPO) which is equal to <30%. Whereas the experimental adsorption of metal ion with the mixture of MWCNTs-D2EHPA-TOPO showed an enhanced effect (95%) in the adsorption of copper, nickel and zinc with a shift of metal ion distribution which may be due to acidic organophosphorous extractants [28]. Therefore, MWCNTs impregnated with D2EHPA-TOPO seems to be a better adsorbent for simultaneous adsorption of copper, nickel and zinc.

### 3.1. Effect of pH

In the SPE studies, the pH of the aqueous solution is an important operational parameter for the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of the ionization of the adsorbing metal ions by chemical reaction [29]. Thus, the role of hydrogen ion concentration was examined on the copper, nickel and zinc ion adsorption efficiency. Due to this important point, the effect of pH has been investigated in the range of 2–7 with the addition of dilute  $\text{H}_2\text{SO}_4$  or NaOH. The adsorption values for the analyte metal ions are presented in Fig. 1. From the figure, it is observed that the quantitative adsorption of copper 98%, nickel 96% and zinc 95% was obtained at  $\text{pH } 5.0 \pm 0.1$ . However, at lower pH values, the percentage of adsorption was decreased. This is due to the fact that the decrease in percentage adsorption at below  $\text{pH } 3.0 \pm 0.1$  reflects a reduction of negative surface charge density on MWCNTs. Therefore, the presence of a negative charge (after impregnation with D2EHPA-TOPO) on MWCNTs surface over the acidic range was the main reason for Cu, Ni and Zn adsorption. Protons ( $\text{H}^+$ ) should be considered as a competitive ion in the adsorption process. Therefore, very low adsorption of the metal



**Fig. 2.** Effect of dosage of MWCNTs impregnated with D2EPHA-TOPO (conditions: adsorbent varied from 100 to 600 mg, concentration of copper, nickel and zinc metal ions:  $500 \mu\text{g L}^{-1}$ , flow rate  $2 \text{ mL min}^{-1}$ ).

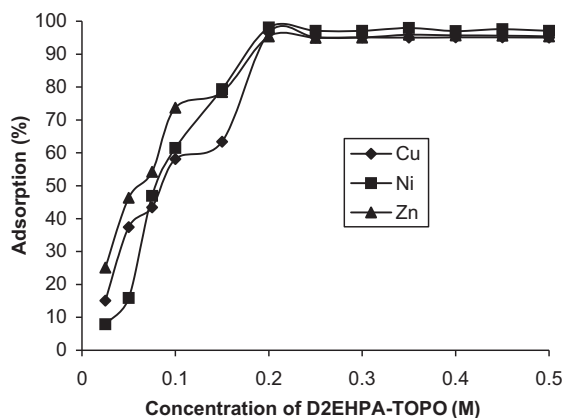
takes place from high acidic solutions [30]. However, at higher ( $\text{pH} > 5.5$ ) values, the adsorption efficiency decreased, it is probably due to increase in precipitation of metal ions in the form of hydroxyl complexes  $\text{Cu}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  and partial dissolution of D2EHPA. These results are in good agreement with those described by previous work [31]. This effect also results in non-permeation of the complex Cu-D2EHPA-TOPO, Ni-D2EHPA-TOPO and Zn-D2EHPA-TOPO species formed at these pH values [14]. Therefore, further adsorption studies were carried out at  $\text{pH of } 5.0 \pm 0.1$ .

### 3.2. Effect of amount of MWCNTs

In order to determine the effect of amount of MWCNTs impregnated with D2EHPA-TOPO on the pre-concentration of copper, nickel and zinc, the amount of adsorbent was varied in the range of 100–600 mg for MWCNTs and the column height occupied the volume of 0.2–1.2 cm. The synthetic aqueous sample solution containing  $500 \mu\text{g L}^{-1}$  each of copper, nickel and zinc metal ions were passed through the column and the solution pH was maintained to 5.0. The results are given in Fig. 2. It could be seen from the figure, that above 100 mg of adsorbent the quantitative adsorption of analyte metal ions were gradually increased, but 500 mg of adsorbent reached a plateau with an efficiency of 95%. This is expected because more binding sites for metal ions are available at higher dosage of adsorbent impregnated with D2EHPA-TOPO [29]. However, increasing dosage of adsorbent and column height above 500 mg and 1.0 cm for MWCNTs, yielded no increase in the metal ion adsorption percentage. Therefore, further studies were performed with 500 mg of MWCNTs impregnated with D2EHPA-TOPO.

### 3.3. Effect of carrier concentration

The effect of equimolar (D2EHPA-TOPO) concentration on the adsorption of copper, nickel and zinc ion has been investigated in the range of  $0.025\text{--}0.5 \text{ mol L}^{-1}$ . The results are presented in Fig. 3. From the figure, it is clear that the adsorption of metal ions increased with increase in extractants concentration. In the extractants concentration range  $0.025\text{--}0.30 \text{ mol L}^{-1}$ , the adsorption percentage increased from 15.80 to 95.90% in the case of copper, 7.50 to 96.20% in the case of nickel and 23.50 to 94.80% in the case of zinc. The adsorption of D2EHPA-TOPO increases almost linearly with increasing D2EHPA-TOPO concentration and



**Fig. 3.** Effect of concentration of D2EHPA-TOPO (conditions: concentration of copper, nickel and zinc metal ions:  $500 \mu\text{g L}^{-1}$ , flow rate  $2 \text{ mL min}^{-1}$  and extractant concentrations  $0.3 \text{ mol L}^{-1}$ ).

