

8-Hydroxyquinoline grafted nanoporous SBA-15 as a novel solid phase extractor for preconcentration of trace amount of Copper

Reza Arab¹, Leila Hajiaghababaei^{1,*}, Alireza Badiei², Mehdi Karimi²,
Mohammad Reza Ganjali³ and Ghodsi Mohammadi Ziarani⁴

¹ Department of Chemistry, Yadegar -e- Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran.

² School of Chemistry, College of Science, University of Tehran, Tehran, Iran.

³ Center of Excellence in Electrochemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran.

⁴ Department of Chemistry, Alzahra University, Tehran, Iran.

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Abstract

In this study, the potential of 8-Hydroxyquinoline grafted SBA-15 to extract of Cu²⁺ cations from aqueous solutions was investigated. SBA-15 nanoporous silica was chemically grafted with 8-Hydroxyquinoline groups according to the procedure in the literature. The presence of organic groups in the silica framework was demonstrated by FTIR spectrum. The grafted product showed the BET surface area 458 m²g⁻¹ and pore diameter 54 Å, based on adsorption-desorption of N₂ at 77 °K. Flame atomic absorption spectrometry was used to determination of the ions concentration in the recovery and sample solution. The effects of several variables (amount of adsorbent, stirring time, pH and the presence of other metals in the medium) were studied. Cu²⁺ ions were completely extracted at pH= 4.5-7 after stirring for 15 minutes. The maximum capacity of the adsorbent was found to be 31.25 mg of Cu²⁺ per each gram of 8-Hydroxyquinoline grafted SBA-15. The minimum amount of acid for stripping of ions from grafted SBA-15 was tested and the preconcentration factor of the method was found 50. Finally, the proposed method was successfully applied as a new solid extractor to preconcentration and determination of trace amounts of Cu²⁺ ions in spiked distilled and tap water samples.

Keywords: Cu²⁺; Flame Atomic Absorption Spectrometry; Grafted SBA-15; Preconcentration; Water Samples; 8-Hydroxyquinoline.

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INTRODUCTION

Direct analysis of trace elements in aqueous samples is a difficult task because of the low concentration levels of elements and the complex matrix which interferes with the determination. Therefore, in order to achieve accurate and reliable results, a preconcentration and matrix elimination step prior to instrumental measurements may be required [1-3]. Liquid-liquid extraction [4] and solid phase extraction [5, 6] are widely employed for preconcentration of trace amounts of these ions. The use of classical liquid-liquid extraction

method is usually time-consuming, labor-intensive and requires relatively large volumes of high purity solvents. Also, disposal of the utilized solvent can create a severe environmental problem. But, solid phase extraction is interested due to their simplicity, high concentration factor and low consumption of harmful organic solvents. Up to now, various solid phase extractor such as green tea leaves [7], silica gel [8-10], composites [11], silanized glass beads [12] and resin [13, 14] have been used. These materials have several problems like low mechanical and thermal stability and

* Corresponding Author Email: lhajiaghababaei@yahoo.com

weak chemical union with the metals. Recently, many researchers have been attracted into the nanomaterials. Nanostructure materials have some important physi-chemical properties which make them particularly attractive as extraction or separation media for various species [15-19]. A variety of functional groups can be grafted or incorporated on the large surface of nanomaterials to increase the affinity towards target compounds [20-25]. There are examples of the use of nanoporous materials for adsorption and preconcentration of metal ions [26-36]. However these examples are limited and further work needs to introduce the new solid phase extractors.

One of the trace elements is copper which require for the proper functioning of many important enzyme systems. Copper-containing enzymes include ceruloplasmin, cytochrome-c oxidase, tyrosinase, monoamine oxidase, lysyl oxidase and phenylalanine hydroxylase [37]. Therefore, copper is an essential element in body, but excess amount of copper is toxic. For example, Wilson disease is an autosomal recessive disorder that leads to copper toxicity because copper accumulates in the liver, brain and eyes [38]. Wilson disease affects the hepatic intracellular transport of copper and its subsequent inclusion into ceruloplasmin and bile. Thus, the determination of Cu^{2+} in water samples is warranted by the narrow window of concentration between essentially and toxicity.

Therefore, in this study, potential of 8-Hydroxyquinoline grafted SBA-15 nanoporous silica as a new adsorbent for simple and fast preconcentration of copper ions from environmental samples was examined.

EXPERIMENTAL PROCEDURES

Reagents

8-hydroxyquinoline (assay 99%) Hydrochloric acid 35% (ACS grade) and Pluronic P₁₂₃ ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Mac = ca. 5800) were purchased from Sigma-Aldrich (USA) and 3-piperazinepropyltriethoxysilane (PPTES, purity 99%) was purchased from Shondong wanda company (China). All the solvents including toluene (purity 99%), CH_2Cl_2 (grade 99.8%), ethanol (grade 99.9%) were obtained from Merck (Germany). All the above materials were used without any further purification. Analytical grade nitrate salts of sodium, potassium, manganese, magnesium, cobalt, nickel, zinc, cadmium, lead,

ferrous, chromium, silver and copper (all from Merck) were of the highest purity available and used without any further purification. Doubly distilled water (DDW) was used in all experiments. The stock solutions of the metal ions were 1000 mg L^{-1} solution in DDW and the working standard solutions were prepared by diluting them to the desired concentration.

