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Preconcentration of Zn(II) from Sample Water by Phenyl-iminodiacetic Acid Grafted Multiwalled Carbon Nanotubes

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Abstract: phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes were prepared by grafted phenyl-iminodiacetic acid groups onto multi-walled carbon nanotubes via a diazotation reaction. The stability of chemically phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes. The application of this phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes for sorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. Zn(II) was found to exhibit the highest affinity towards extraction by these phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for Zn(II) to occur by phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes. The potential applications of phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes for selective extraction of Zn(II) to occur from aqueous solution were successfully accomplished as well as pre- concentration of low concentration of Zn(II) (60 pg ml^{-1}) from natural tap water with a pre-concentration factor of 100 for Zn(II) off-line analysis by flame atomic absorption analysis.

Keywords*:* Preconcentration; Zn(II); phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes

INTRODUCTION

Zinc is considered as an essential micronutrient for humans, plants and animals. It plays an important role in several biochemical processes [1]. Zinc deficiency slows growth and development of the neonate. Zinc deficiency also leads to cognitive defects and impairs the immune system [2]. However, if it is in excess, it can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress [3]. Therefore, it is of great importance and significance for environment science and life science to separate and determine trace zinc in water samples. Although very sensitive analytical techniques, such as FAAS [4, 5, 19-20], ICP-MS [6] and ICP-AES [7] are used for the determination of trace zinc, it is impossible to directly determine the amount of zinc in water samples owing to the low concentration of zinc. In order to achieve accurate and reliable results, preconcentration step is necessary when the concentration of zinc is too low to be directly determined. Solid-phase extraction (SPE) is one of the most effective preconcentration methods because of simplicity, rapidity, high preconcentration factor and high recovery. The procedures for separation and preconcentration of zinc had been reported extensively [4–13]. Polyurethane foam loaded with 2-[2-(6- methyl-benzothiazolylazo)]-4-bromophenol [8] was used for separation of zinc in natural water samples. Silica gel functionalized with 1, 5-bis (di-2-pyridyl) methylene thiocarbohydrazide [7], 1,8-dihydroxyanthraquinone [9] were used for the preconcentration of zinc in water samples. Ion flotation [10], Amberlite XAD-2 [11, 12], solvent extraction using LIX 84 I [13], poly (ethylene terephthalate), naphthalene [17,18] were also used for the separation of zinc in diverse samples.

However, using microcrystalline triphenylmethane loaded with malachite green as solid-phase extracting to separate and preconcentrate Zn (II) has not been reported in any literature. The aim of this work was to apply a thiazolylazo reagent, 5-[1(H)-Benzotriazole methylene]-8-quinolinol (BTMQ) in a CPE procedure for determination of Zinc in water samples. Some analogous compounds of BTMQ such as 2-(6-methyl-2-benzothiazolylazo)-5- diethyl aminophenol (MBTAE) [22–24] and 2-(2-thiazolylazo)- 5-diethylaminophenol (TADAP) [25–27] have been applied as a precolumn derivatizing reagent in high-performance liquid chromatography (HPLC). Another analogue, 2-(6-bromo-2- benzothiazolylazo)-5-diethyl aminophenol,was synthesized and applied to the spectrophotometric determination of nickel [28] and zirconium [29]. According our knowledge, the use of BTMQ in analytical procedures has not been reported before.

For instance, Yan's group utilized L-cysteine to modify multiwalled carbon nanotubes (MWCNTs) resulting in a novel extractant for preconcentration of Cd (II) [33]. Unlike pristine MWCNTs, the sorption of Cd (II) onto the modified MWCNTs is not influenced by ionic strength in a wide range. Similar strategy also has been used by Chang and his coworkers to exploit

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ethylenediamine-grafted MWCNTs extractant [34]. The new extracting shows higher adsorption capacities for SPE of Cr (III), Fe(III) and Pb(II).

