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APPLICATION OF MULTIWALLED CARBON NANOTUBES MODIFIED BY DIETHYL DITHIOPHOSPHATE AMMONIUM FOR SELECTIVE SOLID PHASE EXTRACTION OF ULTRA TRACES Ni(II) AND Co(II) IN RIVER WATER SAMPLES

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ABSTRACT. In the present study, preconcentration followed by solid phase extraction of heavy metal ions, Ni(II) and Co(II) using the multiwalled carbon nanotubes (MWCNTs) and complexing reagent diethyl dithiophosphate ammonium (DDPA) were investigated and characterized by flame atomic absorption spectroscopy (FAAS). A series of experimental parameters, including sample pH, concentration of diethyldithiophosphate ammonium (DDPA), sample flow rate, eluting solution and the effect of interfering ions have been investigated systematically. The calibration graph was linear in the range of 0.4-100 μg L^{-1} and 0.7-120 for Ni(II) and Co(II), respectively . Under optimized conditions, the limit of detections (LOD) were 0.1 and 0.2 μg L^{-1} for Ni(II) and Co(II), respectively. The method was successfully applied to the preconcentration and separation of Ni(II) and Co(II) in some water samples from rivers located in industrial and nonindustrial areas.

Keywords: *Solid phase extraction; diethyl dithiophosphate ammonium (DDPA); Multiwalled carbon nanotubes; river water samples; Flame atomic absorption spectrometry, Ni(II) and Co(II)*

1. INTRODUCTION

Heavy metals at trace levels in environment are generally problem for human living. Industry and traffic are the main sources of traces metal ions in environment.[1]

The high consumption of nickel and cobalt-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling and disposal. Thus, the determination of trace amounts of nickel and cobalt in biological and environmental samples is important in the fields of

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environmental analysis, process control and medicine. Toxicological effects of large amounts of cobalt include vasodilatation, flushing and cardiomyopathy in human and animals.[2] Nickel can cause allergic reactions and that certain nickel compounds maybe carcinogenic. The determination of cobalt and nickel in natural water samples of environmental interest in which it is found at very low concentrations requires the use of preconcentration methods coupled to atomic spectrometric methods.[3]

Solid-phase extraction (SPE) is one of the most employed preconcentration methods that can be applied in off-line or online systems, with the advantage of possible automatization. SPE consists of the retention of metal species (or its derivatives) on the appropriate solid sorbent packed in a column or microcolumn and the later desorption with the adequate solvent. Thus, the concentration and separation of the analyte from the rest of sample matrix is achieved.[4] Solid-phase extraction (SPE), owing to its flexibility, absence of emulsion, simplicity, sampling in the field, safety, and ease of automation, is a preferred method for separation and enrichment of the target. SPE requires that the adsorbent possess a stronger selective adsorption ability.[5]

Carbon nanotubes (CNTs) are one of the most commonly used building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a very interesting material. CNTs have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels.[6]

CNTs have become attractive materials, since its discovery in 1991, because of their novel structure characteristics.[7-16] Recently, Carbon nanotubes as an adsorbent for the preconcentration of traces heavy metals have become very popular.[17-31]

In the presented work, the analytical potential of MWCNTs as an adsorbent for the preconcentration of traces heavy metals cobalt and nickel ions using DDPA as chelating agent was investigated. The procedure, using a solid phase extraction column loaded with MWCNTs as sorbent, for the preconcentration of traces of understudy metals in water samples prior to their determination by flame atomic absorption spectrometry (FAAS).

2. RESULTS AND DISCUSSION

To achieve a sufficiently high efficiency of a solid phase extraction procedure, it is essential to optimize various factors containing, pH, amounts of DDPA and adsorbent, sample volume, elution conditions such as volume and concentration of eluent, flow rate of solution and matrix ions.

2.1. Effect of pH

The pH value plays an important role with respect to the adsorption of different ions on CNTs.[32] To evaluate the effect of pH on the extraction efficiency of Ni(II) and Co(II) as DDPA chelates adsorb on multiwalled carbon nanotubes, the pH of the sample solutions, were adjusted to fit in the range of 1–8. It is observable in Fig. 1, quantitative recoveries (>95%) were obtained for all studied ions at the pH range of 3.5–5.0. So, the pH 4 was selected for all subsequent studies.

