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Solid phase extraction of trace cobalt (II) in industrial wastewaters by modified nanotube carbon carboxyl and its determination with flame atomic spectroscopy

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ABSTRACT: Applying a simple and selective sample preparation procedure prior to instrumental analysis is the most important and crucial step in an analytical process. Up to now, various sample preparation techniques based on solid phase extraction (SPE) systems have been developed to isolate various types of analytes from different matrices. In the method presented for preconcentration and measurement of trace amounts of cobalt (II) ions in aqueous samples, carbon nanotubes functionalized with carboxyl were used for improving the extraction and preconcentration action. Measurement of Co^{2+} ion concentration in aqueous solutions was performed by flame atomic absorption spectroscopy. The parameters including the extraction including pH, amount and type of desorption solvent, extraction time, the effect of other ions, etc. were optimized. The concentration factor, level of detection (LOD) of the method, and relative standard deviation (RSD %) were obtained as 20.83, 6 $\mu g.L^{-1}$, and 1.16%, respectively.

Keywords: *Carbon nanotubes functionalized with carboxyl; Co (II) ion; FAAS; Flame atomic absorption spectroscopy; Preconcentration; SPE.*

INTRODUCTION

Cobalt, at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2012).The direct determination of trace metals especially toxic metal ions such as Co, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden, *et al.*, 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones, *et al.*, 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar, *et al.*, 1998; Caroli, *et al.*, 1991). The application of solid phase extraction technique for pre- concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova, *et al.*, 1993). The normal and selective solid

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phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan, *et al.*, 1997), filter paper (Leyden, *et al.*, 1975), cellulose (Gennaro, *et al.*, 1983) and ion exchange resins (Grote, *et al.*, 1985). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau, *et al.*, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek, *et al.*, 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening, *et al.*, 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1997; Mahmoud, *et al.*, 1997; Tong, *et al.*, 1990; Dadler, *et al.*, 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Co(II) (Mahmoud, 1998; Mahmoud, 1999) and pre-concentration of various cations (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2009; Thurman, 1998; Pawliszyn, 1997; Izatt, *et al.*, 1996; Hagen, *et al.*, 1990; Krueger, 1995; Yamini, *et al.*, 1994; Shamsipur, *et al.*, 1999; Shamsipur, *et al.*, 2001; Brunner, *et al.*, 2003; Zelder, *et al.*, 2004; Boll, *et al.*, 2005; Nayebi, *et al.*, 2006; Moghimi, *et al.*, 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng, *et al.*, 1998).

Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova, *et al.*, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi, *et al.*, 2010). Sorption of Co(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini, *et al.*, 2010) was also reported. 2-Amino-1- cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver(I), Co(II) and palladium(II) (Moghimi, *et al.*, 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin, *et al.*, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros, *et al.*, 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin, *et al.*, 2000) are also sulfur containing silica gel phases.

Therefore, in this work, we report on the first application of MWCNTs-COOH as a novel sorbent for MSPE of gemfibrozil from human serum and pharmaceutical wastewater samples prior to spectrofluorometric determination at FAAS after excitation.

EXPRIMENTAL

Instrumentation

Determination of Co^{2+} by PG-990 flame atomic absorption spectrometer equipped with HI-HCl according to the recommendations of the manufacturers. The pH measurements used by Sartorius model PB-11.

Materials

In this research, the following materials have been used for the experiments: carbon nanotubes functionalized with carboxyl, hexahydrate cobalt (II) nitrate, thiosemicarbazide ligand, buffer, and nitric acid. Thiosemicarbazide ligand (CH_5N_3S) was prepared from Darmstadt, Germany of Merck. Carbon nanotube functionalized with carboxyl

Preparation of the solutions and standards

Co^{2+} solution with the concentration of 200 ppm was prepared by dissolving 0.099 g hexahydrate cobalt (II) nitrate and by bringing the volume to 100 mL. The required solutions were prepared by diluting the mother solution. Through consecutive dilution of the 200 ppm solution, solutions with concentrations of 1, 3, 5, and 10 ppm were prepared as the standard.

Synthesis of carboxylic functionalized carbon nanotubes

A total of 4.0 g of MWCNTs was refluxed with 100 mL concentrated HNO_3 under stirring conditions at 120°C. The obtained MWCNTs-COOH was filtered by 1.2 mcm filter paper, and was then washed with deionized water to reach neutral pH. After that, it was placed inside an oven at 60°C in order to dry off completely (Moghimi, *et al.*, 2012).

The initial experiment of Co^{2+} extraction for determining the suitable absorbent

The method for extraction and ion recovery of cobalt by nanotubes is as follows: first, 0.2 g of thiosemicarbazide ligand and 0.3 g of nanotube (with the amine and carboxylic functions) were dissolved in the lowest amount of acetone, and then dried. Four 50 mL balons were adopted, and 0.05 g of nanotubes with the amine function was poured into one of the balloons. Thereafter, 0.05 g nanotube with carboxylic function, 0.05 g mixture of ligand and amine nanotube, and 0.05 g mixture of ligand and carboxylic nanotube were added to each further balloon. Next, 1 mL buffer with a pH of 4.5 was added to each balloon and a solution with an analyte concentration of 2 ppm was prepared. These four solutions were shaken at room temperature for 20 min, then centrifuged for 15 min and the top solution was injected into atomic absorption device.