Apparatus

Low-angle X-ray scattering measurements were performed on an X'Pert Pro MPD diffractometer using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). N_2 adsorption-desorption isotherms were obtained using BELSORP-minill instrument at liquid nitrogen temperature (-196 °C). All samples were degassed at 100 °C before performing measurements. The Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations were applied on sorption data using BELSORP analysis software to calculate physical properties of materials such as specific surface area, pore diameter, pore volume and pore size distribution. The Fourier transform infrared (FT-IR) spectra of samples were recorded on RAYLEIGH WQF-510A apparatus. Transmission electron microscopy (TEM) was performed on Zeiss EM900 instrument at an accelerating voltage of 80 kV. Samples were dispersed in ethanol using an ultrasonic bath and a drop of the ethanol mixture was placed on a lacey carbon-coated copper grid for analysis. Thermogravimetric analysis (TGA) was carried out in a TGA Q50 V6.3 Build 189 instrument in air atmosphere from ambient temperature to 800 °C with a ramp rate of 20 °C/min in air atmosphere. The quantitative analysis of the concentration of the species was performed through measuring the absorbance of the solutions on a PG-990 flame atomic absorption spectrometer (England PG Company), with hollow cathode lamps and an air-acetylene burner. The instrumental parameters were as follows: wavelength 324.7 nm, slit width: 0.4 nm and lamp current: 5.0 mA. Deuterium lamp background correction was also used. The FAAS determination of other cations was performed under the recommended conditions for each metal.

Synthesis of 8-Hydroxyquinoline grafted SBA-15

The detailed synthesizing procedure was previously reported [39]. In summary, in one container, 5-chloromethyl-8-hydroxyquinoline (yellow powder) was prepared by mixing given

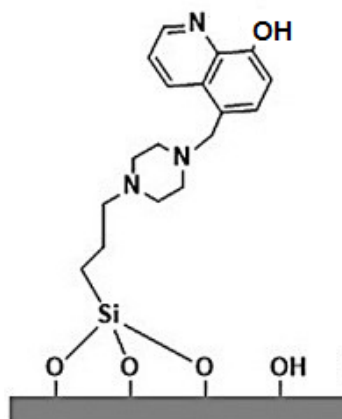


Fig. 1. Structure of 8-hydroxyquinoline grafted on SBA-15 (HQ-SBA-15).

amount of 8-hydroxyquinoline, HCl, formaldehyde under HCl gas flow at 0 °C for 5h. In another one, piperazine-functionalized SBA-15 (denoted as P-SBA-15) was prepared by mixing given amount of SBA-15, toluene and PPTES under Argon atmosphere for 6 h. Then, the resultants of two containers were mixed with triethylamine

and 5-chloromethyl-8-hydroxyquinoline in CH_2Cl_2 following reflux for 24 h resulting in 8-hydroxyquinoline grafted on SBA-15 (Fig. 1) (denoted as HQ-SBA-15).

Sample extraction procedure

The general extraction procedure using the HQ-SBA-15 involved adding 10 mg of HQ-SBA-15 to suitable volumes of 3 mg L^{-1} solution of Cu^{2+} and stirring the mixture for at least 15 min. Then, the adsorbent was filtered and the extracted ions were stripped using 40 mL of 4.0 mol L^{-1} solution of nitric acid into 40 mL volumetric flask. Finally, Cu^{2+} content in extracted and stripping solution was determined by FAAS.

RESULTS AND DISCUSSION

Characterization of HQ-SBA-15

The structure of SBA-15 and HQ-SBA-15 were confirmed by their XRD, N_2 adsorption-desorption, TEM and TGA data (Fig. 2). XRD patterns of the both materials (Fig. 2a) showed three diffractions, a single intense diffraction near $2\theta = 1$ indexed to (100) plane and two weak peaks near $2\theta = 2$

