

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

Ali Moghimi^{1*}, Mohammad Yari²

¹Department of Chemistry, Islamic Azad University, Tehran Medical Branch, Tehran, Iran

²Department of Chemistry, Islamshahr Branch Islamic Azad University, Islamshahr, Iran

*Corresponding Author: Ali Moghimi, Department of Chemistry, Islamic Azad University, Tehran Medical Branch, Tehran, Iran, Email: alimoghimi@iauvaramin.ac.ir

ABSTRACT

A novel, simple, sensitive and effective method has been developed for Preconcentration of Mo (II) on magnetic nano-Fe₃O₄chitosan/graphene oxide solid-phase extraction adsorbent. A novel method applied a solid phase extraction (SPE) dispersive with magnetic nano-Fe₃O₄chitosan/graphene oxide sorbent was established for the Preconcentration of trace quantities of Mo (II) and was identified by flame atomic absorption spectrometry (FAAS). Some of the significant factors were nominated and optimized. Through the optimized circumstances the boundary of detection (LOD) and boundary of quantification (LOQ) were 49.6, 163.7 ng L⁻¹ and the offered method has a good reproducibility 0.90% (RSD %). The enrichment factor was 200 and the percentage of recovery was in the range of 97-100%. The technique was effectively used to for recovering the Mo (II) in several kinds of water samples.

Keywords: magnetic nano-Fe₃O₄chitosan/graphene oxide, Preconcentration, SPE, Preconcentration, FAAS, Mo (II)

INTRODUCTION

The properties of nanomagnetic particles research on their functionality as magnetic carrier (Leyden et al, 1976). Also in medical imaging uses such as magnetic resonance imaging (MRI) it commonly, generated from industrial processes including electroplating, smelting, battery manufacturing, mining, metallurgy, and refining (Leyden et al, 1976; Narin et al, 2000; Akama et al, 2000; Ohta et al, 2001; Cyclic et al, 1997; Moghimi et al, 2012).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan et al, 1997), filter paper (Leyden et al, 1975), cellulose (Gennaro et al, 1983) and ion exchange resins (Grote et al, 1985). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau et al, 1989). The surface of

silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek et al, 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al, 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger 1979). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud 1997; Mahmoud et al, 1997; Tong et al, 1990; Dadler et al, 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-

containing compounds are dithiocarbamate derivatives for selective extraction of Co(II) (Mahmoud 1998; Mahmoud 1999) and preconcentration of various cations (Leyden et al, 1976; Narin et al, 2000; Akama et al, 2000; Ohta et al, 2001; Cuculic et al, 1997; Moghimi et al, 2009; Thurman 1998; Pawliszyn 1997; Izatt et al, 1996; Hagen et al, 1990; Krueger 1995; Yamini et al, 1994; Shamsipur et al, 1999; Shamsipur et al, 2001; Brunner et al, 2003; Zelder et al, 2004; Boll et al, 2005; Moghimi et al, 2007; Moghimi, Chinese Journal of Chemistry 2007,25, 640; Moghimi, Chinese Journal of Chemistry 2007, 10, 1536; Moghimi, Environmental chemistry an Indian journal 2007) and 2-mercaptobenzo thiazol-modified silica gel for on-line preconcentration and separation of silver for atomic absorption spectrometric determinations (Qiao sheng et al, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova et al, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi et al, 2010). Sorption of Co (II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini et al, 2010) was also reported. 2-Amino-1-cyclopentene-1-dithio carboxylic acid (ACDA) for the extraction of silver(I), Co(II) and palladium(II) (Moghimi et al, 2009s), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin et al, 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros et al, 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin et al, 2000) are also sulfur containing silica gel phases.

In the present work, magnetic nano-Fe₃O₄/chitosan/graphene oxide was employed for production of solid phase. The synthesized and characterized new sorbent magnetic nano-Fe₃O₄/chitosan/graphene oxide was utilized for preconcentration of Mo (II) from water samples. Determination of Mo (II) concentration was achieved by GF-AAS after preconcentration procedure.

MATERIALS AND METHODS

Reagents and Chemicals

The analytical grade D.W. (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 Mo standard solution was prepared from Mo(NO₃)₂·4H₂O (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 1-ethyl-3-(3-dimethylaminopropyl) carbon diimide hydrochloride, chitosan and graphene oxide was purchased from BDH, UK. Mo nitrate, Mo (NO₃)₂, cadmium nitrate, Mo (NO₃)₂ and NiCl₂·6H₂O 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).