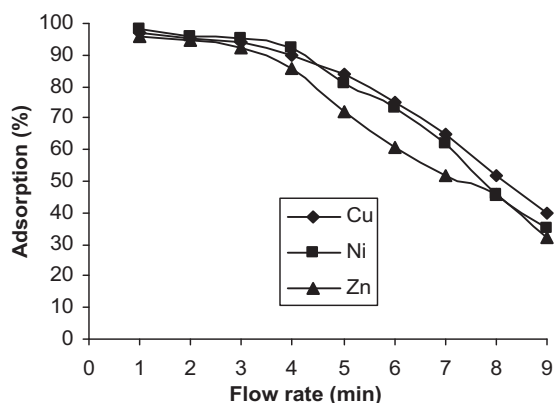
levels off at the concentration are higher than  $0.30 \text{ mol L}^{-1}$ . This is because more binding sites for the metal ions are available at higher dosage of extractants concentration. The results demonstrate that the quantitative adsorption (95%) of the working metal is possible in the range of above  $0.2 \text{ mol L}^{-1}$  D2EHPA-TOPO. Therefore,  $0.3 \text{ mol L}^{-1}$  D2EHPA-TOPO was found to be more effective in separating those metal ions.

### 3.4. Effect of flow rate

The quantitative adsorption of metal ions on the solid phase extraction studies are based on the flow rate of the synthetic aqueous sample solution. The influence of flow rate of the aqueous sample on the adsorption of copper, nickel and zinc ions have been investigated in the range of  $1\text{--}9 \text{ mL min}^{-1}$ . The results are presented in Fig. 4. From the figure, it is seen that the adsorption value for metal ions was quantitative in the range of  $1\text{--}4 \text{ mL min}^{-1}$ . The optimum flow rate was found as  $4 \text{ mL min}^{-1}$  for copper and  $3 \text{ mL min}^{-1}$  for nickel and zinc. Hence, to obtain the quantitative adsorption of metal ions from the synthetic aqueous sample solution, the flow rate was maintained at  $2 \text{ mL min}^{-1}$ .

### 3.5. Desorption studies

Different type of eluents were used for the desorption of the analyte complex loaded on to the MWCNTs impregnated with



**Fig. 4.** Effect of sample flow rate on MWCNTs impregnated with D2EHPA-TOPO (conditions: adsorbent of MWCNTs:  $500 \text{ mg}$ ; pH  $5.0 \pm 0.1$ , concentration of copper, nickel and zinc metal ions:  $500 \mu\text{g L}^{-1}$ ; flow rate  $2 \text{ mL min}^{-1}$  and extractant concentrations  $0.3 \text{ mol L}^{-1}$ ).

**Table 1**

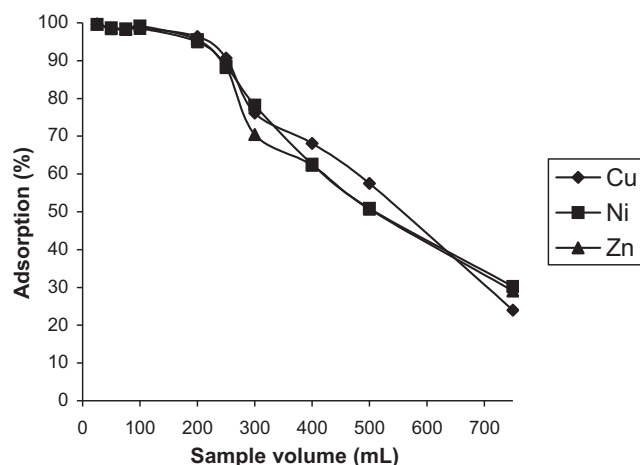
Influence of various eluents on the desorption of copper, nickel and zinc-D2EHPA-TOPO complex from MWCNTs adsorbent (eluent volume:  $10 \text{ mL}$ ,  $N=5$ ).

Acid	Recovery (%)		
	Copper	Nickel	Zinc
$1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	53.3	62.5	55.6
$2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$	72.8	78.6	72.6
$1 \text{ mol L}^{-1} \text{ HCl}$	71.5	69.2	63.7
$2 \text{ mol L}^{-1} \text{ HCl}$	78.6	75.9	82.6
$1 \text{ mol L}^{-1} \text{ HNO}_3$	79.8	82.7	84.3
$2 \text{ mol L}^{-1} \text{ HNO}_3$	98.6	97.9	98.4

D2EHPA-TOPO were evaluated at  $2 \text{ mL min}^{-1}$  flow rate of the each eluent. In the present study, varying concentrations of inorganic acids such as  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ ,  $1.0 \text{ mol L}^{-1} \text{ HCl}$ ,  $2.0 \text{ mol L}^{-1} \text{ HCl}$ ,  $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and  $2.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  were evaluated for the desorption of copper, nickel and zinc. The results are summarized in Table 1. From the table, it is clear that the maximum quantitative recovery of copper, nickel and zinc was obtained with  $2.0 \text{ mol L}^{-1} \text{ HNO}_3$  eluent, while the minimum was obtained with  $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ . In addition, the concentrations of all the metal ions were quantitatively recovered from the column with  $10 \text{ mL}$  eluent volume. The order of stripping efficiency by the acids for copper, nickel and zinc ions from the loaded adsorbent using D2EHPA-TOPO was found to be  $\text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4$ . For achieving higher enrichment factor  $10 \text{ mL}$  of  $2.0 \text{ mol L}^{-1} \text{ HNO}_3$  was recommended for further subsequent works.

