

Preconcentration of Cu(II) with magnetic nanocomposite sorbents prior to determination by Flame Atomic Absorption Spectrometer

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ABSTRACT: A simple, highly sensitive, accurate and selective method for determination of trace amounts of Cu²⁺ in water samples. In this paper, Chitosan was used to encapsulate nano-Fe₃O₄ and produce a nano-Fe₃O₄-CHITOSAN sorbent based new sorbent was prepared. This was treated with ethylenediamine (ED) in another solvent-free procedure for the formation of a novel nano-Fe₃O₄-Chitosan-ED. Flame atomic absorption spectrometer was utilized for determination of Cu(II). The analytical features for sorption were found to be 5.2; 4.3 mL min⁻¹, and 55.0 mL for pH, flow rate and sample volume, respectively. HNO₃ was used as eluent and maximum preconcentration factor was found to be 200. Elution parameters were also determined as 4 mL min⁻¹; 0.6 mol L⁻¹ and 5.1 mL for flow rate, eluent concentration and eluent volume, respectively. Limit of detection and limit of quantification were found to be 49.6 and 163.7 ng L⁻¹, respectively. Validation of the developed method was performed using certified reference material (TMDA-53.3). The methodology was applied for determination of Cu(II) in natural water samples and satisfactory results were obtained.

Keywords: Chitosan; Flame Atomic Absorption Spectrometer; Nano-Fe₃O₄-Chitosan; Preconcentration; Water

INTRODUCTION

Copper, at trace concentrations, acts as both a micronutrient and a toxicant in marine and fresh water systems (Leyden, *et al.*, 1976; Narin, *et al.*, 2000; Akama, *et al.*, 2000; Ohta, *et al.*, 2001; Cuculic, *et al.*, 1997; Moghimi, *et al.*, 2012). The direct determination of trace metals especially toxic metal ions such as Cu, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden, *et al.*, 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte

of interest (Jones, *et al.*, 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar, *et al.*, 1998; Caroli, *et al.*, 1991). The application of solid phase extraction technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova, *et al.*, 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic

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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 Cu(II) (Mahmoud, 1998, Mahmoud, 1999) and pre-concentration 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; Nayebi, *et al.*, 2006;

Moghimi, *et al.*, 2007; Moghimi, 2007) and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng, *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 Cu(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini, *et al.*, 2010) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), Cu(II) and palladium(II) (Moghimi, *et al.*, 2009), 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. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, nano-Fe₃O₄-Chitosan-ED. On the other hand, in terms of economy it is much cheaper than those in the market, like C18 SPE mini-column.

In the present work, nano-Fe₃O₄-Chitosan-ED was employed for production of solid phase. The synthesized and characterized new sorbent nano-Fe₃O₄-Chitosan-ED was utilized for preconcentration of Cu(II) from water samples. Determination of Cu(II) concentration was achieved by FAAS after preconcentration procedure.

EXPERIMENTAL

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 copper standard solution was prepared from Cu(NO₃)₂·4H₂O (Merck) and diluted as required to the µg L⁻¹ levels. BDH Limited, Poole, England. Chitosan, (purity > 99.55%), sodium hydroxide (NaOH) and ethylenediamine (ED) was purchased from BDH, UK. Lead nitrate, Pb(NO₃)₂, cadmium nitrate, Cd(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).

Synthesis of magnetic nano-Fe₃O₄ sorbent

The magnetic nano-iron oxide was first synthesized according to a previously reported method. 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 formed black precipitate, nano-Fe₃O₄, 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-Fe₃O₄-Chitosan sorbent

The magnetic Chitosan-graphen oxide nanocomposite was prepared by the addition of 20.0 mL of Chitosan to 10.0 g of nano-Fe₃O₄ sorbent. This mixture was heated under stirring at 80-90°C for 3 hours the product nano-Fe₃O₄-Chitosan 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 magnetic Chitosan-graphen oxide nanocomposite sorbent

A 10.0 g sample of nano-Fe₃O₄-Chitosan 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-Fe₃O₄ Chitosan-TETA sorbent was heated to dryness in an oven at 60°C.