Apparatus

A Philips X Pert-Pro diffractometer (Mo K α λ =1.54060 Å, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized Fe₃O₄-encapsulated-DOP nano-sorbent. Determination of Mo(II) in solutions were carried out by Perkin Elmer Analyst 200 GF-AAS 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, Help Scientific a 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 enrichment experiments.

Preparation of Magnetic Nano-Fe₃O₄ Sorbent

The novel magnetic nano-iron oxide was first synthesized according to a previously reported method (Moghimi et al. 2019)... A 6.1 g sample of FeCl₃·6H₂O and 4.2 g FeSO₄·7H₂O 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 former black precipitate, nano-Fe₃O₄, was then washed several times with

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

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-Fe₃O₄-Encapsulated-Chitosan/Graphene Oxide Sorbent

Graphene oxide (0.1 g) dispersion was synthesised by solvating graphene oxide for 3 h in ultrapure water. A solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (0.05 M) and N-hydroxyl succinimide (0.05 M) was mixture to the graphene oxide dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of graphene oxide (Moghimi et. al.2019). The pH of the producing solution was maintained at 7.0 using dilute sodium hydroxide.

Magnetic chitosan (0.1g) and graphene oxide solution were mixture in a flask and dispersed in distilled water by ultrasonic dispersion for 20 min. After ultrasonic dispersion, the mixed solutions were stirred at 60 °C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7. Then, the obtained Synthesize collected by the aid of an adsorbent magnet and dried in a vacuum oven at 50 °C. The obtained product nano-Fe₃O₄-encapsulated-chitosan/graphene oxide (Moghimi et. al, 2019)

Preparation of Solid Phase

Adsorption characteristics of Mo (II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of magnetic nano-Fe₃O₄ chitosan/graphene oxide. Sorbent for

extraction of Mo (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, desorption of eluent, ion concentration and interfering ions and calibration curve.

General procedure

50 ngml⁻¹Mo (II) content was prepared as a 100 ml solution. This solution was added to the magnetic nano-Fe₃O₄-chitosan/graphene oxide sorbent. Absorption of the nano-Fe₃O₄- chitosan /graphene oxide sorbent by using buffer solution, its pH was modified to 3.0, followed the container was shaken for 25min in order to allow easier Mo (II) ions (Moghimi et. al. 2019).

At the end of this stage, thenano-Fe₃O₄-chitosan /graphene oxide sorbent which had been formed on the bottom layer of the beaker was removed through applying an external field with 2.0T magnetic powers and was immediately decanted outside the supernatant. Mo (II) ions determinate 1 ml of 1molL⁻¹ ion of eluent was injected into GF-AAS.

RESULTS AND DISCUSSION

Surface morphology

Figures 1a and b show the morphology and size of magnetic nano-Fe₃O₄-chitosan/graphene oxide sorbent as shown in Figures 1a and b. The particles of nano-Fe₃O₄-chitosan/graphene oxide 339 sorbent retained a homogenous distribution in the range of 340 5.0–20.0 nm.

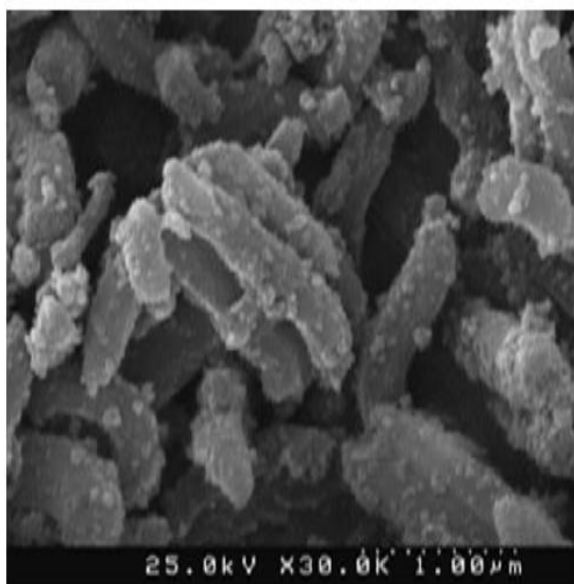
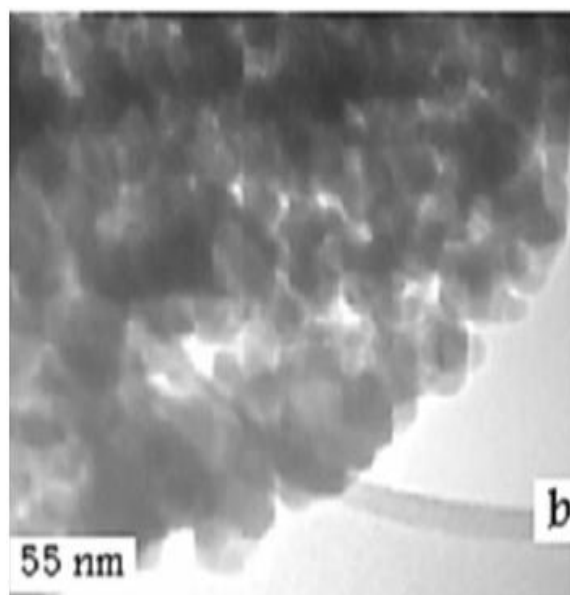