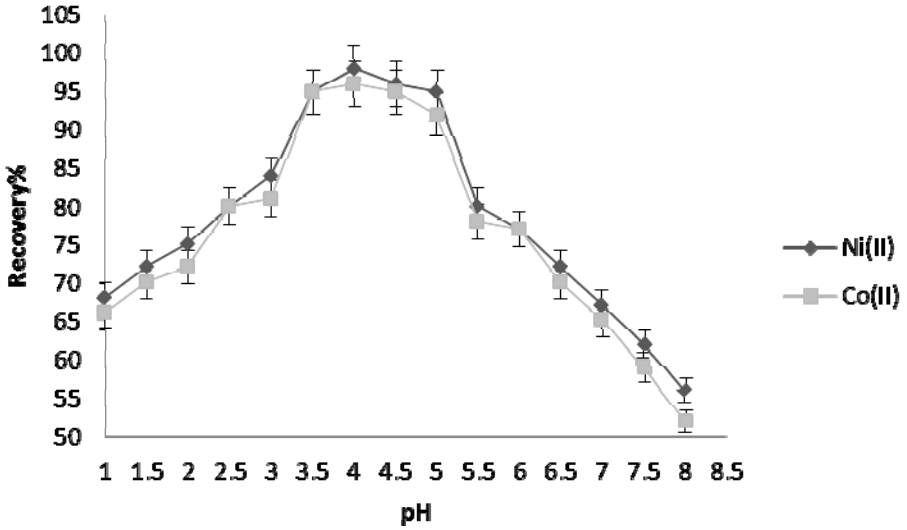

Figure 1. The effect of pH on the recoveries of 1.0 μg L^{-1} Ni(II) and Co(II) (N= 3.0.)

2.2. Effect of eluent type

The elution of the absorbed analytes could be achieved by using an appropriate eluent solution capable of effectively striping them from the MWCNTs and bring them into the solution.[33] Thus, the effects of various eluents (nitric acid, hydrochloric acid and acetic acid) on the recoveries of Ni(II) and Co(II) ions from multiwalled carbon nanotubes modified with DDPA were also investigated. The results are shown in Table 1.

Table 1. Effect of different eluting solutions on the Recoveries of 1µg L^{-1} Ni(II) and Co(II). (N=3)

Eluent	Recovery %	
	Ni(II)	Co(II)
1 mol L^{-1} HNO_3	86±1	84±1
1.5 mol L^{-1} HNO_3	89±3	86±2
2 mol L^{-1} HNO_3	96±2	95±4
1 mol L^{-1} HCl	79±5	81±4
1.5 mol L^{-1} HCl	80±2	71±1
2 mol L^{-1} HCl	75±4	75±5
1 mol L^{-1} CH_3COOH	61±3	72±4
1.5 mol L^{-1} CH_3COOH	80±2	78±3
2 mol L^{-1} CH_3COOH	76±3	71±1

The results indicated that 2 mol L^{-1} HNO_3 was sufficient for quantitative elution (>95%). Furthermore, the influence of eluent volume (2.0–10 mL) on the recoveries was studied by using 2 mol L^{-1} HNO_3. By adding 4.5 mL of 2 mol L^{-1} HNO_3, quantitative recoveries were obtained for all analyte ions. The recoveries were not quantitative for the other eluents listed in Table 1. Therefore, 4.5 mL of 2 mol L^{-1} HNO_3 was used as eluent for further work.

2.3. Effect of amount of chelating agent

To evaluate the effect of ligand on the recovery of metal ions, different amounts of DDPA solution (5×10^{-4} mol L^{-1}) in the range of 0-5 mL was investigated. As presented in Fig. 2, the recoveries of analyte ions increased with increasing amounts of DDPA added and reached a constant value over 95% with at least 2.5 mL. The recovery values of analytes were quantitative at the amounts of ligand range of 2.5- 5. Hence, 2.5 mL of ligand was selected for subsequent studies. At lower concentrations, the amount of ligand is insufficient to extract all the analyte in the solution. But at higher concentrations, all the analyte species were used, thus, Process of complex formation was stop and the percentage of recoveries remained nearly constant, in other words, the Limiting factor is analyte concentration.

