Fabrication method of extracting of Co(II) in water samples by synthesis MG-Chi/Fe$_3$O$_4$

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ABSTRACT: A flame atomic absorption spectrophotometric (FAAS) method for the determination of trace Co(II) after adsorption of synthesis modified with methionine-glutaraldehyde schiff's base (MG-Chi/Fe$_3$O$_4$) nano-biosorbent has been developed. Applying a facile and accessible sample preparation method is highly important before the experimental analysis process. In the current study, a technique was introduced for preconcentration and analysis of trace amounts of Co(II) ions in water samples. The important parameters in the analytical procedure of Co(II) ions were optimized such as the pH of extraction, amount and type of elution solvent, time of extraction, and the effect of another ion. Analytical parameters such as the concentration factor, the limit of detection (LOD) of the technique, and relative standard deviation (RSD %) were achieved as 20, 10.0 μg L^{-1}, and 2.8%, respectively.

Keywords: Co(II) ion, Modified with methionine-glutaraldehyde schiff's base, (MG-Chi/Fe$_3$O$_4$) nano-biosorbent, Preconcentration of heavy metals, SPE.

INTRODUCTION

The properties of nanomagnetic particles research on their functionality as magnetic carrier [1,2]. Also in medical imaging use ssuch as magnetic resonance imaging (MRI) It commonly, generated from industrial processes including electroplating, smelting, battery manufacturing, mining, metallurgy, and refining [2,3]. Cadmium might Co to pancreatic cancer, renal toxicity, and enhanced tumor growth. The US Environment Protection Agency (US-EPA) has classified it as one of the group B1 carcinogenic elements [4]. The maximum allowable total cadmium in drinking water has been set at a concentration of 0.03 mg.L^{-1} by the World Health Organization (WHO) [5]. The direct determination of cadmium in water samples by flame atomic absorption spectrometry (FAAS) is very difficult due to the low concentration of cadmium ions and also interfering because of influences of the components of the matrix. Therefore, separation and preconcentration steps are often required to achieve accurate, sensitive and reliable results by FAAS. Several techniques including precipitation/co-precipitation [6], liquid-liquid extraction [7] cloud point extraction [8] and solid-phase extraction [9] (SPE) have been developed for the separation and preconcentration of trace cadmium Among all

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methods, solid-phase extraction is the most common technique used for preconcentration of an analyte in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [9,10]. In recent years a new kind of SPE, magnetic solid-phase extraction (MSPE), has attracted so much attention. The MSPE is based on magnetic materials as sorbent, which can be isolated from the matrix quickly by using a magnet. Compared with other isolation methods, MSPE can improve the extraction efficiency and simplify the process of preprocessing. In recent year, the application of nanomaterial's such as activated carbon [11-14], Different methods, co-extractant ligands has attracted considerable attention [15,16]. However, the use of classical extraction methods for this purpose is usually for the Extraction and separation of Co ions have been suggested including liquid chromatography [17] supercritical fluid extraction [18,19], flotation [24], aggregate film formation [25], liquid membrane [26], column adsorption of pyrocatechol violet-Co complexes on activated carbon [27], ion pairing [28], ion pairing [29], preconcentration with yeast [30], and solid phase extraction using C_{18} cartridges and disks [31-34]. Consequently, in the current investigation, the researchers focused on the first application of MG-Chi/Fe_3O_4 as a novel adsorbent for dispersive solid-phase and extraction of Co^{2+} wastewater samples before the flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation
The determination of Co^{2+} by PG-990flame atomic absorption spectrometer is equipped with HI-HCl which was done according to the recommendations of the manufacturers. Accordingly, the pH measurements were used by Sartorius model PB-11.

Materials
Individual stock solutions of Co(II), were prepared by direct dissolution of the appropriate amount of salt in 1% HNO_3. By stepwise dilution of the stock solutions, a mixed working solution was prepared. Chitosan was purchased from Sigma-Aldrich (Darmstadt, Germany), with a deacetylation rate>90%, nitrate salt of Co(II), magnetite particle (Fe_3O_4) with particle size less than 20 nm, glutaraldehyde 25%, piperidine, ethylene diamine tetra acetic acid (EDTA), and ethanol absolute (all with purity greater than 99.5%) and methionine (with purity greater than 99%) were prepared from Merck (Darmstadt, Germany). The pH of the solution was adjusted by the addition 2 ml of acetate buffer (acetic acid/sodium acetate) 1.0 mol L^{-1} with pH= 5.5.

Synthesis of modified with methionine-glutaraldehyde schiff's base (MG-Chi/Fe_3O_4)
modified with methionine-glutaraldehyde schiff's base (MG-Chi/Fe_3O_4) nano-biosorbent showed great adsorption ability when 4 sorption-desorption cycles had been accomplished [35].

