Original Article

Separation of Trace Amount of Trace Cobalt (II) In Water Samples by Modified Fe₃O₄@ Quillaja Sapogenin 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 dispersive 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, with $Fe_3O_4@$ quillaja Sapogenin 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 20.0, 6 µg.L⁻¹, and 1.14%, respectively.

Keywords: Fe₃O₄@ quillaja Sapogenin, flame atomic absorption spectroscopy, Co (II) ion, SPE, Preconcentration, FAAS

INTRODUCTION

Co at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems ^[1-8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Co can bind to the cell membrane and hinder the transport process through the cell wall. Co at nearly 40ng mL⁻¹ is required for normal metabolism of many living organisms ^[9, 10]. On the other hand, Co 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 Co is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) ^[11, 12] as well as spectrometric methods ^[13, 14].

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 ^[15, 16]. 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 allo ws higher flow-rates; reduced channeling

resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed ^[17].

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium ^[18, 19] and lead ^[20]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead ^[21, 22], copper ^[23-25], silver ^[26, 27], mercury ^[28], cadmium ^[29], palladium ^[29], Ce ^[30] and UO₂ ^[31].

Ionic liquids (ILs) seem well positioned to address this challenge. Due to their wide solubility, and by introducing a surface charge, modification with ILs should enable the preparation of long-term stable and N,N' -

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disalicylideneethylenediamine modified Graphene that can be dispersed in various matrices. To date, investigations into the covalent attachment of an ionic material to graphene surface have been not carried out. In this communication, we report a convenient method to obtain polydisperse N,N' disalicylideneethylenediamine modified Graphenethat are with 1-(3-aminopropyl) functionalized 3methylimidazolium bromide (IL-NH₂)^[32]. The main goal of the present work is development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Co(II) from aqueous media by means of a surfactant coated C_{18} modified with, N,N' -disalicylideneethylenediamine modified Graphene^[32].

Therefore, in this work, we report on the first application of **Fe₃O₄@ quillaja Sapogenin** as a novel sorbent for MSPE of gemfibrozil from human serum and pharmaceutical wastewater samples prior to spectrofluorometric determination at FAAS after excitation.

EXPERIMENTAL

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. XRD was done on the powdered product using a Philips apparatus by the radiation of Co/K α within a 1.54 Å wavelength, and SEM was obtained on a Mira III. Analysis EDX was conducted for the mapping of the nanocomposites elements. Two minutes before the test commenced, a 10mA layer of gold was used to cover the surface of the sample. The magnetic characteristics of the sample were identified via vibrating sample magnetometer (SAMX; Model: MIRA III) at the ambient temperature.

Materials

In this research, the following materials have been used for the experiments: **Fe₃O₄@ quillaja Sapogenin**, hexahydrate cobalt (II) nitrate, thio-semi-carbazid ligand, buffer, and nitric acid. thio-semi-carbazide ligand (CH₅N₃S) were prepared from Darmstadt, Germany of Merck.

Preparation of magnetic nanoparticles (Fe₃O₄)

Magnetic nanoparticles (MNPs) precipitated in the alkali solution of Fe(III) and Fe(II) (molar ratio 2:1) at 80 °C via the standard co-precipitation method reported by Liu et al. ^[31]

FeCl₃.6H2O (10 mmol, 2.7 gr) and FeSO₄.7H2O (10 mmol, 1.39 gr) were slowly added to a vortex of deoxygenated distilled water (100 ml). The dispersion was vigorously stirred at 80 °C under N2 protection. In the next step, the reaction mixture was suddenly incorporated with ammonium hydroxide by a volume of 7.5 mm. Adding the base to the solution of Fe²⁺/Fe³⁺ salt led to the formation of MNPs, a black precipitate. The reaction was preceded for another 60 min, and the mixture was cooled to room temperature. The

resulting black precipitate was isolated using the implementation of an external magnetic field. It was then washed four times with water followed by drying in vacuum at room temperature ^[29].

Preparation of nano-Fe₃O₄@ Quillija Sapogenin

A mixture of synthesized nano-Fe₃O₄ (1.5 g) and Quillaja Saponin (2.5 g) in 30 mL ethanol stirring via Stirring rod for 20 minutes at ambient temperature. After the reaction mixture, the product was removed by a magnet and dried at room temperature, 3.96 g product was obtained.

