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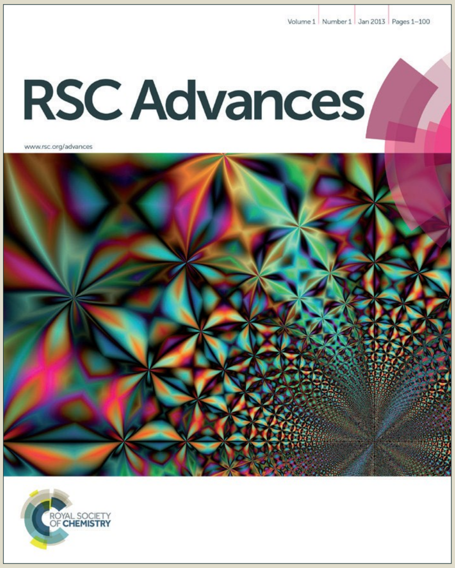

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Triethylenetetramine modified multiwalled carbon nanotube for efficient enrichment of Pb(II), Cu(II), Ni(II) and Cd(II) before FAAS detection

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Abstract

A novel, accurate and easy separation and preconcentration procedure has been established in the presented work. Triethylenetetramine modified multiwalled carbon nanotubes (TETA- MWCNT) was prepared and used as an efficient adsorbent for solid phase extraction of heavy metal ions. This modification for multiwalled carbon nanotubes results in making the surface of MWCNT rich with amino group which has a strong interaction with heavy metal ions. The characterization and surface morphology of TETA- MWCNT was evaluated by FT-IR and SEM. The parameters for the developed solid phase extraction procedure were investigated. The optimum conditions were obtained at pH 7, and 8 mL of 3 M nitric acid as eluent. The LOD values were 3.7 μg L^{-1}, 0.5 μg L^{-1}, 2.4 μg L^{-1} and 0.3 μg L^{-1} for Pb(II), Cu(II), Ni(II) and Cd(II), respectively. The relative standard deviations (RSDs) were found to be 1.4 %, 4.7 %, 2.9 % and 4.2 % for Pb(II), Cu(II), Ni(II) and Cd(II), respectively. The method was validated by using the method for certified reference materials (TMDA-53.3 fortified water and TMDA-64.2 Lake Ontario water). The TETA- MWCNT was applied for enrichment of Pb(II), Cu(II), Ni(II) and Cd(II) from water, cigarette and fertilizer samples.

Keywords: Solid phase extraction, triethylenetetramine, carbon nanotube, heavy metals, water, cigarette, fertilizer samples

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1. Introduction

Nowadays, the pollution with heavy metals has become the most dangerous source for health hazard. In addition, they have been spread in all environments around. Hence, to keep human safety, it is important to monitor heavy metals in environmental samples.[1-8] However, the presence of high quality instruments such as atomic absorption spectroscopy and inductively coupled plasma mass spectroscopy, sample pretreatment is needed to purify the samples as well as to enrich the heavy metals to be suitable for the instruments detection limits.[9-14] Among various preconcentration procedures such as liquid-liquid extraction (LLE),[15] dispersive liquid-liquid microextraction (DLLME) [16] and cloud point extraction (CPE),[17] Solid phase extraction (SPE) is the most stable procedure for heavy metals preconcentration purposes. It showed high repeatability, selectivity, economic and can be used with samples of large volumes.[18, 19] The process depend on two important steps; adsorption of the analyte from large volume samples, and then elution with suitable solvent. To control these two steps, the selection of adsorbent with suitable chemical and physical properties is the most important decision. The best adsorbent should be chemically stable in strong acidic condition, porous, with high surface area and including functional groups in its surfaces.[1, 18] MWCNTs have showed the superior properties as adsorbent for heavy metals. They have high tensile strength, stability in acid and basic medium, as having the ability to interact with various organic and inorganic analytes.[20-26]

Tuzen and Soylak have used MWCNT to speciation of chromium(III) and chromium(VI) and reported a detection limit of 0.90 μg L^{-1}.[21] Stafiej and Pyrzynska have evaluated the carbon nanotubes (CNTs) for solid phase extraction of some metals including Cu(II), Co(II), Ni(II), Zn(II), Pb(II), Mn(II) and Cd(II).[22] Chen et al., have investigated single-walled carbon nanotubes (SWCNTs) for separation of Cu(II), Co(II) and Pb(II) before inductively coupled plasma mass spectrometry (ICP-MS) and reported a detection limit of 39, 1.2 and 5.4 μg L^{-1} for Cu(II), Co(II) and Pb(II), respectively.[24] Duran et al., have applied multiwalled carbon nanotubes (MWNTs) in presence of o-cresolphthalein complexone for preconcentration of some heavy metals ions of copper, cobalt, nickel and lead with a detection limit between 1.64–5.68 μg L^{-1}.[25] Tavallali and Fakhraee have been used l-(2-pyridylazo)-2-naphthol (PAN) with multiwalled carbon nanotubes (MWNTs) for preconcentration of Cd^{2+} with limit of detection of 0.43 μg L^{-1}.[26] Skorek et al., have developed a dispersive micro solid-phase extraction (DMSPE) by multiwalled carbon nanotubes (MWCNT) and combined with energy-dispersive X-ray fluorescence (EDXRF) spectrometry for detection of nickel, cobalt, copper, and lead ions in presence of ammonium pyrrolidinedithiocarbamate (APDC)