The parameters influencing extraction and recovery of Co^{2+}

To find the optimal conditions for achieving the maximum efficiency of extraction and recovery, the effect of different factors including the pH of the solution, suitable washing solution, washing solution volume, extraction time, etc. was examined. For this purpose, one parameter was considered variable, while other parameters were kept constant.

The effect of pH on Co^{2+} extraction

To investigate the effect of pH on absorption of Co^{2+}, first none 2 ppm solutions with a volume of 50 mL in relation with Co^{2+} were prepared, where the effect of aqueous solution on the recovery of Co^{2+} was examined within the pH range of 2 and 10. For adjustment of pH, buffer was used. The method that was used for adjustment of the solution pH involved the following procedure: 2 ppm solutions were poured into beakers and the electrode of pHmeter was floated in it. Then, by adding suitable volumes of the buffer, the pH was adjusted at the desired values (2, 3, 4, 5, 6, 7, 8, 9, and 10). Following adjustment of pH of the solution, 0.05 g of a mixture of the carbon nanotube functionalized with carboxyl and ligand was added to each solution. It was then placed inside a shaker for 20 min, and the mixture was then centrifuged. After that, the top solution of the test tube was put aside and Co^{2+} concentration in it was determined by flame atomic absorption spectroscopy.

The effect of the level of the adsorbent for Co^{2+} extraction

First, seven 2 ppm solutions with a volume of 50 mL in relation with Co^{2+} were prepared, and then poured into seven flasks. The solutions were then adjusted at pH=10 (optimal pH) and different amounts of the nanotube (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) were added to them. They were then placed inside a shaker for 20 min, and the mixtures were then centrifuged and the top solution of the test tube was injected by flame atomic absorption spectrophotometry.

The effect of shaking time on the extraction of Co^{2+}

In order to find the extraction time, 50 mL of 2 ppm solution in relation with Co^{2+} which was adjusted at pH=10 was poured and 0.05 g of the carbon nanotube functionalized with carboxylic and ligand was added to each of them. They were then shaken inside a shaker at the times of 3, 7, 10, 15, 18, 20, and 25 min. following the centrifugation, the concentration of Co^{2+} of the top solution of the tube was determined by flame atomic absorption spectrophotometry.

The effect of different types of desorption for recovery of Co^{2+} ion

First, six 2 ppm solutions with a volume of 50 mL in relation with Co^{2+} were prepared under optimal conditions and then poured into six flasks and the solutions were adjusted at the optimal pH (pH=10), and 0.05 of the carbon nanotube functionalized with carboxyl and ligand was added to them. They were then placed inside a shaker for 20 min, and after that the mentioned mixtures were centrifuged. Next, the top solution was put aside and the obtained deposit was poured into the flasks, to which 7 mL of the following desorption was added: HNO_3 (3M), HNO_3 (1M), HNO_3 (0.1 M), NaOH (0.1 M), H_2SO_4 (0.1 M). They were then placed inside a shaker device for 20 min. The obtained mixture was then centrifuged and Co^{2+} concentration of the top solution of the test tube was determined by flame atomic absorption spectrophotometry.

Optimizing the volume of the desorption solvent for extraction of Co^{2+}

In order to select the suitable volume of the solvent for extraction of Co^{2+}, first 50 mL of 2 ppm solution in relation with Co^{2+} adjusted at the optimal pH was poured into six small balloons, to each of which 0.05 g carbon nanotube functionalized with carboxyl and ligand was added. They were then placed inside a shaker for 20 min. the mixture was then centrifuged and the top solution was put aside and the deposits were poured into six flasks, to each of which 5, 7, 9, 12, 14, 16, and 18 mL of nitric acid 0.1 M (the optimal desorption). They were then placed inside shaker for 20 min and the mixture was then centrifuged. Finally, the concentration of Co^{2+} in the top solution of the tube was determined by flame atomic absorption spectrophotometry.

The effect of the volume of the sample solution (break through volume)

After finding the best pH value of the sample solution which is suitable desorption solvent for complete washing of Co (II) ion off the absorbent, the maximum volume of the aqueous solution including Co^{2+} should be determined. To investigate the effect of the volume of the sample solution, six 2 ppm solutions were prepared under optimal conditions except for pH adjustment. Then, nothing was added to the first solution. However, 50, 100, 200, 300, and 450 mL water and 0.02, 0.04, 0.08, 0.12, and 0.18 g of ligand were added to the other solutions. Then, the pH was adjusted and they were placed inside shaker for 20 min (optimal time). The mixture was then centrifuged and eventually washed with 12 mL of nitric acid 0.1 M. It was then placed inside the shaker again for 20 min. Next, the resulting mixture was centrifuged and then Co^{2+} concentration in the top solution of the centrifuged tube was determined by flame atomic absorption spectrophotometry.

Determination of the control standard deviation (S_b)

First, to prepare the blank solution (control), four 50 mL balloons were washed and dried and then 50 mL of deionized water at pH=10 was added to 0.05 g of the carbon nanotube functionalized with carboxyl and ligand. They were then placed inside shaker for 20 min and centrifuged and eventually washed with 12 mL nitric acid 0.1 M. They were then placed inside the shaker again for 20 min. the mixture was centrifuged and the absorption was measured by flame atomic absorption spectrophotometry.