### 3.6. Effect of sample volume

The effect of synthetic aqueous sample volume on the adsorption of copper, nickel and zinc-impregnated with MWCNTs-D2EHPA-TOPO has been investigated in the range of  $25\text{--}750 \text{ mL}$  and keeping the metal ion concentration fixed at  $500 \mu\text{g L}^{-1}$ . The column flow rate was  $2 \text{ mL min}^{-1}$ . The results are presented in Fig. 5. From the figure, it is seen that the adsorption of metal can be achieved quantitatively (95%) by sample volume up to  $250 \text{ mL}$ . Above  $250 \text{ mL}$ , the quantitative adsorption decreased gradually. As sample volume increases, the concentration of analyte decreases. It is generally observed that the dilute solutions of copper, nickel and zinc at ppb levels may not be identical at higher concentrations. This feature may be responsible for the low adsorption as sample volume increases. In the present study, a highest pre-concentration



**Fig. 5.** Effect of sample volume on the adsorption of MWCNTs impregnated with D2EHPA (conditions: adsorbent of MWCNTs:  $500 \text{ mg}$ ; pH  $5.0 \pm 0.1$ , concentration of copper, nickel and zinc metal ions:  $500 \mu\text{g L}^{-1}$ ; sample volume varied from  $25$  to  $750 \text{ mL}$ ; flow rate  $2 \text{ mL min}^{-1}$ ; and extractant concentrations  $0.3 \text{ mol L}^{-1}$ ).

**Table 2**Tolerance levels of interfering ions for the adsorption copper, nickel and zinc–D2EHPA–TOPO complex from MWCNTs adsorbent (volume 100 mL,  $N=5$ ).

Ion	Added as	Concentration ( $\text{mg L}^{-1}$ )	MWCNT impregnated with 0.3 D2EHPA–TOPO. Adsorption of copper (%) <sup>a</sup>	MWCNT impregnated with 0.3 D2EHPA–TOPO. Adsorption of nickel (%) <sup>a</sup>	MWCNT impregnated with 0.3 D2EHPA–TOPO. Adsorption of zinc (%) <sup>a</sup>
Na <sup>+</sup>	NaCl	1000	97.0 ± 2.0	97.0 ± 6.0	97.0 ± 2.0
K <sup>+</sup>	KNO <sub>3</sub>	1000	96.0 ± 3.0	98.0 ± 5.0	98.0 ± 3.0
Ca <sup>2+</sup>	CaCl <sub>2</sub> ·3H <sub>2</sub> O	1000	97.0 ± 2.0	97.0 ± 7.0	97.0 ± 4.0
Mg <sup>2+</sup>	MgCl <sub>2</sub>	1000	96.0 ± 3.0	97.0 ± 2.0	98.0 ± 6.0
Cl <sup>-</sup>	NaCl	1000	96.0 ± 2.0	96.0 ± 2.0	97.0 ± 4.0
NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	1000	96.0 ± 4.0	98.0 ± 6.0	97.0 ± 7.0
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1000	98.0 ± 3.0	97.0 ± 5.0	98.0 ± 5.0
PO <sub>4</sub> <sup>3-</sup>	KH <sub>2</sub> PO <sub>4</sub>	1000	96.0 ± 2.0	96.0 ± 4.0	97.0 ± 4.0
Cd <sup>2+</sup>	Cd (NO <sub>3</sub> ) <sub>2</sub>	25	98.0 ± 2.0	98.0 ± 3.0	97.0 ± 6.0
Mn <sup>2+</sup>	MnSO <sub>4</sub>	25	97.0 ± 2.0	98.0 ± 6.0	97.0 ± 4.0
Fe <sup>3+</sup>	FeCl <sub>3</sub>	50	98.0 ± 3.0	98.0 ± 5.0	98.0 ± 6.0
Pb <sup>2+</sup>	Pb (NO <sub>3</sub> ) <sub>2</sub>	25	98.0 ± 2.0	97.0 ± 7.0	98.0 ± 5.0
Co <sup>2+</sup>	CoCl <sub>2</sub>	25	98.0 ± 2.0	98.0 ± 5.0	98.0 ± 4.0
Ag <sup>2+</sup>	AgNO <sub>3</sub>	25	96.0 ± 3.0	97.0 ± 6.0	96.0 ± 6.0
Cr <sup>6+</sup>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	25	95.0 ± 3.0	95.0 ± 3.0	95.0 ± 3.0

<sup>a</sup> Mean ± standard deviation based on the five replicates.

factor was found to be 25, the adsorbed metal ions eluted with 10 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub> in the pre-concentration and separation of copper, nickel and zinc metal ion.

### 3.7. Effect of interfering ions

The influence of possible matrix ions in the environmental samples and the effect of some transition metals have been investigated for this study. The effect of potential interfering ions on the determination of copper, nickel and zinc was studied by adding known concentration of various metals ions in an aqueous solution. The concentration of copper, nickel and zinc was fixed at 500  $\mu\text{g L}^{-1}$  and the concentration of interfering metal ions varied from 25 to 1000  $\text{mg L}^{-1}$ . The results are presented in Table 2. The results revealed that the alkaline and alkaline earth metals are normally present in the drinking water and did not retain through the column due to the low solubility constant of their chelates under the experimental conditions [16]. But, some of the heavy metal ions can be adsorbed through organic phase of D2EHPA–TOPO and the carrier adsorption of D2EHPA–TOPO caused metal complex formation with various metal ions such as Cd, Pb, Cr and Fe. At higher concentration (1000  $\text{mg L}^{-1}$ ) of Cd, Pb, Cr and Fe metal ions, there was an interference with pre-concentration of copper, nickel and zinc ions. In this case, the tolerance limit of the some heavy metal ions concentration was set, as the diverse ions amount require causing ±4% error in the determination of copper, nickel and zinc ions, because of the levels of some heavy metal ions in these samples are lower than their interference level.