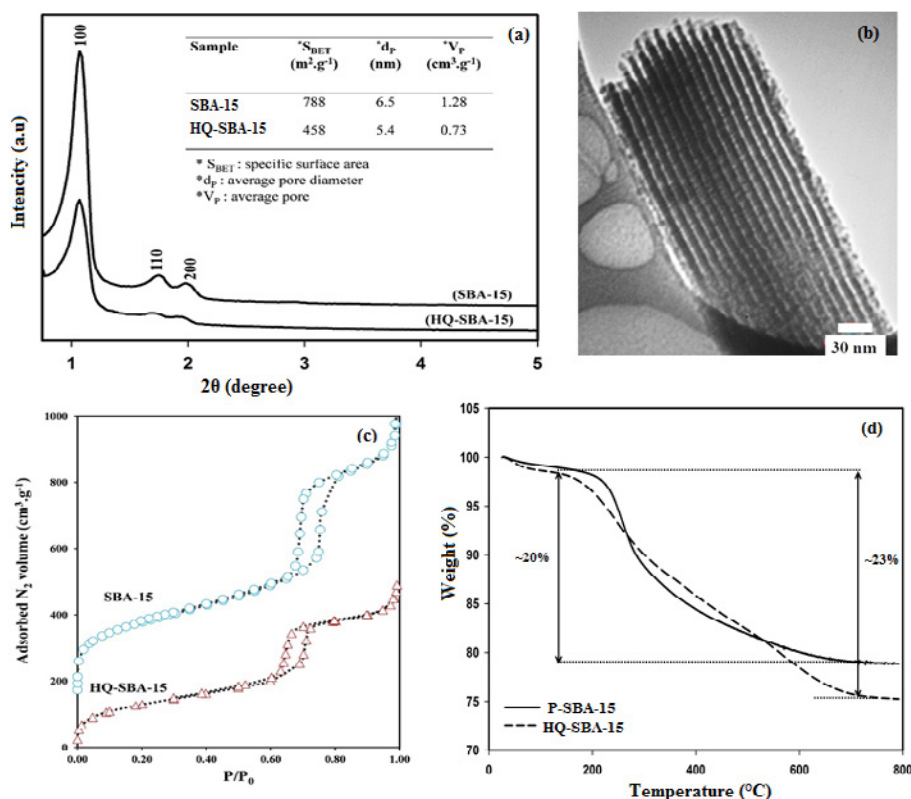


Fig. 2. a. XRD diffractions and textural parameters of SBA-15 and HQ-SBA-15, b. TEM images of SBA-15, c. N_2 adsorption-desorption isotherms of SBA-15 and HQ-SBA-15, and d. TGA curves of P-SBA-15 and HQ-SBA-15.

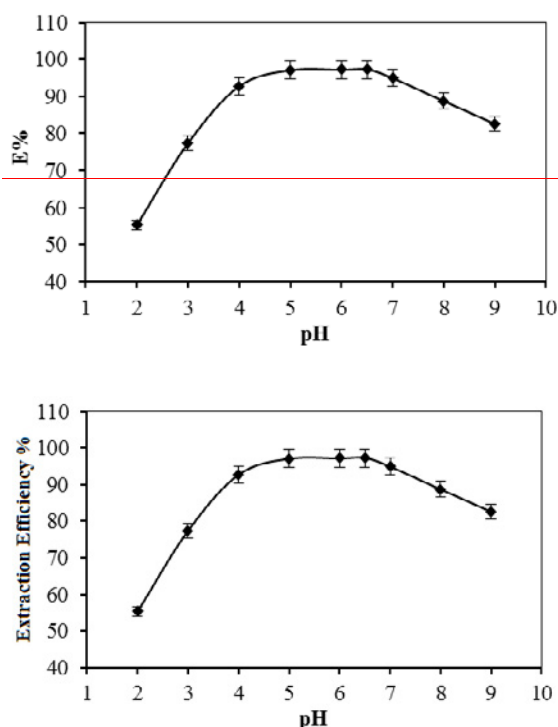


Fig. 3. Effect of pH on the percent of extraction of Cu²⁺ ions.

indexed to the (110) and (200) planes, implying the presence of a long – range periodic order and two – dimensional hexagonal (p6mm) mesostructures for the both materials [40]. TEM image of SBA-15 displayed two dimensional channels throughout the particle (Fig. 2b).

A type IV standard IUPAC isotherm (corresponded to the mesoporous materials) and H1 type hysteresis loop (characteristic of highly ordered structure) of the materials were confirmed by N₂ adsorption – desorption implying that the pores of original SBA-15 did not block after modification steps and the channels are still open (Fig. 2c) [41]. Specific surface area (S_{BET}), average pore diameter (d_p) and average pore volume (V_p) of SBA-15 and HQ-SBA-15 are given in the inset of Fig. 2a.

The attachment of the organic parts was confirmed by FT-IR spectra of the materials. The observed bands were as below: 1- bands located around 800, 960, 1100, 1640 and 3434 cm⁻¹ in both spectra assigned to the symmetric stretching vibrations of Si-O, symmetric stretching vibration of Si-OH, asymmetric stretching vibrations of Si-O-Si vibrations, physically absorbed water molecules and stretching vibrations of OH groups, respectively, 2- bands around 1415 and within

2865-2960 cm⁻¹ ranges were related to stretching vibrations of –CH₂– groups of propyl chain, 3- band corresponded to the phenolic OH appeared at 1376 cm⁻¹ and the bands corresponded to the aromatic C=C and C=N ring vibration of the attached 8-HQ group appeared at 1471, 1505 cm⁻¹ [42].

The amount of the attached piperazine ligand and 8-hydroxyquinoline to the surface of SBA-15 was estimated by TGA curves. Organic moieties were eliminated in the range of 150-700 °C [43] estimated to be ~20% for P-SBA-15 and 23% for HQ-SBA-15. 3% difference between the two percentages was related to the amount of grafted 8-hydroxyquinoline which estimated to be about 0.19 mmol.g⁻¹ (Fig. 2d).

The influence of the pH on the Cu²⁺ ions extraction efficiency

The pH is an important factor affecting the removal of metal ions from aqueous solutions. Effect of pH on metal sorption is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites. The extraction of the Cu²⁺ ions by the HQ-

SBA-15 adsorbents was evaluated at different pH values in the range of 2.0 to 9.0. The changes in the solution pH were created using 1 mol L⁻¹ solutions of nitric acid or sodium hydroxide. The results are shown in Fig. 3. As can be seen, Cu²⁺ can be extracted quantitatively by the HQ-SBA-15 in the pH range of 4.5 -7. It could be due to the charge-dipole interaction between metal ions and nitrogen atoms of HQ-SBA-15. But at higher acidic media (pH ≤ 4), the nitrogen atoms of the adsorbent could be protonated and reduces the stability of the complexes. The decrease in extraction efficiency above the pH value of 7.0 might be justified by the formation of the Cu²⁺ ion hydroxy complexes in the solution. Therefore, it was decided to use a pH value of about 4.5 -7 as a compromise for the extraction of Cu²⁺. Similar results have been observed in previous study on preconcentration of copper and other ions with aminobenzenesulfonamide functionalized SBA-15 [27], diethylenetriamine functionalized SBA-15 [28] and SBA-15 modified with 4-amino-5-hydrazino-1, 2, 4-triazole-3-thiol [45].

