Extraction and determination of Ni(II) by Histidine functionalized multi-walled carbon nanotubes adsorbed on surfactant coated C_{18} SPE column

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Abstract

A novel, simple, sensitive and effective method has been developed for preconcentration of Ni on Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) solid-phase extraction adsorbent. The stability of a chemical (MWCNTs-His), especially in concentrated hydrochloric acid, was then used as a recycling and pre-concentration reagent for further uses of (MWCNTs-His). The method is based on selective chelation of Ni(II) on surfactant coated C_{18}, modified with Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His). The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated C_{18} adsorbs 40 mg of the Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) base which in turn can retain 20.0 ± 0.9 mg of each of the two ions. The limit of detection (3σ) for Ni(II) was found to be 5.40 ng 1^{-1}. The enrichment factor for both ions is 100.

Keywords: Determination of Ni, Pre-concentration**,** Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His), FAAS.

1.0 Introduction

Ni at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [1-3].This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Ni can bind to the cell membrane and hinder the transport process through the cell wall. Ni at nearly 40ng mL^{-1} is required for normal metabolism of many living organisms . On the other hand, Ni is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Ni is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) as well as spectrometric methods [4,5].

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriative performation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time. The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed.

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium and lead.Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead, copper, silver, mercury, cadmium, palladium,Ce and UO$_2$ [6-9].

The main goal of the present work is the development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Ni(II) from aqueous media by means of a surfactant coated C18 modified with Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) (I, shown in Fig. 1).

Such a determination has not been reported in the literature. The structure of Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) is shown in Fig. 1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, MWCNTs-His or SDS. On the other hand, in terms of economy, it is much cheaper than those in the market, like the C$_{18}$ SPE mini-column.

2.0 Materials and methods

2.1. Reagents and Apparatus

All solutions were prepared with doubly distilled deionized water. C$_{18}$ powder for chromatography with a diameter of about 50 µm was obtained from Katayama Chemicals. It was conditioned before use by being suspended in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl solfate(SDS) was obtained from Merck and used without any further purification. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were purchased from Aldrich. Histidine (Guangfu Fine Chemical Research Institute, Tianjin, China) was used to prepare MWCNTs-His.

2.2. Synthesis of MWCNTs-His

Fig. 1 illustrates the scheme for the synthesis of MWCNTs-His. Briefly, the oxidized MWCNTs (MWCNT-COOH) were prepared as reported elsewhere [28]. The MWCNT-COOH was dispersed with EDC and NHS in DMF, and stirred for 5 h.

Then the product was separated and dried under vacuum before mixed with histidine in anhydrous DMF and stirred for 24 h. After the resultant solid was washed with DMF and DDW, the prepared MWCNTs-His was dried under vacuum [30].
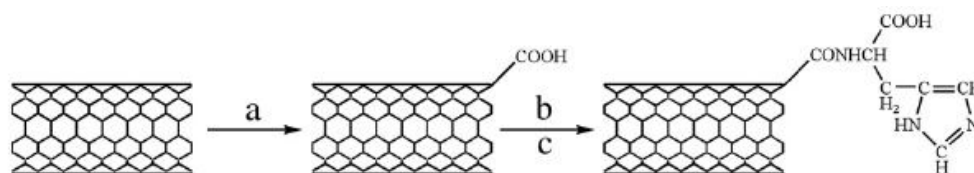

Figure-1: Schematic of Synthesis and structure of MWCNTs-His.

2.3. Column preparation

MWCNTs-His (40 mg) were packed into an SPE mini-column (6.0 cm ×9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L^{-1} HNO$_3$ and DDW were passed through the column to clean it.

2.3. Apparatus

The pH measurements were conducted with an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of MWCNTs-His were carried out from the KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was performed with a Perkin-Elmer.