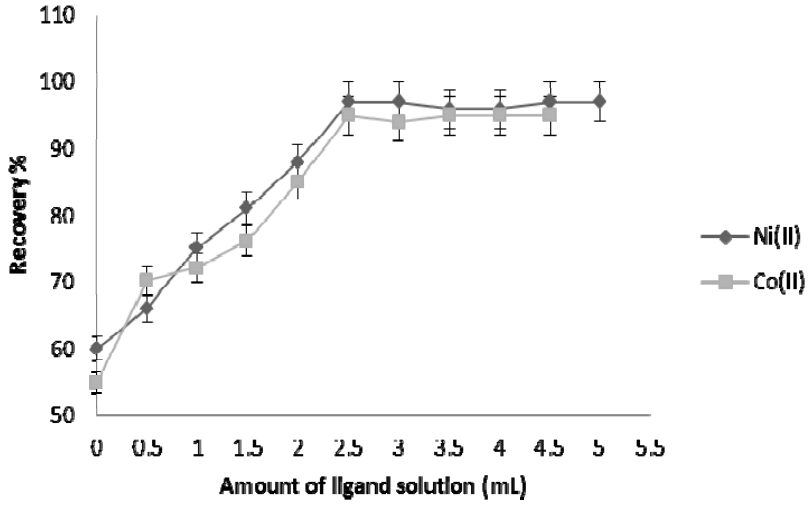

Figure 2. Effect of amount of ligand solution on the recoveries of analytes.

2.4. Effect of amounts of adsorbent (MWCNTs)

To estimate the impact of adsorbent mass on the recovery of metal ions, different amounts of adsorbent (50-400), packed into an SPE column, were investigated, following the preconcentration procedure. The recoveries of metal ions increased with increasing amounts of adsorbent. In the less amounts than 150 mg, the resultant recoveries were low because of by-passing of the liquid in the SPE column.[29] Quantitative recoveries of target ions were obtained in the range of 150–300 mg. Therefore, 150 mg of MWCNTs was the amount selected for further studies.

2.5. Effect of the sample volume

A higher preconcentration factor is obtainable by increasing the sample to eluent volume ratio by either decreasing the eluent volume or increasing the sample volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution by passing 50–600 mL of sample solutions. The effects of sample volumes on the recoveries of the two analytes are shown in Fig. 3. The results showed that the maximum sample volume could be up to 500 mL with the recovery >95%. Therefore, 500 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. The preconcentration factor (PF) is calculated by the ratio of the highest sample volume (500 mL) and the lowest eluent volume (4.5 mL). The preconcentration factor was calculated as 111.0

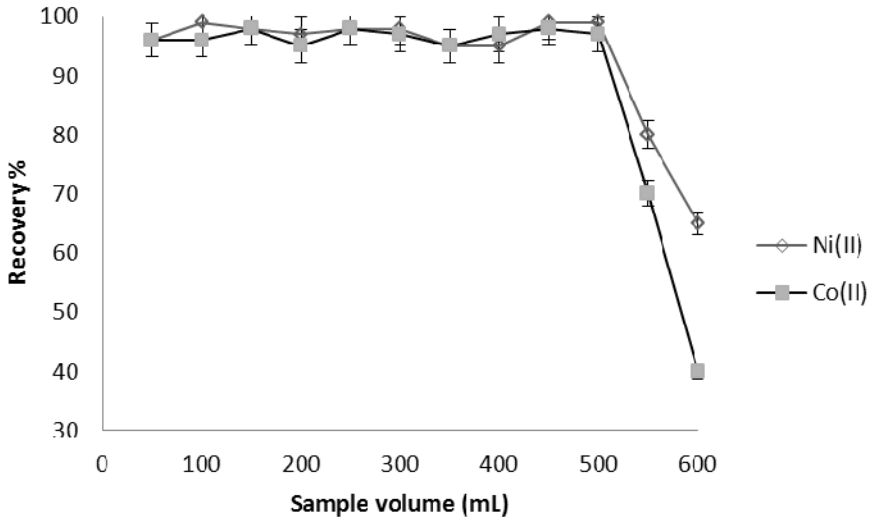

Figure 3. Effect of sample volume on the recoveries of 1.0 μg L^{-1} Ni(II) and Co(II) (N= 3.0)