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achieving detection limits of 0.43, 0.11, 0.46, 0.15 μg L^{-1} for Co(II), Ni(II), Cu(II), and Pb(II) respectively.[27] ALqadami et al., have applied MWCNT for preconcentration of As, Bi, Cd, Pb, Hg and Ti from cosmotic samples before determination by ICP-AES.[28] Their results showed a limit of 2.4, 4.08, 0.3, 2.1, 1.8, and 1.8 ng·mL^{-1}, for As, Bi, Cd, Pb, Hg and Ti respectively. However, the chemical modification of the MWCNT is still the most significant improvement of their adsorption capacity.[14]

This work aimed to firstly used TETA- MWCNT as a novel adsorbent for efficient solid phase extraction of Pb(II), Cu(II), Ni(II) and Cd(II) from water, cigarette and fertilizer samples in literature. The most important factors have been evaluated including, pH of the metal solution, eluent type and amount, coexisiting ions, initial sample volume and adsorption/recovery tests.

2. Materials and Methods

2.1. Reagents and solutions

Reverse osmosis purified water (18.2 MΩ cm, Millipore) was used for solution preparation. Heavy metal stock solutions with concentrations of 1000 mg L^{-1} (Sigma, St. Louis) were diluted daily to prepare solutions for all tests. Distilled water was used for preparation of all solutions. All chemicals were in analytical grade. Multiwalled carbon nanotubes and triethylenetetramine disulfate was purchased from Sigma, St. Louis. TMDA-53.3 fortified water and TMDA-64.2 Lake Ontario water (National Water Research Institute, Ontario, Canada) was used as water certified reference material for trace analyte analysis.

2.2. Instruments

A Perkin-Elmer Model 3110 (Norwalk, CT, USA) flame atomic absorption spectrometer equipped with a hollow cathode lamp (HCL) and an air/acetylene flame as an atomizer was used for the measurements. The flame AAS operating parameters were as follows: wavelength (nm) 283.3 (Pb), 324.8 (Cu), 232.0 (Ni) and 228.8 (Cd); lamp type and lamp current HCL 15 mA for Pb, 15 mA for Cu, 30 mA for Ni, and 12 mA for Cd, respectively; air/acetylene flow rate (l min^{-1}) 9.5/2.3; burner height 65 mm; slit width 0.7 nm. The absorbance measurements were performed with the continuous aspiration mode of FAAS.

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The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). Scanning electron microscope (SEM) images were obtained on a LEO 440 SEM with an accelerating voltage of 20 kV.

2.3. Preparation of triethylenetetramine modified MWCNT

The synthesis of triethylenetetramine modified MWCNT was done according to the steps described in literature studies with some modifications.[30, 31] In details, 2 g of MWCNT was oxidized with 200 mL conc. HNO_3 for 18 h at 60 ºC. Then the product was filtered, washed with distilled water until pH of the filtrate become 7. The obtained oxidized MWCNT was dried overnight in the oven at 60 ºC. Thereafter, 1 g of the dry oxidized MWCNT was reacted with 50 mL of 5% (v/v) thionyl chloride ($SOCl_2$) in toluene, for 3h at 70 ºC, then $SOCl_2$ was removed by Rotary evaporator, and the product washed 3 times with ethanol. Then, the produced MWCNT -CO-Cl was refluxed with 50 ml of (1%) triethylene tetraamine disulfate. The product was filtered, washed with ethanol and deionized water and dried overnight in the oven at 60 ^{o}C.

2.4. SPE procedure using triethylenetetramine modified MWCNT (TETA- MWCNT)

The Pb(II), Cu(II), Ni(II) and Cd(II) solutions with concentrations from 0.01 to 0.05 mg L^{-1} were adjusted to pH 7 using phosphate buffer solution. Then, the mixture was allowed to pass through a glass column containing 0.2 g of the TETA- MWCNT which was preconditioned with the same buffer. Then the system was washed with 10 mL distilled water. After that, the adsorbed heavy metals were eluted with 8 mL of 3 M nitric acid. Then, the concentrations of analytes in the eluent solution was analysed by flame atomic absorption spectrometer.