### 3.8. Adsorption capacity of MWCNT

The adsorption capacity of MWCNTs was determined by studying the maximum amount of the adsorbed metal ions namely copper, nickel and zinc retained on the column. The resulting aqueous solution was passed through the column containing MWCNTs impregnated with D2EHPA–TOPO. The effect of the adsorption capacity of metal ions at pH 5.0 was investigated with 100 mL of aqueous sample solution containing 500  $\mu\text{g L}^{-1}$  each of copper, nickel and zinc. After passing the solution through column containing (0.1 g of MWCNTs), the sample was determined by flame atomic absorption spectroscopy. The adsorption capacity of MWCNTs was found to be 4.90  $\text{mg g}^{-1}$  for copper, 4.78  $\text{mg g}^{-1}$  for nickel and 4.82  $\text{mg g}^{-1}$  for zinc, respectively, which was stable for 15 cycles. Beyond 15 cycles, there was a decrease in the adsorption capacity of carbon nanotubes. In order to investigate the adsorption capacity, reproducibility was taken for this study. MWCNTs

were washed with hexane; the mixture was dried at 75 °C and was impregnated with D2EHPA–TOPO. The pre-concentration and separation method at optimum condition was carried out for five experiments and the adsorption efficiency was found to be 98.8%, 97.4% and 98.5% for copper, nickel and zinc ions, which indicate good reproducibility of results.

### 3.9. Analytical parameters

In order to estimate the analytical performance of the present pre-concentration and separation method, firstly, synthetic model solution containing different amount of copper, nickel and zinc with varying concentration from 5  $\mu\text{g}$  to 15  $\mu\text{g}$  was prepared. The results are given in Table 3. From the table, it is clear that the quantitative adsorption of those elements was in the range of 96–98% and the accuracy of the proposed method is satisfactory. The resulting solutions were submitted to the pre-concentration and separation procedure. Good agreement was obtained between the added and found analyte content using the recommended procedure.

### 3.10. Detection limit

The detection limit of the present work was calculated under optimal conditions after the application of pre-concentration and separation procedure of blank solutions analysed by FAAS. The detection limit based on the three times the standard deviation of the blank ( $k=3$ ,  $n=5$ ) was 50  $\mu\text{g L}^{-1}$  for Cu, 40  $\mu\text{g L}^{-1}$  for Ni and 60  $\mu\text{g L}^{-1}$  for Zn. The detection limits of metal ions were 50  $\mu\text{g L}^{-1}$  found to be all the analyte ions. The comparative data for recent

**Table 3**The copper, nickel and zinc determinations in spiked test solutions (volume 100 mL,  $N=5$ ).

Ion	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	R.S.D.	Adsorption (%) <sup>a</sup>
Cu	5.0	4.96 ± 0.20	4.1	99.0 ± 0.2
	10.0	9.91 ± 0.30	3.0	99.0 ± 0.1
	15.0	14.98 ± 0.70	4.6	99.0 ± 0.8
Ni	5.0	4.98 ± 0.40	8.0	99.0 ± 0.6
	10.0	9.86 ± 0.80	8.1	98.0 ± 0.6
	15.0	14.88 ± 0.20	1.3	99.0 ± 0.2
Zn	5.0	4.92 ± 0.10	2.0	98.0 ± 0.4
	10.0	9.84 ± 0.70	7.1	98.0 ± 0.4
	15.0	14.89 ± 0.60	4.0	99.0 ± 0.2

<sup>a</sup> Mean ± standard deviation based on the five replicates.

**Table 4**  
Comparative data from some recent studies on copper, nickel and zinc.

Analytes	Method and instrumental detection	PF	Detection limit	R.S.D. (%)	References
Nickel	SPE on surfactant-coated alumina/AAS	300	40 g/L	2.4	[32]
Nickel	SPE on aminocarboxylic amphoteric resin/DRS	–	50 g/L	<5	[33]
Copper	SPE on Amberlite XAD-2/AAS	50	0.8–23.2 g/L	<5	[34]
Copper	CPE/CE	15.9–16.3	0.12–0.26 g/L	0.74–1.8	[35]
Copper, nickel and zinc	SPE on MWCNTs impregnated with D2EHPA-TOPO/AAS	25	50 µg/L	<10	Present method

Note. CPE: cloud point extraction; SPE: solid phase extraction; PF: pre-concentration factor; DL: detection limit.

studies are summarized in Table 4. It can be seen that the adsorption of copper, nickel and zinc was  $96 \pm 5.0$  at 95% confidence level.

### 3.11. Analysis of real samples

The present proposed method for copper, nickel and zinc was applied to natural water and electroplating industrial wastewater. The samples were collected and stored in pre-cleaned polyethylene pet bottles. Before analysis, the samples were filtered through Whatmann 41 filter paper. Then these samples were passed through the column loaded with MWCNTs impregnated with D2EHPA-TOPO and the proposed pre-concentration and separation method was applied under optimal experimental conditions as determined before. The results of natural water samples and wastewater are presented in Table 5. Satisfactory results were obtained for spiked analyte ions for the quantitative adsorption of metal ions. The adsorption was higher than 96%, which indicates the capability of the SPE system in the determination of copper, nickel and zinc ions present in the real samples and the accuracy of the proposed method is also satisfactory.