Optimization of HQ-SBA-15 amount

To determine the best amount of required HQ-SBA-15 for maximum extraction of Cu²⁺ ions, experiments were conducted using different amounts of the HQ-SBA-15. As it is seen from results in Fig.4., initially, the extraction efficiency of Cu²⁺ ions increased with the amount of the functionalized SBA-15 and finally, this reaches an almost constant value. This can be attributed to the higher number of the available adsorption sites with increasing of the adsorbent amount. Similar results have been observed in previous study on preconcentration of copper and other ions with functionalized mesoporous silica materials [27, 28, 36, 44]. The later extraction tests were carried out using the minimum optimal value of 10 mg of HQ-SBA-15 because Cu²⁺ can be extracted quantitatively using 10 mg of adsorbent.

The effect of the extraction time on extraction efficiency

The effect of time on the extraction efficiency was studied using a series of solutions containing

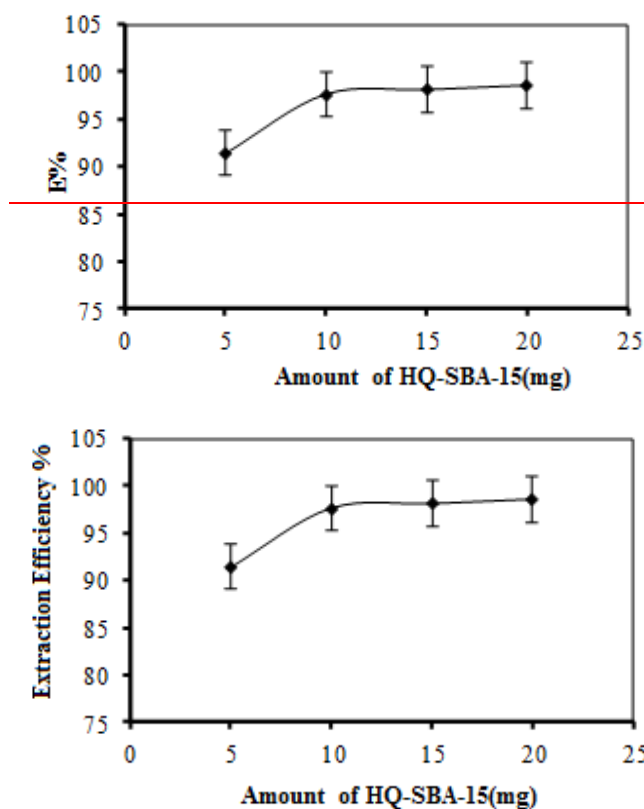


Fig. 4. Effect of amount of HQ-SBA-15 on the percent of extraction of Cu²⁺ ions.

75 μg of Cu^{2+} ions, and the results are presented in Fig. 5. It is easy to note that the extraction rapidly increases during the initial stage, but this trend lessens over time. The fast adsorption process could be attributed to the presence of numerous active sites on the HQ-SBA-15 and strong attraction forces between the active functional groups of the adsorbent and Cu^{2+} ions. These findings were consistent with previous study [27, 28, 44]. Based on the data, after 5 min more than 90% of the total Cu^{2+} content is extracted and after 15 min it reaches about 98%. In this light 15 min was chosen as the optimal contact time for further evaluations.

The effect of the volume of acid on the stripping of Cu^{2+}

Some experiments were carried out in order to choose a proper volume of nitric acid for the recovery of Cu^{2+} ions after extraction by the HQ-SBA-15. The ions were stripped with varying volumes of acid. Results showed (Fig. 6) that, 40 mL of 4.0 mol L^{-1} nitric acid solution can accomplish the quantitative elution of Cu^{2+} ions from the HQ-SBA-15.

Break through volume determination

The break through volume of the sample solution was studied by dissolving 75 μg of the Cu^{2+} ions in 250, 500, 1000 and 2000 mL of water, and the recommended procedure was followed. In all cases, the extraction by HQ-SBA-15 was found to be quantitative. Thus the break-through volume for the method should be greater than 2000 mL. As recovery of Cu^{2+} ions was done with 40 mL nitric acid, thus, preconcentration factor is 50.

Capacity of the HQ-SBA-15

The maximum capacity of HQ-SBA-15 was determined by adding adsorbent to 25 mL portions of an aqueous solution containing 2500 μg Cu^{2+} and stirring it for 15 minutes and passing the resulting mixture through a paper filter, followed by determination of the retained metal ions using FAAS. The maximum capacity was found to be $31.25 (\pm 1.7) \text{ mg Cu}^{2+}$ per gram of HQ-SBA-15.