2.5 Applications to real samples

For real samples applications, cigarette and fertilizer samples were collected from Kayseri city, Turkey. The obtained samples were washed with distilled water, dried at 80 °C for 48 h, ground, and digested as described in literature.[18] 1.0 g of each sample was taken in a Teflon beaker separately and then 20 mL of concentrated nitric acid (65% w/w) was added. The mixture was heated until dryness. After cooling, a mixture of concentrated nitric acid (15 mL) and hydrogen peroxide (5 mL) was added; the mixtures were heated until dryness. The digested samples were dissolved in 10 mL of distilled water. Then, the described procedure for SPE given in Section 2.4 was applied for digested samples.

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Water samples including tap water, waste water, sea water, dam water and valley water were collected from Turkey. The water samples were filtered through 0.45-µm membrane filters. Then, the described procedure for SPE given in Section 2.4 was applied for water samples.

3. Results and discussion

3.1. Characterization of the prepared adsorbent (TETA- MWCNT)

The FT-IR spectras of multiwalled carbon nanotubes (MWCNT) and triethylenetetramine modified MWCNT (TETA- MWCNT) are shown in Fig. 1. When MWCNT was modified by triethylenetetramine, several new peaks appeared in the spectrum assigned as follows: the typical bands at 3321 cm^{-1}, 2957, 1725 cm^{-1}, 1637 cm^{-1}, 1460 cm^{-1}-1383 cm^{-1} and 1241-1066 cm^{-1} due to OH stretching vibration of COOH (carboxyl group), -CH_2 stretching vibration, C=O stretching vibration, –NH bending vibration of NH groups on triethylenetetramine, C-N stretching vibrations and C-O stretching vibrations, respectively.

Information about the surface morphology of MWCNT and TETA- MWCNT can be obtained by studying the scanning electron microscopy (SEM) micrographs that are presented in Fig. 2a and Fig. 2b. The morphology of the MWCNT and TETA- MWCNT shows important differences. Especially, the formation of porous surface for TETA- MWCNT is seen. This porous surface morphology of TETA- MWCNT is providing a large exposed surface area for adsorption of analytes.

By the modification of MWCNT with TETA in the presented work; the surface of MWCNT has rich with amino group. It has a strong interaction with heavy metal ions for the adsorption of the analyte elements.

3.2. Development of the SPE using TETA- MWCNT

Herein, the parameters for optimizing the solid phase extraction (SPE) including; pH of the metal solution, eluent type and amount, coexisting ions, initial sample volume and adsorption/recovery were evaluated in order to identify the optimum conditions for real samples applications. The prepared (TETA- MWCNT) is an amino rich adsorbent and its interaction with heavy metals is expected to be pH dependent. Therefore, the changing pH of the metal solution from 2 to 7.5 was investigated. Results indicated that at lower pH, the recovery was low, while at higher pH of 6 and 7, the quantitative recoveries were obtained (Fig. 3). This may be attributed to the strong competition between H^+ ions and metal ions in

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the strong acidic medium, while this effect is lower at pH of 6 and 7. Based on these results, a pH of 7 was selected for subsequent work and real sample analysis.

For optimization of the desorption condition to elute the adsorbed metals from TETA-MWCNT surfaces, different concentrations from hydrochloric acid and nitric acid were tested and the recoveries were investigated (Fig 4). Results indicate that in case of using hydrochloric acid, partial recoveries were achieved which is not suitable for preconcentration purposes. While in case of using nitric acid, the quantitative recoveries were achieved with 3 M nitric acid solution. For further optimization, the amount of 3 M nitric acid was investigated by testing 3, 5, 8 mL. The quantitative recovery was achieved with 8 mL of the 3 M nitric acid. Therefore, 8 mL of 3 M nitric acid was selected for the further experiments. TETA- MWCNT can be used as high as greater than 100 experiments without any loss in its sorption behavior.

By transfer from standard solutions of heavy metals to the real sample applications, the complicated matrices retard the extraction procedure. Therefore, different matrix should be optimized. [29, 32-41] In order to evaluate the effect of presence of coexisting ions on the recoveries of Pb(II), Cu(II), Ni(II) and Cd(II), the matrix ions have been tested. The calculated recoveries in each case are presented in Table 1. It can be concluded from these results that the developed SPE procedures were applicable in the presence of tested ions. These confirm that the developed SPE procedure is matrix-independent.