Determination of the accuracy and replicability of the method (RSD%)

To determine the accuracy, first 50 mL of 2 ppm solution in relation with Co^{2+} adjusted at pH=10 was poured into four beakers, to each of which 0.05 g of the carbon nanotube functionalized with carboxyl and ligand was added. They were then stirred inside shaker for 20 min. the mixture was then centrifuged and eventually washed with 12 mL nitric acid 0.1 M and then placed inside the shaker again for 20 min. Finally, following solidification of the mixture, Co^{2+} concentration in the filtered solution was determined by flame atomic absorption spectrophotometry.

The linear range and calibration curve

To determine the linear range, first 50 mL of 10, 80, 200, and 800 ppb solutions in relation with Co^{2+} adjusted at pH=10 was poured into four balloons, to each of which 0.05 g carbon nanotube functionalized with carboxyl and ligand was added. They were then stirred in a shaker for 20 min and the mixture was the centrifuged and eventually washed with 12 mL of nitric acid 0.1 M. it was then placed inside the shaker again for 20 min. eventually, the mixture was centrifuged and absorption of Co^{2+} in the top solution of the centrifuged tube was determined by flame atomic absorption spectrophotometry.

Disturbances on extraction of Co^{2+}

To investigate the effect of disturbance of other ions on the extraction of Co^{2+}, some 2 ppm solutions in relation with Co^{2+} adjusted at pH=10 were prepared with the volume (break through volume), and certain amounts of interfering factors and different ions were added to the initial solution. Then, 0.05 g of carbon nanotube functionalized with carboxyl and ligand was added to each solution. They were then stirred inside shaker for 20 min, and then centrifuged and eventually washed with nitric acid 0.1 M and placed inside the shaker again for 20 min. next, the concentration of Co^{2+} in the top solution of the centrifuge tube was determined by flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was completed by nanotubes and optimal conditions were found for it, several real water samples were analyzed. The real samples which were studied were: well water in Pishva Town was collected with a temperature of 20°C and pH=7.1 in 23.8.95 at 9:45 and the drinking water of this town was collected at 21°C, pH=7.3 in 23.8.95 at 10:00. Finally, a fish farming sample was collected at 22°C, pH=6.20 in 23.8.95 at 11:20. First, three suitable bottles were prepared for the sampling of each sample. The inner part of the bottles was washed with ordinary water and distilled water. Once the bottles dried completely, label ‘suitable’ was attached on them. To collect water samples, dry and clean beakers which had already been washed were used. To begin the analysis of the samples, their colloidal and suspended particles should be removed. For this purpose, the samples were passed through a 0.22μm filter. Next, 100 mL of the samples was poured into beakers. Their pH was adjusted at 10 and to each sample nanotube and ligand were added. They were stirred for 20 min, and the mixture was then centrifuged. Finally, they were washed with nitric acid 0.1 M and placed inside shaker again for 20 min. Eventually, following centrifugation of the mixture, absorption of cobalt ion was determined in the solution under filter by flame atomic absorption spectrophotometry. In the first stage, the sample itself was injected into the device without any cobalt ion, where in water samples, the device showed no absorption. Indeed, to determine certain amounts of cobalt present in the water samples, standard elevation method was used, and this stage was performed as with the first stage. The only difference was that 0.5 mL of 200 ppm solution in relation with Co^{2+} was added to the samples. Eventually, absorption of cobalt ion was determined in the solution under filter by flame atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

This section deals with analysis resulting from the research experiments. The results obtained in the experimental chapter, calibration curve, and the parameters influencing the extraction (e.g. pH, time, temperature effect, etc.) of cobalt ion by the carbon nanotubes are discussed and following presentation of a scientific justification, overall conclusion of this research is stated. The tests conducted to confirm the nanotubes functionalized with carboxyl

This compound is two stretching vibrational bands related to C-O bond belonging to the carbon attached to carboxylic group, which is observed at 1107.78 cm^{-1}. On the other hand, two stretching vibration bands associated with C=O bond of carboxylic group can be seen at 1593.65 cm^{-1}. Eventually, a strong vibration is also observed at 3384.12 cm^{-1} belonging to the stretching vibration of O-H bond. Emergence of absorption peaks at 1593.65 and 1105.37 cm^{-1} evidently introduces carboxylic groups on the carbon nanotubes.

Investigation of the results obtained from XRD spectrum

Here, to determine the size of carbon nanotubes,

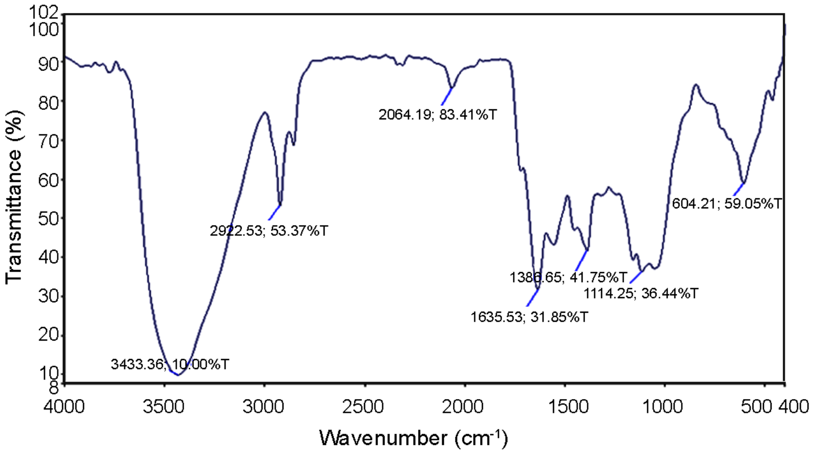

Fig. 1. FT-IR spectrum of the carbon nanotubes and ligand before the absorption Co(II)