### 3.12. Characterization of adsorbent

The FT-IR spectra of pure D2EHPA, TOPO, MWCNTs and D2EHPA-TOPO have been recorded and IR adsorption frequencies

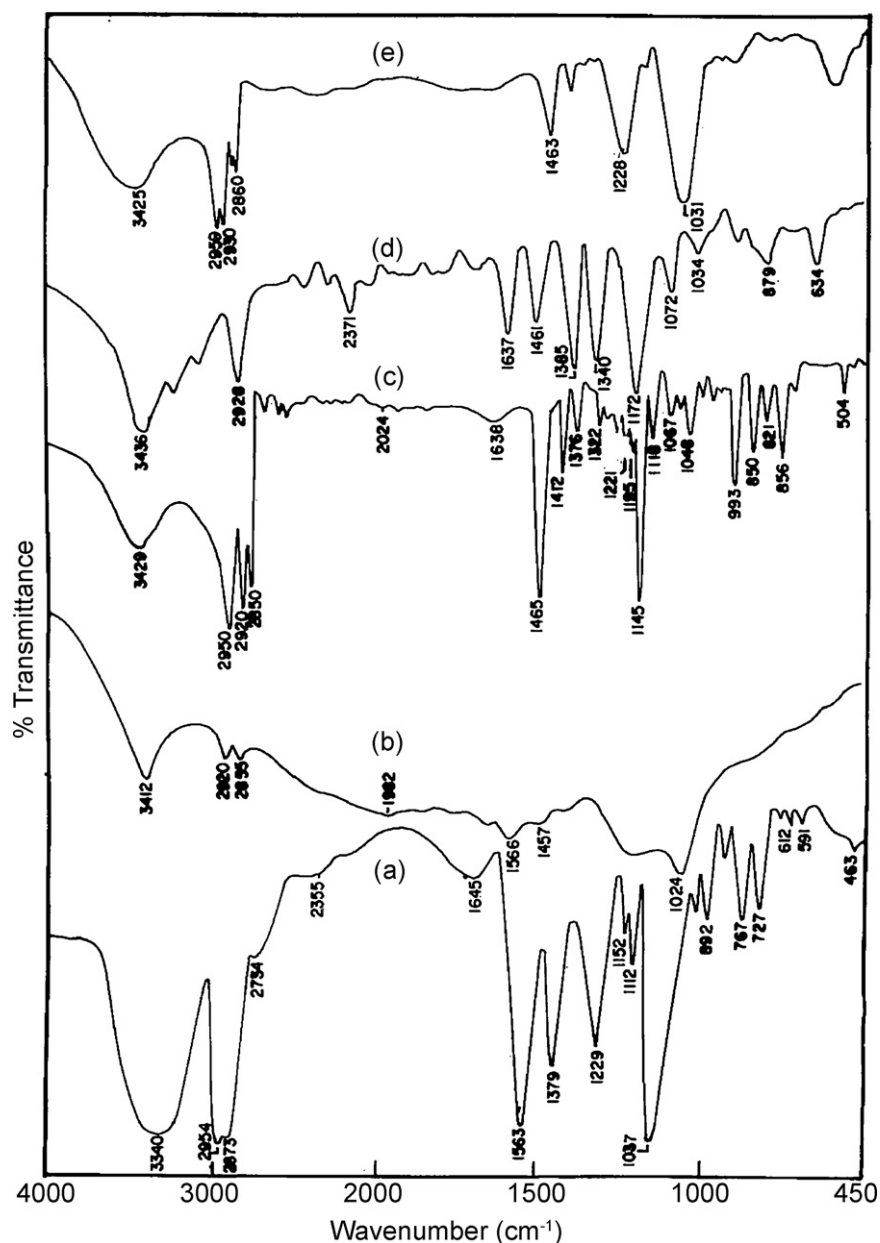
are presented in Fig. 6(a)–(e). From the figures, it is clear that for pure D2EHPA, P–O–C group showed intense absorption band around  $1031 \text{ cm}^{-1}$ . This group appears to have two stretching frequencies, one primarily due to the stretching of the P–O bond and the other due to the O–C band stretching for D2EHPA in MWCNTs. On the other hand, two bands are at  $1145 \text{ cm}^{-1}$  and  $1125 \text{ cm}^{-1}$  due to P–O stretching of TOPO in MWCNTs. But, it was not possible to specifically distinguish in the case of MWCNTs-D2EHPA-TOPO, because P–O–H group may overlap in the same frequency.

On the other hand, it can be seen that in MWCNTs adsorbent contains mixture of both extractants (D2EHPA-TOPO) and the P=O stretching frequency has been assigned at  $1226 \text{ cm}^{-1}$ . The bands corresponding to alkyl moieties have been identified at 2928–2863, 1461 and  $1380 \text{ cm}^{-1}$ . When the D2EHPA-TOPO interacts with any metal ion, the phosphoryl bond is highly affected. The FT-IR spectra of the free D2EHPA-TOPO and analyte ions show that the P=O band occurred at 1229 and  $1221 \text{ cm}^{-1}$ , respectively. The intensity of the P=O band corresponding to the free D2EHPA-TOPO of the copper, nickel and zinc concentration in the organic phase. The relative intensity of the band for free D2EHPA-TOPO (P–O–H) at  $1034 \text{ cm}^{-1}$  was found to be different in FT-IR spectra at  $1032 \text{ cm}^{-1}$  which is a very small difference. The relative intensity of the band for free D2EHPA (P–O–H) was found to be  $1034 \text{ cm}^{-1}$ , since there were two groups (P–O–C and P–O–H) overlapped in this frequency.