As the pre-concentration factor increase, the efficiency of the extraction procedure is improved. The preconcentration factor is calculated based on the initial sample volume and the final eluent volume. In the proposed work, the sample volume was evaluated at different intervals including 25, 50, 100, 250, 500, 750, 900 and 1000 mL. The results shown in Fig. 5 revealed that the developed SPE procedure is efficient and quantitative recovery can be obtained up to 900 mL. Therefore, the pre-concentration factors were calculated as 113 for Pb(II), Cu(II), Ni(II) and Cd(II), when using 8 mL of 3M nitric acid as eluent.

3.3. Analytical Features

One of the most important features of the SPE is the limit of detection (LOD). Therefore, the optimized conditions were applied, and the LOD (N=7) was calculated based on eq. (1)

$$LOD = \frac{3 * STD}{PF} \quad (1)$$

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Where, STD is the standard deviation of seven blank readings, and PF is the pre-concentration factor. The analytical performances of the presented method were given Table 3. With 100 mL sample volume and with 3 parallel columns, at a sample flow rate of 5.0 mL min^{-1}, sampling frequency of 8 h^{-1} was obtained.

The determination of Pb(II), Cu(II), Ni(II) and Cd(II) in TMDA-53.3 fortified water and TMDA-64.2 Lake Ontario water certified reference materials were applied to evaluate the developed SPE procedure. The results shown in Table 3 indicate that the recovered concentrations were in agreement with the concentrations in the certified reference materials. Furthermore, the addition/ recovery methods were operated at optimized conditions. The results in Table 4 showed that the quantitative recovery was not less than 97 %.

An urgent interest has been devoted for monitoring of elements at trace levels in environmental samples to avoid the human exposure with them, [9, 42-45] the proposed SPE procedure was applied for the preconcentration of Pb(II), Cu(II), Ni(II) and Cd(II), from water, cigarette and fertilizer samples. The concentrations of Pb(II), Cu(II), Ni(II) and Cd(II), are given in Table 5. The results reveal the suitability and applicability of the developed SPE procedure for real samples with different matrix mediums.

A comparison between preconcentration works in literature and presented work has been given in Table 6. The procedure presented is simple and accurate for the preconcentration and flame atomic absorption spectrometric determination of lead, copper, nickel and cadmium at trace levels. The obtained LODs and preconcentration factor are generally better than those obtained by some presented methods given in Table 6.

4. Conclusion

The combination of carbon nanotubes with triethylenetetraamine has led to an improvement for the application as solid phase extraction (SPE) sorbent. This can be attributed to the presence of amino groups which has strong interaction with the heavy metals such as Pb(II), Cu(II), Ni(II) and Cd(II). The optimum conditions for application of this adsorbent (TETA- MWCNT) for SPE were obtained at pH 7, and 8 mL of 3 M nitric acid was used as eluent. The quantitative recoveries were achieved up to sample volume of 900 mL. The preconcentration factor was 113. The developed SPE was applied for determination of Pb(II), Cu(II), Ni(II) and Cd(II) in water, cigarette and fertilizer samples.

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Figure captions

Figure 1. FT-IR spectra of triethylenetetraamine modified carbon nanotubes (A) and multiwalled carbon nanotubes (B).

Figure 2a and 2b. SEM images of multiwalled carbon nanotubes and triethylenetetraamine modified carbon nanotubes.

Figure 3. Effect of the pH on the recovery of Pb(II), Cu(II), Ni(II) and Cd(II) (N=3).

Figure 4. Effect of the eluent type and concentration on the recovery of Pb(II), Cu(II), Ni(II) and Cd(II) (N=3).

Figure 5. Effect of sample volume on the recovery of Pb(II), Cu(II), Ni(II) and Cd(II) (N=3).

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Table 1. Effect of matrix on the recovery of Pb(II), Cu(II), Ni(II) and Cd(II) (N=3).

Coexisting ion		Na(I)	K(II)	Fe(III)	Cr(III)	Ca(II)	SO_4^{2-}	Cl^-	CO_3^{2-}	**Al**(III)	**Hg**(II)	**Mn**(II)	**Zn**(II)	F^-
Added as		$NaNO_3$	KCl	$Fe(NO_3)_3.9H_2O$	$Cr(NO_3)_3.6H_2O$	$CaCl_2$	Na_2SO_4	KCl	Na_2CO_3	$Al(NO_3)_3.7H_2O$	$Hg(NO_3)_2.6H_2O$	$Mn(NO_3)_2.6H_2O$	$Zn(NO_3)_2.6H_2O$	NaF
Concentration (mg/L)		20000	1000	20	10	200	200	1000	800	10	10	10	10	500
Recovery %	Pb(II)	92±0	98±6	97±3	94±3	96±8	92±6	98±3	98±7	97±5	93±7	103±5	106±8	98±6
	Cu(II)	96±3	95±3	100±4	96±0	98±5	98±2	94±0	95±5	86±4	100±6	98±3	96±4	95±3
	Ni(II)	99±1	89±2	91±6	86±4	95±0	90±1	95±4	95±5	80±5	95±6	66±2	68±3	89±2
	Cd(II)	96±2	90±4	94±2	98±2	98±3	97±0	94±1	94±2	79±6	100±6	73±2	93±3	90±4

