Graphene Oxide Nanosheets Modified with 8-Hydroxylquinoline for the Solid Phase Extraction, Preconcentratrion and Flame Atomic Absorption Spectrometric Determination of Copper in Black Tea, Rice and Red Pepper Samples

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A graphene oxide sorbent was modified with 8-hydroxyquinoline and used for solid phase extraction and selective determination of copper using flame atomic absorption spectrometry. In this method, 5 mg of modified sorbent was added to 50 ml of aqueous solution containing 100 µg l^{-1} of Cu(II) at pH = 3. The sorbent/aqueous solution mixture in the flask was stirred for 30 min and then centrifuged. Copper was desorbed from sorbent by 2 ml of 1 M HCl, afterwards. The effect of several variables upon extraction efficiency, like: extraction time, pH adjustment and sorbent amount was studied. Under experimental conditions, the enrichment factor of 23 was obtained by using of 50 ml of sample solution. The working dynamic range was from 5 to 800 ng ml^{-1}. The limit of detection, limit of quantification and relative standard deviation were 2.16 ng ml^{-1}, 6.51 ng ml^{-1}, and 3% for eight determinations of 100 µg l^{-1} of Cu(II), respectively. The method was successfully applied for the determination of Cu(II) in black tea, rice and red pepper samples.

Keywords: Graphene oxide, Modification, 8-Hydroxylquinoline, Copper, Food samples

INTRODUCTION

Trace heavy metals are essential micro-nutrients with a variety of biochemical functions in all living organisms. Copper is an environmentally harmful pollutant causing irritation of nose and throat, nausea, vomiting, and even high doses can cause damage to liver and kidneys. Therefore, due to the positive and negative effects and the toxicity of trace amounts on human health and the environment, many researchers are interested in the analysis of copper contents of the environmental and the food samples [1,2].

Various methods including liquid-liquid extraction [3], solid phase extraction (SPE) [4], cloud point extraction (CPE) [5], and solid phase microextraction (SPME) [6], liquid liquid microextraction (LPME) [7] have been developed.

Among these pretreatment methods, solid-phase extraction (SPE) as an interesting method for separation and preconcentration of metal ions in environmental samples has been developed and widely utilized because of its higher enrichment factors, simplicity, absence of emulsion, safety with respect to hazardous samples, less time-consuming, minimal costs due to low consumption of reagents, and the ability to combine with different detection techniques whether in on-line or off-line mode [8]. For SPE, the sorbent material used is crucial for determining the selectivity and sensitivity of the method. Adsorbents with excellent performance such as large specific surface area and high adsorptive capacity can be chosen.

Nowadays, nanotechnology has been intensively applied in separation science and other research fields [9]. Many research groups have focused on the use of nanosheets such as graphene and modified graphene [10-12], in many scientific area, especially solid-phase extraction (SPE). Because of their high surface area, nanosheets provide high interfacial area making mass transfer and equilibrium achievement quicker.

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Modified nanocompounds have a wide application in separation of heavy metals. For example, chitosan/graphene oxide nanocomposite has been used for adsorption of lead (3), and graphene as solid sorbent has been used for extraction and determination of Co, Ni, Cu, Pb in water samples [9]. Silver, cadmium, copper, mercury and lead were extracted from various food samples using 3-(trimethoxy silyl)-1-propanethiol coated Fe_3O_4 nanoparticles [13].

8-Hydroxyquinoline (8-HQ), known as oxine, is a monoprotic, bidentate chelating agent. It contains an oxygen donor atom and a nitrogen donor atom that can both bind to metal atoms.

In this work, we synthesize a new sorbent for extraction, pre-concentration and determination of trace amounts of copper. Firstly, graphene oxide is physically modified through the immobilization of 8- hydroxyquinoline (8-HQ) onto GO surfaces. Then, it is used to enhance the removal of Cu(II) from aqueous samples. The primary results show that the modified GO obtains 25% adsorption of Cu(II) ion more than the unmodified adsorbent. The adsorption parameters are also studied. Recycling and regeneration of the 8-HQ/GO used are investigated, and also desorption conditions are optimized. The introduced new sorbent is successfully applied for determination of copper in different samples, such as black tea, rice and red pepper.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade. Potassium permanganate ($KMnO_4$), hydrochloric acid, sulfuric acid, nitric acid, 8-hydroxy quinoline, H_2O_2, NaOH, and graphite powder (50 mesh) were all purchased from Merck (Darmstadt, Germany). The stock standard solutions containing 1000 mg l^{-1} of Cu(II) were daily prepared by dissolving appropriate amounts of standard solutions daily through serial dilutions of the stock solution with deionized water prior to analysis. All vessels in the experiments were kept in 10% HNO_3 for at least 24 h and subsequently washed with deionized water before application.

