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Preconcentration of Hg(II) with novel nano-Fe_3O_4- sorbents prior to determination by CVAAS

A. Moghimi

Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran

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ABSTRACT: A novel, simple, sensitive and effective method has been developed for preconcentration of Hg(II) on nano-Fe_3O_4-DOP-ED solid-phase extraction adsorbent. In this paper, Dioctyl phthalate (DOP) was used to encapsulate nano-Fe_3O_4 and produce a nano-Fe_3O_4-DOP sorbent based new sorbent was prepared. This was treated with ethylenediamine (ED) in another solvent-free procedure for the formation of a novel nano-Fe_3O_4-DOP-ED. Flame atomic absorption spectrometer was utilized for determination of Hg(II). Some of the important parameters on the preconcentration and complex formation were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ) were 49.6, 163.7 ng L^{-1} and the proposed method has a good reproducibility 0.90% (RSD %) and preconcentration factor was found to be 200. The methodology was applied for determination of Hg(II) in natural water samples and satisfactory results were obtained.

Keywords: *Cadmium; Central Composite Design; Dioctyl phthalate (DOP) was used to encapsulate nano-Fe_3O_4; Flame Atomic Absorption Spectrometer; Preconcentration; Water*

INTRODUCTION

The properties of nano magnetic particles research on their functionality as magnetic carrier, (Bulut, *et al.*, 2010, Graf, *et al.*, 2007), also in medical imaging uses such as magnetic resonance imaging (MRI) (Ansari, *et al.*, 1999, Margel, *et al.*, 1997), in isolating substances and materials in anions– cations pre-concentration (Afkhami and Moosavi, 2010, White, *et al.*, 2009, Tuutijarvi, *et al.*, 2009, Batterham, *et al.*, 1997, Hummers and Offeman, 1958, Camel, 2003). The determination of Hg is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) (Castillo, *et al.*, 2005, Eaton, *et al.*, 1995) as well as spectrometric methods (Welcher and Boschmann, 1979, Marczenko, 1986). However, due to the presence of Hg in medicinal and environmental samples at low levels, its separation from other elements presents and also the use of a preconcentration step prior to its determination is usually necessary. Different methods, co-extractant ligands have attracted considerable attention (Carasek, *et al.*, 2002, Ceccarini, *et al.*, 2005). However, the use of classical extraction methods for this purpose is usually for the Extraction and separation of Hg ions have been suggested including liquid chromatography (Tuzen, 2009) supercritical fluid extraction (Choi and Choi, 2003, Tuzen, *et al.*, 2004, Karousis, *et al.*, 2011, Smith and March, 2001, Mermoux, *et al.*, 1991, Cataldo, 2003), flotation (Tohidifar, *et al.*, 2013), aggregate film formation (Thistlethwaite and Hook, 2000), liquid membrane (Taguchi, *et al.*, 1997), column adsorption

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(*) Corresponding Author - e-mail: alimoghimi@iauvaramin.ac.ir

of pyrocatechol violet-Hg complexes on activated carbon (Tajodini and Moghimi, 2010), ion pairing (Thistlethwaite and Hook, 2000), ion pairing (Stevens, *et al.*, 2007), preconcentration with yeast (Su, 2003), and solid phase extraction using C_{18} cartridges and disks (Su, *et al.*, 2003, Soylak, *et al.*, 2003, Szabo, *et al.*, 2005, Moghimi, 2014). Solid phase extraction (SPE) or liquid-solid extraction is poplar and growing techniques that are used to sample preparation for analysis. However, the disks modified ligand is a selective approach to separation and pre- concentration of heavy metals in water samples (Moghimi A., Abdouss, 2013, Moghimi, *et al.*, 2007, Tarigh and Shemirani, 2013, Moghimi and Poursharifi, 2012, Moghimi, 2014, Moghimi and Siahkalrodi, 2013, Moghimi and Yari, 2014, Moghimi and Akbarieh, 2014, Moghimi, 2013). In a recent series of papers, (Moghimi, *et al.*, 2012, Moghimi, *et al.*, 2013, Moghimi and Shabanzadeh, 2012) the determinate relies on the esterase activity of a DNA-linked Hg complex. 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 CVAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, nano-Fe_3O_4-DOP-ED. In the present work, nano-Fe_3O_4-DOP-ED was employed for production of solid phase. The synthesized and characterized new sorbent nano-Fe_3O_4-DOP-ED was utilized for preconcentration of Hg(II) from water samples. Determination of Hg(II) concentration was achieved by CVAAS after preconcentration procedure.