Figure1. (a) Images of (a) Scanning Electron Microscopy (SEM)



(b) Transmission Electron Microscopy (TEM) of nano-Fe₃O₄-chitosan/graphene oxide.

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

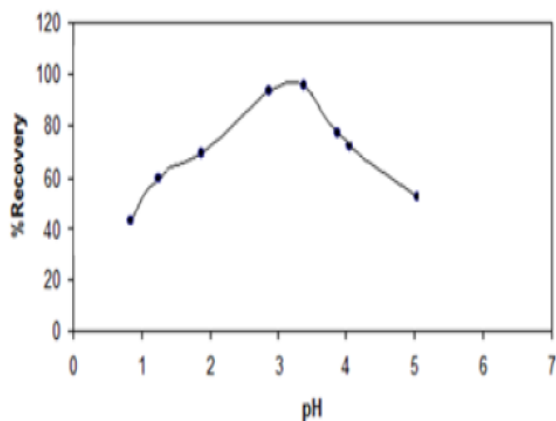


Figure 2. Influence of sample pH and dissolving solvent of nano- Fe₃O₄ -DOP- ED on the percentage recovery of Mo (II).

Effect of Ph

The pH of the sample solution plays important role in retention of metals on sorbent. The pH of the model solutions containing 5 μ g Mo (II) were adjusted to certain value using diluted HNO₃ and NaOH. As shown in Figure 2, the recovery results were not dramatically affected by the change in pH between 4 and 7. According to

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

Factors	For sorption Levels					Factors	For elution Levels				
	- α	-1	0	+1	+ α		- α	-1	0	+1	+ α
pH	3.5	4	5	6	6.5	Flow rate(mL min ⁻¹)	2.3	3	4	5	5.7
Flow rate(mL min ⁻¹)	2.3	3	4	5	5.5	Eluent Concentration(mol L ⁻¹)	0.08	0.25	0.5	0.75	0.92
Sample volume(mL)	8.0	25	50	75	91.4	Eluent Volume	3.3	4	5	6	6.7

Optimization of Variables

Three level full factorial CCD with 20 runs of Optimization and preliminary studies was achieved shows in Table 1. The maximum, minimum and centre values of the variables for sorption and elution. External standard calibration method by GF-AAS was determined the metal concentration

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

Run	X ₁ pH	X ₂ Flow rate(mL min ⁻¹)	X ₃ Sample volume (mL)	Recovery%
1	3	3	25	99.2
2	3.5	3	25	101
3	4	5	25	98.2
4	3.5	5	25	101.3
5	4	3	75	99.4
6	3.5	5	75	99.6
7	4	5	75	104
8	6	5	75	98.5
9	5	4	50	102.6
10	3.3	4	50	96.7
11	4	4	50	97.6
12	3.7	2.3	50	101.4
13	3.7	5.7	50	99.0
14	3.7	4	8.0	100.1

this, pH=3.5 were chosen as centre value for the optimization protocol.

Desorption Reagent

Desorption of Mo(II) were tested 0.5 mol L⁻¹ of HNO₃, HCl, CH₃COOH, H₂SO₄ and H₂O₂ for desorption of Mo(II) from nano- Fe₃O₄ -DOP- ED. The recovery percentages were varied between 9.8-97.4 % except HNO₃ elution experiments. It was showed that HNO₃ is the best as an eluent and the recovery percentage is 95.5 \pm 1.5 %.

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 Mo ions were investigated between 3-20 mL min⁻¹. Quantitative results (> 95%) were obtained up to 10 and 8 mL min⁻¹ for 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.

in solutions. Lists Tables 2 and 3 the experimental design matrix and the results for sorption and elution are given.