Instrumentation
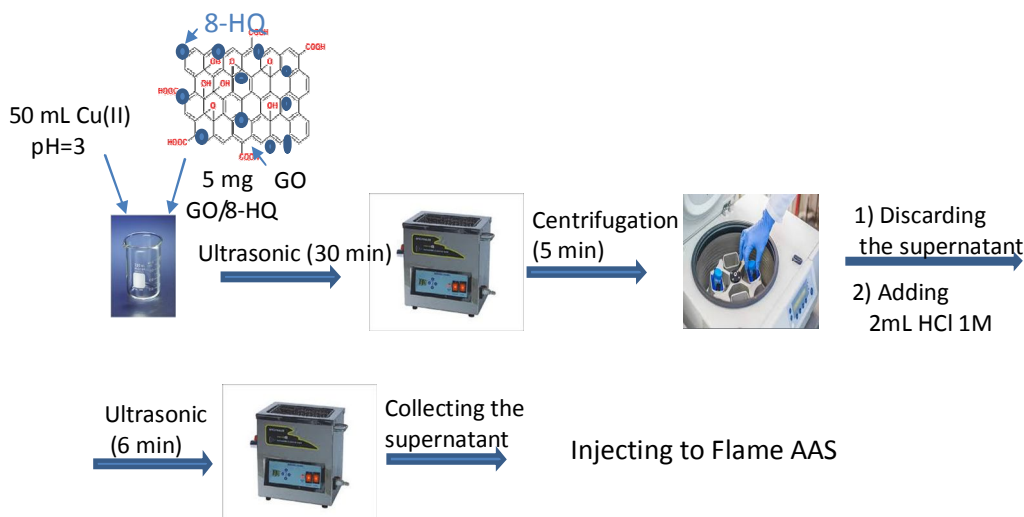
An Atomic Absorption Spectrometer (Shimadzu, AA-670 model, Japan) equipped with flame module was used for determining copper using the manufacturer recommendations. A copper hollow-cathode lamp as the radiation source was used for the absorbance measurements at a wavelength of 328.4 nm and a 3 mA current. All measurements were carried out in an air/acetylene flame. FT-IR spectra in KBr were recorded on a Bruker tensor 27 (Bruker, Germany) spectrometer. A Metrohm model E-691 pH-meter (Herisau, Switzerland), equipped with a combined glass-calomel electrode, was used for determining pH values. SEM images were obtained using a Hitachi S-4160 (Hitachi, Japan) field emission scanning electron microscope operating at 17 kV. An ultrasonic mode Parsonic 7500 was used for dispersion of experimental solutions.

Preparation of 8-HQ/GO Nanocomposite

Prior to preparation of 8-HQ/GO nanocomposite, GO was obtained on the basis of Hummers method [14,15], for which $KMnO_4$ was used as oxidant. In the next step, the GO was modified using 8-HQ [16]. A saturated solution of 8-HQ was prepared by adding an appropriate quantity in 1000 mL of ultra-pure water, sonicating for 2 h and then stirring with a magnetic stirrer for 2 h. The solution was then filtered to remove the undissolved 8-HQ by filtration through Whatman filter paper. In the following step, 10.0 g of GO was added to the saturated solution of 8-HQ and put over the stirrer for 2 days. GO was separated by filtration through a 0.45-µm filter membrane and washed with deionized water to remove excess 8-HQ until the filtrate became colorless. The final product of 8-HQ/GO was dried in an oven at 110 °C overnight.