Reusability of the adsorbent

Some experiments carried out in order to evaluate the reusability of the HQ-SBA-15. The adsorbent was used in some cycles of the

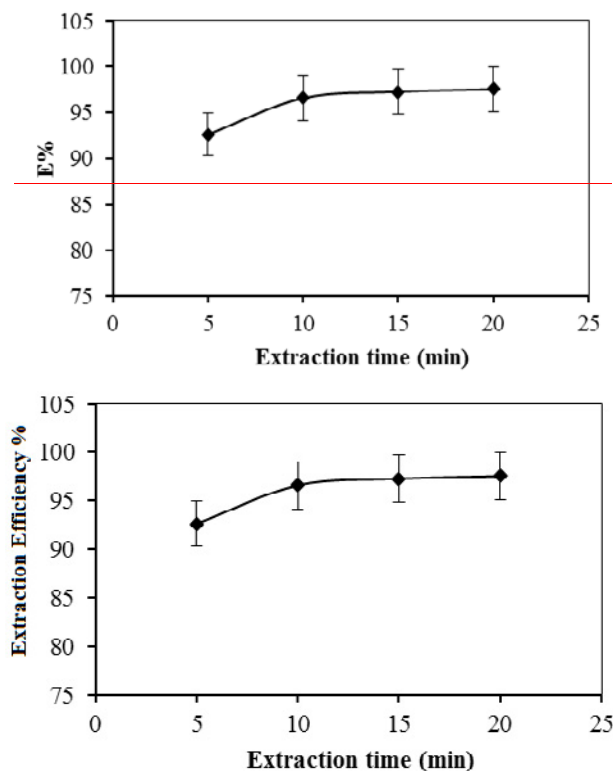


Fig. 5. Effect of extraction time on the percent of extraction of Cu^{2+} ions.



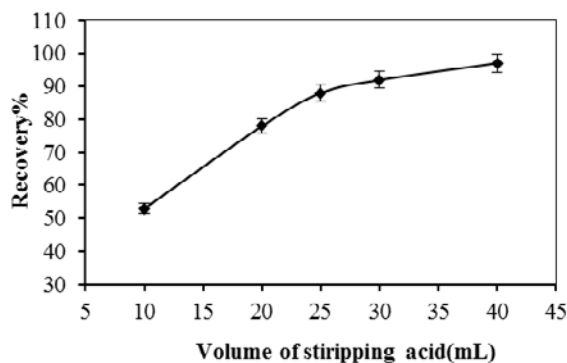


Fig. 6. Effect of volume of stripping acid on the percent of recovery of Cu²⁺ ions.

Table 1. Extraction of copper ions from binary mixtures^a

Divers ions	Amount taken(μg)	%Extraction of Cu ²⁺
K ⁺	2500	99.1 (1.2) ^b
Na ²⁺	2500	95.1 (0.8)
Mg ²⁺	2500	95.9 (1.0)
Ag ⁺	2500	95.4 (0.9)
Cr ³⁺	300	95.2 (0.9)
Pb ²⁺	2000	95.1 (1.5)
Co ²⁺	1500	95.3 (0.8)
Fe ²⁺	300	95.0 (0.9)
Ni ²⁺	2500	95.2 (1.1)
Cd ²⁺	2000	95.0 (0.9)
Zn ²⁺	2000	95.1 (1.3)
Mn ²⁺	2500	95.5 (1.2)

^a Initial samples contained 75μg copper ions in 25 ml water.

^b Values in parentheses are RSDs based on three replicate analysis.

adsorption/desorption process. The extraction efficiency of Cu²⁺ was more than 97.0% up to the fourth cycle and decreased slowly in the next cycles. Therefore, the results proved that the adsorbents could be used at least 4 times without considerable losses in their adsorption efficiency.

Preconcentration of Cu²⁺ ions in binary mixtures

In order to investigate the extraction of Cu²⁺ ions from water solutions containing diverse metal ions, an aliquot of aqueous solution (25 mL) containing 75 μg of Cu²⁺ ions and various amounts of other cations was taken and the recommended procedure was followed, and the results are shown in Table 1. As is obvious from Table 1, Cu²⁺ ions in all mixtures are retained completely by the HQ-SBA-15. High affinity of solid phase for Cu²⁺ ions is probably related to complexation reactions of copper as intermediate acid with the ligand's amine groups as intermediate bases.

Analytical characteristics of the method

The limit of detection, limit of quantitation, precision, accuracy, linear range and regression

equations were the parameters which were used for the method validation.

The limit of detection (LOD) for Cu²⁺ was determined by passing a blank solution through the HQ-SBA-15 under the optimal experimental conditions. The LOD obtained from $C_{LOD} = K_b S_b m^{-1}$ for a numerical factor $K_b = 3$, was 1.0 ng mL⁻¹. " S_b " is standard deviation of blank solution and " m " is the slope of calibration curve. The limit of quantitation, defined as ten times of the S values of blanks, was calculated as 3.3 ng mL⁻¹.

The parameters of the repeatability and reproducibility were investigated in order to assess the precision of the technique. For the repeatability monitoring, 4 replicate standards samples 20 ng mL⁻¹ of Cu²⁺ ion were measured. The Cu²⁺ mean concentrations were found to be 19.9 ng mL⁻¹ and with associated RSD% value of 2.1%.

Regarding the inter-day precision, the same three concentrations were measured for 3 consecutive days, providing mean Cu²⁺ concentrations was found 19.7 ng mL⁻¹ and associated RSD% values of 2.8%.

Certified multi element standard, Cat. No.