Quadratic Eq. (1) and Eq. (2), which were obtained by using data of response values, are showed below for sorption and elution, respectively.

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

15	3.7	4	92.0	99.2
16	3.7	4	50	99.8
17	3.7	4	50	101.0
18	3.7	4	50	98.9
19	3.7	4	50	100.0
20	3.7	4	50	99.8

Table3. Experiments and recovery values for the elution of Mo (II)

Run	X ₁ Flow rate (mLmi ⁻¹)	X ₂ Eluent Concentration (mol L ⁻¹)	X ₃ Eluent volume(mL)	Recovery%
1	3	0.25	4	99.2
2	5	0.25	4	101
3	3	0.75	4	98.6
4	5	0.75	4	100.6
5	3	0.25	6	98.9
6	5	0.25	6	98.9
7	3	0.75	6	100.7
8	5	0.75	6	99.5
9	4	0.5	5	99.5
10	2.3	0.5	5	101.5
11	5.7	0.5	5	97.5
12	4	0.08	5	1003
13	4	0.92	5	98.9
14	4	0.5	3.3	100.9
15	4	0.5	5	98.0
16	4	0.5	5	99.0
17	4	0.5	5	102.0
18	4	0.5	5	99.4
19	4	0.5	5	100.1
20	4	0.5	5	99.2

$$Y=0.512605-0.73420x_1-0.81067x_2-0.97620x_3+0.045582x_1^2+0.171280x_2^2+0.493038x_3^2+1.465720x_1x_2+1.4556159x_1x_3+1.306404x_2x_3 \quad (1)$$

$$Y=0.647745-0.018065x_1-1.241486x_2-0.121647x_3+0.565546x_1^2+1.224434x_2^2+0.33018x_3^2+0.72127x_1x_2+0.06768x_1x_3+0.07180x_2x_3(2)$$

x₁, x₂ and x₃ represents the 1st, 2nd and 3rd factors. Derivatives of the equations in terms of x₁, x₂ and x₃ 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 protocols of trace metal ions can be strongly affected by other ions. For this reason, the effects of matrix ions were researched under optimal conditions. The results revealed that the nano-Fe₃O₄-chitosan/graphene oxide behaves as a neutral ionosphere in the pH

range 3.0 [49, 50] so that the Mo ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the solid phase extraction of Mo (II) ions. The influence of the concentration of sodium acetate ion on Mo recovery was investigated, and the results are given in Table4.

As seen, the percent recovery of Mo²⁺ 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 solid phase extraction 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.

Table4. Optimum preconcentration conditions for Mo (II) by nano-Fe₃O₄-chitosan/graphene oxide

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

Fabrication of Magnetic Nano-Fe₃O₄/chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

Table 5. Separation of Mo from binary mixtures ^a

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Mo 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)
Hg ²⁺	0.44	2.81(2.1)	97.7(2.8)
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 Mo²⁺ and different amounts of various ions in 100 mL water (0.1M acetate ion). ^b Values in parentheses are RSDs based on five individual replicate analyses.

Effect of Sample Volume

The enrichment studies were applied to solutions within the range of 25-1000mL containing 5µg amount of Mo (II) to explore the possibility of enriching at low concentration with high enrichment factor. The recovery value was obtained as 99.8 % at 1000mL sample volume by analysing 5mL eluant and the highest Preconcentration factor was found to be 200.

Analytical Figures of Merit

Accuracy and Relative standard deviation (RSD, %) of the proposed solid phase extraction procedure under optimal conditions were investigated (*n*=5) as 101.0±0.2 % and 2, respectively. Limits of detection 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 49.6ng L⁻¹ for LOD and 163.7ng L⁻¹ for LOQ.

Validation and Application of the Improved Method

The developed procedure was validated by Mo (II) determination in certified reference material. The results are given in Table 6. A statistical evaluation was performed by Student's test and *t* value was calculated as 2.95.

Critical value (4.30) is higher than the calculated one at 95 % confidence level. This test showed no significant difference between Mo (II) concentration obtained from the presented method and the certified value.

Table 6. Analysis of standard reference material

pH	Certified Value	Found Value	Recovery%
CRM(TMDA-53.3)	105±5.0	102±0.2	99.8

Real Sample Analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Mo from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 25 January, 2016), Snow water (Varamin, 10 February, 2016) and Sea water (taken from Caspian Sea, near the Mahmoud-Abad shore) samples were analyzed (Table 7).