Procedure for Solid-phase Extraction of Samples

Extraction procedure of Cu(II) ion was performed by batch equilibrium technique. First, 50 ml of sample solution spiked with the proper amounts of Cu(II) ions (2 µg) was placed in a beaker and its pH was adjusted to 3 by addition of dilute HNO_3 or NaOH. Afterwards, 5 mg of nanocomposite was dispersed into the solution. After ultrasonicating for 30 min, the adsorbent was isolated from the solution by centrifugation at 3500 rpm for 5 min. Subsequently, 2 ml of eluent containing 1 M HCl was introduced to desorb target analytes from the adsorbent

Scheme 1. Procedure for SPE of the target Cu(II) ions using 8-HQ/GO nanocomposite

surface by means of ultrasonicating for 6 min. After that, the supernatant solution was collected and injected into the FAAS system for analysis. Scheme 1 displays the steps for SPE of the target Cu(II) ions using synthesized 8-HQ/GO nanocomposite.

The amount of Cu(II) ion adsorbed on the adsorbent was determined by the difference of the initial concentration (C0) and the equilibrium concentration (Ce). The removal percentage of Cu(II) ion from the solution was calculated using the following relationship:

$$\%\mathrm{Re}moval = \frac{C_0 - C_a}{C_0} \times 100$$

Preparation of Real Samples

The procedure used for the extraction of ions from tea and rice samples was similar to that reported in the literature [17,18]. 10 mg of the dry tea sample (dried at 110 °C) was placed in a 50 ml beaker, followed by the addition of 7 ml of concentrated nitric acid, and the beaker was covered with a glass watch. The beaker was allowed to stand overnight, and the contents were heated on a hot plate (150 °C for 15 min). Then, the sample was cooled, 8 ml of perchloric acid was added, and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was removed and the acid was evaporated to dryness at 150 °C. The residue was completely dissolved in 5 ml of 1 M nitric

acid and the solution was transferred to a 100 ml calibrated flask. Then, the solution was neutralized with a proper NaOH solution and diluted to the mark, and the recommended procedure was followed.

One gram of red pepper sample was placed in a 250 ml beaker, and 100 ml of concentrated HNO₃ (65% w/w) was added to the beaker. The mixture was evaporated near to dryness on a hot plate at about 130 °C for 4 h. After cooling to room temperature, 3 ml of concentrated perchloric acid was added. The mixture was again evaporated near to dryness. The resulting solution was filtrated with deionized water. Finally, the SPE procedure described was applied to the sample solutions [19].

Rock sample: The powdered rock sample of 0.1 g was weighed in a 50 ml Teflon beaker, and 4 ml HNO3, 3 ml HClO₄ and 5 ml HF were added. The mixture was kept for more than 30 min, then evaporated to dryness under 200 °C. The residue was dissolved with 5 ml (1 + 1) HNO₃ by heating. The solution was filtrated, if necessary, and diluted to 100 ml. One milliliter of this solution was transferred into a 100 ml volumetric flask and analyzed by the proposed procedure [20].