Table 2. Determination of copper ions in water samples^a

Samples	Added amount (ng mL ⁻¹)	Concentration of Cu ²⁺ (ng mL ⁻¹) in Distilled water	Concentration of Cu ²⁺ (ng mL ⁻¹) in Tap water
1	0	0.0	6.4 (1.3) ^b
2	20	20.1 (0.7)	26.2 (1.2)
3	30	30.6 (1.0)	35.8 (0.9)

^aCu²⁺ ions were added to 2000 mL water samples

^bRSD based on three replicate analysis

Table 3. Comparison of the proposed method with the previously reported Cu²⁺ ions determination methods using HQ-SBA-15

Adsorbent	Preconcentration Factor	Extraction time (min)	LOD (ng/mL)	pH	Ref.
Magnetically modified MCM-41/piperazine	33	10	0.25	----	31
SBA-15/Diphenyl Carbazon/ SDS	100	15	0.21	7-8	5
SBA-15/Diethylenetriamine	100	15	1.4	3-8	28
SBA-15/8-Hydroxyquinoline	50	15	1.0	4.5-7	This work

90243 (Ag, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, Sr, Zn: 10 mg L⁻¹ each, Al, B, Cr, Li, Mo, Na, Ni, Ti: 50 mg L⁻¹ each, Bi, K, Pb: 100 mg L⁻¹ each) from Sigma–Aldrich was used as certified reference material. The proposed extraction procedure was carried out on the certified reference material. The accuracy of the method was calculated to be 3.1%.

The calibration graph was linear in the range 3-80 ng mL⁻¹ Cu²⁺ under the optimum conditions of the general procedure. The regression equations for Cu²⁺ determination was $A=2.415C+0.0374$ ($R^2=0.997$), where A is the absorbance and C is the metal concentration in solution (ng mL⁻¹).

Application to real sample

To assess the applicability of proposed method in real samples an attempt was made to determine of Cu²⁺ in various water types including spiked distilled water and tap water of Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch. To 2000 mL of the some sample solutions 40 and 60 µg of Cu²⁺ ions were added and to some of the solutions were added nothing. The recommended procedure was followed for all solutions. As shown in Table 2, a good agreement was obtained between the added and measured amount of Cu²⁺ in spiked samples that indicates the capability of the method for the preconcentration and the determination of Cu²⁺ ions in various water types.

Comparison of the proposed method with the previously reported Cu²⁺ ions retention methods using modified SBA-15

In order to verify the capability of the

presented method, it was compared with comparable studies reported earlier which are outlined in Table 3. As is obvious, the results clearly indicate that the present study can afford satisfactory pH ranges, acceptable detection limit, fast extraction time and also high preconcentration factor [5, 28, 31]. Mesoporous materials offer a significantly high surface area to volume ratio, which results in rapid extraction and high extraction efficiencies.

CONCLUSION

The main objective of the present research is development of simple, fast and practically useful preconcentration technique to determination of trace amount of Cu²⁺ ions in water samples. Therefore, HQ-SBA-15 nanoporous silica as a new solid extractor for the preconcentration of Cu²⁺ ions was successfully applied. The enrichment factor of the proposed method was 50 and the maximum capacity the HQ-SBA-15 was found to be 31.25 (±0.94) mg of Cu²⁺ per each gram of adsorbent. The proposed method was applied for determination of ultratrace amounts of Cu²⁺ ions in drinking water. The major advantage of the present extraction procedure are very short sample processing time, reduced channeling results and low consuming of harmful organic solvents.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests.