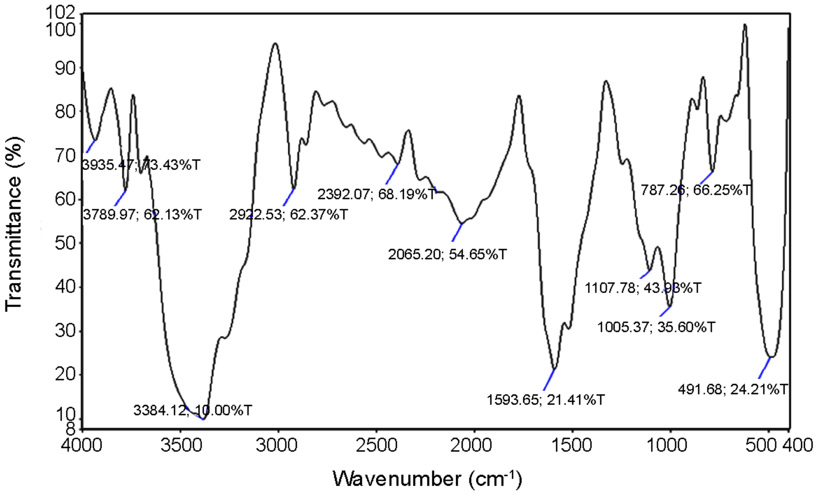

Fig. 2. FT-IR spectrum of the carbon nanotubes and ligand after the absorption Co(II)

sheerer equation (1) was used, which is as follows:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

τ: the mean size of the crystallite (nm)

L: the crystal form coefficient (usually considered as 0.9)

λ: the wavelength of the tube generating x-ray (nm)

β: the peak breadth

θ: diffraction angle

The following figure demonstrates diffraction of carboxyl nanotube, where peak diffraction of θ= 26.5 can be seen. In XRD spectrum, the observed peak is in full congruence with the peaks related to the nanotube compound phase. As the carboxyl nanotube is functionalized, a short peak is expected. This well exists in the spectrum and is the reason of placement of carboxyl groups on the carbon nanotube Fig. 4.

In XRD spectrum below this compound, there is a peak with a high intensity related to carboxylic nanotube in the region θ= 26 and a very weak peak at 42.89°, which have a very sharp and small peaks, respectively (Figs. 4, 5).

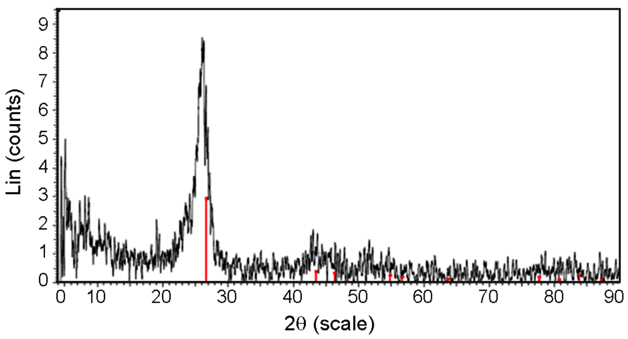

Fig. 3. XRD images of the carbon nanotubes before the absorption

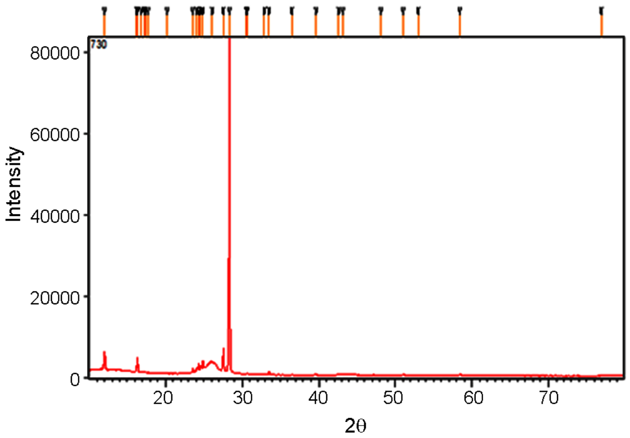

Fig. 4. XRD images of the carbon nanotubes plus ligand before the absorption

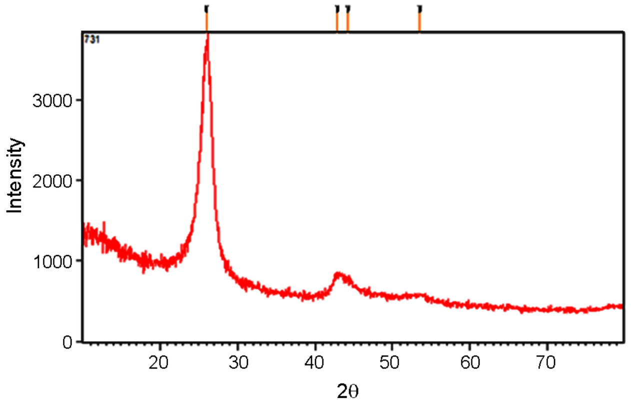

Fig. 5. XRD images of the carbon nanotubes plus ligand after the absorption

The following figure reveals the SEM image of carboxyl nanotube. For the carboxylic nanotube, the size of particles is obtained as 200 nm Fig. 6.

Further, the post-absorption figure of SEM image reveals deposition of the metal of interest on the carboxylic carbon nanotube. Based on the above images, it can be concluded that the thickness of planes has increased. As can be seen in the figure, the carboxylic functional group on the surface of carbon nanotubes can be seen as lighter points Figs.7 and 8.