This paper describes the applications of phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes for selective extraction and solid phase pre-concentration of Zn (II) from aqueous and natural water samples.

EXPERIMENTAL

Reagents and materials

Analytical grade nitrate salts of Hg(II), Mn, Fe and Zn(II) litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II) and copper(II) of reagent grade were of the highest purity. Ultra-pure organic solvents were obtained from E.Merck, Darmstat, Germany, and High Purity deionized water was used throughout the experiments and 3-chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. Organic solvents were dried according to conventional methods. For all solutions double distilled water was used and the buffer solutions were prepared from 1.0M sodium acetate to which different volumes of 1.0M HCl; HNO_3 were mixed and the pH-value of the resulting solution was adjusted with the use of a pH- meter.The main range of diameter, length and specific surface area of the pristine MWCNTs (Chendu Organic Chemicals Co. Ltd., China Academy of Sciences, Chendu, China, http://www.cioc.ac.cn) are 8 nm, 30 μm, and 500 m^2 g^{-1}, respectively. 1,4-benzenediamine, sodium dodecyl benzenesulfonate (SDBS) and sodium chloroacetate (Aladdin Reagent Inc, Shanghai, China, http://www. sigmaaldrich.com) were used without further purification. The preparation of PIDA-WMCNTs was performed by Yang *et al*.[35].The synthesis route of PIDA-MWCNTs is illustrated in Fig. 1.

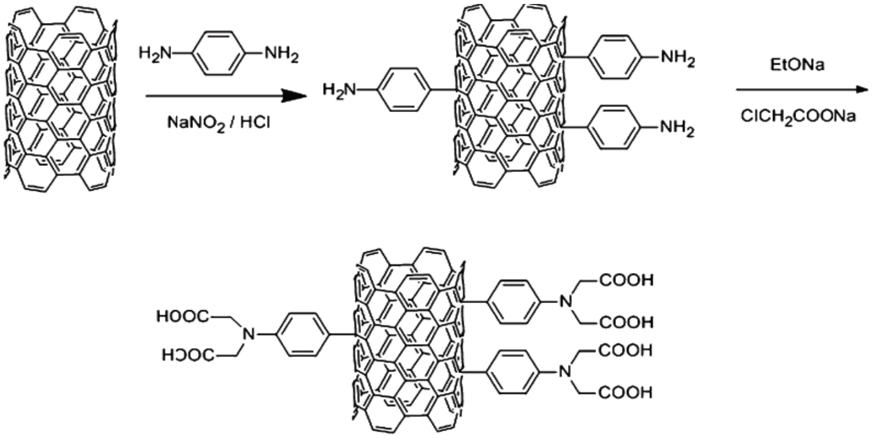

Fig. 1 The synthesis route of PIDA-MWCNTs

Synthesis Apparatus

X-ray photoelectron spectroscopy (XPS) was performed by using a Axis Ultra DLD spectrometer (Kratos Analytical. Ltd., UK) to investigate the functional groups on the surface of PIDA-MWCNTs. A model PSPE01 portable solid-phase-extractor (Green empire environmental protection S&T Co. Ltd., Shanghai, China) was used as solid phase extraction system. The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353)calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn (II) was performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn (II) determinations were performed by a Varian Spect AA-10 plus atomic absorption spectrophotometer.

Batch method procedure

A portion of standard or sample solutions containing Zn (II) was transferred into a 10 mL triangular flask; and the pH values were adjusted to the desired values with 0.1 mol L^{-1} hydrochloric acid and 0.1 mol L^{-1} aqueous ammonia. Then the volume was adjusted to 10 mL with DDW. 10 mg of PIDA-MWCNTs was added; and the mixture was shaken vigorously for 15 min to facilitate adsorption of the metal ions onto the PIDA-MWCNTs. After filtered, the concentration of the metal ions in the solution was determined by FAAS. The extracting was then eluted with HCl at optimum concentration and volume. Then the desorbed metal ions were measured by FAAS.