MATERIALS AND METHODS

Reagents and Chemicals

The analytical grade deionized water was obtained by reverse osmosis system. All containers and glassware were kept overnight in 10% nitric acid and rinsed three times with water before use.1,000 mg L^{-1} stock Hg standard solution was prepared from $Hg(NO_3)_2.4H_2O$ (Merck) and diluted as required to the μg L^{-1} levels. BDH Limited, Poole, England. Dioctyl phthalate, DOP, (purity> 99.55%), sodium hydroxide (NaOH) and ethylenediamine (ED) was purchased from BDH, UK. Hg nitrate, $Hg(NO_3)_2$, cadmium nitrate, $Cd(NO_3)_2$ and $NiCl_2$-$6H_2O$ was purchased from Merck. In interference study, cations were added as nitrates and the anions were added as sodium salts. Feasibility of the suggested method was tested with Lake Ontario water certified reference material (TMDA-53.3, lot 0310).

Synthesis of magnetic nano-Fe_3O_4 sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method (Graf, *et al.*, 2007). A 6.1 g sample of $FeCl_3$-$6H_2O$ and 4.2 g $FeSO_4$-$7H_2O$ were dissolved in 100 mL of distilled water. A total of 25.0 mL of 6.5 M-NaOH was slowly added to the above solution. The reaction mixture was stirred for 4 h using a magnetic stirrer. After the complete addition of NaOH, the formed black precipitate, nano-FejOa, was then washed several times with distilled water, collected in a pure form by the assistance of an external magnetic field and dried in an oven at 70°C.

Synthesis of nano-Fe_3O_4-DOP sorbent

The Fe_3O_4-encapsulated-DOP nano-sorbent was prepared by the addition of 20.0 mL of DOP to 10.0 g of nano-Fe_3O_4 sorbent. This mixture was heated under stirring at 80-90 °C for 3 hands the product nano-Fe_3O_4-DOP sorbent was filtered, washed with methanol, collected in a pure form by a magnetic field and dried in an oven at 70 °C until complete dryness.

Synthesis of magnetic nano- Fe_3O_4 -DOP- ED sorbent

A 10.0 g sample of nano-Fe_3O_4-DOP addition to 5 mL of ED and these two reactants were combined together by heavy grinding and mixing in a mortar for 5 h. The produced nano- Fe_3O_4 DOP-TETA sorbent was heated to dryness in an oven at 60 °C.

Apparatus

A Philips X Pert-Pro diffracrometer (Hg Kα λ= 1.54060 A°, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized Fe_3O_4-encapsulated-DOP nano-sorbent.

Determination of Hg(II) in solutions were carried out by Perkin Elmer AAnalyst200 CVAAS equipped with deuterium background correction. All measurements were performed in an air/acetylene flame. GFL 3005 orbital shaker having speed and time control was used for preparation of the sorbent. During the solid phase extraction experiments, VelpScientifica SP311 peristaltic pump with Tygon tubes was used. A Thermo Orion 5 Star model pH meter, Heidolph MR 3001 K model magnetic stirrer, Sartorius TE214S electronic balance, Eppendorf Research micro pipettes were used for the present work. Funnel tipped glass tube (10x100 mm) equipped with stopcock was used as a column for the preconcentration experiments.

Preparation of Solid Phase

Sorption characteristics of Hg(II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of magnetic nano- Fe_3O_4-DOP-ED sorbent for extraction of Hg(II) ions was studied by the batch equilibrium technique under several experimental controlling factors. These include the effect of pH, contact time, sorbent dosage, initial metal ion concentration and interfering ions.

General procedure

100 mL solution with 50 ngmL^{-1} Hg content was prepared as a sample. This solution was added to the magnetic nano-Fe_3O_4-DOP-ED sorbent and by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25 min in order to allow easier Hg ions absorption of the nano- Fe_3O_4-DOP-ED sorbent (Tarigh and Shemirani, 2013). At the end of this stage, the nano-Fe_3O_4-DOP-ED sorbent which had been formed on the bottom layer of the beaker was removed through applying external field with1.4T magnetic powers and was immediately decanted outside the supernatant. 1 mL of 1 molL^{-1} ion of eluent was injected into CVAAS for measurement of Hg(II) ions concentrations.