REFERENCES

1. Soylak M., Unsul Y. E., (2010), Chromium and iron determinations in food and herbal plant samples by atomic absorption spectrometry after solid phase extraction on single-walled carbon nanotubes (SWCNTs) disk. *Food Chem. Toxicol.* 48: 1511-1515.
2. Anthemidis A. N., Adam I. S. I., Zachariadis G. A., (2010), Poly (Etheretherketone)-turnings a novel sorbent material for lead determination by flow injection flame atomic absorption spectrometry and factorial design optimization. *Talanta.* 81: 996-1002.
3. Stafiej A., Pyrzynska K., (2008), Solid Phase Extraction of Metal Ions Using Carbon Nanotubes. *Microchem. J.* 89: 29-33.
4. Zolotor Y. A., Kuzmin N. M., Pertukhim O. M., Spirakov B. Y., (1986), Liquid-liquid extraction in inorganic analysis: current status and prospects. *Anal. Chim. Acta.* 180: 137-161.
5. Mirabi A., Shokuhi Rad A., Divsalar F., Karimi-Maleh H., (2017), Application of SBA-15/diphenyl carbazon/SDS nanocomposite as solid phase extractor for simultaneous determination of Cu (II) and Zn (II) ions. *Arab. J. for Sci. Eng.* 43: 3547-3556.
6. Hajiaghababaei L., Tajmiri T., Badiei A., Ganjali M. R., Khaniani Y., Mohammadi Ziarani G., (2013), Heavy metals determination in water and food samples after preconcentration by a new nanoporous adsorbent. *Food Chem.* 141: 1916-1922.
7. Kimura M., Yamashita H., Komada J., (1986), Use of green tea as an adsorbent of several metal ions in water. *Bunseki Kagaku.* 35: 400-405.
8. Kubota M., Matseemoto K., Terada K., (1987), Preconcentration of silver (I) with 2-mercaptobenzothiazole loaded silica gel. *Anal. Sci.* 3: 45-48.
9. Zou X., Cui Y., Chang X., Zhu X., Hu Z., Yang D., (2009), **Silica gel surface modified with sulfanilamide for selective solid-phase extraction of Cu(II), Zn(II) and Ni(II).** *Int. J. Environ. An. Ch.* 89: 1043-1055.
10. Soliman E. M., Mahmoud M. E., Ahmed S. A., (2002), Reactivity of Thioglycolic Acid Physically and Chemically Bound to Silica Gel as New Selective Solid Phase Extractors for Removal of Heavy Metal Ions From Natural Water Samples. *Int. J. Environ. An. Ch.* 82: 403-413.
11. Mohammadi M., Sedighi M., Alimohammadi V., (2019), Modeling and optimization of Nitrate and total Iron removal from wastewater by TiO₂/SiO₂ nanocomposites. *Int. J. Nano Dimens.* 10: 195-208.
12. Taguchi S., Yai T., Shimada Y., Goto K., Hara M., (1983), Simultaneous determination of several trace metals by asv after preconcentration by adsorption as padap complexes on C(18)-bonded glass beads. *Talanta.* 30: 169-172.
13. Khan A. S., Chow A., (1986), Sorption of silver, gold and palladium with a polythioether foam. *Talanta.* 33: 182-184.
14. Aydin F. A., Soylak M., (2010), Separation, preconcentration and inductively coupled plasma-mass spectrometric (ICP-MS) determination of thorium(IV), titanium(IV), iron(III), lead(II) and chromium(III) on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin. *J. Hazard. Mater.* 173: 669-674.
15. Sadegh H., Shahryari Ghoshekandi R., Masjedi A., Mahmoodi Z., Kazemi M., (2016), A review on Carbon nanotubes adsorbents for the removal of pollutants from aqueous solutions. *Int. J. Nano Dimens.* 7: 109-120.
16. Khadami R., Alizadeh A., Saeb K., (2014), Synthesis and application of modified magnetic nanoparticles for removal of Cyanide from aqueous solutions. *Int. J. Nano Dimens.* 5: 241-246.
17. Shirsath D. S., Patil B. N., Shirivastava V. S., (2013), Rapid removal of metals from aqueous solution by magnetic nanoadsorbent: A kinetic study. *Int. J. Nano Dimens.* 3: 303-312.
18. Zargarlollahi H., Ghafourian H., (2014), Separation of heavy metal Nickel (II) using a new nano adsorbent ring GZ-BAKI-TAC-Ni-88 from Ni contaminated Water using beshel tire activated Carbon. *Int. J. Nano Dimens.* 5: 197-202.
19. Habibpour R., Vaziri R., (2016), Investigation of structural and electronic properties of small Au n Cu m (n+m≤5) nano-clusters for Oxygen adsorption. *Int. J. Nano Dimens.* 7: 208-224.
20. Maa X., Wanga Y., Gaoa M., Xua H., Li G., (2010), A novel strategy to prepare ZnO/PbS heterostructured functional nanocomposite utilizing the surface adsorption property of ZnO nanosheets. *Catal. Today.* 158: 459-463.
21. Hajiaghababaei L., Badaei A., Ganjali M. R., Heydari S., Khaniani Y., Mohammadi Ziarani G., (2011), Highly efficient removal and preconcentration of lead and cadmium cations from water and wastewater samples using ethylenediamine functionalized SBA-15. *Desalination.* 266: 182-187.
22. Habibi S., Hajiaghababaei L., Badiei A., Yadavi M., Dehghan Abkenar S., Ganjali M. R., Mohammadi Ziarani G., (2017), Removal of Reactive Black 5 from water using carboxylic acid-grafted SBA-15 nanorods. *Desalin. Water Treat.* 95: 333-341.
23. Hajiaghababaei L., Abozari S., Badiei A., Zarabadi Poor P., Dehghan Abkenar S., Ganjali M. R., Mohammadi Ziarani G., (2017), Amino Ethyl-Functionalized SBA-15: A Promising Adsorbent for Anionic and Cationic Dyes Removal. *Iran. J. Chem. Chem. Eng.* 36: 97-108.
24. Kavosi A., Faridbod F., Ganjali M. R., (2015), Solid Phase Extraction of Some Lanthanide Ions by Functionalized SBA-15 from Environmental Samples. *Int. J. Environ. Res.* 9: 247-254.
25. Dolatyari L., Yaftian M. R., Rostamnia S., Seyeddorrajji M. R., (2017), Multivariate Optimization of a Functionalized SBA-15 Mesoporous Based Solid-Phase Extraction for U(VI) Determination in Water Samples. *Anal. Sci.* 33: 769-776.
26. Lam K. F., Yeung K. L., Mckay J., (2007), Selective mesoporous adsorbents for Cr O²⁻ and Cu separation. *Micropor. Mesopor. Mater.* 100: 191-201.
27. Hajiaghababaei L., Ghasemi B., Badiei A., Goldoos H., Ganjali M. R., Mohammadi Ziarani G., (2012), Aminobenzenesulfonamide functionalized SBA-15 nanoporous molecular sieve: A new and promising adsorbent for preconcentration of lead and copper ions. *J. Environ. Sci.* 24: 1347-1354.
28. Hajiaghababaei L., Badiei A., Shojaan M., Ganjali M. R., Mohammadi Ziarani G., Zarabadi-Poor P., (2012), A novel method for the simple and simultaneous preconcentration of Pb²⁺, Cu²⁺ and Zn²⁺ ions with aid of diethylenetriamine