Column SPE procedure

The dynamic capacity is an important parameter for the PIDAMWCNTs in on-line application. The column SPE procedure was used to simulate the on-line test. 30 mg of PIDAMWCNTs was packed in the polytetrafluoroethylene (PTFE) column (50 mm×9.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 5 mL of 0.5 mol L^{-1} HCl

Stability studies

The stability of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phases in different buffer solutions (pH 1–6) and concentrated hydrochloric and nitric acid was studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 ml of the selected solution in 100 ml measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 ml water and dried in an oven at 80°C. Around 100 mg of the treated phase was added to 1.0 ml of 0.1M Zn (II) and 9.0 ml of 0.1M sodium acetate and the mixture was shaken for 30 min by an automatic shaker. The percentage of hydrolysis surface of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phases in different acidic solutions was calculated from the determined µmol g^{-1} value of each treated phase.

Sorption studies

Determination of metal capacity values (µmol g^{-1})

The determination of metal capacity of 13 metal ions, viz. Ba(II), Ca(II), Co(II), Zn(II), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1.0 ml of 0.1M metal ion and 9.0 ml of the buffer solution (pH 1–6 and 0.1M sodium acetate) in 50 ml measuring flask. The mixture was then automatically shaken for 30 min, filtered, washed with 50 ml water and the unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Zn (II) by the static technique. In this, 100 mg of the phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phase was added to 1.0 ml of 0.1M Zn(II) and 9.0 ml of 0.1M sodium acetate in 50 ml measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20,25,30 and 35 min). The mixture was filtered, washed with 50 ml water and the free metal ion was determined as described above.

Determination of the distribution coefficient

About 100 mg of the phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phase was mixed with 50 ml of the metal ion (1 $mgml^{-1}$) in a 100 ml measuring flask and shaken for 3 h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2% nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

Percentage removal of Zn (II) from aqueous solutions

One liter of Zn (II) solution, containing 10, 50 and 100 ng ml^{-1} was passed over a column [27] packed with 500 and 1000 mg each of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub. The flow rate was adjusted to 2.0 ml min^{-1}. The eluents were collected and 5ml was diluted with 20 ml of 2% nitric acid solution and subjected to flame atomic absorption spectrometric analysis (FAAS).

Pre-concentration of Zn (II) from aqueous and natural tap water

Two liters sample solution spiked with 20 pg ml^{-1} of Zn (II) in both double destilled water DDW and natural tap water were prepared and passed over a column packed with 1000 mg of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub with a flow rate of 2ml min^{-1}. Then 10 ml concentrated hydrochloric acid (10.0 M) was then passed over the phase and adsorbed metal ion to desorb the bound-Zn(II). The desorbed metal ion was directly determined by FAAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

RESULTS AND DISCUSSION

Stability studies

The stability of the newly synthesized phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Zn (II), this ion was used to evaluate the stability measurements for the phenyl-iminodiacetic acid grafted multiwalled carbon nanotub [14]. The results of this study proved that the phenyl-iminodiacetic acid grafted multiwalled carbon nanotub is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

However, the use of nitric acid with different concentration values (1.0, 5.0, 10.0 M) was found to change the color of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub from dark brown into reddish brown which is interpreted on the basis of chemical changes of the phenyl-iminodiacetic acid grafted multiwalled carbon nanotub modifier via oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0M hydrochloric acid for more than 1 week.

This test proved a reasonable stability of phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phase compared to non-treated silica gel phases judging from the color change of the two phases as well as the metal capacity values determination of Zn (II) and comparison of these with those of the original non-treated phenyl-iminodiacetic acid grafted multiwalled carbon nanotub phases.

Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix [9]. Finally, the phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phases were also found to be stable over a range of 1 year during the course of this work.