RESULTS AND DISCUSSION

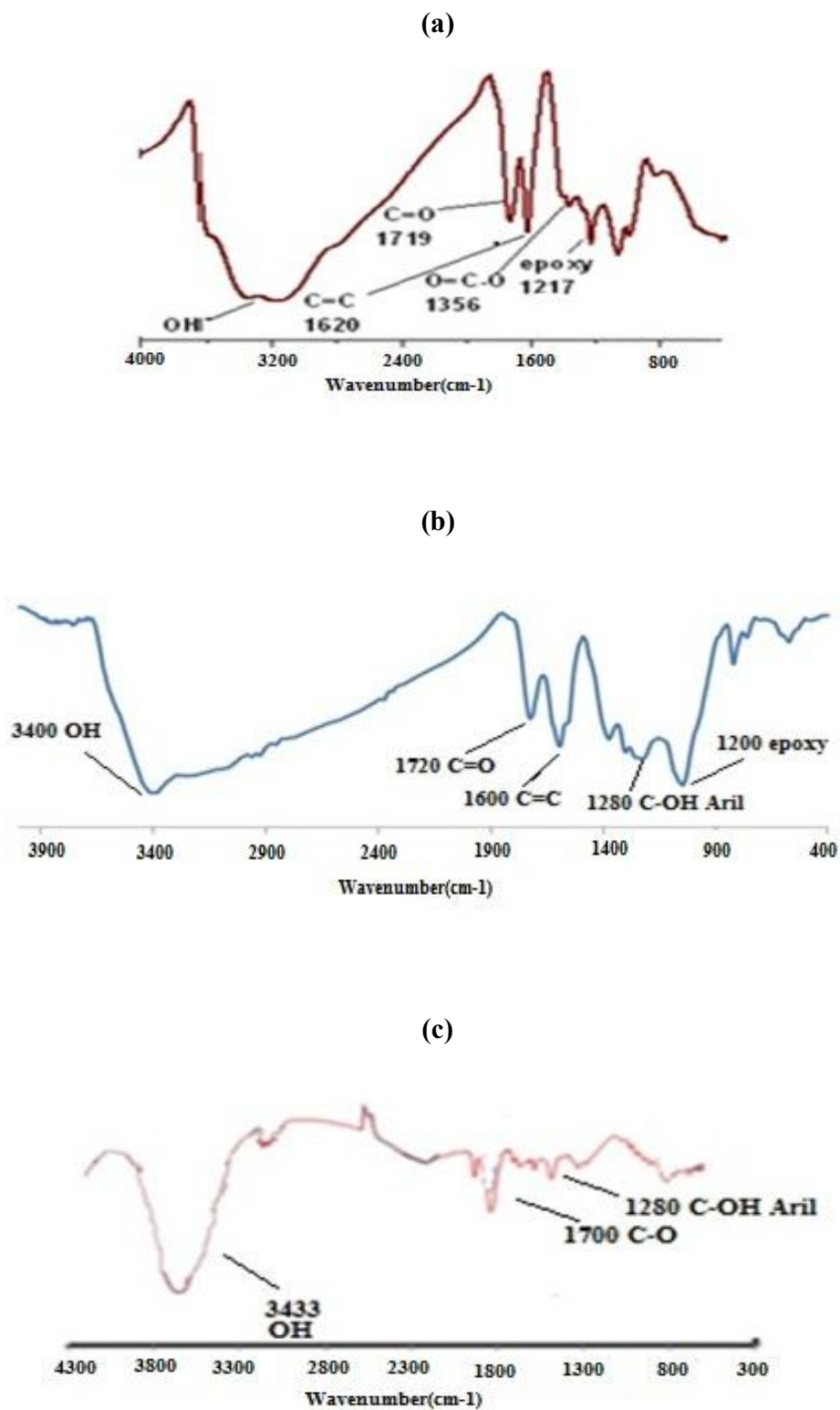In order to select the optimum conditions for the extraction of Cu(II) ions, a 50 ml sample solution

(a)

(b)

(c)

Fig. 1. Infrared spectra of GO (a), 8-HQ/GO nanocomposite (b), and 8-HQ/ (c).

containing 0.1 mg l^{-1} of Cu(II) was used to study SPE efficiency under different conditions. All the experiments were performed in triplicate, and optimal results were applied for real sample analysis.

Characterization

The formation of GO, and 8-HQ/GO nanocomposite were investigated using FT-IR spectrometry. FT-IR spectrum of GO is shown in Fig. 1a. The strong wide absorption band at 3400 cm^{-1} is characteristic of the stretching vibration of hydroxyl groups. There are also bands due to carbonyl C=O and C=C groups (1719 cm^{-1} and 1620 cm^{-1}, respectively), and carboxylic acid O-C=O band (1356 cm^{-1}). FT-IR spectrum of nanocomposite is also shown in Fig. 1b. The band of aryl group at 1280 cm^{-1} can be a confirmation on the formation of 8-HQ/GO nanocomposite adsorbent. We have reported the spectrum of 8-hydroxyquinoline for comparison (Fig. 1c). The typical SEM image of 8-HQ/GO nanocomposite is shown in Fig. 2. SEM observation shows that 8-HQ/GO has a crumbled wave-like structure of GO.

Effect of Ultrasoniction Time

The adsorption of Cu(II) onto 8-HQ/GO can be affected by the ultrasonication time. The effect of ultrasonicate time was examined in the range of 10-90 min with constant experimental conditions. Firstly, according to results (Fig. 3), the extraction recovery was increased with the increase of the ultrasonicate time, and then the extraction efficiency remained almost constant after 30 min. Hence, 30 min was taken as an optimal time for the subsequent experiment.