**Table 5**  
Adsorption copper, nickel and zinc in some natural water samples (volume 100 mL,  $N=5$ ).

	Ion	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	R.S.D.	Adsorption (%) <sup>a</sup>
Tap water	Cu	5.0	$4.98 \pm 0.30$	6.1	99.6
		10.0	$9.93 \pm 0.70$	7.5	99.3
		15.0	$14.89 \pm 0.50$	3.4	99.2
	Ni	5.0	$4.93 \pm 0.20$	4.0	98.6
		10.0	$9.89 \pm 0.60$	6.1	98.9
		15.0	$14.92 \pm 0.80$	5.3	99.4
	Zn	5.0	$4.89 \pm 0.40$	8.2	97.8
		10.0	$9.86 \pm 0.60$	6.1	98.6
		15.0	$14.89 \pm 0.70$	4.7	99.2
Well water	Cu	5.0	$4.93 \pm 0.40$	8.1	98.6
		10.0	$9.92 \pm 0.20$	2.0	99.2
		15.0	$14.85 \pm 0.30$	2.0	99.0
	Ni	5.0	$4.96 \pm 0.20$	4.0	99.2
		10.0	$9.94 \pm 0.40$	4.0	99.4
		15.0	$14.92 \pm 0.10$	1.0	99.5
	Zn	5.0	$4.86 \pm 0.30$	6.1	97.2
		10.0	$9.88 \pm 0.80$	7.1	98.8
		15.0	$14.83 \pm 0.60$	4.0	98.7
Electro plating wastewater	Cu	–	$5.65 \pm 0.40$	7.1	–
		5.0	$10.52 \pm 0.30$	2.9	97.4
		10.0	$15.60 \pm 0.20$	1.3	99.5
	Ni	15.0	$20.59 \pm 0.20$	1.0	99.6
		–	$5.86 \pm 0.50$	8.5	–
		5.0	$10.78 \pm 0.20$	1.9	98.4
	Zn	10.0	$15.82 \pm 0.40$	2.5	99.6
		15.0	$20.84 \pm 0.60$	2.8	99.8
		–	$5.20 \pm 0.40$	7.6	–
		5.0	$10.15 \pm 0.50$	4.9	99.0
		10.0	$15.10 \pm 0.20$	1.3	99.0
		15.0	$20.18 \pm 0.80$	3.9	99.8

<sup>a</sup> Mean  $\pm$  standard deviation based on the five replicates.



**Fig. 6.** (a) FT-IR spectroscopy of pure D2EHPA (without solvent), (b) pure MWCNTs, (c) pure TOPO, (d) D2EHPA-TOPO impregnated with MWCNTs, and (e) MWCNTs-D2EHPA-TOPO complexed with metal ions.

The decrease on absorbance seems to be related to the P–O–H group. Because copper, nickel and zinc metal ions are extracted with D2EHPA-TOPO and the liberation of hydrogen atom into the aqueous phase, while P–O–C group is unchanged. This indicated that the free P–O–H bonds were reduced. It seems that complex Cu, Ni and Zn (D2EHPA) was preferentially formed since it was more stable than Cu–O, Ni–O and Zn–O bonds. After stripping, the analyte ions from the loaded organic phase were analyzed with FT-IR spectra in Fig. 1(e). The spectra show bands at 888 and 1463  $\text{cm}^{-1}$  for P–O–H and P=O respectively. This revealed that the stripping agent did not affect the organic phase and it was also further confirmed by reuse of organic phase. Similar results were observed for Zn, Cu/D2EHPA system [28].

SEM images of pure MWCNTs, modified with D2EHPA and MWCNTs impregnated with D2EHPA-TOPO are presented in

Fig. 7(a)–(d). From the figures it is clear that, the chemical modification of carbon adsorbents surface is extremely irregular, the adsorbent impregnated with D2EHPA-TOPO has the appearance of an agglomerate of globular and cylindrical elements with diameters and lengths of  $\sim 5 \mu\text{m}$  or less. The rugosity and irregularity of the surface prevent an accurate measurement of the impregnating adsorbents. However a comparison of microphotographs obtained from the impregnated and non impregnated (6 copies) adsorbents indicate that the width of the MWCNTs-D2EHPA-TOPO layers ranges between 10 and 20  $\mu\text{m}$ . However, the irregular surface can be considered as a desirable feature, since it increases the effective surface area of the adsorbent, it provides a faster adsorption and desorption of analytes. The modifications of SEM images reveal that the D2EHPA-TOPO fully covered surface of the MWCNTs possesses good adsorption ability.