2.3.1. Preparation of admicell column:

Solution was added to 40 ml of water containing 1.5 g of C_{18}, and 150 mg of the above Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) was loaded after washing acetone, 1mol l^{-1} HNO$_3$ solution and water, respectively. The pH of the suspension was adjusted to 2.0 with the addition of 4 M HNO$_3$ and stirred by a mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remaining C_{18} was washed three times with water, then with 5 ml of 4 M HNO$_3$ and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10mm).

Determination of Ni^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1). A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

2.3.2. Procedure

The pH of a solution containing 100 ng of each Ni(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 ml min^{-1}. The column was washed with 10 ml of water and the retained ions were desorbed with 1 ml of 4 M HNO$_3$ with a flow rate of 2 ml min^{-1}. The desorption procedure was repeated 3 more times. All the acid solutions (4 ml all together) were collected in a 10 ml volumetric flask and diluted to the mark with water. The concentrations of Ni in the solution were determined by FAAS at 283.3.

Diverse ion	Amounts taken (mg) added to 50 mL	% Found	%Recovery of Ni^{2+} ion
Na^+	92.4	$1.19(2.6)^a$	98.7(1.9)
K^+	92.5	1.38(2.1)	98.9(2.6)
Mg^{2+}	14.5	0.8(1.8)	98.7(1.8)
Ca^{2+}	28.3	1.29(2.0)	99.0(1.8)
Sr^{2+}	3.45	2.85(2.2)	98.2(2.0)
Ba^{2+}	2.66	3.16(2.5)	98.3(2.0)
Mn^{2+}	2.64	1.75(2.3)	98.5(1.8)
Co^{2+}	2.17	1.4(2.6)	98.1(2.2)
Ni^{2+}	2.65	2.0(2.6)	98.4(2.4)
Zn^{2+}	2.74	1.97(2.1)	98.7(2.2)
Cd^{2+}	2.53	1.9(2.0)	98.8(2.8)
Bi^{3+}	2.55	2.7(1.4)	98.7(2.7)
Cu^{2+}	2.46	2.81(2.3)	98.7(2.6)
Fe^{3+}	2.60	3.45(2.4)	96.6(2.8)
Cr^{3+}	1.70	2.92(2.6)	97.3(2.4)
UO^{2+}	2.89	1.3(2.4)	98.3(2.2)
NO_3^-	5.8	2.3 (2.3)	98.5(2.6)
CH3COO$^-$	5.0	2.2(2.5)	96.6(2.2)
SO_4^{2-}	5.0	2.9(3.0)	97.7(2.1)
CO_3^{2-}	5.6	1.8(2.5)	99.3(2.5)
PO_4^{3-}	2.5	2.1(2.0)	98.9(2.0)

Table-1:. **Effect of foreign ions on the recovery of 100 ng of Ni.**
Values in parentheses are CVs based on three individual replicate measurements.

2.3.3. Determination of Ni in water samples

Polyethylene bottles were soaked in 1 M HNO_3 overnight, and washed two times with water and used for sampling. The water sample was filtered through a 0.45 µm porous filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0(4 M HNO_3) and passed through the column under a flow rate of 5 ml min^{-1}. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

2.3.4. Speciation of Ni in water samples

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures [26-29]. The chelating cation exchanger (Chelex-100) and anion exchanger, (Dowex 1X-8) resins were washed with 1 M HCl, water, 1 M NaOH and water, respectively. 1.2 g of each resin was transferred to separate polyethylene columns. Each column was washed with 10 ml of 2 M HNO_3 and then

30 ml of water. The C_{18} bounded silica adsorber was conditioned with 5 ml of methanol in a separate column, then with 5 ml of 2 M HNO_3 and at the end with 20 ml of water. 5 ml of methanol was added on top of the adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. Then water was added to it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45 µm filter and then passed through the three column system, Dowex 1X-8, RP-C18 silica adsorber and Chelex-100, respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10 ml of 2 M HNO_3 and the C_{18} column with 10 ml of 1 M HCl.