As can be showed from Table 4 the added Mo ions can be quantitatively recovered from the

water samples used. As is seen, the recovered Mo ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES (Tables 7). In the present study, a new sorbent is prepared by using nano-Fe₃O₄-chitosan/graphene oxide and for Preconcentration of Mo (II) from natural water samples. With nano-Fe₃O₄-chitosan/ graphene oxide was prepared easily and sorbed Mo (II) rapidly. The Preconcentration parameters pH, flow rate and sample volume for sorption procedure was obtained by CCD as 5.2, 4.3mL min⁻¹, 55.0 mL, respectively. Elution parameters, flow rate, eluent

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

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 100 mL of water sample (included 5 µg) passed through the nano-Fe₃O₄-chitosan/graphene oxide column.

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

Sample	Pb ²⁺ added (µg)	Pb ²⁺ determined (ng mL ⁻¹)	ICP-AES
Tap water	0.0	1.78 (3.0) ^a	ND
	10.0	11.68 (3.2)	11.2
Snow water	0.0	4.46 (2.2)	ND
	10.0	14.67 (2.2)	14.3
Rain water	0.0	2.56 (1.9)	ND
	10.0	12.65 (2.7)	12.4
Sea Water	0.0	12.65 (2.6)	12.4
	10.0	22.96 (2.5)	23.5

A Values in parentheses are % RSDs based on five individual replicate analysis, B Not detected

The interference effects of some ions were also researched according to the improved method. The tolerance limits were between 750-10,000 times greater are given 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 Mo enrichment with nano-Fe₃O₄-chitosan/graphene oxide is comparable to, or better than, some of the previously reported nano-Fe₃O₄-chitosan/graphene oxide based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, accurate and repeatable method for determination of Mo (II) after enrichment. This new enrichment procedure can also be applied to some other metal ions.

Table 8. Comparison with other solid phase adsorbents

References	Chelating agent/solid phase adsorbent	Method	Preconcentration factor	Eluent
Moghimi et al, 2012	Dithizone/microcrystalline naphthalene	FAAS	200	7 mol L ⁻¹ HCl
Narin et al, 2000	β-Naphthol/polyurethane foam	Atomic absorptionspectrophotometry	50	0.1 mol L ⁻¹ HNO ₃
Tuzen et al, 2009	Dithizone/silica gel	FAAS	200	10 mol L ⁻¹ HCl
Liu et al, 2010	HgI ₄ ²⁻ -Aliquat-336/naphthalene	Anodic stripping voltammetry	80	Tetraphenyl-borate
Moghimi, 2013	Duolite GT-73 resin	ICP-AES	40	H ₂ SO ₄ -H ₂ O ₂ mixture
Choi et al, 2003	Dithioacetal/SiO ₂	FAAS	5	Water
Tajodini et al 2010	2-ercaptobenzoxazole/chromosorb	FAAS	300	2 mol L ⁻¹ HNO ₃ in acetone
Present work	nano-Fe ₃ O ₄ -chitosan/graphene oxide	GF-AAS	200	HNO ₃

CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the dispersive solid phase extraction of trace amounts of Mo (II) in water samples using magnetic nano-Fe₃O₄chitosan/graphene oxide and its determination by FAAS.

The method developed was simple, reliable, and precise for determining Mo (II) in water. Also,

the proposed method was free of interference compared to conventional procedures to determine Mo (II) [51-57]. The method can be successfully applied to the separation and determination of Mo (II) in binary mixtures.

ACKNOWLEDGEMENTS

The author wish to thank the Chemistry department of Varamin branch Islamic Azad University for financial support