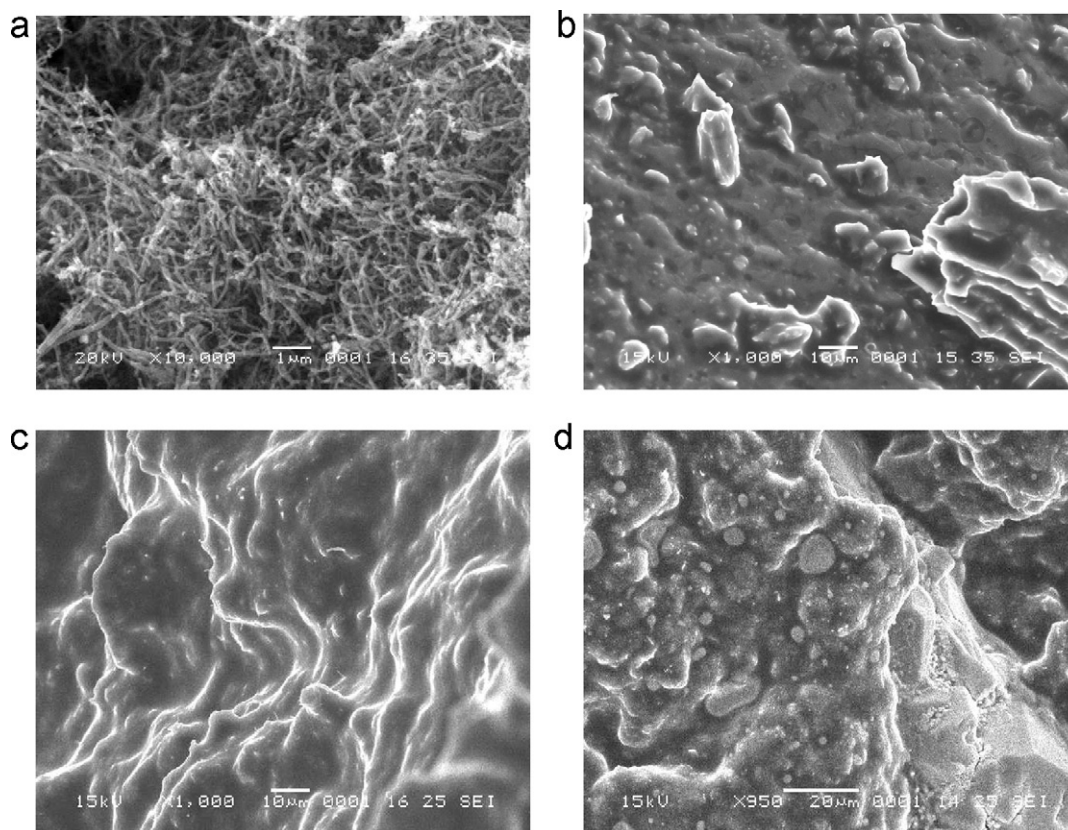


Fig. 7. SEM image of pure (a) MWCNTs, (b) MWCNTs modified with D2EHPA (c) MWCNTs modified with D2EHPA-TOPO, and (d) MWCNTD2EHPA-TOPO with metal ions.

#### 4. Conclusion

The organophosphorous extractants (D2EHPA-TOPO) loaded on MWCNTs is a sensitive and accurate method for preconcentration and separation of copper, nickel and zinc ions in low concentrations. The results presented in this paper have confirmed the applicability of the separation and pre-concentration of copper, nickel and zinc. The percentage adsorption of copper, nickel and zinc increased with increase in D2EHPA-TOPO concentration up to 0.2–0.3 M. Under optimum conditions, the maximum adsorption (96%) was achieved from electroplating wastewater and the detection limit of copper, nickel and zinc ion was  $50 \mu\text{g L}^{-1}$ .

#### Acknowledgement

Mr. S. Vellaichamy is thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, India, for providing financial assistance under the award of Senior Research Fellowship scheme (No: 09/468/(0369)/2007 EMR-I).

#### References

- [1] J. Kozłowska, C.A. Kozłowski, J.J. Kozioł, Transport of Zn (II), Cd (II) and Pb (II) across CTA plasticized membranes containing organophosphorous acids as an ion carrier, *Sep. Purif. Technol.* 57 (2007) 430–434.
- [2] A. Baran, E. Bicak, S.H. Baysal, S. Onal, Comparative studies on the adsorption of Cr (VI) ions on various adsorbents, *Bioresour. Technol.* 98 (2006) 661–665.
- [3] R. Sabry, A. Hafez, M. Khedr, A. Hassani, Removal of lead by an emulsion liquid membrane: Part I, *Desalination* 212 (2007) 165–175.
- [4] S. Baytak, A.R. Turker, Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA, *J. Hazard. Mater. B* 129 (2006) 130–136.
- [5] M. Soylak, N.D. Erdogan, Copper (II)-rubeanic acid coprecipitation system for separation-pre-concentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater. B* 137 (2006) 1035–1041.
- [6] M. Soylak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples, *Talanta* 66 (2005) 1098–1102.
- [7] D. Zendelovska, G. Pavlovska, K. Cundeve, T. Stafilov, Electrothermal atomic absorption spectrometric determination of cobalt, copper, lead and nickel traces in aragonite following flotation and extraction separation, *Talanta* 54 (2001) 139–146.
- [8] F. Gode, E. Pehlivan, Removal of Cr (VI) from aqueous solution by two Lewatitanion exchange resins, *J. Hazard. Mater.* 119 (2005) 175–182.
- [9] Z. Yan, F. Xuliang, Y.E. Zhilong, L.I. Yahong, C.A.I. Weimin, Biosorption of Cu (II) on extracellular polymers from *Bacillus* sp. F19, *J. Environ. Sci.* 20 (2008) 1288–1293.
- [10] V.O. Doroschuk, S.O. Lelyushok, V.B. Ishchenko, S.A. Kulichenko, Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction, *Talanta* 64 (2004) 853–856.
- [11] Y. Guo, B. Din, Y.W. Liu, X.J. Chang, S.M. Meng, M.Z. Tian, Pre-concentration of trace metals with 2-(methylthio) aniline-functionalized XAD-2 and their determination by flame atomic absorption spectrometry, *Anal. Chim. Acta* 504 (2004) 319–324.
- [12] M. Camino, M.G. Bagur, M. Sanchez-Vinas, D. Gazquez, R. Romero, Multivariate optimization of solvent extraction of Cd (II), Co (II), Cr (VI), Cu (II), Ni (II), Pb (II) and Zn (II) as dibenzyl dithiocarbamates and detection by AAS, *J. Anal. Atom. Spectrom.* 16 (2001) 638–642.
- [13] C. Cpara, S. Hasegawa, K. Naito, Collection of iron(III) from homogeneous aqueous solutions on membrane filters using chromazurol B with Triton X-100, *Anal. Sci.* 19 (2003) 265–268.
- [14] M. Soylak, I. Narin, U. Divrikli, S. Saracoglu, L. Elci, M. Dogan, Pre-concentration-separation of heavy metal ions in environmental samples by membrane filtration-atomic absorption spectrometry combination, *Anal. Lett.* 37 (2004) 767–780.
- [15] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration and determination of copper, nickel, cobalt, lead and iron content using a surfactant coated alumina, *Bull. Chem. Soc. Jpn.* 79 (2006) 432–436.
- [16] A.M. Starvin, T.P. Rao, Removal and recovery of mercury (II) from hazardous waste using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, *J. Hazard. Mater.* 13 (2004) 329–334.
- [17] M. Tuzen, M. Soylak, L. Elci, M. Dogan, Column solid phase extraction of copper, iron and zinc ions at trace levels in environmental samples on Amberlite XAD-7 for their flame atomic absorption spectrometric determinations, *Anal. Lett.* 37 (2004) 1185–1201.
- [18] S. Baytak, A.R. Turker, The use of *Agrobacterium tumefaciens* immobilized on Amberlite XAD-4 as a new biosorbent for the column pre-concentration of