Investigation of the influential factors on Co^{2+} extraction

Investigation of the effect of pH on Co^{2+} extraction

The results of this investigation are provided in Table 1 and Fig. 9. As the results in the table indicate, at pH=10, cobalt absorption has been maximized, while at lower and higher pHs, the extent of absorption declines, suggesting that at pH<10 absorption of ions cannot occur completely.

Investigation of the effect of nanotube level for Co^{2+} extraction

The results of this investigation are provided in Fig. 10. As the results in the table reveal, at 0.05 g of the nanotube, the absorption percentage and recovery of Co^{2+} have been maximized.

Investigation of the effect of time on Co^{2+} extraction

The results of this experiment have been presented in Fig. 11. There results indicate that over time, the extent of absorption increases, as the ions present in the solution find more opportunity to be absorbed in the absorbent's sites. Therefore, quantitative extraction of cobalt ion within a period longer than 20 min becomes possible and within durations longer than 20 min and more, the reaction occurs completely.

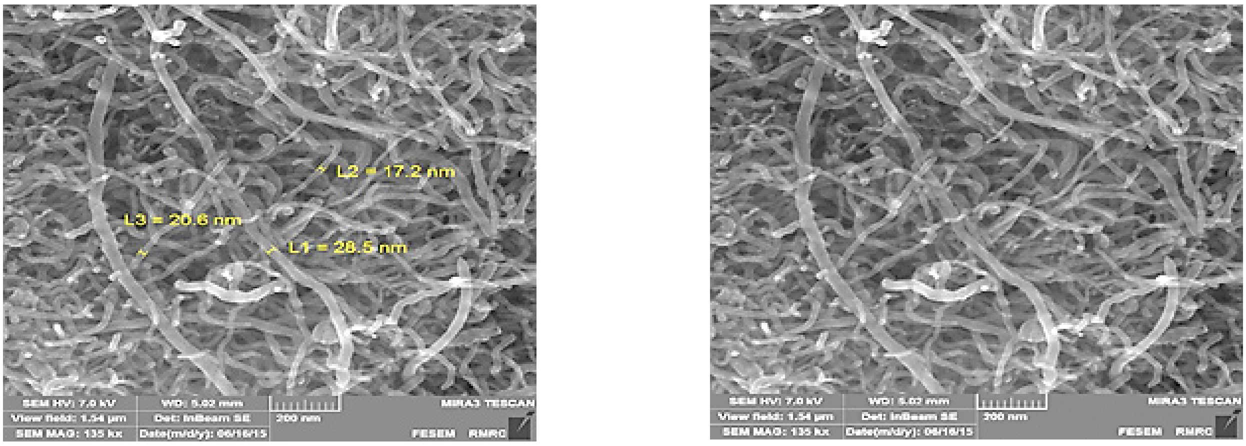

Fig. 6. SEM related to the carbon nanotubes before the absorption ligand

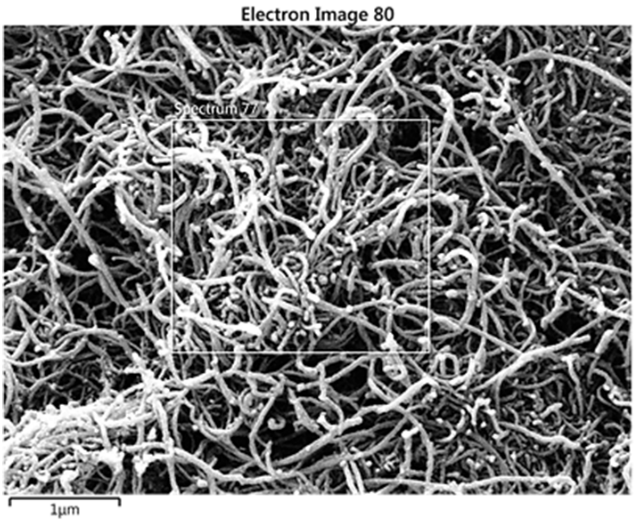

Fig .7. SEM of carbon nanotubes added ligand before the absorption Co^{2+}

Investigation of the effect of type of different desorption solvent for recovery of Co^{2+}

Based on the results (Table 2), sodium hydroxide cannot be used as a suitable desorption and these bases do not have a complete detergence power. Thus, mineral acids with certain concentrations, H_2SO_4 and HNO_3 were used. Based on the results (Table 2), the results of this table suggest that all acids have a good detergence power for Co^{2+}, but the recovery percentage of nitric acid is far greater than that of other acids. An acidic environment causes dissolution of possible deposits and increased recovery of these ions. However, the results that were obtained for HNO_3 were better than H_2SO_4, such that 0.1 M solution washed 92.54% of the cobalt ion off the absorbent. For this reason, for the rest of studies, nitric acid 0.1 M was sued as the desorption solution.

