Original Article

Separation of method of dispersive solid phas exteraction mercury (II) from water solution using of FE_3O_4 @ quillaja sapogenin

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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 Hg (II) ions in aqueous samples, Fe_3O_4@quillaja Sapogenin was synthesized for improving the extraction and preconcentration action. Measurement of Hg^{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 µg.L^{-1}, and 1.16%, respectively.

Keywords: Fe_3O_4@quillaja Sapogenin was synthesized, graphite furnace atomic absorption spectroscopy, Hg (II) ion, SPE.

Introduction

The properties of nanomagnetic particles were studied on their functionality as magnetic carrier [1, 2] also in medical imaging used as magnetic resonance imaging(MRI). It commonly, generated from industrial processes including electroplating, smelting, battery manufacturing, mining, metallurgy, and refining [2, 3]. Mercury caused to decrease pancreatic cancer, renal toxicity, and enhanced tumor growth. The US Environment Protection Agency (US-EPA) has classified it as one of the group B_1 carcinogenic elements [4]. The maximum allowable total Mercury in drinking water has been set at a concentration of 0.03 mg/L by the World Health Organization (WHO)[5]. The direct determination of Mercury in water samples by flame atomic absorption spectrometry (FAAS) is very difficult due to the low concentration of Mercury ions and also interfering 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 Mercury. Among all 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 to other isolation methods, MSPE can improve the extraction efficiency and simplify the process of preprocessing. In recent year, the application of nanomaterials such as activated carbon [11],

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Different methods, co-extractant ligands has attracted considerable attention [12, 13]. However, the use of classical extraction methods which is usually for the extraction and separation of Hg ions has been suggested including liquid chromatography [14] supercritical fluid extraction [15, 16], flotation [17], aggregate film formation [18], liquid membrane [19], column adsorption of pyrocatechol violet-Hg complexes on activated carbon [20], ion pairing [21], ion pairing [22], preconcentration with yeast [23], and solid phase extraction using C_{18} cartridges and disks [24].

Recently, our goal is to products such as construction for magnetic nanoparticle iron oxide by covering it with organic materials initiate in plants. The Licorice plant, Quillaja Saponaria (sapogenin), is one of those organic material which is a huge evergreen plant with leathery and bright leaves. They also have thick bark and are originally from Peru, China, and the semi-arid regions of Chile.[10] Their barks are very rich in saponins and also plant glycosides which primarily exist in the aquatic animals and plants. Chemically, saponins are steroids or triterpene glycosides possessing a wide variety of activities that are related to cancer, anti-inflammatories, antiallergics, and antivirals affecting the physiology of the heart and blood systems, as well as molluscicidal activities. [11, 25, 26]

For optimization of the system and exploration of structure-activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Hg^{2+} in low concentration. The chelated ions were desorbed and determined by GF-AAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, magneticnano-Fe_3O_4chitosan/graphene oxide.

Therefore, in this work, we report on the first application of Fe_3O_4@quillaja Sapogenin as a novel sorbent for dispersive solid phase exteractionHg^{2+}wastewater samples prior to spectrofluorometric determination at GF-AAS after excitation.

Experimental

Instrumentation

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

Materials

In this research, the following materials have been used for the experiments: Quillaja Saponin functionalized with carboxyl, hexahydrate Hg (II) nitrate, thio-semi-carbazid ligand, buffer, and nitric acid. thio-semi-carbazide ligand (CH_5N_3S)were prepared from Darmstadt, Germany of Merck.

preparation of the solutions and standards

Hg^{2+} solution with the concentration of 200 ppm was prepared by dissolving 0.099 g hexahydrate Hg (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.

Preparation of magnetic nanoparticles (Fe_3O_4)

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. [23].

$FeCl_3.6H_2O$ (10 mmol, 2.7 gr) and $FeSO_4.7H_2O$ (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 Fe^{2+}/Fe^{3+} 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 [24, 27].

Preparation of nano-Fe_3O_4@ Quillija Sapogenin

A mixture of synthesized nano-Fe_3O_4 (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.

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

To investigate the effect of pH on absorption of Hg^{2+}, first 2.0 ppm solutions with a volume of 50 mL in relation with Hg^{2+} were prepared, where the effect of aqueous solution on the recovery of Hg^{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 Sample container 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 nano-Fe_3O_4@ Quillija Sapogenin 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 Hg^{2+} concentration in it was determined by flame atomic absorption spectroscopy.