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Table 2. Analytical characteristics of the method

	LOD (µg L^{-1})	RSDs, %	Calibration Curve	Linear range mg L^{-1}
Pb(II)	3.7	1.4	A= 0.0006 + 0.007 C	1.0-20.0
Cu(II)	0.5	4.7	A = 0.0031 + 0.008 C	0.5-10.0
Ni(II)	2.4	2.9	A= -0.0026 + 0.032 C	0.5-10.0
Cd(II)	0.3	4.2	A=-0.0002 + 0.042 C	0.1-6.0

A=Absorbance value obtained FAAS, C= Concentration of analyte, mg L^{-1}.

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Table 3. Determination of Pb(II), Cu(II), Ni(II) and Cd(II) in TMDA-53.3 and TMDA-64.2 certified reference materials (N=3).

	TMDA-53.3 fortified water			**TMDA-64.2 Lake Ontario water**		
	Certified value µg L^{-1}	Found µg L^{-1}	Recovery %	Certified value µg L^{-1}	Found µg L^{-1}	Recovery %
Pb(II)	349	340±11	97	286	300±9	105
Cu(II)	308	299±1	97	270	263±1	97
Ni(II)	311	329±5	106	260	260±5	100
Cd(II)	118	122±2	103	264	262±2	99

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Table 4. Addition and recovery of analytes from tap water (N=3).

Analyte	Added, µg L^{-1}	Found µg L^{-1}	Recovery, %
Pb(II)	0.0	[a] BDL	-
	1.0	1.00±0.12	100
	3.0	3.02±0.12	101
Cu(II)	0.0	0.03±0.005	-
	0.1	0.09±0.00	97
	0.2	0.20±0.01	100
Ni(II)	0.0	0.30±0.06	-
	2.8	2.80±0.09	100
	5.0	5.43±0.09	100
Cd(II)	0.0	BDL	
	1.3	1.29±0.07	100
	2.4	2.39±0.10	100

[a] BDL: Below of the detection limit.

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Table 5. Determination of analyte elements in water, cigarette and fertilizer samples (N=3).

Analyte	Water Samples, µg L^{-1}				Cigarette mg kg^{-1}	Fertilizer mg kg^{-1}
	Waste water	**Sea water**	**Dam water**	**Valley water**		
Pb(II)	110±4	140±3	80±2	BDL	BDL	BDL
Cu(II)	4.0±0.0	7.0±0.0	6.0±0.0	2.0±0.0	0.8±0.0	BDL
Ni(II)	90±3	8.0±0.5	120±1	6.0±0.1	3.0±0.1	4.0±0.1
Cd(II)	150±1	190±2	150±1	7.0±0.0	3.0±0.1	BDL

[a] BDL: Below of the detection limit.

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Table 6. Comparison between the developed SPE procedure and other methods from the literature

Technique	Instrument	Preconcentration Factor	LOD (μg L^{-1})	Ref.
SPE/L-cysteine functionalized multi-walled carbon nanotubes (MWCNTs-cysteine)	FAAS	33	Cd: 0.28	11
SPE/multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo)resorcinol	FAAS	15	Pb: 7.2, Ni: 4.3, Zn: 1.1, Cd: 2.8	18
Coprecipitation/ -(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one	FAAS	100	Pb: 1.2, Cu: 0.5, Cr: 0.2, Zn: 0.7	33
Dispersive liquid–liquid microextraction sodium diethyldithiocarbamate,	FAAS	-	Cd: 20 ng g^{-1}, Pb: 140 ng g^{-1}	46
SPE/ Triethylenetetramine modified multiwalled carbon nanotubes (TETA- MWCNT)	FAAS	113	Pb: 3.7, Cu: 0.5, Ni: 2.4, Cd: 0.3	This work