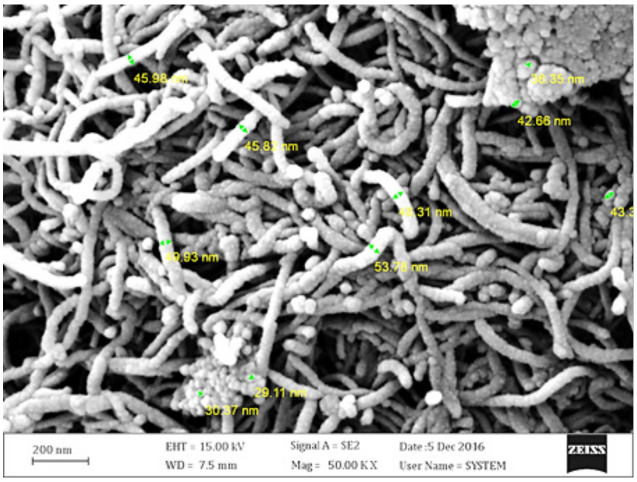

Fig. 8. SEM of the carbon nanotubes after the absorption Co^{2+}

Table 1. The changes in the recovery percentage versus pH of the sample solution in relation with Co^{2+}

pH	Absorption
2	7.2)^{a})0.0664
3	13.1))0.0506
4	0.9))0.0402
5	0.9))0.0299
6	1.8))0.0201
7	0.4))0.0112
8	1.6))0.0073
9	1.4))0.0051
10	7.2))0.0024

$^{a)}$ measurement RSD following three replications

Investigation of optimization of the effect of volume of desorption solvent for Co^{2+} recovery

After investigation and selection of the type of optimal desorption, the volume of this solvent was studied, with the results collected in Table 3 and Fig. 13. The volume of 7 mL for nitric acid was chosen as the optimal volume for washing.

Changes in the recovery percentage in terms of changes in the volume of desorption solvent Fig. 12.

Investigation of the effect of volume of the sample solution (determination of the break through volume)

Following optimization of the parameters of the pH of the sample solution and desorption solvent, etc., for complete washing of Co^{2+} off the absorbent, the maximum volume of the water solution containing Co^{2+} should be determined. The break through volume for pre-concentration method is a volume where with the

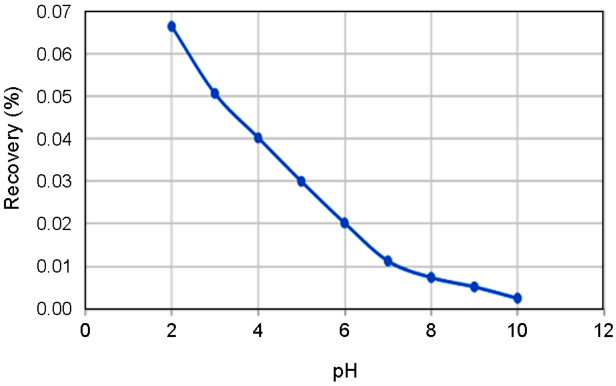

Fig. 9. The effect of pH in the Co^{2+} absorption

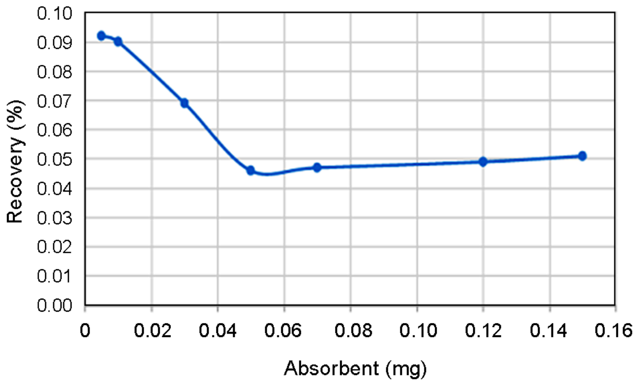

Fig. 10. The effect of absorption Co^{2+} of the absorbent

Table 2. Selection of the suitable desorption for recovery of Co^{2+}

Solvent	Recovery(%)
M HNO_3 0.1	0.2)^{a})92.54
HNO_3 1M	0.5))75.04
$HNO_3$3M	0.2))78.89
H_2SO_4 0.1M	0.5))73.99
$H_2SO_4$1M	0.3))74.86
NaOH 0.1 M	0.2))69.86

$^{a)}$ measurement RSD after three replications

Table 3. Determination of the optimal volume of the desorption solvent

Solvent volume	Recovery (%)
5 ml	0.4)^{a})45.68
ml 7	0.6))60.4
9 ml	0.5))78.62
12 ml	0.7))92.96
14 ml	0.1))88.3
16ml	0.1))88.8
18ml	0.4))90.1

$^{a)}$ measurement RSD following three replications

passage larger than that volume over the solid phase, all analyte ions are not kept on the absorbent and some of the analyte ions pass over it without inhibition. On the other hand, if the volume of the experimental solution is less than the break through volume, with the passage of that volume, all analyte ions are kept on the solid phase. The results (Table 4) and Fig. 13 indicate that up to 250 mL of ions is absorbed by the nanoabsorbents and if the sample volume is larger than this value, part of the Co^{2+} will not be kept on the absorbent and pass over the absorbent with no inhibition. Based on the break through volume definition, it can be stated that the break through volume in this study is 250 mL and if the volume of the sample solution which includes Co^{2+} is over 250 mL, cation absorption does not occur completely and thus if the sample volume is 250 mL and passed over the absorbent and then washed with 12 mL of the desorption solvent, the concentration factor will be obtained as 30. This means that the concentration of Co^{2+} in 7 mL of the desorption solvent which has been passed over the absorbent grows by 20.8 times the concentration of Co^{2+} present in the initial experimental solution. Based on (Table 4), the break through volume calculations is as follows:

Effect of determination of the break through volume on measurement of Co^{2+} the sample Fig. 13.