• Fe₃O₄@ quillaja Sapogenin acid solution

Fe3O4@ quillaja Sapogenin solution (0.01 mol 1^{-1}) was prepared by dissolving 0.9433 g of the disodium salt hydrate of Fe₃O₄@ quillaja Sapogenin in 250 ml of water.

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 200ppm solution, solutions with concentrations of 1, 3, 5, and 10 ppm were prepared as the standard.

The initial experiment of Co²⁺ extraction for determining the suitable absorbent

The method for extraction and ion recovery of cobalt by Nano-Fe₃O₄@Qs is as follows: first, 0.2 g of thiosemicarbazide ligand and 0.3 g of Nano-Fe₃O₄@Qs (with the amine and Fe₃O₄@ quillaja Sapogenin) were dissolved in the lowest amount of acetone, and then dried. Four 50-mL balons were adopted, and 0.05 g of Nano-Fe₃O₄@Qs with the amine function was poured into one of the balloons. Thereafter, 0.05 g Fe₃O₄@ quillaja Sapogenin, 0.05 g mixture of ligand and amine Nano-Fe₃O₄@Qs, and 0.05 g mixture of ligand and 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 2ppm 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 Co²⁺ extraction

To investigate the effect of pH on absorption of CO^{2+} , first none 2.0ppm 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 (2,3,4,5,6,7,8,9,10). Following adjustment of pH of the solution, 0.05 g of a mixture of the with Fe₃O₄@ quillaja Sapogenin 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 Co²⁺ concentration in it was determined by flame atomic absorption spectroscopy.

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

First, seven 2.0 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 Nano-Fe₃O₄@Qs (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 Co²⁺

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 Fe₃O₄@ quillaja Sapogenin 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 2.0ppm 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 Fe₃O₄@ quillaja Sapogenin 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 desorptions was added: HNO₃ (3M), HNO₃ (1M), HNO₃ (0.1 M), NaOH (0.1 M), H₂SO₄ (0.1 M). They were then placed inside a shaker device for 20 min. The obtained mixture was then centrifuged and Co²⁺ 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 Fe₃O₄@ quillaja Sapogenin 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 Co²⁺ 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 Co²⁺ concentration in the top solution of the centrifuged tube was determined by flame atomic absorption spectrophotometry.

Determination of the control standard deviation $(S_{\mbox{\tiny b}})$

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 Fe₃O₄@ quillaja Sapogenin 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 2.0ppm solution in relation with Co^{2+} adjusted at pH=10 was poured into four beakers, to each of which 0.05 g of the Fe₃O₄@ quillaja Sapogenin 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 Fe₃O₄@ quillaja Sapogenin 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 Co²⁺

To investigate the effect of disturbance of other ions on the extraction of Co^{2+} , some 2.0ppm 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 Fe₃O₄@ quillaja Sapogenin 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 Nano- $Fe_3O_4@Qs$ 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 Nano-Fe₃O₄@Qs 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 200ppm solution in relation with Co²⁺ was added to the samples. Eventually, absorption of cobalt ion was determined in the solution under filter by flame atomic absorption spectrophotometry.

RESULT AND DISCUSSION

Nano-Fe₃O₄@Qs/CoCl was synthesized within two steps. Firstly, we synthesized nano-Fe₃O₄ by Fe²⁺ and Fe³⁺ ions' coprecipitation, and then the product of the first step was mixed with Quillaja Sapogenin (Scheme 1).



Scheme 1

The magnetically heterogeneous adsorbent, nano-Fe₃O₄@Qs, is characterized by Fourier transform infrared (FT-IR) spectroscopy, vibrating sample magnetometer (VSM), Energy dispersive X-ray spectroscopic (EDX) analysis), X-ray diffraction (XRD), Electron Microscopy (SEM), and thermo gravimetric analysis (TGA).