2.6. Flow rates of sample and eluent solutions

The impact of flow rates of sample and eluent solutions are very important in solid phase extraction studies due to retention of analyte ions on column system. Low flow rates can be time consuming. The flow rates were investigated in the range of 1–10 mL min^{-1} and under the optimum conditions (pH and eluent type). It was found when the flow rates of the sample and eluent solutions were at the range of 1.0-6.0 and 1.0-7.0 mL min^{-1}, the recoveries of analytes were quantitative. At higher flow rates, there was a decrease in the recovery in that there was not sufficient contact time between MWCNTs and sample solution. Therefore, a flow rate of six milliliters per minute was chosen as the optimum flow rates of the sample and eluent solutions.

2.7. Effect of foreign ions

The effects of common coexisting ions on the adsorption of the analytes on MWCNTs were investigated. The obtained results were presented in Table 2. The tolerance limit is defined as the ions had no significant interferences in the preconcentration and determination of the analyses. This is due to the low adsorbing capacity or rates for interfering ions. It can be seen that the presence of major coexisting ions has no obvious influences on the determination of the analytes under the selected conditions.

Table 2. Effect of interfering ions on determination of 1.0 μg L^{-1} Ni(II), and Co(II) (N= 3).

Ion	Concentration (mg L^{-1})	Recovery (%)[a]	
		Ni(II)	Co(II)
Na^+, Cl^-, Li^+ I^-, K^+, Ca^{2+}	10000	97±1	96±2
Mg^{2+}, Ag^+ Br^-, $C_2O_4^{-2}$	8000	99±2	96±3
SO_4^{-2}, CO_3^{-2}, F^-	6000	97±1	99±3
NO_3^-, PO_4^{-3},	3000	96±1	98±2
HCO_3^{-2}, CH_3COO^-	1500	99±1	97±3
Pb^{2+}, Hg^{2+}	500	95±3	96±3
Mo^{5+}	250	97±1	97±2
Mn^{2+}, Sn^{4+}	100	99±3	97±1
Cr^{3+}, Al^{3+}, Cd^{2+}	10	95±1	97±2

[a] Mean ± standard deviations.

2.8. Adsorption capacity

For investigation of the adsorption capacity of multiwalled carbon nanotubes, 0.1 g MWCNTs was added to 50 ml of solution containing 1.0 mg of metal ions at pH 4.0. After shaking for 30 min, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 100 ml and determined by flame atomic absorption spectrometry. This procedure was repeated for each analyte ions separately. The capacity of modified MWCNTs for Ni(II), and Co(II) were found to be 76.1 and 70.5 mg g^{-1}, respectively.

2.9. Analytical performance

Using the optimized experimental conditions, calibration curves of enrichment process were linear in the range of 0.4-100 μg L^{-1} and 0.7-120 for Ni(II), and Co(II), respectively . The detection limits, based on three times of the standard deviation of 10 runs of blank solution, were found to be 0.1 and 0.2 μg L^{-1} for Ni(II), and Co(II), respectively. The relative standard deviation (RSD), twelve determinations of 1.0 μg L^{-1} of Ni(II), and Co(II) were 4.0 and 2.6%, respectively (N=12). The correlation coefficients for Ni(II), and Co(II) were 0.9997, 0.9995, respectively. The preconcentration factor for the proposed method was 111.0.

2.10. Analytical applications

The solid phase extraction procedure was also applied to the determination of Ni(II), and Co(II) in water samples from rivers located in industrial and nonindustrial areas. Various amounts of analytes were also spiked to these water samples. The results are given in Table 3. A good agreement was obtained between the added and measured Ni(II), and Co(II) amounts. The accuracy of the method was verified by the analysis of samples spiked with known amounts of the analytes.

Table 3. The results for determination of Ni(II) and Co(II) in various river water samples.