Effect of pH

The acidity of solution plays an important role for metal adsorption on 8-HQ/GO. In order to improve the extraction efficiency of Cu(II) from aqueous solution, the effect of pH adjustment upon recoveries of Cu(II) onto 8-HQ/GO was investigated in our experiment. The pH was adjusted by 0.1 M HCl and 0.1 M NaOH. The studied pH range was from 2.0-9.0. The recovery of Cu(II) at each pH value was calculated. The results of the effect of pH on the recovery values are presented in Fig. 4. It was observed that if the higher pH value is adjusted, the lower adsorption of Cu(II) is achieved. At the higher pH values, the low adsorption

probably was due to the hydrolysis of Cu(II) [21]. Accordingly, pH 3.0 was selected for the subsequent work and analysis of the real samples.

Effect of Sample Volume

In order to obtain high preconcentration factor, the effect of sample volume on the sorption behavior of Cu(II) on 8-HQ/GO was investigated by passing 25-250 ml of sample solutions containing 5 µg Cu(II) according to the recommended procedure. Quantitative recovery (>95%) was obtained up to a sample volume of 50.0 ml and the adsorbed Cu(II) could be eluted with 2 ml of HCl. Thus, an enrichment factor of 25 was achieved by this method. In our procedure, a sample volume of 50.0 ml was used for routine analysis (Fig. 5).

Effect of Graphene Dosage

In order to choose the optimum amount of the adsorbent (8-HQ/GO) for the extraction of Cu(II), different quantities of nanocomposite were tested in the range of 2.5-15 mg. As shown in Fig. 6, the maximum extraction efficiency was obtained using 5 mg and when the amount of adsorbent was above 5 mg, the recovery remained almost invariant. According to the results, 5 mg graphene was selected for the further analysis.

Desorption Conditions

The effect of desorption time was also studied, and it was observed that the copper ions could be completely desorbed within 6 min time interval and more desorption time is not necessary. To obtain a high enrichment factor, a suitable eluent should be used. The eluent should desorb the adsorbed analytes quantitatively using its small volume. The obtained results showed that 2 ml of 1 M HCl solution is suitable for the elution of copper.