Apparatus

A Philips X Pert-Pro diffractometer (Cu Kα λ=1.54060

Å, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized magnetic Chitosan-graphen oxide nanocomposite. Determination of Cu(II) in solutions were carried out by Perkin Elmer Analyst 200FAA Se 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, Velp-Scientifica 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 (10×100 mm) equipped with stopcock was used as a column for the preconcentration experiments.

Preparation of Solid Phase

Sorption characteristics of Cu(II) ions by magnetic nano-sorbents by the batch equilibrium technique. The applicability of magnetic Chitosan-graphen oxide nanocomposite sorbent for extraction of Cu(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 ng mL⁻¹ copper content was prepared as a sample. This solution was added to the magnetic magnetic Chitosan-graphen oxide nanocomposite 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 copper ions absorption of the magnetic Chitosan-graphen oxide nanocomposite sorbent (Tuzen, *et al.*, 2009). At the end of this stage, the magnetic Chitosan-graphen oxide nanocomposite sorbent which had been formed on the bottom layer of the beaker was removed through apply in an external field with 1.4 T magnetic powers was immediately decanted out side the supernatant. 1 mL of 1 mol L⁻¹ ion of eluent was injected into FAAS for measurement of Cu(II) ions concentrations.

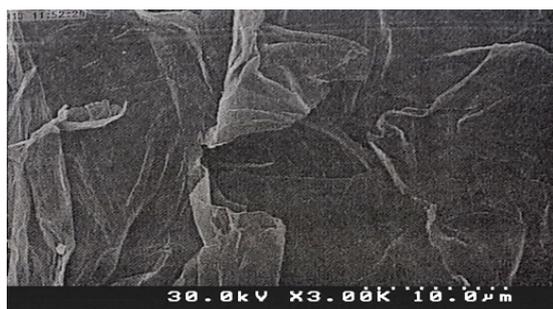


Fig. 1. Image of Scanning Electron Microscopy (SEM) of magnetic Chitosan-graphen oxide nanocomposite

RESULTS AND DISCUSSION

Surface morphology

Figs. 1a and b show the morphology and size of magnetic Chitosan-graphen oxide nanocomposite sorbent as shown in Fig. 1. The particles of magnetic Chitosan-graphen oxide nanocomposite 339 sorbent retained a homogenous distribution in the range of 340 5.0–20.0 nm.

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 Cu(II) were adjusted to certain value using diluted HNO₃ and NaOH. As shown 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 centred value for the optimization procedure.

Desorption reagent

0.5 mol L⁻¹ of HNO₃, HCl, CH₃COOH, H₂SO₄ and H₂O₂ were tested for desorption of Cu(II) from magnetic Chitosan-graphen oxide nanocomposite. The recovery percentages were varied between 5.7–87.9% except HNO₃ elution experiments. It was observed 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 copper ions were inves-

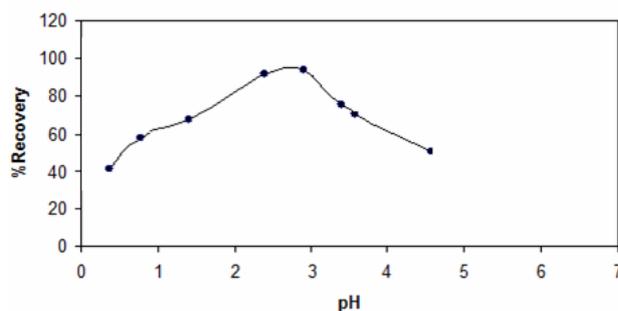


Fig. 2. Influence of sample pH and dissolving solvent of magnetic Chitosan-graphen oxide nanocomposite on the percentage recovery of Cu(II)

tigated 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.