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 Hg^{2+} adjusted at pH=10 was poured into four balloons, to each of which 0.05 g nano-Fe_3O_4@ Quillija Sapogenin 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 0.10 M. It was then placed inside the shaker again for 20 min. eventually, the mixture was centrifuged and absorption of Hg^{2+} in the solution of the centrifuged tube was determined by flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was completed by nano-Fe_3O_4@ Quillija Sapogenin, optimal conditions were found for it, and several real water samples were analyzed. The real samples 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 Sample container 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 Sample container. Their pH was adjusted at 10 and to each sample nano-Fe_3O_4@ Quillija Sapogenin 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 Hg 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 Hg ion, where in water samples, the device showed no absorption. Indeed, to determine certain amounts of Hg present in the water samples, standard elevation method was used, and this stage was performed like the first stage. The only difference was that 0.5 mL of 200ppm solution in relation with Hg^{2+} was added to the samples. Eventually, absorption of Hg 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 Hg^{2+} ion by the carbon naotubes are discussed and following presentation of a scientific justification, overall conclusion of this research is stated.

The results obtained from FT-IR spectroscopy of (A) nano-Fe_3O_4, (B) nano-Fe_3O_4@Qs, (C) nano-Fe_3O_4@Qs/HgCl are presented in Fig1. The existence of stretching vibration of Fe-O was concluded by results obtained from FT-IR spectroscopy of nano-Fe_3O_4 (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- Fe_3O_4@Qs, Quillija Sapogenin (B) indicates that Quillija Sapogenin covers the magnetic nano-Fe_3O_4. 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 FT-IR spectrum of nano-Fe_3O_4@Qs/HgCl (C) shows a characteristic peak at 415 cm^{-1} that may correspond to O–Ni–O bending vibrations. 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}.

In comparison with nano-Fe_3O_4@Qs, bonding Ni to the Qs shifts Fe–O stretching vibrations to lower wave range (from 626 cm^{-1} to 615 cm^{-1}). The stretching vibrations of O–H bonds are observed at 3383 cm^{-1} overlapping with stretching vibrations O–H bonds Hg –OH are observed at 3375 cm^{-1}.

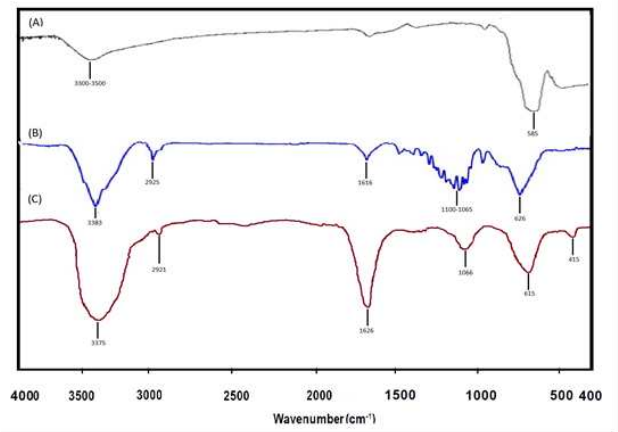

Figure 1- FT-IR spectra of (a) nano-Fe_3O_4, (b) nano-Fe_3O_4@Qs, (c) nano-Fe_3O_4@Qs/HgCl

Phase purity and structure of nano-Fe_3O_4 (A), nano-Fe_3O_4@Qs (B), and nano-Fe_3O_4@Qs/NiCl (C) are studied by means of high angle X-ray diffraction analysis (XRD) (Fig. 2).

The bare Fe_3O_4 shows diffraction peaks at 2 θ = 30.3821°, 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 Fe_3O_4 patch described in the literature (Fig. 2A) [28].

The same peak was also observed on the XRD diffraction pattern of nano-Fe_3O_4@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 2θ = 19.8° and 21.3°, is related to the sapogenin coating of nano-Fe_3O_4 (fig.2 B). The XRD of nano-Fe_3O_4@Qs/HgCl pattern shows the structure is amorphous.