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8-HQ/GO Reuse

The stability and potential regeneration of 8-HQ/GO were investigated. The 8-HQ/GO could be reused after ultrasonication with 1 M HCl for 10 min and washing with 10.0 ml deionized water and in the following isolating from the solution by centrifugation at 3500 rpm for 5 min and drying at 40 °C. It was stable up to at least 5 adsorptions-elution cycles without significant decrease in the recovery
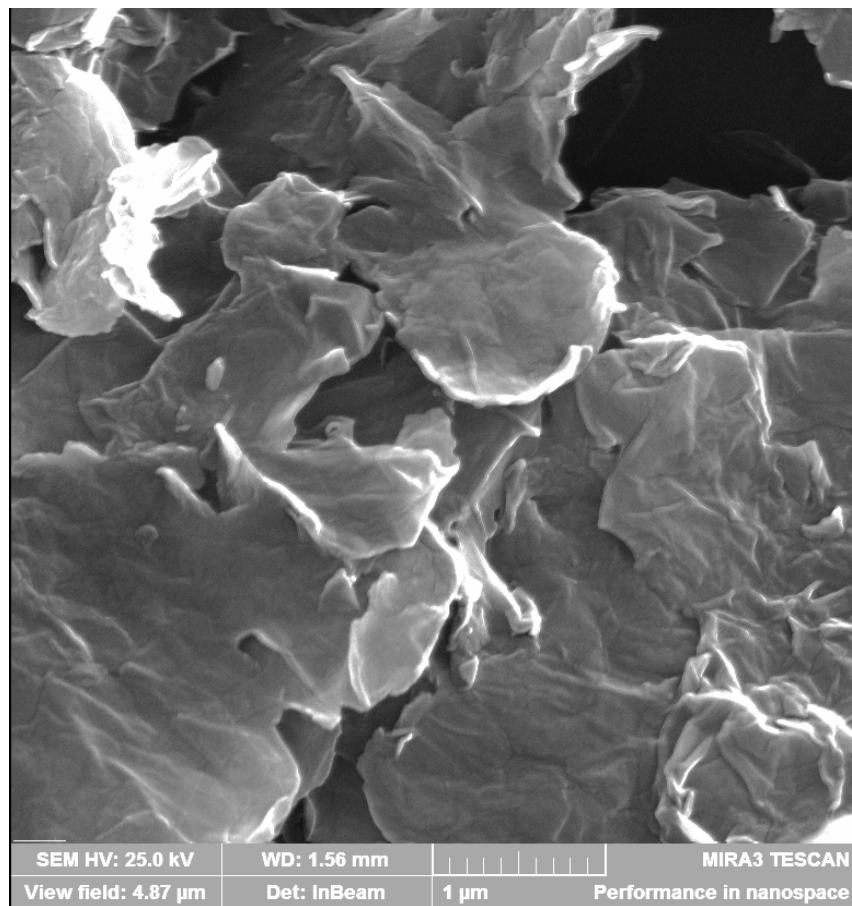
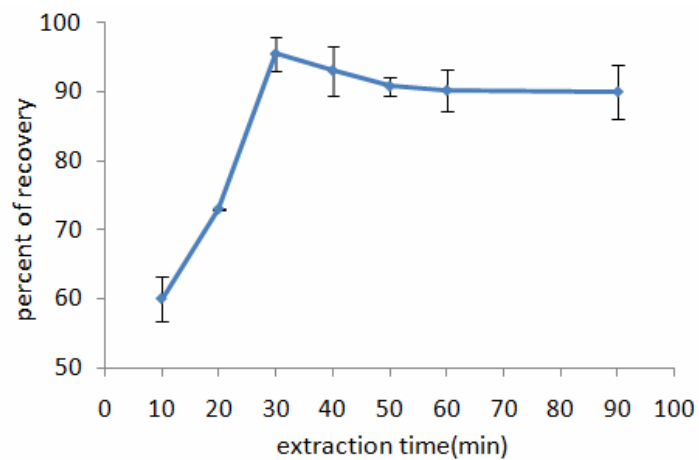**Fig. 2.** The SEM image of 8-HQ/GO nanocomposite.

Fig. 3. Effect of extraction time on extraction efficiency of Cu(II) ion. Extraction conditions: water sample volume, 50 ml; pH, 3; eluent type, 1 M HCl; Adsorbent amount, 5 mg; concentration of Cu(II), 100 µg l^{-1}.
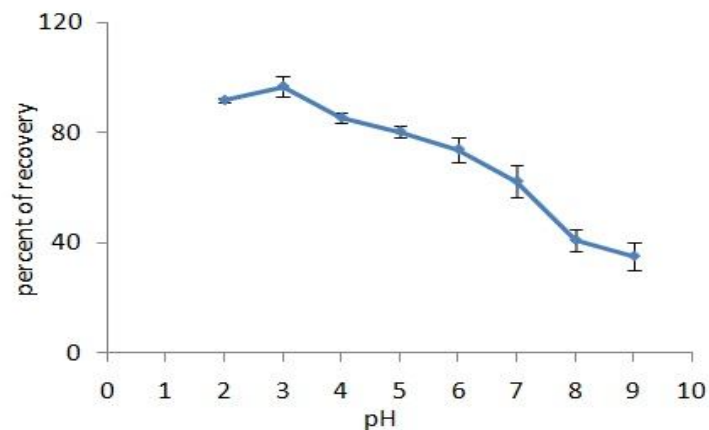
Fig. 4. Effect of pH on the recovery of Cu(II) from 8-HQ/GO nanocomposite adsorbent. Extraction conditions: water sample volume, 50 ml; extraction time, 30 min; extraction eluent type, 1 M HCl; adsorbent amount, 5 mg; concentration of Cu(II), 100 µg l^{-1}.
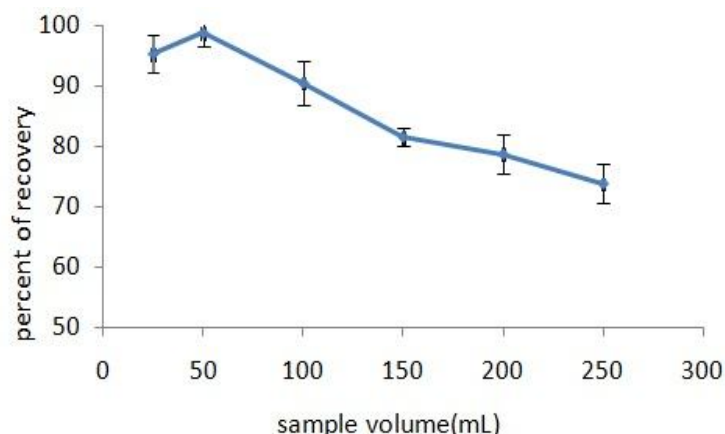