Diverse ion	Amounts taken (mg) added to 50 mL	% Found	%Recovery of Ni^{2+} ion
Na^+	92.4	1.19(2.6)[a]	98.7(1.9)
K^+	92.5	1.38(2.1)	98.9(2.6)
Mg^{2+}	14.5	0.8(1.8)	98.7(1.8)
Ca^{2+}	28.3	1.29(2.0)	99.0(1.8)
Sr^{2+}	3.45	2.85(2.2)	98.2(2.0)
Ba^{2+}	2.66	3.16(2.5)	98.3(2.0)
Mn^{2+}	2.64	1.75(2.3)	98.5(1.8)
Co^{2+}	2.17	1.4(2.6)	98.1(2.2)
Ni^{2+}	2.65	2.0(2.6)	98.4(2.4)
Zn^{2+}	2.74	1.97(2.1)	98.7(2.2)
Cd^{2+}	2.53	1.9(2.0)	98.8(2.8)
Bi^{3+}	2.55	2.7(1.4)	98.7(2.7)
Cu^{2+}	2.46	2.81(2.3)	98.7(2.6)
Fe^{3+}	2.60	3.45(2.4)	96.6(2.8)
Cr^{3+}	1.70	2.92(2.6)	97.3(2.4)
UO^{2+}	2.89	1.3(2.4)	98.3(2.2)
NO_3^-	5.8	2.3 (2.3)	98.5(2.6)
$CH3COO^-$	5.0	2.2(2.5)	96.6(2.2)
SO_4^{2-}	5.0	2.9(3.0)	97.7(2.1)
CO_3^{2-}	5.6	1.8(2.5)	99.3(2.5)
PO_4^{3-}	2.5	2.1(2.0)	98.9(2.0)

[a]: Values in parentheses are CVs based on three individual replicate measurements.
Table-2: Effect of foreign ions on the recovery of 100 ng of Ni

The flow rate of eluents was 1 ml min^{-1}. The Ni content of each eluted solution was determined by FAAS.

3.0 Results and discussion

3.1. Stability studies

The stability of the newly synthesized MWCNTs-His 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 Ni(II), this ion was used to evaluate the stability measurements for the MWCNTs-His phase [14]. The results of this study proved that the MWCNTs-His is more resistant than the chemically adsorbed analog, especially in 1.0, 5.0 and 10.0 M hydrochloric acid with a hydrolysis percentage of 2.20, 6.10 and 10.50 for each phase, respectively.

Thus, these stability studies indicated the suitability of each 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 MWCNTs-His phases were also found to be stable over a range of 1 year during the course of this work.

MWCNTs-His are insoluble in water. Primary investigations revealed that surfactant coated C_{18} could not retain Ni(II) cations, but when modified with the MWCNTs-His, it retains these cations selectively. It was then decided to investigate the capability of the MWCNTs-His as a ligand for simultaneous preconcentration and determination of Ni on admicell.

The C_{18} surface in acidic media (1<pH<6) attracts protons and becomes positively charged. The hydrophilic part of SDS (-SO_3^-), is attached strongly to these protons. On the other hand, the MWCNTs-His are attached to the hydrophobe part of SDS and retain small quantities of metallic actions[22].

3.1. Effect of pH

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Ni(II) was studied in the pH range of 1-10. The pH of the solution was adjusted by means of either 0.01 M H NO_3 or 0.01M NaOH.
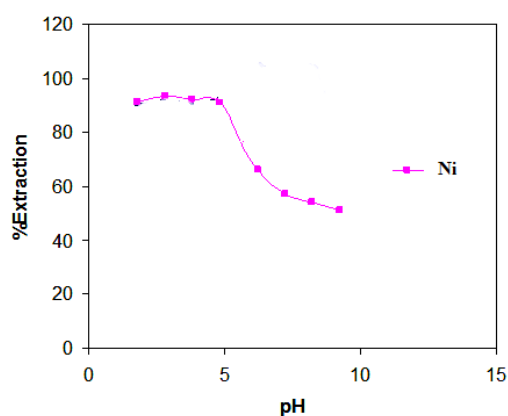