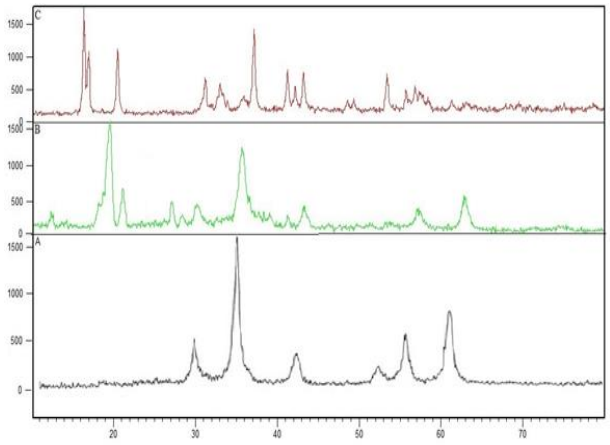

Figure 2- XRD patterns of the (a) nano-Fe_3O_4, (b) nano-Fe_3O_4@Qs, (c) nano-Fe_3O_4@Qs/HgCl.

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 were 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.

Study the effect of pH on Hg^{2+} extraction

The results of this investigation are provided in Table 1.As the results in the table indicate, at pH=10, Hg 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. As shown in Fig. 3, to détermine the amont of nano-Fe_3O_4@ Quillija Sapogenin requise for effective removal of Hg^{2+}, différent amont of the nano-Fe_3O_4@ Quillija Sapogenin (50 mg) for modification of nano-Fe_3O_4@ Quillija Sapogenin with fixes amont (3 mg) and its effect for the removal of $Hg^{2+}$from 20 mL solutions of mercury ion (50 µg/L) were investigated.

Table 1- The changes in the recovery percentage versus pH of the sample solution in relation with Hg2+

pH	Absorption
2	0.0664(2.2)[a]
3	0.0506(2.1)
4	0.0402(2.9)
5	0.0299(2.9)
6	0.0201(2.8)
7	0.0112(2.4)
8	0.0073(2.6)
9	0.0051(2.4)
10	0.0024(2.2)

a)measurement RSD after three replications

Investigation of the effect of type of different desorption solvent for recovery of Hg^{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 Hg^{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 Hg^{2+} ion absorbent. So for the rest of studies, nitric acid 0.10 M was sued as the desorption solution.

Table 2- Selection of the suitable desorption for recovery of Hg^{2+}

Solvent	Recovery (%)
HNO_3 0.1M	92.58(1.2)[a]
HNO_3 1M	75.14(1.5)
$HNO_3$3M	78.89(1.2)
H_2SO_4 0.1M	73.90(1.5)
$H_2SO_4$1M	74.80(1.3)
NaOH0.1 M	69.89(1.2)

a)measurement RSD after three replications

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

After investigation and selection of optimal desorption, the volume of this solvent was studied, with the results collected in Table 3. The volume of 12 mL for nitric acid was chosen as the optimal volume for washing.

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

Solvent volume	Recovery (%)
5 ml	45.67(1.4)[a]
7ml	60.99(2.6)
9 ml	78.68(2.5)
12 ml	92.97(2.7)
14 ml	88.6(2.1)
16ml	88.5(2.1)
18ml	90.4(2.4)

a) Measurement RSD following three replications

Investigation the effect of break through volume

Following optimization of the pH of the sample solution and desorption solvent, etc., to eluting the Hg^{2+}in the absorbents, the maximum volume of the water solution containing Hg^{2+} should be determined. If the volume of 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 Fig 3 indicate that up to 250 mL of ions is absorbed by the nano absorbents and if the sample volume is larger than this value, part of the Hg^{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 Hg^{2+} is over 250 mL, 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 Hg^{2+} in 7 mL of desorption solvent which has been passed over the absorbent grows by 20.8 times. Based on, the break through volume calculations is as follows:

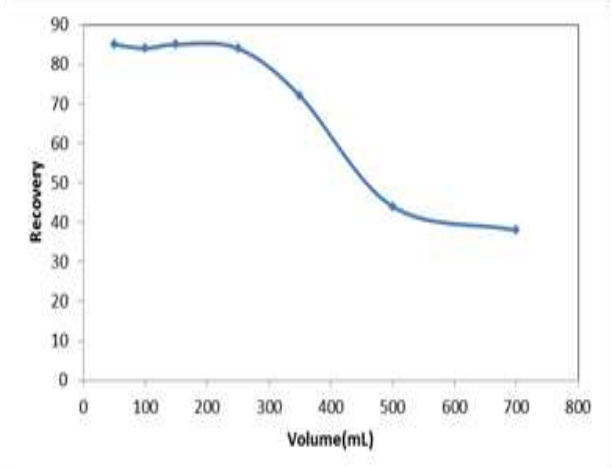

Figure 3- Effect of determination break through volume of the sample solutions on the recovery percentage of Hg^{2+}

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 Fig.4, the calibration curve of the method is as follows and the line equation is $Y=0.001X+ 0.0122$. and $R^2=0.9995$.