REFERENCES

- [1] Akama Y., Ito M., Tanaka S. (2000) (Selective separation of cadmium from cobalt, copper, iron (III) and zinc by water-based two-phase system of tetrabutylammonium bromide.), *Talanta* 52:645-651.
- [2] Alexandrova A., Arpadjan S. (1993) (Elimination of sulfide interference by sodium hypochlorite solution in the cold vapor atomic absorption spectrometric determination of mercury using tin (II) reduction in alkaline medium), *Analyst* 118:1309-1313.
- [3] Arpadjan S., Vuchkova L., Kostadinova E. (1997) (Study of the adsorption behavior of heavy metal ions on nanometer-size titanium dioxide with ICP-AES), *Analyst* 122: 243-250.
- [4] Boudreau S.P., Cooper W.T. (1989) (Analysis of thermally and chemically modified silica gels by heterogeneous gas-solid chromatography and infrared spectroscopy), *Anal. Chem.* 61: 41-47.
- [5] Boll, I., Kramer, R., Brunner, J.; Mokhir, A. (2005) (Oligonucleotide-Templated Reactions for Sensing Nucleic Acids,) *J. Am. Chem. Soc.* 27:7849-7855.
- [6] Brunner, J., Mokhir, A., Kramer, R. (2003) (Copper (II)-Quenched Oligonucleotide Probes for Fluorescent DNA Sensing), *J. Am. Chem. Soc.* 125:12410-12415.
- [7] Bruening M.L., Mitchell D.M., Bradshaw J.S., Izatt R.M., Bruening R.L. (1991) (Removal of cesium from alkaline waste solution: Part II – Column ion exchange study), *Anal. Chem.* 63 21-27.
- [8] Campderros M.E., Acosta A., Marchese J. (1998) (Selective separation of copper with Lix 864 in a hollow fiber module), *Talanta* 47:19-23.
- [9] Caroli C., Alimanti A., Petrucci F., Horvath Z. (1991) (Selective pre-concentration and solid phase extraction of mercury (II) from natural water by silica gel-loaded dithizone phases), *Anal. Chim. Acta.* 248: 241-247.
- [10] Choi, Y.S., Choi, H.S. (2003) (Studies on Solvent Sublimation of Trace Heavy Metals by Continuous Flow System as Ternary Complexes of 1, 10-Phenanthroline and Thiocyanate Ion), *Bull. Korean Chem. Soc.* 24:222-228.
- [11] Cuculic V., Mlakar M., Branica M. (1997) (Synergetic adsorption of copper (II) mixed ligand complexes onto the SEP-PAK C18 column), *Anal. Chim. Acta* 339:181-189.
- [12] Dadler V., Lindoy L.F., Sallin D., Schlaepfer C.W. (1987) (Selective pre-concentration and solid phase extraction of mercury (II) from natural water by silica gel-loaded dithizone phases), *Aust. J. Chem.* 40:1557-1563.
- [13] Gennaro M.C., Baiocchi C., Campi E., Mentasti E., Aruga R. (1983) (Undesirable and harmful metals in wines Determination and removal), *Anal. Chim. Acta* 151: 339-344.
- [14] Graf D, Molitor F, Ensslin K, Stampfer C, Jungen A, Hierold C. (2007), *Nano Lett.*, 7:238–42.
- [15] Grote M., Kettrup A. (1985) (Liquid-liquid extraction of noble metals by formazans: Analytical Applications of Silver Extraction by ortho-Substituted Formazans), *Anal. Chim. Acta* 175: 239-244.
- [16] Izatt R.M., Bradshaw J.S., Bruening R.L. (1996) (, *Pure Appl. Chem.* 68:1237-1242.
- [17] Jones J.S., Harrington D.E., Leone B.A., Bramstedt W.R. (1983) (Determination of trace elements in analytical-reagent grade sodium salts by atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry after preconcentration by column solid phase extraction), *Atom. Spectrosc.* 4: 49-57.
- [18] Hagen D.F., Markell C.G., Schmitt G.A. (1990) (Enhanced biosensor performance for on-site field analysis of explosives in water using solid-phase extraction membranes), *Anal. Chim. Acta* 236:157-163.
- [19] Harvey D., Clifford C. Hach (1950) "Bis (N, N'- Disalicylalethylenediamine)-μ - Aquodico balt (II)". In *org. Synth. Inorganic Syntheses* 3: 196–201.
- [20] Hummers W.S., Offeman RE., (1958), Preparation of graphitic oxide, *J. Am. Chem. Soc.*, 80 :1339-1344.
- [21] Kaiss .R., Waleed .F and Mohammed A., (2007) "Synthesis and Photolysis of Some
- [22] Transition Metal Complexes of Schiff Base Ligand Derived From Ethylene
- [23] Diamine and Salicylaldehyde", *J. of Al-Anbar university for pure science* 1 (1).
- [24] Krueger C.J., Fild J.A. (1995), (Method for the analysis of triadimefon and ethofumesate from dislodgeable foliar residues on turfgrass by solid-phase extraction and in-vial elution) *Anal. Chem.* 67: 3363-3369.
- [25] Kvitek R.J., Evans J.F., Carr P.W. (1982) (Denaturation of purple membranes at the air/water interface studied by SEM), *Anal. Chim. Acta* 144: 93-98.
- [26] Leyden D. E., Luttrell G.H., Nonidez W.K., Werho D.B. (1976) (Adsorption of Co(II) and Cu (II) on silica gel surface modified with pyridinium ion from acetone and ethanol solutions), *Anal. Chem.* 48:67-72.
- [27] Leyden D.E., Luttrell G.H., Sloan A.E., De Angelis N.J. (1976) (Automated separation and preconcentration of copper (II) from natural