Sample	Added (μg L^{-1})		Found [a] (μg L^{-1})		Recovery (%)	
	Ni(II)	Co(II)	Ni(II)	Co(II)	Ni(II)	Co(II)
River Water [b]	-	-	80.14	43.12	-	-
	100	100	181.4	140.40	100.7	98.1
	200	200	280.4	238.30	100.09	98.02
River Water [c]	-	-	78.45	36.12	-	-
	100	100	172.15	140.30	96.47	103.07
	200	200	273.74	235.63	98.30	99.8
River Water [d]	-	-	65.8	31.57	-	-
	100	100	167.11	127.74	100.79	97.08
	200	200	261.8	239.13	98.50	103.26
River Water [e]	-	-	8.85	3.97	-	-
	100	100	108.99	107.16	100.13	103.06
	200	200	201.01	203.24	96.25	99.64

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence (N = 5)
[b] From karoon river, located in an industrial area
[c] From zayande rood river, located in an industrial area
[d] From khour musa, located in an industrial area
[e] From pole zohre located in an nonindustrial area

4. CONCLUSIONS

In this work, MWCNTs were successfully modified with DDPA and applied as enrichment material for SPE coupled with FAAS for determination of Ni(II) and Co(II). High sensitivity and selectivity, and also the good detection limits and high preconcentration factor (PF=111.0) are from the advantages of the work. The proposed method was proved to be simple, rapid and reliable and could be used for studied metal ions determination in environmental

samples. The high accuracy of the proposed method was confirmed by recovery test with standard addition method. The possible interference of some important ions was investigated and no important interference was encountered. The MWCNTs has great potential as an adsorbent for the preconcentration and determination of trace/ultra-trace metal ions in complex samples.

3. EXPERIMENTAL

3.1. Apparatus

A Metrohm pH-meter (model 691, Switzerland) was used in order to adjust the pH at desirable values. A Chemtech Analytical Instrument model CTA-3000 atomic absorption spectrometer (Bedford, England) equipped with a flame burner was used for analysis of the understudy metals, including lamp currents and wavelength were those recommended by the manufacturer. All metals were measured under optimized operating conditions by FAAS with an air–acetylene flame.

3.2. Standard solutions and reagents

Ultrapure water was used throughout the work. All chemicals were of analytical reagent grade. All the plastic and glassware were cleaned by soaking in 10% HNO3 solution and then rinsed with distilled water prior to use. Standard solutions (1000 mg l^{-1}) of Co(II) and Ni(II) ions were prepared from high purity compounds, supplied by E. Merck (Darmstadt, Germany). The working standard solutions were prepared by diluting stock standard solution. A 5×10^{-4} mol L^{-1} solution of DDPA reagent was prepared by dissolving an appropriate amount of DDPA in 10 mL ethanol and diluting to 100 mL in a volumetric flask. McIlvaine's buffer solution in the pH range of 1-8 was used to adjust pH values and made by mixing 0.2 mol L^{-1} phosphoric acid and 0.1 mol L^{-1} Acetic acid. Multiwalled carbon nanotube was purchased from Aldrich, (Germany). The BET (Brunauer-Emmett-Teller) surface area and density of nanotubes were 300 m^2 g^{-1} and 2.1 g mL^{-1}, respectively.

3.3. Preparation of the column

150 mg of Multiwalled nanotube was packed into a glass column, 120 mm in length and 20 mm in diameter, and blocked by small portion of glass wool at the both ends to prevent loss of the adsorbent. In order to clean the column, prior to use, 1.5 mol L^{-1} HNO_3 solution and water were passed through the column to clean it. Then, the column was conditioned to the desired pH values with McIlvaine's buffer solution. The column was conditioned with distilled water during the passing time for the next experiments.

3.4. Recommended procedure

A standard solution containing 0.4-100 μg L^{-1} of Ni(II) and 0.7-120 μg L^{-1} of Co(II) and and the pH value was adjusted to the desired value with McIlvaine's buffer solution. Then DDPA was added to form the metal DDPA chelates and the solutions were passed through the column gravitationally. The metal ions retained on the column were eluted with desired volume and concentration of nitric acid solution and determined by FAAS.

3.5. Sample preparations

The river water samples were collected from the rivers located in industrial and nonindustrial areas. The water samples were filtered through a 0.45 μm PTFE Millipore filter. After adjusting to the desired pH values, the solutions were passed through the column gravitationally.

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