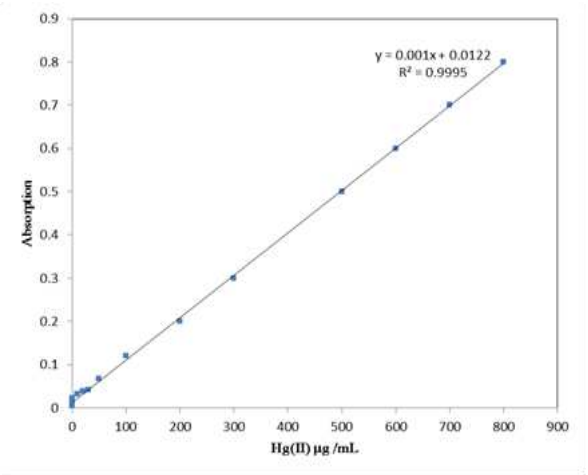

Figure 4 - Calibration curve of the proposed method by SPE-AAS.

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

A disturbing ion is an ion which causes a certain change of over ±5% in the absorption and recovery of Hg^{2+}. To investigate the effect of disturbance of other ions on Hg^{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 4, in the presence of external ions, Hg recovery occurs with ±5% changes and the external ions have no special effect on the measurement and cause no disturbance.

Table 4- The effect of interfering ions on recovery of Hg^{2+}

Ions	Added value(ppm)	Recovery percentage Hg(II)
Na^+	200	89.15(2.7)[a]
Zn^{2+}	5.0	93.95(2.3)
K^+	200	91.73(2.6)
Mg^{2+}	100	91.93(2.8)
Cu^{2+}	5.0	91.84(2.2)
Cl^-	308.7	89.15(2.1)

NO_3^-	317	91.76(2.1)
SO_4^{2-}	400	91.97(1.9)

a) Measurement RSD after three replications

Determining the method's limit of detection

The lowest Hg^{2+} 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 detection of is a method is a concentration of an experimental sample where the device response to it, (which is significantly different with the response of control sample) and is defined as follows. The limit of detection is the lowest amount of Hg^{2+}, where the presented method is able to detect it. Based on the presented definition, Therefore, LOD can be calculated6.0 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 Hg 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 Hg^{2+} 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 Hg^{2+} was performed according to the concentration and separation method. Indeed, to determine certain amounts of the Hg present in the water samples, standard elevation method was used. The results of this analysis have been shown in Table 5. As can be observed, in the water samples, in Tap water of Pishva–Varamin in 27 Jan 2020 and industrial wastewater Charmshar Varamin in 30jan 2018, there is a larger amount of Hg^{2+} than in the experimented water samples. However, in other samples, there is less Hg. Based on this, the efficiency and power of preconcentration and Hg measurement can be deduced.

Table 5- the results of measurement of Hg in real samples

Sample	Hg(II) added(µg)	Hg(II) found in FAAS(µg)
Well water of pishva	0.0	N.D[b]
	5.0	5.020(1.9)[a]
Tap Water of pishva	0.0	0.064(2.7)
	5.0	5.06(2.5)
Industrial wastewater Charmshar Varamin	0.0	0.04(2.0)
	5.0	5.04(2.9)

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 [27-31].The proposed method is one of the best systems for measurement of very trace amounts of metal ions including Hg in water samples. Another point in application of nano-Fe_3O_4@ Quillija Sapogenin absorbent is that instead of applying the proposed ligand, one can place other nano-Fe_3O_4@ Quillija Sapogenin 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 Hg^{2+} by this absorbent and obtain a lower limit of detection value.

Conclusion

In comparison with other methods reported for separation and measurement of Hg (II), this method enjoys considerable advantages which 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 Hg^{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 Hg (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 Hg^{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 Hg (II) in water samples.

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