The results obtained from FT-IR spectroscopy of (A) nano-Fe₃O₄, (B) nano-Fe₃O₄@Qs, are presented in Fig1. The existence of stretching vibration of Fe-O was concluded by results obtained from FT-IR spectroscopy of nano-Fe₃O₄ (A), which indicates an obvious signal in 585 cm⁻¹. Furthermore, the broadness of the band at the range within 3300 to 3500 cm⁻¹ has resulted from stretching vibrations of OH group. Existence of Fe-O stretching vibration in conjunction with absorptions of nano- Fe₃O₄@Qs, Quillija Sapogenin (B) indicates that Quillija Sapogenin covers the magnetic nano-Fe₃O₄. Wideband at 3383 cm⁻¹ as a result of the OH groups' stretching vibrations in addition to the absorption bands around 2925 cm⁻¹ demonstrate the stretching vibrations of the C–H bonds, the 1619 cm⁻¹ band corresponds to the H–O–H bending vibration. The absorption bands around 1065 and 1100 cm⁻¹ demonstrate the vibrations of the C–O bonds.

The peak at 615 cm⁻¹ corresponding to stretching vibrations of Fe–O groups, the 1626 cm⁻¹ band corresponds to the H– O–H bending vibration. The absorption bands around 2921 cm⁻¹ demonstrate the stretching vibrations of the C–H bonds, the stretching vibrations of O–H bonds are observed at 3375 cm⁻¹.



Fig. 1. FT-IR spectra of (a) nano-Fe₃O₄, (b) nano-Fe₃O₄@Qs, (c) nano-Fe₃O₄@Qs/CoCl

Phase purity and structure of nano-Fe₃O₄ (A), nano-Fe₃O₄@Qs (B), and nano-Fe₃O₄@Qs/Co(C) are studied by means of high angle X-ray diffraction analysis (XRD) (Fig. 2). The bare Fe₃O₄ shows diffraction peaks at $2 \Theta = 30.3821^{\circ}$, 35.7917° , 42.7496° , 52.6891° , 56.3597° and 61.64854° with FWHM equal to 0.4723, 0.4723, 0.4723, 0.7872, 0.6298 and 0.6298 correspond respectively to the cubic structure of the pure Fe₃O₄ patch described in the literature (Fig. 2A) [^{30]}.

The same peak was also observed on the XRD diffraction pattern of nano-Fe₃O₄@Qs, which indicates the preservation

of the structure of the crystalline spinel ferrite core during the process of cellulose coating. Moreover, the other different peaks at $2\Theta = 19.8^{\circ}$ and 21.3° , is related to the sapogenin coating of nano-Fe₃O₄ (fig.2 B). The XRD of nano-Fe₃O₄@Qs/CoCl pattern shows the structure is amorphous.

The peaks at $2\Theta = 12.5^{\circ}$, 19° , 21° , 27° were also observed in the Fe₃O₄@Qs (Fig2. C). The diffraction peaks at $2\Theta = 16.5^{\circ}$, 49° , 53.5° correspond to CoCl cores and the sharp peak at around $2\Theta = 37$ indicates the existence of nano-Fe₃O₄@Qs and bonding of Hg to Qs shell.



Fig. 2. XRD patterns of the (a) nano-Fe₃O₄, (b) nano-Fe₃O₄@Qs, (c) nano-Fe₃O₄@Qs/CoCl.

In Fig. 2 (a) and 2 (b) and 2 (i) FTIR test of the adsorbent is shown. The wave numbers were from 3409.40 to 3411.93 (cm⁻¹) which was associated with the tensile vibration of OH⁻. The 1615.93 and 1619.31 (cm⁻¹) wave numbers can be assigned to the vibrations of hydroxyl groups. The increase of bands intensity is caused due to the bonds between the OH - and COO- groups. The wave numbers range between 500 and 800 cm⁻¹ are related to the chemical bond between the oxygen and Al, Mg or Fe. The shift of band from 1615.93 to 1619.31 (cm⁻¹) in the spectrum is related to effect of cadmium adsorption that shows cadmium uptake on LDH adsorbent.

Thermo-gravimetric analysis (TGA) has been conducted at the temperature range of 0-800 °C (Fig. 3). The TGA (A) it is related to nano-Fe₃O₄@Qs. The curve shows three mass-loss steps. Firstly, weight loss was small (about 12.64%) from 20

to 135 °C is related to the removal of moisture and solvent of the catalyst. Afterward, the weight loss observed in two steps, the main weight loss was about (35.27%) and observed in the range of 170–510 °C, is related to the decomposition of Quillija Sapogenin units through the formation of cellulose and other compounds, and another weight loss is between 640° C to 800° C.