- iron (II), cobalt (II), manganese (II) and chromium (III), *Talanta* 65 (2005) 938–945.
- [19] E. Kenduzler, A.R. Turker, Determination of iron, manganese and zinc in water samples by flame atomic absorption spectrophotometry after pre-concentration with solid phase extraction on to Ambersorb 572, *Anal. Sci.* 18 (2002) 917–921.
- [20] S. Tokalioglu, T. Oymak, S. Kartal, Determination of palladium in various samples by atomic absorption spectrometry after pre-concentration with dimethyl glyoxime on silica gel, *Anal. Chim. Acta* 511 (2004) 255–260.
- [21] A. Barbosa, M. Segatelli, A. Pereira, A. Santos, L. Kubota, P. Luccas, C. Tarley, Solid phase extraction for Pb (II) ions enrichment based on multiwall carbon nanotubes on-line to flame atomic absorption spectrometry, *Talanta* 71 (2007) 1512–1519.
- [22] P.M. Ajayan, T. Ichihashi, S. Iijima, Distribution of pentagons and shapes in carbon nano-tubes and nano-particles, *Chem. Phys. Lett.* 202 (1993) 384–388.
- [23] C.C. Carrion, R. Lucena, S. Cardenas, M. Valcarcel, Surfactant coated carbon nanotubes as pseudophases liquid–liquid extraction, *Analyst* 132 (2007) 551–559.
- [24] K. Sarangi, B.R. Reddy, R.P. Das, Extraction studies of cobalt (II) and nickel (II) from chloride solutions using Na-Cyanex 272. Separation of Co(II)/Ni(II) by the sodium salts of D2EPHA, PC88A and Cyanex 272 and their mixtures, *Hydrometallurgy* 2 (1999) 253–265.
- [25] M. Benamor, Z. Bouariche, T. Belaid, M.T. Draa, Kinetic studies on cadmium ions by Amberlite XAD7 impregnated resins containing di(2-ethylhexyl) phosphoric acid as extractant, *Sep. Purif. Technol.* 59 (2008) 74–84.
- [26] N.E. Belkhouche, M.A. Didi, R. Romero, J.A. Jonsson, D. Villemin, Study of new organophosphorous derivatives carriers on the selective recovery of M(II) and M(III) metals, using supported liquid membrane extraction, *J. Membr. Sci.* 284 (2006) 398–405.
- [27] A.B. Barbosa, M.G. Segatelli, A.C. Pereira, A.S. Santos, L.T. Kubota, P.O. Luccas, C.R.T. Tarley, Solid phase extraction system for Pb (II) ions enrichment based on multiwall carbon nanotubes coupled on-line to flame atomic absorption spectrometry, *Talanta* 71 (2007) 1512–1519.
- [28] J.L. Cortina, N. Miralles, A.M. Sastre, M. Aguilera, Solid–liquid extraction studies of divalent metals with impregnated resins containing mixtures of organophosphorous extractants, *React. Funct. Polym.* 32 (1997) 221–229.
- [29] O.S. Amuda, A.A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, *Biochem. Eng. J.* 36 (2007) 174–181.
- [30] N.A. Kabbashi, M.A. Atilh, A.A. Mamun, M.E.S. Mirghami, M.D.Z. Alam, N. Yahya, Kinetic adsorption of application of carbon nanotubes for Pb(II) removal from aqueous solution, *J. Environ. Sci.* 21 (2009) 539–544.
- [31] C. Cella, D. Bauer, Diphasic acido-basic properties of organophosphorous acids, *Solvent Extr. Ion. Exch.* 6 (5) (1988) 819–833.
- [32] F. Shemirani, S.D. Abkenar, Pre-concentration and determination of trace nickel using 1-(2-pyridylazo)-2-naphthol (PAN) immobilized on surfactant-coated alumina, *J. Anal. Chem.* 59 (4) (2004) 327–330.
- [33] O.P. Kalyakina, O.N. Kononova, S.V. Kachin, A.G. Kholmogorow, Sorption pre-concentration and determination of nickel in wastes of heat power industry by diffuse reflection spectroscopy, *Bull. Korean. Chem. Soc.* 24 (2) (2003) 173–177.
- [34] P. Bermejo-Barrera, M.A. Nancy, D.L. Cristina, B.B. Adela, Use of Amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol as a pre-concentration system for river water prior to determination of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> by flame atomic absorption spectroscopy, *Microchim. Acta* 142 (1–2) (2003) 101–108.
- [35] A.N. Tang, D.Q. Jiang, X.P. Yan, Cloud point extraction pre-concentration for capillary electrophoresis of metal ions, *Anal. Chim. Acta* 507 (2004) 199–204.