Figure-2: Extraction percentage of Ni(II) against pH

Column	River water(50ml) Ni(µg)	sample water (1000ml)[a] Ni(µg)	Tap water (1000ml) Ni(µg)
Dowex 1X8	-	-	-
Silica C-18	-	-	-
Chelex-100	0.018(4.5)[b]	0.108(3.1)	0.106(2.6)

[a]: This was a solution containing 0.1 µg of each cation in 1000 ml of distilled water.
[b]: Values in parentheses are CVs based on three replicate analyses. The samples are the same as those mentioned in Table 4.

Table-3: Results of speciation of Ni in different samples by the three columns system

The results indicate that complete chelation and recovery of Ni(II) occurs in a pH range of 2-4 shown in Fig. 2. It is probable that at higher pH values, the

cations might be hydrolyzed and complete desorption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18}, pH=2.0 was chosen for further studies.

3.2 Effect of flow rates of solutions

The effect of the solution's flow rate of the cations on their chelation on the substrate was also studied. It was indicated that flow rates of 1-5 ml min^{-1}would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and a MWCNTs-His has been reported in the literature [21,22]. A flow rate of 1-2 ml min^{-1}for desorption of the cations with 4 ml of 4 M HNO$_3$has been found suitable. Higher flow rates need a larger volume of acid. Hence, flow rates of 5 ml min^{-1}and 2 ml min^{-1}were used for sample solution and eluting solvents throughout, respectively.

3.3. Effect of the MWCNTs-His quantity

To study an optimum quantity of the MWCNTs-His on quantitative extraction of Ni, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns, the sorbent of which were modified with various amounts, between 10-50 mg of the MWCNTs-His. The best result was obtained on the sorbent which was modified with 40 mg of the MWCNTs-His.

3.4. Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted

into 10 ml solution, the enrichment factor for both cations is 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follows; 500 ml of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replicates was found to be 20.0±0.9 µg of each cation. The limit of detection (3σ) for the cations[30] were found to be 5.40 ngl^{-1}for Ni ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Ni(II).

3.5. Effect of foreign ions

The effect of foreign ions was also investigated on the measurements of Ni. Here a certain amount of foreign ion was added to 50 ml of the sample solution containing 100 ng of each Ni(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of Ni are listed in Table 2. As it is observed, it is possible to determine Ni without being affected by the mentioned ions.

3.6. Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of Ni were determined in different water samples namely: distilled water, tap water of Tehran (taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2013), snow water (Tehran, 7 February, 2013), and two synthetic samples containing different cations. The results are tabulated in Table 3. As it is seen, the amounts of Ni added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three columns system. It is possible to precon- centrate and at the same time

separate the neutral metal complexes of MWCNTs-His, anionic complexes and free ions from each other by this method.[27]. Water samples were passed through the three connected columns: anion exchanger, C_{18}-silica adsorber and chelating cation exchanger. Each species of Ni is retained in one of the columns; anionic complexes in the first column, neutral complexes of MWCNTs-His in the second, and free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4. According to the results, it is indicated that Ni is present only as cations. On the other hand, the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. We have proposed a method for the determination and preconcentration of Ni in water samples using surfactant coated C_{18} impregnated with a Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His)base. The proposed method offers a simple, highly sensitive, accurate and selective method for the determination of trace amounts of Ni(II) in water samples.

4.0 Conclusion

In the present work, a novel, simple, sensitive and effective method has been developed for preconcentration of Ni on Histidine functionalized multi-walled carbon nanotubes (MWCNTs-His) solid-phase extraction adsorbent. The stability of MWCNTs-His especially in concentrated hydrochloric acid, was then used as a recycling and pre-concentration reagent, and the results were encouraging, however further studies are in progress to further optimize the process.

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