The TGA (B) it is related to nano-Fe₃O₄@Qs/CoCl. The curve shows two mass-loss steps. Firstly, a weight loss (39.49%) from 90°C to 416 °C is related to the removal of moisture and solvent and some organic compounds of the catalyst. Subsequently, and other weight loss steps, the main weight loss (39.85%) from 422°C to 800 °C, It is related to metals and some organic compounds.



Fig. 3. Thermal gravimetric analysis pattern of (a) nano-Fe₃O₄@Qs, (b) nano-Fe₃O₄@Qs/CoCl.

In order to determine the content of the elements nano- $Fe_3O_4@Qs$, EDS analysis was performed (Fig.4). As shown, the results of EDS Nano $Fe_3O_4@Qs$ indicate the presence of

C, Fe, and O. Also, the EDS results were confirmed the nano- Fe_3O_4 and Quillija were combined in Fig 4.



Fig. 4. EDS diagram of nano-Fe₃O₄@Qs

The existence of the expected elements in the structure of the nano-Fe₃O₄@Qs/CoCl was approved by EDX analysis (energy-dispersive X-ray spectroscopy) (Fig.5). The EDX

results clearly confirm the presence Fe, O, Hg, Cl, C elements in this catalyst. The results indicate that the catalyst has been made.



Fig. 5. EDS diagram of nano-Fe₃O₄@Qs/CoCl

The magnetic properties of nano-Fe₃O₄ (A), nano-Fe₃O₄@Qs (B), and nano-Fe₃O₄@Qs/CoCl were characterized at room temperature by a vibrating sample magnetometer (VSM), and their curves are presented in Fig. 6.

All of the samples indicate a typical superparamagnetic behavior. So, the saturation magnetization of nanoparticles is

70.0 emu/g (Fig.6a), which is less than its bulk counterparts (92.0 emu/g) ^[6]. The nano-Fe₃O₄@Qs/CoCl magnetization was less than 30.0 emu/g of particles, so the result showed lower than nano-Fe₃O₄. This might result from the formation of a Sapogenin shell and Hg shell as a double layer around the nano-Fe₃O₄ core.



Fig.6. Magnetization loops of (a) nano-Fe₃O₄, (b) nano-Fe₃O₄@Qs and (c) nano-Fe₃O₄@Qs/CoCl.

Investigation of the effect of pH on Co²⁺ extraction The results of this investigation are provided in Table 1 and **Fig 7.** 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.

Table1.percentagerelation with	The e versu th Co ²⁺	changes is pH of the	in e sa	the mple :	recovery solution in
рН		A	bsor	ption	

0.0664(3.2)^a

2

3

4	0.0402(2.9)
5	0.0299(2.9)
6	0.0201(1.8)
7	0.0112(2.4)
8	0.0073(2.6)
9	0.0051(2.4)
10	0.0024(2.2)

a) measurement RSD following three replications





Investigation of the effect of Nano-Fe $_3O_4@Qs$ level for Co $^{2+}$ extraction

The results of this investigation are provided in Fig 8. As the results in the table reveal, at 0.05 g of the Nano-Fe₃O₄@Qs,

the absorption percentage and recovery of Co^{2+} have been maximized.



Fig 8. The effect of absorption Co²⁺ of the absorbent

Investigation of the effect of time on Co^{2+} extraction The results of this experiment have been presented in Fig 9. 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 9. In the recovery percentage effect of extraction time Co²⁺

Investigation of the effect of type of different desorption solvent for recovery of Co²⁺

Based on the results (Table 4-4), 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 HNO₃ 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.

Table 2.Selection of the recovery of Co ²⁺	e suitable desorption for
Solvent	Recovery (%)
HNO ₃ 0.1 M	92.54(0.2) ^a
HNO ₃ 1M	75.04(0.5)
HNO ₃ 3M	78.89(0.2)
$H_2SO_4 0.1M$	73.99(0.5)
H_2SO_41M	74.86(0.3)
NaOH 0.1 M	69.86(0.2)

a) measurement RSD after three replications

Investigation of optimization of the effect of volume of desorption solvent for Co²⁺ 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.