Metal capacity in various controlling factors

The metal capacity values determined in µmol g^{-1} for the phenyl-iminodiacetic acid grafted multiwalled carbon nanotube in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase. Table 1 compiles the µmol g^{-1} values for the 13 tested metal ions, viz) Zn(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cd(II), Cr(III) and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of µmol g^{-1} extracted values from the metal ion solution for most tested metal ions on the pH-value [20, 25].

The maximum value was found to be mainly at higher pH-values (pH 5–6 and 0.10M NaOAc). Second, is the strong affinity of the phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase for extraction and removal of Zn(II) from aqueous solution compared to other tested metal ions, as shown by the higher µmol g^{-1} values by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phases(25).

Table 1**.** Metal capacity values determined in µmol g^{-1a}

pH	Zn(II)	Pb(II)	Hg(II)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)	Ca	Mg	Ba
NaOAc	248	59	52	20	-	14	43	63	19	23	20	30
6	217	45	36	58	-	35	64	91	39	21	28	38
5	136	33	23	69	10	50	69	75	20	35	29	29
4	55	25	15	50	44	25	38	60	10	30	15	20
3	34	12	10	28	30	14	38	45	5	25	10	13
2	23	7	8	18	23	10	25	25	00	15	5	6
1	2	3	3	13	3	4	15	14	00	2	00	2

[a] Values are based on n=3 with standard deviation of 4.

This behavior of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube –loaded sulfur containing compounds for selective extraction and removal of Zn(II) from aqueous and natural water sample is well documented [19,20] and reported based on different governing rules [17]. Third are the notably high µmol g^{-1} values determined for chemically phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase in comparison with values found as given in Table 1. The comparison between the metal sorption properties of chemically and physically- phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phases has been extensively studied [21] and the results presented in this work are consistent with the surface activity of the donor atoms responsible for metal ion interaction, sorption, extraction and selective removal. In the case of the physically adsorbed phase, some of these donor atoms are involved in physical adsorption processes with the active surface, leading to the minimization of the reactivity of such donor atoms for metal interaction and binding processes. The product, phenyl-iminodiacetic acid grafted multiwalled carbon nanotube, in this case is tuned with the active donor atoms (N) directed with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, are the general orders of metal capacity values for all tested metal ions by the two phases which are in many respects consistent and similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Zn (II) as well as the higher metal uptake behavior of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube . The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as µmol g^{-1} and correlated to that determined at 30 min shaking time. Fig. 1 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase and Zn (II). One minute shaking time was found to be sufficient to establish 84% of the determined µmol g^{-1} value at 30 min whereas 10 min shaking time led to 88% extraction. The data and results presented in this section reveal the superiority of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase as previously declared in the stability studies (Section 3.1).

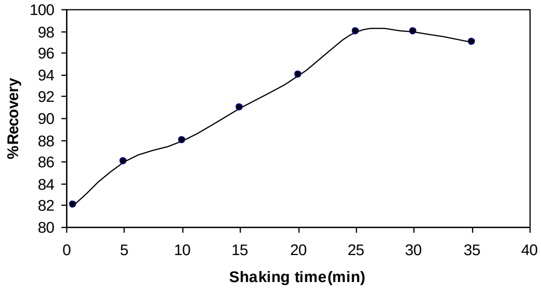

Fig 1. Effect of shaking time (min) on the percentage extraction of Zn(II) by the phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phases.

Table 2 **.** Distribution coefficient (K_d) values of various metal ions

Metal ions	K_d
Mn(II)	89
Fe(III)	77
Co(II)	76
Ni(II)	65
Cu(II)	700
Cd(II)	499
Cu(II)	118
Zn(II)	12600
Pb(II)	130