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 centred values of the variables for sorption and elution. The metal concentration in solutions was determined with external standard calibration method by FAAS. The experimental design matrix and the results for sorption and elution are given in Table 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.

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

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

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.

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

Factors	For sorption levels					Factors	For elution levels				
	$-\alpha$	-1	0	+1	$+\alpha$		$-\alpha$	-1	0	+1	$+\alpha$
pH	3.0	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

Interference effects

The preconcentration procedures of trace metal ions can be strongly affected by other ions. For this reason, the effects of matrix ions were investigated under optimal conditions. The results revealed that the magnetic Chitosan-graphen oxide nanocomposite behaves as a neutral ionophore in the pH range 3.0 (Liu, *et al.*, 2010) so that the copper 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 Cu(II) ions. The influence of the concentration of so-

dium acetate ion on copper recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Cu²⁺ 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

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

Run	X ₁ Flow rate (mL min ⁻¹)	X ₂ Eluent Concentration (mol L ⁻¹)	X ₃ Eluent 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	100.7
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

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 Cu(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 analyzing 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 under optimal 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 Cu(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 value (4.30) is higher than the

Table 4. Optimum preconcentration conditions for Cu(II) by GO-H2P

Optical condition			
orption		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

Table 5. Separation of copper from binary mixtures ^a

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Cu 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 10 µg Cu²⁺ 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.

calculated one at 95% confidence level. This test showed no significant difference between Cu(II) concentration obtained from the presented method and the certified value.

Real sample analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water

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 copper added to 1000 mL of different water samples (containing 0.1 M acetate at pH= 3.0).

Sample	Cu ²⁺ added (µg)	Cu 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.

Table 8: Comparison of published results of several solid phase adsorbents methods for determination of Cu(II).

Ref.	LOD ($\mu\text{g/L}$)	RSD (%)	Sorbent	Technique
Narin <i>et al.</i> , 2009	9.5	-	Lanthanum hydroxide	FIA-AAS
Shojai <i>et al.</i> , 2015	20	2.9%	1,5-Diphenylcarbazine	FIA-AAS
Moghimi, 2014	49	2.5%	Titanic silicate	ICP-AES
Present work	0.049	0.21%	nano- Fe_3O_4 -Chitosan-ED	Several methods

(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 copper ions can be quantitatively recovered from the water samples used. As is seen, the recovered copper 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 magnetic Chitosan-graphen oxide nanocomposite and for preconcentration of Cu(II) from natural water samples. Magnetic Chitosan-graphen oxide nanocomposite was prepared easily and sorbed Cu(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 GO-H2P column. The interference effects of some ions were also investigated according to the improved method. The tolerance limits were between 750-10,000 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 Cu preconcentration with magnetic Chitosan-graphen oxide nanocomposite is comparable to, or better than, some of the previously reported magnetic Chitosan-graphen oxide nanocomposite based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, accurate and repeatable method for determination of Cu(II) after preconcentration. This new enrichment procedure can also be applied to some other metal ions.