RESULTS AND DISCUSSION

Surface morphology

Figs. 1a and b show the morphology and size of magnetic nano-Fe_3O_4-DOP-ED sorbent as shown in Figs. 1a and b. The particles of nano-Fe_3O_4-DOP-ED 339 sorbent retained a homogeneous distribution in the range of 340 5.0–20.0 nm.

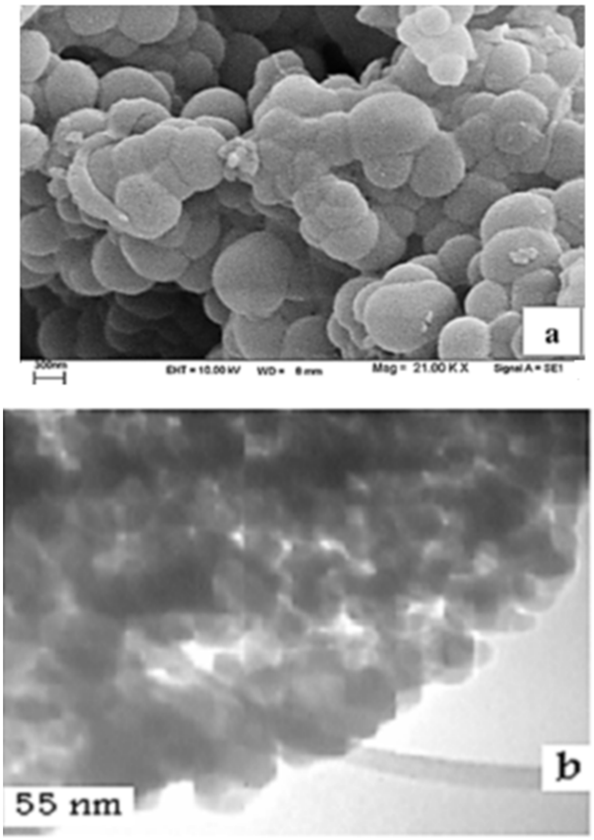

Fig. 1. Images of (a) Scanning Electron Microscopy (SEM) and (b) Transmission Electron Microscopy (TEM) of magnetic nano-Fe_3O_4-DOP-ED

Effect of pH

The pH of the sample solution plays an important role in retention of metals on sorbent. The pH of the model solutions containing 5μg Hg(II) were adjusted to certain value using diluted HNO_3 and NaOH. As shown

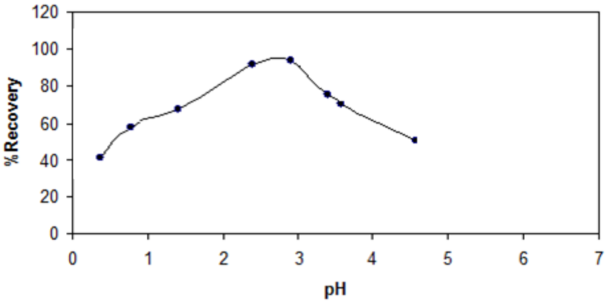

Fig. 2. Influence of sample pH and dissolving solvent of nano-Fe_3O_4-DOP-ED on the percentage recovery of Hg(II).

Table 1. Levels and the real values of factors utilized in CCD.

Factors	For sorption Levels -α	-1	0	+1	+α	Factors	For elution Levels -α	-1	0	+1	+α
pH	3.3	4	5	6	6.7	Flow rate (mL min^{-1})	2.3	3	4	5	5.7
Flow rate (mL min^{-1})	2.3	3	4	5	5.7	Eluent Concentration (mol L^{-1})	0.08	0.25	0.5	0.75	0.92
Sample volume (mL)	8.0	25	50	75	92.0	Eluent Volume	3.3	4	5	6	6.7

in Fig. 2, the recovery results were not dramatically affected by the change in pH between 4 and 7. According to this, pH= 3.0 were chosen as centre value for the optimization procedure.