The initial experiment of Co^{2+} extraction for determining the suitable adsorbent
The procedure for extraction and recovery of Co ions by MG-Chi/Fe_3O_4 is as follows; in the first step, 0.2 g of thiosemicarbazone ligand and 0.3 g of MG-Chi/Fe_3O_4 and were dissolved in the little amount of acetone, and then it dried. Four 50-mL ballons were adopted, and then 0.05 g of MG-Chi/Fe_3O_4 was poured into one of the balloons. Afterward, 0.05 g MG-Chi/Fe_3O_4 with carboxylic function, 0.05 g combination of ligand and amine MG-Chi/Fe_3O_4, and 0.05 g mixture of MG-Chi/Fe_3O_4 were added to each other balloons. Thereupon, a 1 ml buffer solution with a pH of 4.5 was added to balloons and a 2 ppm solution was prepared with an analyte. Four solutions were shaken at 25°C for 20 min, then these solutions for 15 min were centrifuged and the supernatant injected into an atomic absorption apparatus.

The effect of adsorbent amount for Co^{2+} extraction
Seven 2.0 ppm solutions with 50 mL of Co^{2+} were provided and poured into seven flasks. Seven solutions were adjusted at pH= 10 (optimum pH) and different amounts of the adsorbent (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) added to flasks. The mixtures were

shaken for 20 min, and then the mixtures were centrifuged and the top solution of the examine tube injected in flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was performed by the adsorbent, optimal conditions were achieved for it, and MG-Chi/Fe$_3$O$_4$ ple real aqueous samples were investigated. The real samples were as follows; well and drinking water in Pishva Town were collected with temperatures of 20 and 22°C, pH= 7.1, 7.3 in 23.8.95 at 9:45, 10:00, respectively. Finally, a fish farming sample was collected at, pH= 6.20 in 23.8.95 at 11:20. First, these suitable bottles were provided for the sampling of samples. The bottles were washed first with ordinary and distilled water. The bottles dried completely, and the 'suitable' label was attached to each bottle. To collecting of water samples, the used containers sample dried and cleaned and they had already been washed. For the analysis of the samples in the first stage, colloidal and suspended particles were removed. To this aim, the water samples passed through 0.22 μm filters. Next, the volume of 100 mL of samples was poured into the sample container. The pH of samples was adjusted at 10 and then, nanotube and ligand were added to samples. They stirred for 20 min and the mixture was then centrifuged. Then, they were washed with HNO$_3$ 0.1 M and were shaken again for 20 min. Finally, following the centrifugation of the mixture, absorption of Co ion was identified from the filtered solution by flame atomic absorption spectrophotometry. In the first step, the sample itself was injected into the apparatus without any Co ion, wherein water samples, the device displayed no absorption. To identify certain amounts of Co of the samples, the method of standard elevation was used. This stage was accomplished like the first step, the only discrepancy was that 0.5 mL of 200 ppm solution with Co^{2+} added to the water samples. Finally, the absorption of Co ion was identified from the filtered solution by flame atomic absorption spectrophotometry.

RESULT AND DISCUSSION

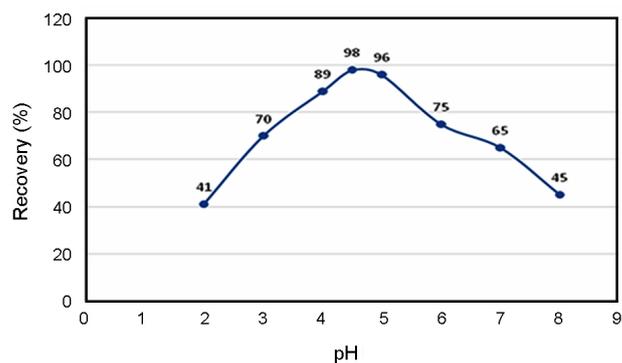This section deals with the results of the research ex-

Fig. 1. The effect of pH in the Co^{2+} extraction

periments. The results achieved in the experimental chapter, calibration curve, and the factors influencing the extraction (e.g. pH, temperature effect, time, etc.) of Co^{2+} ion by the MG-Chi/Fe$_3$O$_4$ are discussed which are followed in the presentation of scientific justification and overall conclusion of the study.

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

The results of this study are provided in Fig. 1. indicate, at pH= 5, Co adsorption was maximized, while at lowest and highest pHs, the extent of adsorption declines, inferring that at pH<5 adsorptions of Co^{2+} ions cannot occur completely. As revealed in Fig. 1, to determine the amount of MG-Chi/Fe$_3$O$_4$ required for effective removal of Co^{2+}, different amounts of the MG-Chi/Fe$_3$O$_4$ for modification of MG-Chi/Fe$_3$O$_4$ with fixes amount (3 mg) and its effect for the removal of Co^{2+} from 20 mL solutions of cobaltion (50 μg/L) were investigated.