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REFERENCES

- 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.
- 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.
- 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.
- 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.
- Boll, I., Kramer, R., Brunner, J.; Mokhir, A., (2005). Oligonucleotide-Templated Reactions for Sensing Nucleic Acids. *J. Am. Chem. Soc.*, 27:7849-7855.
- Brunner, J., Mokhir, A., Kramer, R., (2003). Copper(II)-Quenched Oligonucleotide Probes for Fluorescent DNA Sensing. *J. Am. Chem. Soc.*, 125:12410-12415.
- 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.
- Campderros, M.E., Acosta, A., Marchese, J., (1998). Selective separation of copper with Lix 864 in a hollow fiber module. *Talanta*, 47:19-23.
- 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.
- Choi, Y.S., Choi, H.S., (2003). Studies on Solvent Sublation 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.
- Cuculic, V., Mlakar, M., Branica, M., (1997). Synergistic adsorption of Copper(II) mixed ligand complexes onto the SEP-PAK C18 column. *Anal. Chim. Acta*, 339:181-189.
- 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.
- 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.
- Graf, D., Molitor, F., Ensslin, K., Stampfer, C., Jungen, A., Hierold, C., (2007). Spatially resolved Raman spectroscopy of single- and few-layer graphene. *Nano Lett.*, 7:238-42.
- 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.
- Izatt, R.M., Bradshaw, J.S., Bruening, R.L., (1996). Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic. *Pure Appl. Chem.*, 68:1237-1242.
- 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 pre-concentration by column solid phase extraction. *Atom. Spectrosc.*, 4: 49-57.
- 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.
- Harvey, D., Clifford, C., (1950). Bis(N,N'-Disicalyalethylenediamine)- μ -Aquadicobalt(II). *Inorg. Synth.*, 3: 196–201.
- Hummers, W.S., Offeman, R.E., (1958). Preparation of graphitic oxide. *J. Am. Chem. Soc.*, 80:1339-1344.
- Kaiss, R., Waleed, F., Mohammed, A., (2007). Synthesis and Photolysis of Some Transition Metal Complexes of Schiff Base Ligand Derived From Ethylene Diamine and Salicylaldehyde. *J. Al-Anbar univ. pure sci.*, 1 (1).
- 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.
- 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.
- 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.
- Leyden, D.E., Luttrell, G.H., Sloan, A.E., DeAngelis, N.J., (1976). Automated separation and precon-

- centration of Copper(II) from natural waters using a column treatment. *Anal. Chim. Acta*, 84: 97-102.
- Leyden, D.E., Luttrell, G.H., (1975). Comparison of chelating agents immobilized on glass with chelex 100 for removal and preconcentration of trace copper(II). *Anal. Chim.*, 47:1612-1616.
- 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. *Mater. Lett.*, 64:2236-2239.
- 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.
- Mahmoud, M.E., (1997). Silica-immobilized formyl-salicylic acid as a selective phase for the extraction of Iron(III). *Talanta*, 44: 15-21.
- 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.
- Mahmoud, M.E., (1998). in: *Proceeding of the 25th FACSS Conference, Austin, TX, USA, 11–15 October*.
- Mahmoud, M.E., (1999). Selective solid phase extraction of Mercury(II) by silica gel-immobilized-dithiocarbamate derivatives. *Anal. Chim. Acta*, 398: 297-302.
- McAllister, M.J., Abdala, A.A., McAllister, M.J., Ak-say, I.A., Prudhomme, R.K., (2007). *Langmuir*, 23:10644-9.
- Moghimi, A., Ghiasi, R., Abedin, A.R., Ghammamy, S., (2009). Solid phase extraction of Cd(II) using mesoporous organosilicas and determination by FAAS. *Afr. J. Pure Appl. Chem.*, 3 (3): 051-059.
- Moghimi, A., Tajodini, N., (2010). Preconcentration of Copper(II) in Water Samples Using Polyurethane Foam/2-(6'-Ethyl-2'-benzothiazolylazo) chromotropic Acid. *Asian J. Chem.*, 22(5): 3325-3334.
- Moghimi, A., (2006). Preconcentration and determination of Fe (III) using octadecyl silica membrane disks and flame atomic absorption spectrometry. *Orient. J. Chem.*, 22 (3): 527-532.
- Moghimi, A., (2007). Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry. *Chinese J. Chem.*, 25(10): 640-645.
- Moghimi, A., (2008). Preconcentration of Copper(II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry. *J. Korean Chem. Soc.*, 52(2):155-163.
- Moghimi, A., Ghammamy, S., (2007). *Environ. Chem. Indian J.*, 2 (3): 51.
- 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. *Mat. Sci. Res. India*, 3(1a): 27-32.
- Moghimi, A., Abdouss, M., (2012). Preconcentration of Ni(II) from sample water by modified poly (ethylene terephthalate)-grafted-acrylic acid/acrylamide fiber. *Afr. J. Pure Appl. Chem.*, 6(8):110-118.
- Moghimi, A., (2014). Separation and extraction of Co(II) using magnetic Chitosan nanoparticles grafted with β -cyclodextrin and determination by FAAS, *Russ. J. Phys. Chem. A*, 88(12): 2157-2164.
- 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.
- 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.
- Nayebi, P., Moghimi, A., (2006). Preconcentration and Determination of copper(II) by 1-(2-Pyridyl Azo)-2-Naphthol(PAN) modified Octadecyl Silica. *Orient. J. Chem.*, 22(3):507-512.
- Ohta, K., Tanahasi, H., Suzuki, T., Kaneco, S., (2001). Preconcentration of trace copper with yeast for river water analysis. *Talanta*, 53: 715-722.
- Pawliszyn, J., (1997). *Solid-Phase Microextraction, Theory and Practice*, Wiley-VCH, New York.
- Qiaosheng, P., Qiaoyu, S., Zhide, H., Zhixing, S.,