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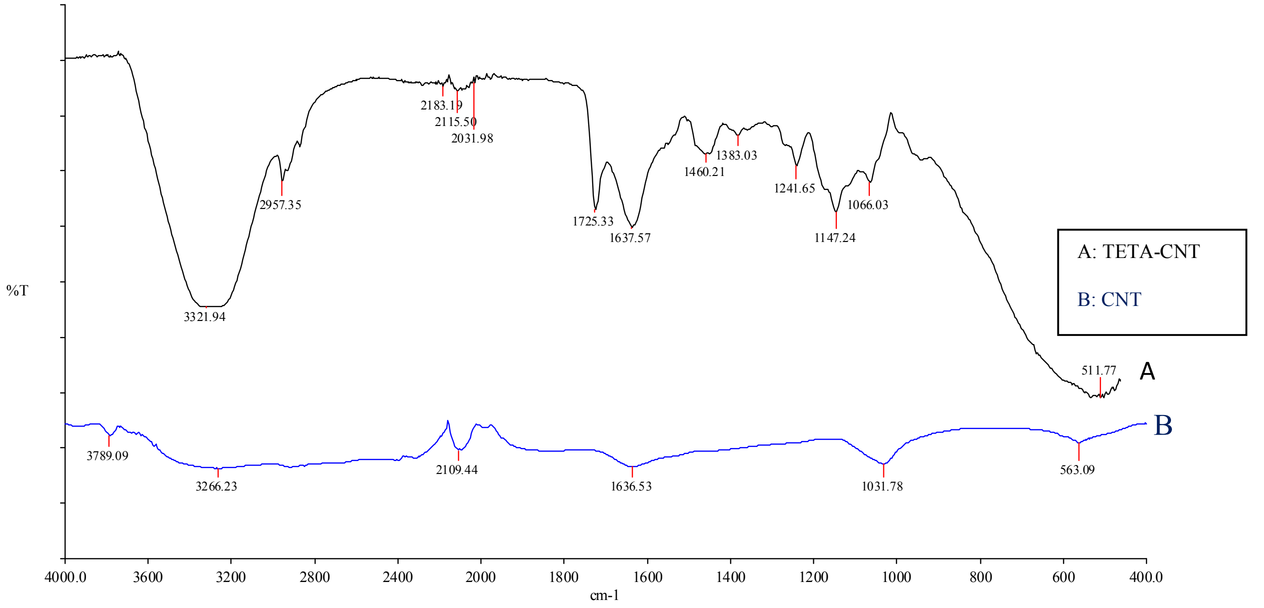

Figure 1.

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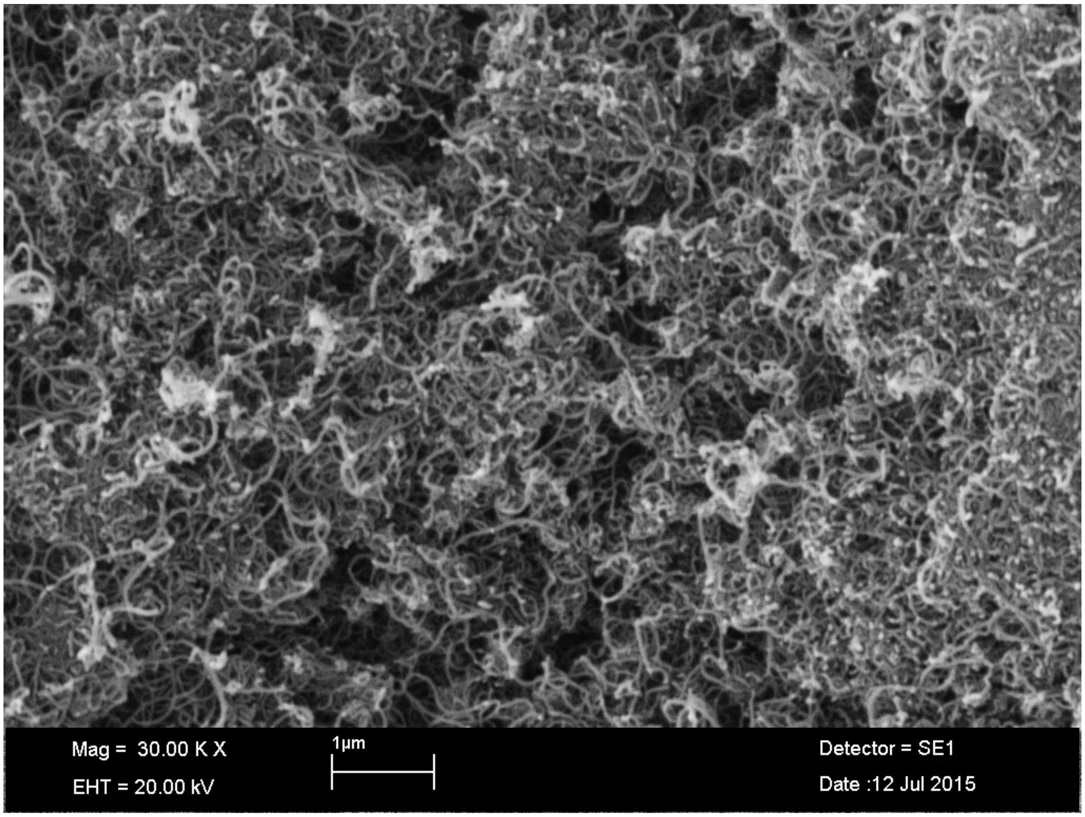

Figure 2a.