Desorption reagent

0.5 mol L^{-1} of HNO$_3$, HCl, CH$_3$COOH, H$_2$SO$_4$ and H$_2$O$_2$ were tested for desorption of Hg(II) from nano-Fe$_3$O$_4$ -DOP- ED. The recovery percentages were varied between 5.7-87.9 % except HNO$_3$ elution experiments. It was observed that HNO$_3$ is the best as an eluent and the recovery percentage is 95.5±1.5 %.

Table 2. Experiments and recovery values for the sorption of Hg(II)

Run	X$_1$ pH	X$_2$ Flow rate (mL min^{-1})	X$_3$ Sample volume (mL)	Recovery (%)
1	4	3	25	99.1
2	6	3	25	102
3	4	5	25	98.6
4	6	5	25	101.4
5	4	3	75	99.6
6	6	5	75	99.4
7	4	5	75	105
8	6	5	75	98.6
9	5	4	50	102.4
10	3.3	4	50	96.6
11	6.7	4	50	97.1
12	5	2.3	50	102.7
13	5	5.7	50	98.4
14	5	4	8.0	101.6
15	5	4	92.0	99.0
16	5	4	50	99.8
17	5	4	50	101.5
18	5	4	50	98.8
19	5	4	50	101.0
20	5	4	50	99.7

Table 3. Experiments and recovery values for the elution of Hg(II)

Run	X$_1$ pH	X$_2$ Flow rate (mL min^{-1})	X$_3$ Sample volume (mL)	Recovery (%)
1	3	0.25	4	99.6
2	5	0.25	4	103
3	3	0.75	4	98.5
4	5	0.75	4	101.6
5	3	0.25	6	99.7
6	5	0.25	6	99.8
7	3	0.75	6	101.6
8	5	0.75	6	99.6
9	4	0.5	5	99.7
10	2.3	0.5	5	101.8
11	5.7	0.5	5	97.1
12	4	0.08	5	1007
13	4	0.92	5	98.8
14	4	0.5	3.3	101.7
15	4	0.5	5	99.8
16	4	0.5	5	99.1
17	4	0.5	5	101.1
18	4	0.5	5	98.4
19	4	0.5	5	100.5
20	4	0.5	5	99.0

Effect of flow rate on sorption and elution

The retention of a metal ion on the sorbent also depends on the flow rate of the sample solution. Thus, the both effect of flow rate of the sample and eluent on the sorption and desorption of Hg ions were investigated between 3-20 mL min^{-1}. Quantitative results (> 95%) were obtained up to 10 and 8 mL min^{-1} for

Table 4. Optimum preconcentration conditions for Hg(II) by nano- Fe3O4 -DOP- ED

Optical condition			
sorption		**elution**	
pH	2.9	Flow rate (mL min^{-1})	4.1
Flow rate (mL min^{-1})	4.3	Eluent concentration (mol L^{-1})	0.6
Sample volume (mL)	55	Eluent volume (mL)	5.1

sorption and elution, respectively. In order to avoid an abrupt change in adsorption and increase the contact time of the sample solution with the sorbent, flow rate was selected as 4 mL min^{-1} for sorption and elution.

Optimization of variables

Optimization of the preliminary studies was achieved by a three level full factorial CCD with 20 runs. Table 1 lists the maximum, minimum and centre values of the variables for sorption and elution. The metal concentration in solutions was determined with external standard calibration method by CVAAS. The experimental design matrix and the results for sorption and elution are given in Tables 2 and 3. Quadratic Eq. (1) and Eq. (2), which were obtained by using data of response values, are given below for sorption and elution, respectively.

$$Y = 0.512150 - 0.72565\ x_1 - 0.70169\ x_2 - 0.98326\ x_3 + +0.056583 x_1^2 +0.171215\ x_2^2 + 0.493058\ x_3^2 + 1.565734\ x_1x_2 + 1.5556039\ x_1x_3 +1.606564\ x_2x_3 \quad (1)$$

$$Y = 0.683345 - 0.018065\ x_1 - 1.220286\ x_2 - 0.130547\ x_3 + +0.576546\ x_1^2 +1.235334\ x_2^2 + 0.33238\ x_3^2 + 0.071217\ x_1x_2 + 0.06884\ x_1x_3 +0.07096\ x_2x_3 \quad (2)$$

x_1, x_2 and x_3 represents the 1st, 2nd and 3rd factors. Derivatives of the equations in terms of x_1, x_2 and x_3 were equalized to zero and solved using Microsoft® Excel. The real values presented in Table 4 obtained from CCD and used as optimal conditions for further experiments.