Concentration factor = break through volume / the desorption solvent volume = 250/12 = 20.8

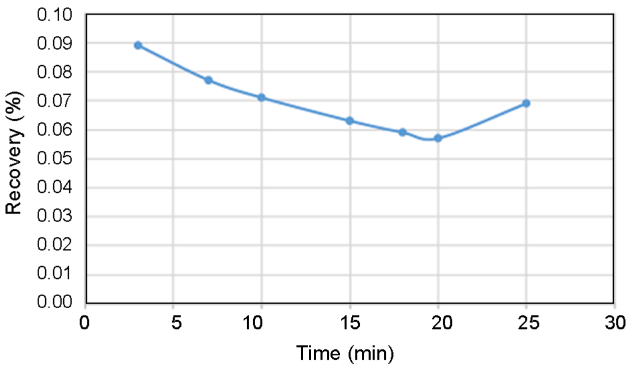

Fig. 11. In the recovery percentage effect of extraction time Co^{2+}

Determination of the blank standard deviation (S_b)

The replicability or accuracy of any method is an important factor in determining its validity and reliability. To examine the method's replicability, the results

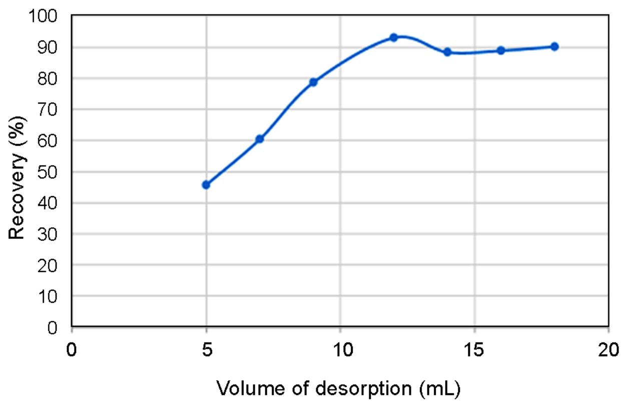

Fig. 12. Effect of optimization volume of desorption solvent for Co^{2+} recovery

Table 4. investigation of the effect of solution volume in the sample

V(ml)	Recovery (%)
50	78.2(1.0) [a]
100	80.5(0.4)
150	77.7(0.9)
250	76.5(1.2)
350	68(1.7)
500	45.0(1.1)

[a] measurement RSD following three replications

of investigation of four blank solutions (deionized water) have been collected in Table 5.

Based on the results obtained in Table 4-12, the blank standard deviation has been obtained as follows:

$S_b = 0.0004$

4-3-8 Determination of the accuracy and RSD% of the method

This parameter is used for investigation of the experimental accuracy and proximity of studied data. According to Table 6, $\overline{X}$ or the mean of recoveries and S or standard deviation have been calculated for three measurements and the relative standard deviation (RSD) has been obtained for three replications.

The linear range and calibration curve of the method

To determine the linear range in analysis, a calibration curve should be plotted. This diagram is not linear across all concentrations and various factors cause the calibration curve to lie in the linear range and follow Beyer Law. Based on Table 7 and Diagram 4-7, the calibration curve of the method is as follows and the line equation is Y=X0.0020+0.0531 and R^2= 0.9985.

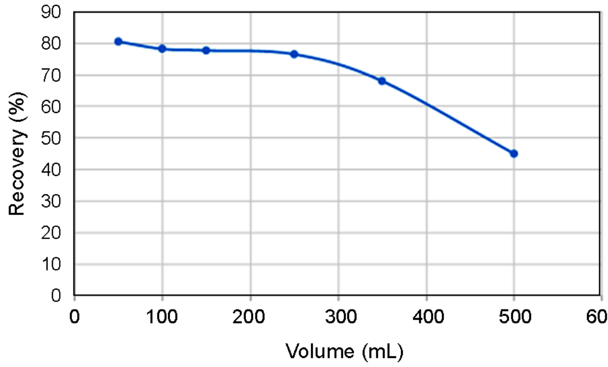

Fig. 13. Effect of determination break through volume of the sample solutions on the recovery percentage of Co^{2+}

Table 5. Measurement RSD following three replications

Sample	Device response
1	0.021(0.7) [a]
2	0.020(1.1)
3	0.021(0.7)
4	0.021(0.9)

[a] measurement RSD following three replications

Table 6. Determination of %RSD of the method

Sample	Absorption
1	0.043(0.7) [a]
2	0.42(1.1)
3	0.043(0.7)
4	0.043(0.9)

$$\overline{X} = 04275 \qquad S_b = 0.0005$$

$$RSD(\%) = \frac{S}{\overline{X}} \times 100 = \frac{0.0005}{X0.04275} \times 100 = 1.16\%$$

Investigation of the effect of disturbances on measurement of Co^{2+}

A disturbing ion is an ion which causes a certain change of over ±5% in the absorption and recovery of Co^{2+}. To investigate the effect of disturbance of other ions on Co^{2+} extraction, certain amounts of interfering factors were added to the initial solution and the experiment was done at break through volume. Absorption of the recovered solution is measured with flame atomic absorption and then compared against the solution absorption resulting from the recovery of the sample which lacks the interfering ion. As can be seen in Table 8, in the presence of external ions, Co recovery occurs with ±5% changes and the external ions have no special effect on the measurement and cause no disturbance.