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

Based on the results, the extent of absorption increases, and the Co ions present in the solution find more chance to be adsorbed in the adsorbent's sites. Therefore, the quantitative extraction of Co ion is possible for a period of longer than 20 min, and within durations longer than 20 min and more, the reaction happens completely.

Survey of the effect of type of various desorption solvent for recovery of Co^{2+}

Based on the results (Table 1), NaOH cannot be used as appropriate desorption and these bases do not possess a complete detergence power. Therefore, mineral

Table 1. Selection of the appropriate desorption for recovery of Co^{2+}

Solvent	Recovery (%)
HNO_3 0.1M	90.20(2.5) [a]
HNO_3 1M	81.32(2.4)
HNO_3 3M	70.55(2.3)
H_2SO_4 0.1M	71.34(2.7)
H_2SO_4 1M	70.10(2.8)
NaOH 0.1M	60.22(2.0)

a) measurement RSD after three replications

acids with determined concentrations, H_2SO_4, and HNO_3 were applied. As shown in Table 1, the results of this table offer that all acids contain a good detergence power for Co^{2+}, but the recovery percentage of HNO_3 is higher than that of other acids. In an acidic environment, the possible deposits dissolved and recovery of these ions increased. However, the results obtained from nitric acid were better than H_2SO_4, in that 0.1 M of solution washed 92.54% of the Co^{2+} ion adsorbent. So, for the rest of the experiments, nitric acid 0.10 M was used as the desorption solution.

Survey of optimization of the volume effect of desorption solvent for Co^{2+} recovery
After the investigation and choice of optimal desorption, the volume of solvent was investigated, with the results which are shown in Table 2. The volume of 10 mL for HNO_3 was selected as the optimal volume for washing.

Investigation the effect of breakthrough volume
Following the optimization of the pH of the desorption solvent and sample solution, etc., to elute the Co^{2+} in the adsorbents, the maximum volume of the

Table 2. The optimum volume of the desorption solvent

Solvent volume (mL)	Recovery (%)
5	41.20(2.9) [a]
7	50.60(2.6)
9	60.15(2.7)
10	90.07(2.7)
12	89.35(2.6)
15	89.47(2.5)
20	89.00(2.4)

a) Measurement RSD following three replications

Table 3. Investigations of the effect of solution volume in the sample

V (mL)	Recovery (%)
50	87.90(2.4) [a]
100	74.20(2.5)
150	76.70(2.6)
250	75.50(2.6)
350	57.60(2.4)
500	37.50(2.4)

a) Measurement RSD following three replications

aqueous solution containing Co^{2+} should be measured. If the volume of the test solution to be less than the breakthrough volume, and passaging of that volume, all analytes are kept in the solid phase. The results in (Table 3) verify that up to 250 mL of ions are adsorbed by the nano adsorbents and if the sample volume is greater than this value, some of the Co^{2+} is not kept on the adsorbent and pass over the adsorbent with no inhibition. Also with definition by the concept of breakthrough volume, it can be reported that the breakthrough volume in the current study is 250 mL and if the sample solution volumes which includes Co^{2+} is over 250 mL, adsorption does not occur completely and hence if 250 mL of sample volume is passed over the adsorbent and then with 12 ml of the desorption solvent washed, the concentration factor could not be achieved as 30. This concept that the concentration of Co^{2+} in 7 mL of desorption solvent which was passed over the adsorbent grows by 20 times. Based on the related results (Table 3), the breakthrough volume calculations are as follows:

The linear range and a calibration curve of the method
To assess the linear range in the analysis method, a calibration curve should be plotted. This curve is not linear across all concentrations and different factors cause the calibration curve to the situation in the linear range and follow from Beyer Law. the calibration curve of the method is as conform and the line equation is y= 0.005x+0.049 and R^2= 0.995.

Study of the effect of disturbances on the measurement of Co^{2+}
A disturbing ion is an ion that causes a certain variation of over ±5% in the adsorption and recovery of

Co²⁺. To study the effect of disturbance of other ions on Co²⁺ extraction, a certain quantity of interfering factors added to the initial solution, and the experiment was performed at breakthrough volume. Absorption of the recovered solution is analyzed with flame atomic absorption and then compared versus the solution absorption resulting from the sample recovery which lacks the interfering ion. As can be shown in Table 4, in the presence of external ions, Co recovery occurred with ±5% variations and the external ions had no particular effects on the analysis and cause no disturbance.