- (1998). Application of 2-mercaptobenzothiazole self-assembled monolayer on polycrystalline gold electrode as a nanosensor for determination of Ag(I). *Analyst*, 123:239-243.
- Saitoh, T.; Matsuhima, S.; Hiraide, M., (2004). Application of Self-Assembled System Based on Ionic Surfactants Adsorbed onto Oxides Surface in. *J. Chromatogr. A*, 1040: 185-191.
- Shamsipur, M., Ghiasvand, 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 Microdroplet Followed by Direct GFAAS Determination. *Anal. Chem.*, 71:4892-4897.
- Shamsipur, M., Ghiasvand, A.R., Sharghi, H., (2001). Selective preconcentration of ultra-trace Copper(II) using octadecyl silica membrane disks modified by a recently synthesized glyoxime derivative. *Int. J. Environ. Anal. Chem.*, 82:23-29.
- Shojai, M., Moghimi, A., 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.
- Takehima, M., Yokoyama, T., Imamoto, M., Asaba, H., (1969). Technetium labeling of bi, tri and tetradentate ligands derived from 2-aminocyclopentene-1-dithiocarboxylic acid: Characterization and biodistribution of their oxo and nitrido 99mtechnetium complexes. *J. Org. Chem.*, 34:730-735.
- Taylor, K.Z., Waddell, D.S., Reiner, E.J. (1995). Application of Multiwall Carbon Nanotubes as a Solid-Phase Extraction Sorbent for Chlorobenzenes. *Anal. Chem.*, 67: 1186-1192.
- Tajodini, N, Moghimi, A., (2010). Preconcentration and Determination of Ultra Trace Cobalt(II) in Water Samples Using Co(II)-Imprinted Diazoaminobenzene- Vinylpyridine Copolymers. *Asian J. Chem.*, 22(5): 3335-3344
- Thurman, E.M., Mills, M.S., (1998). *Solid-Phase Extraction, Principles and Practice*, Wiley, New York.
- Tong, A., Akama, Y., Tanaka, S., (1990) Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay. *Anal. Chim. Acta*, 230: 179-185.
- Tuzen, M., Soylak, M., Citak, D., Ferreira, H.S., Korn, M.G.A., Bezerra, M.A., (2009). A Preconcentration System for Determination of Copper and Nickel in Water and Food Samples Employing Flame Atomic Absorption Spectrometry. *J. Hazard. Mater.*, 162: 1041-1047.
- Unger, K., (1979). Porous silica: its properties and use as support in column liquid chromatography. *Elsevier, Amsterdam*, 16: 64-68.
- Yamini, Y., Ashraf-Khorassani, M., (1994). Extraction and determination of linear alkylbenzenesulfonate detergents from the aquatic environment using a membrane disk and gas chromatography) *High Resolut. J. Chromatogr.*, 17:634-639.
- Zelder, F.H., Brunner, J., (2005). Chemical control of biomolecular interaction modules. *R. Chem. Commun.*, 902-911.

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