Table 3. Determination ofthe desorption solvent	f the optimal volume of
Solvent volume	Recovery (%)
5 ml	45.68(0.4) ^a
7 ml	60.4(0.6)

9 ml	78.62(0.5)
12 ml	92.96(0.7)
14 ml	88.3(0.1)
16ml	88.8(0.1)
18ml	90.1(0.4)

a) Measurement RSD following three replications

Changes in the recovery percentage in terms of changes in the volume of the desorption solvent Fig 10.



Fig 10. Effect of optimization volume of desorption solvent for Co²⁺ recovery

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 Co²⁺ off the absorbent, the maximum volume of the water solution containing Co²⁺ should be determined. The break through volume for pre-concentration method is a volume where with the 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 11 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 Co²⁺ 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 Co²⁺ 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:

Table 4.6volume in the sample	of the effect of solution
V(ml)	Recovery (%)
50	80.5(1.0) ^a
100	78.2(0.4)
150	77.7(0.9)
250	76.5(1.2)
350	68(1.7)
500	45(1.1)

a) Measurement RSD following three replications

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



Fig 11. Effect of determination break through volume of the sample solutions on the recovery percentage of Co^{2+.}

Concentration factor = break through volume/the desorption solvent volume= $\frac{250}{12} = 20.8$

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

Table 5.Measurementreplications	RSD following three
Sample	Device response
1	$0.021(1.5)^{a}$
2	0.020(3.1)
3	0.021(1.5)
4	0.021(0.9)

a) Measurement RSD following three replications

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

$S_b=0.0004$

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.

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)	

$\% \text{RSD} = \frac{s}{\bar{x}} \times 100 = \frac{0.0005}{\bar{x}0.04275} \times 100 = 1.14\%$

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 fig12, the calibration curve of the method is as follows and the line equation is Y=X0020.0 + 0.0531 and $R^2=0.9985$.

Table 7. The calibration curve for measurement of

Co ²⁺		
Primary standard solution concentration μg.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 after three replications



Fig. 12. Calibration curve of the proposed method by SPE-AAS.

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

A disturbing ion is an ion which causes a certain change of over $\pm 5\%$ in the absorption and recovery of Co²⁺. To investigate the effect of disturbance of other ions on Co²⁺ 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 $\pm 5\%$ changes and the external ions have no special effect on the measurement and cause no disturbance.

Table 8. The effect of interfering ions on recovery of Co ²⁺		
Ions	Added value(ppm)	Recovery percentage Co(II)
Na ⁺	200	89.15(1.7) ^a
Zn^{2+}	5.0	93.93(2.3)
K*	200	91.78(2.6)
Mg^{2+}	100	91.96(1.8)
Cu ²⁺	5.0	90.87(1.6)
Cl ⁻	308.7	89.18(1.4)
NO ₃ ⁻	317	95.79(2.1)
SO_4^{2-}	400	94.95(2.9)

a) measurement RSD after three replications

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 sample 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. 6.0 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 Co²⁺ and washed and then injected into the device. It was found that the device does not show a considerable absorption. In the second time, increase in the Co2+ 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 20 jan 2020 and industrial wastewater Charmshar Varamin in 14 jan 2020, 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.

Table 9. The results of measurement of cobalt in real samples		
Somplo	Cobalt(II)	Cobalt(II) found in

Sample	added(µg)	FAAS(µg)
Well water of pishva	0.0	$N.D^b$
	5.0	$5.1(1.3)^{a}$
Tap Water of pishva	0.0	0.079(2.2)
	5.0	5.06(1.9)
Industrial wastewater Charmshar Varamin	0.0	0.04(2.0)
	5.0	5.04(1.9)

a) Measurement %RSD after three replications

b) Not Detection

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 [6, 20]. 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 Nano-Fe₃O₄@Qs absorbent is that instead of applying the proposed ligand, one can place other ligands on the Nano-Fe₃O₄@Qs 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.

CONCLUSION

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 Co2+ 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 Co²⁺ 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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