Interference effects

The preconcentration procedures of trace metal ions can be strongly affected by other ions. For this reason,

Table 5. Separation of Hg from binary mixtures [a]

Diverse ion	**Amounts taken (mg)**	**% Found**	**%Recovery of Hg^{2+} ion**
Na^+	92.4	1.15(2.4)[b]	98.7(1.8)
K^+	92.5	1.32(2.3)	98.5(2.9)
Mg^{2+}	14.5	0.7(1.2)	98.9(1.8)
Ca^{2+}	26.3	2.25(3.0)	98.5(1.6)
Sr^{2+}	2.45	2.85(2.5)	98.4(2.0)
Ba^{2+}	2.66	3.16(2.1)	98.3(2.3)
Mn^{2+}	2.66	1.75(2.2)	97.3(2.8)
Co^{2+}	2.16	1.4(2.3)	99.1(2.9)
Ni^{2+}	1.65	2.0(2.4)	98.5(2.6)
Zn^{2+}	2.78	1.97(2.1)	98.4(2.2)
Cd^{2+}	2.55	1.92.0)	98.2(2.8)
Pb^{2+}	0.54	2.7(1.9)	97(2.7)
Ag^+	2.63	3.45(2.9)	96.6(2.9)
Cr^{3+}	1.73	2.92(2.30	97.3(2.4)
UO^{2+}	2.84	2.8(2.1)	98.3(2.7)

[a] Initial samples contained 10µg Pb^{2+} and different amounts of various ions in 100 mL water (0.1 M acetate ion).

[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table 6. Analysis of standard reference material

pH	Certified value	Found value	Recovery%
CRM (TMDA-53.3)	118.0±5.5	125±8.6	98.8

Table 7. Recovery of Pb added to 1000mL of different water samples (containing 0.1Macetate at pH= 3.0).

Sample	Pb^{2+} added (μg)	Pb^{2+} determined ($ng.mL^{-1}$)	ICP-AES
Tap water	0.0	1.74(1.4)[a]	ND
	10.0	11.98(3.2)	11.7
Snow water	0.0	4.45(2.4)	ND
	10.0	14.97(2.0)	14.7
Rain water	0.0	2.65(2.3)	ND
	10.0	12.75(2.4)	12.3
Sea Water	0.0	12.64(2.3)	12.5
	10.0	22.93(2.0)	23.1

[a] Values in parentheses are %RSDs based on five individual replicate analysis

[b] Not detected

the effects of matrix ions were investigated under optimal conditions. The results revealed that the nano-Fe_3O_4-DOP-ED behaves as a neutral ionosphere in the pH range 3.0 (Moghimi, 2012, Moghimi, 2007) so that the Hg ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Hg(II) ions. The influence of the concentration of sodium acetate ion on Hg recovery was investigated, and the results are shown in Table 4.

As seen, the percent recovery of Hg^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative. Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.The tolerance limit of coexisting ions was given in Table 5.The experiments indicated that, no further sample treatment or masking reagents are needed.

Effect of sample volume

The preconcentration studies were applied to solutions within the range of 25-1000 mL containing 5 μg amount of Hg(II) to explore the possibility of enriching at low concentration with high enrichment factor. The recovery value was obtained as 98.7 % at 1000 mL sample volume by analysing 5 mL eluate and the highest preconcentration factor was found to be 200.

Analytical figures of merit

The accuracy and precision (RSD %) of the proposed solid phase extraction procedure underoptimal conditions were investigated (n= 10) as 102.0±0.2 % and 2, respectively. Limits of detection (LOD) and the limits of quantification (LOQ) were obtained by using a criterion signal-to-noise ratio of 3 and 10, respectively. The results were calculated 49.6 ng L^{-1} for LOD and 163.7 ng L^{-1} for LOQ.