Determining the method's limit of detection
The lowest Co²⁺ concentration or weight in a sample that could be determined with a certain confidence level is called the limit of detection (LOD), which is defined as follows. The LOD of a method is a concentration of an analysis sample where the device response to concentration (which is significantly different from the response of the control sample) is defined as follows; the limit of detection is the lowest amount of Co²⁺, where the presented method can detect it. Based

on the presented definition, LOD can be calculated by the following relation;

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

Where S_b and m are the standard deviations of the blank signal and the slope of the calibration curve, respectively. Therefore, LOD can be calculated at 10.0 ppb.

Determination of Co in natural tap water samples
In addition, the effect of packing amount of silica gel phase is also evident in Table 5, where the near completion of Co removal was accomplished by the use of 5 mg phase. The results of the preconcentration of Co from aqueous solutions are presented in Table 5 of Co from DDW and natural tap water samples. Real samples marked 1 to 5, were collected at the at the distances of 5, 100, 250, 350 and 500 metres of the total waste water of electroplating plants in the eastern parts of Varamin, respectively. The total results obtained by the recommended procedure and ICP-AES have compared in Table 6. As it is seen, the results obtained by

Table 4. The effect of interfering ions on the recovery of Co²⁺

Ions	Added value (ppm)	Recovery percentage Co(II)
Na⁺	200	88.92(2.3)ª
Zn²⁺	5.0	90.84(2.5)
K⁺	200	86.88(2.5)
Mg²⁺	100	86.78(2.7)
Cu²⁺	5.0	89.73(2.7)
Cl⁻	200	84.18(2.8)
NO₃⁻	300	93.28(2.9)
SO₄²⁻	400	92.94(2.9)

a) Measurement RSD after three replications

Table 5. Determination of Co in real water samples

Sample	Taken amount (µg)	cold vapor atomic absorption spectrometry (CVAAS) (µg)	Recovery (%)
Tap water (Tehran, Iran)	0	4.0(2.6)ª	-
	30	34.08(2.6)	97.5
Tap water (Pakdasht, Tehran, Iran)	0	1.5(2.7)	-
	30	35.1(3.0)	97.0
Mineral water (Damavand Company)	0	N.Dᵇ	-
	30	30.12(3.0)	95

a) Values in parentheses are RSD based on four replicated analyses.

b) No adsorption, passes through column

Table 6. Comparison of the total results of the proposed method with ICP-AES [a].

Sample	Co^{2+} (mg.mL^{-1}) SPE- FAAS	Co^{2+} (mg.mL^{-1}) ICP-AES	F-test [c]	T-test [d]
1	16.0±2.5[b]	16.1±1.7	3.1	0.5
2	12.6±2.3	12.7±1.5	1.8	0.8
3	7.0±2.8	7.1±1.7	2.7	0.9
4	3.0±2.3	3.1±1.1	2.0	0.6
5	1.5±2.9	1.5±1.9	2.1	0.7

a) All real samples were diluted 50 times before analysis.

b) Mean ± standard deviations based on five individual replicate analyses.

c) Tabulated F-value for (4,4) degrees of freedom at p (0.95) is 6.39.

d) Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.

the proposed method and ICP-AES are in agreement with each other. Moreover, as it is expected, the Co(II) concentration decreases as the distance from the electroplating plants increases.

A comparison between the current method and other methods

A comparison of this method with other methods verified that the current method is more accurate, easiest, and faster as it had smaller relative standard deviation values in comparison with other methods [36-53]. The current method is one of the foremost systems for determining the very trace amounts of heavy metal ions including Co in aqueous samples. Another point in the usage of nanotube adsorbent is that instead of using the proposed ligand, one can put other ligands on the adsorbent which to adsorb mineral ions, thereby measuring trace amounts of metal ions. A wide variety of ligands can be used given their properties, which act selective towards one or several ions and applying this set, preconcentration, and determination of cations can be carried out. Using flame atomic absorption and solid drop microextraction, single-drop liquid-liquid extraction, and homogeneous liquid-liquid extraction with other devices, one can determine trace amounts of Co^{2+} by this adsorbent and achieve a smaller limit of detection value.

CONCLUSIONS

In comparison with other procedures reported for measurement of Co(II), this method has considerable advantages that are easy and inexpensive and can be applied quickly for environmental aqueous samples. Furthermore, it minimizes the utilization of organic, toxic, and costly solvents. Moreover, the design and development of this procedure for separation, measurement, and preconcentration of Co^{2+} are essential considering its importance in various industries and the little concentration of Co^{2+} ion in most samples. Therefore, this research aims to present an effective, selective, cost-effective, and simple method for measurement of the level of Co(II) across different environmental aqueous samples (in this research, the limit of detection, the value of breakthrough volume, and RSD has been obtained). This research indicated that the measurement of Co^{2+} occurs at an appropriate level without the interference of any other interfering factor and thus the current method can be applied easily in the measurement of the quantity of Co(II) in aqueous samples.

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