Table 7. The calibration curve for measurement of Co^{2+}

Primary standard solution concentration $\mu g.L^{-1}$	Absorption
20	0.06(3.8) [a]
80	0.066(1.3)
200	0.09(1.4)
500	0.144(0.1)
800	0.204(0.5)

[a] measurement RSD following three replications

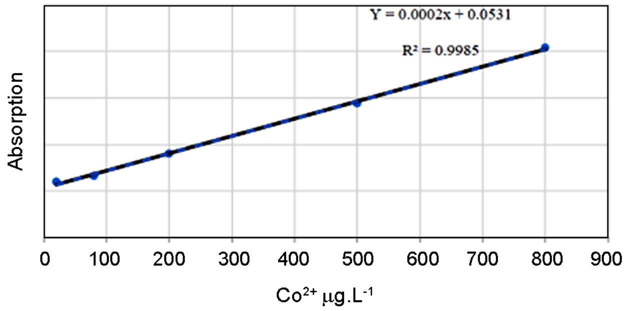

Fig. 14. Calibration curve of the proposed method by SPE-AAS.

Determining the method's limit of detection

The lowest concentration or weight of the sample which can be measured with a certain confidence level is called limit of detection, which is defined as follows. The limit of detection of a method is a concentration of an experimental sample where the device response to it is significantly different with the response of control sample, which is defined as follows. A concentration of the experimental samples whose signal is equal to blank signal plus three times of the standard deviation resulting from the solution. The limit of detection is the lowest amount of Co^{2+}, where the presented method is able to detect it. Based on the presented definition, LOD can be calculated by the following relation:

$$LOD = \frac{3S_b}{m}$$

Where, S_b is the standard deviation for the blank signal and m is the slope of calibration curve. Based on the performed experiments, S_b= 0.0004 and the slope of the calibration curve is 0.0002.
Therefore, LOD can be calculated as follows.

$$LOD = \frac{3 \times 0.0004}{0.0002} = 6.0 \text{ ppb}$$

Investigation of the obtained results on real samples

Once the optimal conditions of the method were obtained, to investigate the implement ability of the method on real samples, the level of cobalt was measured across various water and biological samples at the break through volume (250 mL). In the first stage, the sample itself was studied without addition of certain amounts of Co^{2+} and washed and then injected into the device. It was found that the device does not

Table 8. The effect of interfering ions on recovery of Co^{2+}

Ions	Added value(ppm)	Recovery percentage Co(II)
Na^+	200	89.18(1.7) [a]
Zn^{2+}	5.0	93.95(3.3)
K^+	200	91.78(1.6)
Mg^{2+}	100	91.99(0.8)
Cu^{2+}	5.0	91.80(1.2)
Cl^-	308.7	89.18(1.1)
NO_3^-	317	91.78(2.1)
SO_4^{2-}	400	91.99(1.9)

a) measurement RSD after three replications

Table 9. the results of measurement of cobalt in real samples

Sample	Cobalt(II) added(µg)	Cobalt(II) found in FAAS(µg)
Well water of pishva	0.0	N.D [b]
	5.0	5.1(1.0) [a]
Tap Water of pishva	0.0	0.079(2.1)
	5.0	5.08(1.7)
Industrial wastewater Charmshar Varamin	0.0	0.05(2.3)
	5.0	5.05(1.9)

a) Measurement %RSD after three replications

b) Not Detection

show a considerable absorption. In the second time, increase in the Co^{2+} was performed according to the concentration and separation method. Indeed, to determine certain amounts of the cobalt present in the water samples, standard elevation method was used. The results of this analysis have been shown in Table 9. As can be observed, in the water samples, in Tap water of Pishva-Varamin in 27 Jan 2017 and industrial wastewater Charmshar Varamin in 30 Jan 2017, there is a larger amount of cobalt than in the experimented water samples. However, in other samples, there is less cobalt. Based on this, the efficiency and power of preconcentration and cobalt measurement can be deduced.

A comparison between the presented method and other methods

Comparison of the proposed method with other methods indicates that the proposed method is more accurate, simpler, and faster as it had lower relative standard deviation values in comparison with other methods (Moghimi, *et al.*, 2009; Moghimi, 2013; Narin, *et al.*, 2000). The proposed method is one of the best systems for measurement of very trace amounts of metal ions including cobalt in water samples. Another point in application of nanotube absorbent is that instead of applying the proposed ligand, one can place other ligands on the nanotube which is able to absorb mineral ions, thereby determining trace amounts of heavy metals. A wide variety of ligands can be used given their properties, which act selective towards the one or several ions, and using this set, preconcentration and measurement of cations can be performed. Using flame atomic absorption and micro extraction with solid drop and single-drop liquid-liquid extraction, homogeneous liquid-liquid extraction and other devices, one can measure trace amounts of cobalt by this absorbent and obtain a lower limit of detection value.

CONCLUSIONS

In comparison with other methods reported for separation and measurement of cobalt (II), this method enjoys considerable advantages in that it is simple and inexpensive and can be used quickly for environmental samples including natural water. In addition, it minimizes usage of organic, toxic, and expensive solvents. Furthermore, design and development of this method for preconcentration, separation, and measurement of Co^{2+} are essential considering its significance in different industries and the low concentration of this ion in most samples. Therefore, the aim of this research is to present an efficient, selective, inexpensive, and simple method for evaluation of the level of cobalt (II) across different samples (in this research, the value of break through volume, limit of detection, and RSD has been obtained).This research indicated that measurement of Co^{2+} occurs at an acceptable level without interference of any other interfering agent and thus the presented method can be used easily in measurement of the amount of cobalt (II) in water samples.

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