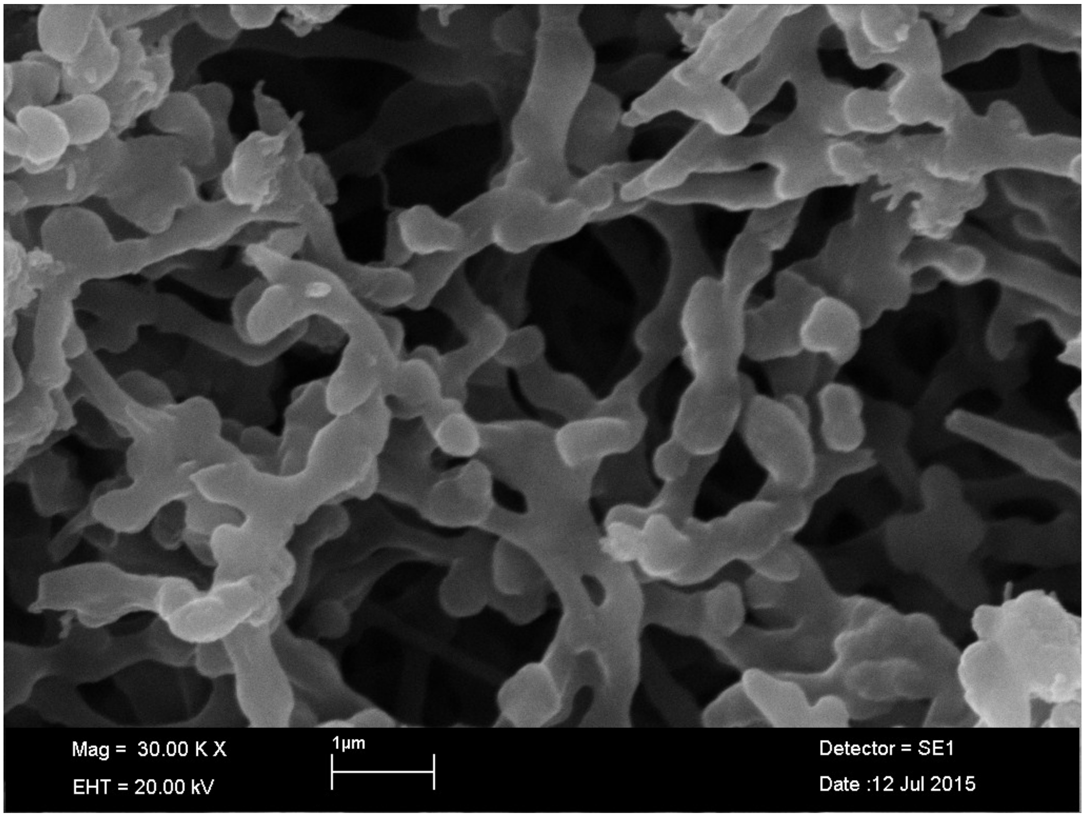

Figure 2b.

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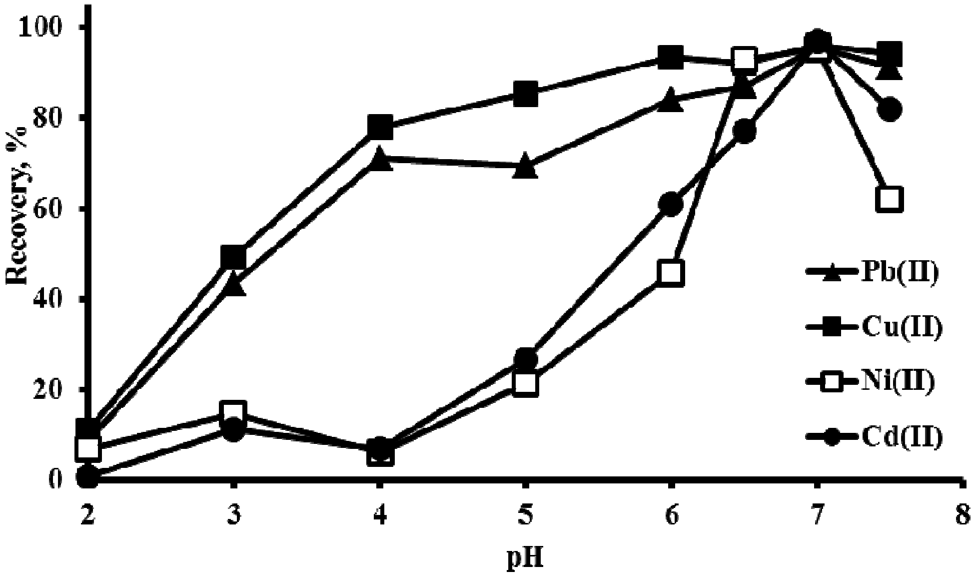