Fabrication of Magnetic Nano-Fe₃O₄/chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

- waters using a column treatment), *Anal. Chim. Acta* 84: 97-102.
- [28] Leyden D.E., Luttrell G.H. (1975), *Anal. Chim.* 47:1612-1616.
- [29] Liu J., Wang Y., Xu S., & Sun D.D., (2010), Synthesis of graphene soluble in organic solvents by simultaneous ether-functionalization with octadecane groups and reduction *Materials Letters*, 64 :2236-2239.
- [30] Mahmoud M.E. (1997), (Silica gel-immobilized Eriochrome black-T as a potential solid phase extractor for zinc (II) and magnesium (II) from calcium (II)), *Talanta* 45: 309-314.
- [31] Mahmoud M.E. (1997) (Silica-immobilized formylsalicylic acid as a selective phase for the extraction of iron (III)), *Talanta* 44: 15-21.
- [32] Mahmoud M.E., Soliman E.M. (1997) (Study of the selective extraction of iron (III) by silica-immobilized 5-formyl-3-aryloxy-salicylic acid derivatives), *Talanta* 44:1063-1071.
- [33] Mahmoud M.E., in: Proceeding of the 25th FACSS Conference, Austin, TX, USA, and 11–15 October, 1998.
- [34] Mahmoud M.E. (1999), (Selective solid phase extraction of mercury (II) by silica gel-immobilized-dithiocarbamate derivatives), *Anal. Chim. Acta* 398: 297-302.
- [35] McAllister M.J., Abdala A.A., McAllister M.J., Aksay I.A., Prudhomme R.K., (2007), *Langmuir*, 23:10644–9.
- [36] Moghimi, A. Ghiasi R., Abedin A.R., Ghammamy S. (2009) (Solid phase extraction of Cd (II) using mesoporous organosilicas and determination by FAAS), *African Journal of Pure and Applied Chemistry*, 3 (3): 051-059.
- [37] Moghimi A., Tajodini, N. (2010) (Preconcentration of Copper (II) in Water Samples Using Polyurethane Foam/2-(6-Ethyl-2'-benzothiazolylazo) chromo tropic Acid), *Asian Journal of Chemistry*22 (5): 3325-3334.
- [38] Moghimi, A. (2006), *Oriental Journal of Chemistry*, 22(3):527-532.
- [39] Moghimi, A. (2007), (Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry), *Chinese Journal of Chemistry*, 25(10): 640-645.
- [40] Moghimi, A. (2008), (Preconcentration of Copper (II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry *Chinese Journal of Chemistry*), *Journal of the Korean Chemical Society* 52(2):155-163.
- [41] Moghimi, A., Ghammamy S. (2007), *Environmental chemistry an Indian journal*, 2(3).
- [42] Moghimi A., Tehrani M.S., Waqif Husain S. (2006) (Preconcentration and Determination of Copper (II) Using Octadecyl Silica Membrane Disks Modified by 1, 5-Diphenylcarbazide and Flame Atomic Absorption Spectrometry), *Material Science Research India* 3(1a): 27-32.
- [43] Moghimi, A., Abdouss M. (2012) Preconcentration of Ni (II) from sample water by modified poly (ethylene terephthalate)-grafted-acrylic acid/acryl amide fiber), *Afr. J. Pure Appl. Chem.* 6(8):110-118.
- [44] Moghimi, A., (2014). Separation and extraction of Co (II) using magnetic chitosan nano particles grafted with β -cyclodextrin and determination by FAAS, *Russ. J. Phys. Chem. A*, 88(12): 2157-2164.
- [45] Moghimi, A., (2013).Detection of trace amounts of Pb (II) by schiff base-chitosan-grafted multi walled carbon nano tubes, *Russ. J. Phys. Chem. A*, 87(7) (2013):1203–1209.
- [46] Moghimi A, Yari M, (2019). (Review of procedures involving separation and Solid Phase Extraction for the determination of cadmium using spectrometric techniques) *Journal of Chemical Reviews* 1 (1), 1-18.
- [47] Nambiar D.C., Patil N.N., Shinde V.M., (1998), (Liquid-liquid extraction of mercury (II) with triphenylphosphine sulphide: Application to medicinal and environmental samples), *Fresenius J. Anal. Chem.* 360: 205-212.
- [48] Narin I., Soylak M., Elic L., Dogan M. (2000),(An Evaluation of Loading Rate of Dust, Pb, Cd, and Ni and Metals Mass Concentration in the Settled Surface Dust in Domestic Houses and Factors Affecting Them), *Talanta* 52: 1041-1047.
- [49] Ohta K., Tanahasi H., Suzuki T., Kaneco S. (2001), (Preconcentration of trace copper with yeast for river water analysis), *Talanta* 53: 715-722.
- [50] Pawliszyn J. (1997), *Solid-Phase Micro extraction, Theory and Practice*, Wiley-VCH, New York.
- [51] Qiaosheng P., Qiaoyu S., Zhide H., Zhixing S. (1998), (Application of 2-mercaptobenzo thiazole self-assembled monolayer on polycrystalline gold electrode as a nano sensor for determination of Ag (I)) *Analyst* 123 :239-243.
- [52] Saitoh T., Matsuhima S., Hiraide M., (2004), *J. Chromatogr. A*, 1040:185-191.
- [53] Shamsipur M., Ghiasv and A.R., Yamini Y. (1999) (Synthesis of a New α -Dioxime Derivative and Its Application for Selective Homogeneous Liquid-Liquid Extraction of Cu (II) into a Micro droplet Followed by Direct GFAAS Determination), *Anal. Chem.* 71:4892-4897.
- [54] Shamsipur M., Ghiasv and A.R., Sharghi H. (2001) (Selective preconcentration of ultra trace

Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)

- copper (II) using Octadecyl silica membrane disks modified by a recently synthesized glyoxime derivative), *Int. J. Environ. Anal. Chem.* 82:23-29.
- [55] Shojai, M., Moghimi, A., Reza Asghari, R., (2015). Preconcentration of Pb (II) on Micro Crystalline Naphthalene Modified with Organic-Solution-Processable Functionalized-Nano Graphene, *Elixir Appl. Chem.*, 82: 32605-32609.
- [56] Takeshima, M., Yokoyama, T., Imamoto, M., Asaba, H. (1969), (Technetium labeling of bi, tri and tetra dentate legends derived from 2-aminocyclopentene-1-dithiocarboxylic acid: Characterization and bio distribution of their oxo and nitrido 99mtechnetium complexes), *J. Org. Chem.*, 34:730-735.
- [57] Taylor K.Z., Waddell D.S., Reiner E.J. (1995), (Application of Multi walled Carbon Nano tubes as a Solid Phase Extraction Sorbent for Chloro benzenes), *Anal. Chem.* 67; 1186-1192.
- [58] Tajodini, N, Moghimi A., *Asian Journal of Chemistry* (2010) (Preconcentration and Determination of Ultra Trace Cobalt(II) in Water Samples Using Co(II)-Imprinted Diazo amino benzene- Vinyl pyridine Copolymers) 22(5): 3335-3344
- [59] Thurman E.M., Mills M.S. (1998), *Solid-Phase Extraction, Principles and Practice*, Wiley, New York.
- [60] Tong A., Akama Y., Tanaka S. (1990), (Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay) *Anal. Chim. Acta* 230: 179-185.
- [61] Tuzen M., Soylak M., Citak D., Ferreira H.S., Korn M.G.A., Bezerra M.A., (2009), *J. Hazard. Mater.* 162:1041-1047. Unger K., *Porous Silica*, Elsevier, Amsterdam, 1979.
- [62] Yamini Y., Ashraf-Khorassani M. (1994), (Extraction and determination of linear alkyl benzene sulfonate detergents from the aquatic environment using a membrane disk and gas chromatography) *High Resolute J. Chromatogr* 17:634-639.
- [63] Zelder, F.H., Brunner, J., Kramer (2005) (Chemical control of bio molecular interaction modules), *R. Chem. Commun.*, 902-911.

Citation: Ali Moghimi, Mohammad Yari, "Fabrication of Magnetic Nano-Fe₃O₄chitosan/Graphene Oxide sorbents by New Method and Application in Solid Phase Extraction for Preconcentration of Mo (II)", *Research Journal of Nanoscience and Engineering*, vol 3 (3), pp.14-23, 2019.

Copyright: © 2019 Ali Moghimi, This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.