Validation and application of the improved method

The developed procedure was validated by Hg (II) determination in certified reference material. The results are given in Table 6. A statistical evaluation was performed by Student's t test and t value was calculated as 2.95. Critical t value (4.30) is higher than the calculated one at 95 % confidence level. This test showed no significant difference between Hg(II) concentration obtained from the presented method and the certified value.

Table 8. Comparison with other solid phase adsorbents

Eluent	Preconcentration factor	Method	Chelating agent/solid phase adsorbent	References
7 mol L^{-1} HCl	200	CVAAS	Dithizone/microcrystalline naphthalene	(Moghimi and Shabanzadeh, 2012)
0.1 mol L^{-1} HNO_3	50	Atomic absorption spec-trophotometry	β-Naphthol/polyurethane foam	(Xie, *et al.,* 2008)
10 mol L^{-1} HCl	200	CVAAS	Dithizone/silica gel	(Goswami, *et al.,* 2003)
Tetraphenyl-borate	80	Anodic stripping voltammetry	HgI_4^{2-}-Aliquat-336/naphthalene	(Moghimi, 2012)
H_2SO_4 –H_2O_2 mixture	40	ICP-AES	DuoliteGT-73 resin	(Moghimi, 2007)
Water	5	CVAAS	Dithioacetal/SiO_2	(McAllister, *et al.,* 2007)
1 mol L^{-1} HBr	50	CVAAS	Hexathia18 crown-6 tetraone/Empore disk	(Pourreza, *et al.,* 2012)
1 mol L^{-1} HBr	100	CVAAS	1,5-Diphenylcarbazone/SDS coated alumina	(Ekinci Dogan and Akcin, 2007)
HNO_3	–	ICP-AES	1,5-Bis(2-pyridyl)-3-sulfophenylmethylene) thiocarbonohydrazide/Dowex anion exchange resin	(Moghimi, 2014)
6 mol L^{-1} HCl	50	CVAAS	4-(2-Pyridyl azo) resorcinol/nano-sized SiO_2	(Ghaedi, *et al.,* 2006)
2 mol L^{-1} HNO_3 in acetone	300	CVAAS	2-Mercaptobenzoxazole/chromosorb	(Ensafi, *et al.,* 2003)
HNO_3	200	CVAAS	nano- Fe_3O_4 -DOP- ED	Present work

Real sample analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Hg from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2015), Snow water (Varamin, 6 February, 2015) and Sea water (taken from Caspian Sea, near the Mahmoud-Abad shore) samples were analyzed (Table 7). As can be seen from Table 4 the added Hg ions can be quantitatively recovered from the water samples used. As is seen, the recovered Hg ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES (Table 7).

CONCLUSIONS

In the present study, a new sorbent is prepared by using nano-Fe_3O_4-DOP-ED and for preconcentration of Hg(II) from natural water samples. With nano-Fe_3O_4-DOP-ED was prepared easily and sorbed Hg(II) rapidly. The preconcentration parameters pH, flow rate and sample volume for sorption procedure was obtained by CCD as 5.2, 4.3 mL min^{-1}, 55.0 mL, respectively. Elution parameters, flow rate, eluent concentration and eluent volume were also obtained as 4.1 mL min^{-1}, 0.6 mol L^{-1} and 5.1 mL, respectively. Enrichment factor was found to be 200 when 1000 mL of water sample (included 5 µg) passed through the nano-Fe_3O_4-DOP-ED column. The interference effects of some ions were also investigated according to the improved method. The tolerance limits were between750-10,000 times greater as can be seen in Table 5. The mean recovery values for spiked water samples were satisfactory and confirmed the validity of the method. Additionally, mean %RSD value was 2 and showed that the precision of the method is quite good. Preconcentration factor, LOD, RSD, eluent type and concentration and detection technique of present work was compared with literature data in Table 8. In most cases, suggested method for Hg preconcentration with nano-Fe_3O_4-DOP-ED is comparable to, or better than, some of the previously reported nano-Fe_3O_4-DOP-ED based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, accurate and repeatable method for determination of Hg(II) after preconcentration. This new enrichment procedure can also be applied to some other metal ions.

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AUTHOR (S) BIOSKETCHES

Ali Moghimi, Associate Professor, Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran, *Email: alimoghimi@iauvaramin.ac.ir ; kamran9537@yahoo.com*