The distribution coefficient (K_d) data of the tested metal ions with the two newly phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phases are summarized in Table 2. It is evident that Zn (II) is the strongest absorbed metal ion by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase. The distribution coefficient values of Zn (II) by the loaded phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase were found to be much higher than those reported for ion exchange resins containing phenyl-iminodiacetic acid grafted multiwalled carbon nanotube derivatives [9]. In addition, the K_d values for Zn(II) by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase were found to come on the second place after Zn(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxil donor groups present in phenyl-iminodiacetic acid grafted multiwalled carbon nanotube for binding with Zn(II) [19,20]. On the other hand, the various tested metal ions as shown in Table 2 were found to exhibit lower tendency to bind with phenyl-iminodiacetic acid grafted multiwalled carbon nanotube judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Zn(II) and the lower ones for the other metal ions, except Zn(II), provide an additional evidence for the suitability of these two newly phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase for selective extraction of Zn(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase is consistent with the reported data.

Percentage removal of Zn(II) from aqueous solution

The use of a column technique is a common procedure for extraction, separation and selective extraction of metal ions from various aquatic systems [10]. The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes [14–16]. This property enables the pre-concentration of metal ions at very low trace levels. The percentage removal of metal ions from aqueous solutions is essential for the evaluation of the method described and suggested here. This is mainly dependent on several well-known factors such as the type and amount of packing stationary and mobile phases and the flow rate of the mobile phase [21]. In this study, we attempted to evaluate the percentage recovery of Zn(II) with different spiked concentrations, namely 10, 50 and 100 ng ml^{-1} from 1 l of 0.1M NaOAc solution by the application of two different amounts (500 and 1000 mg) of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase packing. The results of the percentage removal of Zn (II) from aqueous solutions are presented in Table 3 which clearly demonstrates the suitability and validity of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase for removal and extraction of Zn(II). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Zn (II) removal was accomplished by the use of 1000 mg phase.

Table 3. Percentage removal of Zn(II) from aqueous solutions by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase [a]

Zn(II) spiked (ng ml^{-1})	Phase (mg)	Percentage removal
10	500	94±4
50	500	96±4
100	500	97±3
10	1000	99±3
50	1000	95±2
100	1000	96±4

[a] Values are based on triplicate analysis.

Table 4. Preconcentration of Zn (II) from DDW and natural tap water samples [a].

Phase (mg)	Sample Volume(mL)	Zn(II)spiked (pg ml^{-1})	Preconcentration reagent	Preconcentration factor	Zn(II)detected[a] (ng ml^{-1})	Percentage removal
1000	2000 Tap water (Saveh)	20	10.0ml of 10.0M HCl	200	3.95±2.6	99.8±1.8
1000	2000 DDW	20	10.0ml of 10.0 M HCl	200	3.94±2.7	98.7±1.6

[a] Values are corrected for blank concentration of water samples and based on triplicate analysis.

Selective pre-concentration of Zn(II) from natural water for off-line FAAS

This study was undertaken in order to evaluate the potential application of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase for pre-concentration of trace levels of Zn (II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW (2 l) were spiked with 20 pg ml^{-1} of Zn(II). Several pre-concentration reagents are well-known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl [9] as well as ethylenediaminetetraacetic acid [25]. However, some of these reagents are usually characterized by adsorption on the surface of phenyl-iminodiacetic acid grafted multiwalled carbon nanotube which lead to severe change in the nature of packing material as well as non-reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Zn(II), by 10.0M HCl acid is found to be high without causing any notable change to the chemical nature of the organic phenyl-iminodiacetic acid grafted multiwalled carbon nanotube. Therefore, 10.0 ml of 10.0M HCl was used for the elution of the adsorbed Zn (II) from the column bed. The pre-concentration factor targeted from this study is 100 as given in Table 4. As the results indicate, the off-line detection results of the eluted and pre-concentrated Zn(II) are very good with a satisfactory pre-concentration factor which can be further increased to 500-fold by simply increasing the water sample volume to 5 l instead of 2 l. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed selective extraction, removal and pre-concentration of Zn(II) by phenyl-iminodiacetic acid grafted multiwalled carbon nanotube phase

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