- functionalized SBA-15 nanoporous silica compound. *Int. J. Environ. An. Ch.* 92: 1352-1364.
29. Lee B., Kim Y., Lee H., Yi J., (2001), Synthesis of functionalized porous silicas via templating method as heavy metal ion adsorbents: the introduction of surface hydrophilicity onto the surface of adsorbents. *Micropor. Mesopor. Mat.* 50: 77-90.
 30. El-Nahhal I. M., Chehimi M., Selmane M., (2017), Synthesis and Structural Characterization of G-SBA-IDA, G-SBA-EDTA and G-SBA-DTPA Modified Mesoporous SBA-15 Silica and Their Application for Removal of Toxic Metal Ions Pollutants. *Silicon.* 3: 981-993.
 31. Kanani N., Bayat M., Shemirani F., Ghasemi J. B., Bahrami Z., Badiei A., (2017), Synthesis of magnetically modified mesoporous nanoparticles and their application in simultaneous determination of Pb(II), Cd(II) and Cu(II). *Res. Chem. Intermed.* 3: 1689-1709.
 32. Bibby A., Mercier L., (2002), Mercury(II) Ion Adsorption Behavior in Thiol-Functionalized Mesoporous Silica Microspheres. *Chem. Mater.* 14: 1591-1597.
 33. Ganjali M. R., Hajiaghababaei L., Badaei A. R., Saberyan K., Salavati-Niasari M., Mohammadi Ziarani G., Behbahani S. M. R., (2006), A novel method for fast enrichment and monitoring of hexavalent and trivalent chromium at the ppt level with modified silica mcm-41 and its determination by inductively coupled plasma optical emission spectrometry. *Quim. Nova.* 29: 440-443.
 34. Ganjali M. R., Hajiaghababaei L., Norouzi P., Pourjavid M. R., Badaei A. R., Saberyan K., Ghannadi maragheh M., Salavati-Niasari M., Mohammadi Ziarani G., (2005), Novel Method for the Fast Separation and Purification of Molybdenum(VI) from Fission Products of Uranium with Aminofunctionalized Mesoporous Molecular Sieves (AMMS) Modified by Dicyclohexyl-18-Crown-6 and S-N Tetradentate Schiff's Base. *Anal. Lett.* 38: 1813-1821.
 35. Ganjali M. R., Daftari A., Hajiaghababaei L., Badaei A. R., Saberyan K., Mohammadi Ziarani G., Moghimi A., (2005), Pico level monitoring of silver with modified hexagonal mesoporous compound (mcm-41) and inductively coupled plasma atomic emission spectrometry. *Water Air Soil Poll.* 173: 71-80.
 36. Ganjali M. R., Hajiaghababaei L., Badaei, A. R., Mohammadi Ziarani G., Tarlani A., (2004), Novel method for the fast preconcentration and monitoring of a ppt level of lead and copper with a modified hexagonal mesoporous silica compound and inductively coupled plasma atomic emission spectrometry. *Anal. Sci.* 20: 725-729.
 37. Linder M. C., Hazeigh-Azam M., (1996), Copper biochemistry and molecular biology. *Am. J. Clin. Nutr.* 63: 797S-811S.
 38. Harris Z. L., Gitlin J., (1996), Genetic and molecular basis for copper toxicity. *Am. J. Clin. Nutr.* 63: 836S-841S.
 39. Karimi M., Badieia A., Mohammadi Ziarani G., (2016), Fluorescence-enhanced optical sensor for detection of Al³⁺ in water based on functionalised nanoporous silica type SBA-15. *In Chem. Papers.* 70: 1431-1438.
 40. Karimi M., Badiei A., Mohammadi Ziarani G., (2015), A single hybrid optical sensor based on nanoporous silica type SBA-15 for detection of Pb²⁺ and I⁻ in aqueous media. *RSC Advances.* 5: 36530-36539.
 41. Karimi M., Badiei A., Mohammadi Ziarani G., (2016), A click-derived dual organic-inorganic hybrid optical sensor based on SBA-15 for selective recognition of Zn²⁺ and CN⁻ in water. *Inorg. Chim. Acta.* 450: 346-352.
 42. Karimi M., Badiei A., Lashgari N., Afshani J., Mohammadi Ziarani G., (2015), A nanostructured LUS-1 based organic-inorganic hybrid optical sensor for highly selective sensing of Fe³⁺ in water. *J. Lumin.* 168: 1-6.
 43. Karimi M., Badiei A., Mohammadi Ziarani G., (2016), SBA-15 Functionalized with Naphthalene Derivative for Selective Optical Sensing of Cr₂O₇²⁻ in Water. *Anal. Sci.* 32: 511-516.
 44. Behbahani M., Akbari A. A., Amini M. M., Bagheri A., (2014), Synthesis and characterization of pyridine-functionalized magnetic mesoporous silica and its application for preconcentration and trace detection of lead and copper ions in fuel products. *Anal. Methods.* 6: 8785-8792.
 45. Ivasschen J. R., Jorgetto A. O., Wondracek M. H. P., Silva A. C. P., Zara L. F., Pedrosa V. A., Rocha B. P., Saeki M. J., Castro G. R., (2018), Adsorptive properties of mesoporous silica modified with Lewis base molecule and its application in the preconcentration of Cu(II), Co(II), and Cd(II) from aqueous media. *Turk. J. Chem.* 42: 547-561.