Figure 3.

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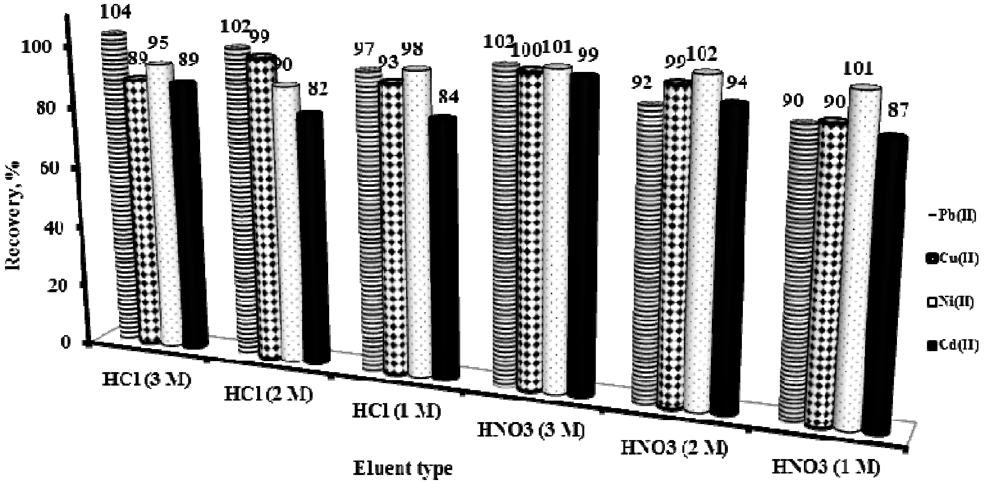

Figure 4.

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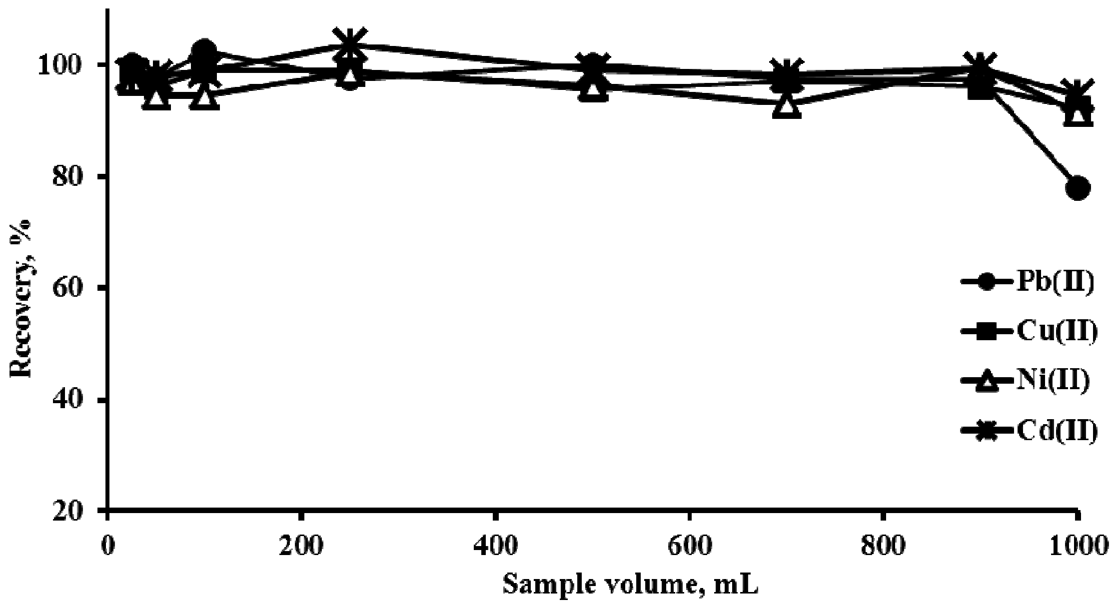

Figure 5

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