Fig. 5. Effect of sample volume on extraction efficiency of Cu(II) ion. Extraction conditions: extraction time, 30 min; pH, 3; eluent type, 1 M HCl; adsorbent amount, 5 mg; concentration of Cu(II), 100 µg l^{-1}.

of Cu(II).

Effect of Interfering Ions

The effect of other ions in the extraction of Cu(II) on 8-HQ/GO was studied under optimized conditions. Solutions containing 100 µg l^{-1} Cu(II) and different concentrations of other ions were prepared and subjected to the preconcentration procedure. The tolerance limit of the coexisting ions is defined as the largest amount making the recovery of Cu(II) less than 95%. The results, summarized

in Table 1, showed that within ±5% error range, the presence of major cations and anions has no significant influence on the adsorption of Cu ion under the selected conditions.

Analytical Performance

Under optimized conditions, a linear dynamic range for Cu(II) was obtained by preconcentration of a series of Cu(II) standards according to the procedure outlined above. The curve was linear from 5-800 µg l^{-1} with a correlation
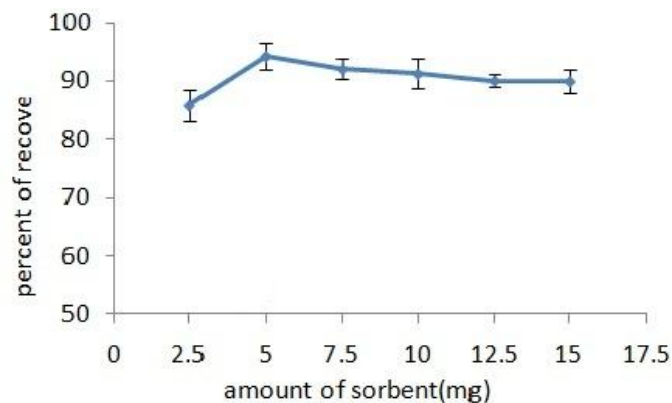
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Fig. 6. Effect of 8-HQ/GO nanocomposite amount on the extraction efficiency of Cu(II) ion. Extraction conditions: water sample volume, 50 ml; extraction time, 30 min; pH, 3; eluent type, 1 M HCl; concentration of Cu(II), 100.

Table 1. Tolerance Limits of Interfering Species in the Determination of 100 µg l^{-1} of Cu(II)

Coexiting ions	Added as	Interference to copper ion ratio $(C_{ion}/C_{Cu})^a$
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	1000
Ag^+	$AgNO_3$	10
Co^{2+}	$CO(NO_3)_2.6H_2O$	1000
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	50
Pb^{2+}	$Pb(NO_3)_2$	50
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	10
Al^{3+}	$Al(NO_3)_3.9H_2O$	50
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	1000
Ca^{2+}	$Ca(NO_3)_2$	1000
K^+	KNO_3	1000
Na^+	$NaNO_3$	1000
F^-	NaF	1000
NO_3^-	KNO_3	1000
Cl^-	$NaCl$	1000
SO_4^{2-}	Na_2SO_4	1000

[a]At this ratio interfering effect was observed.

Table 2. Displaying of Various Parameters of Proposed Method Compared to Previous Reported Approaches for SPE of Cu(II)

Method	Extraction method	Linear range (ng ml^{-1})	LOD (ng ml^{-1})	RSD (%)	EF	Ref.
FAAS	DLLME[a]	0.2-20	0.05	1.5-3.5	55	[22]
FAAS	SPE[b]	10-340	1.9	2.1	33	[23]
FAAS	Coprecipitation	-	1.32	2.5	20	[24]
FAAS	DLLME	50-2000	3.0	5.1	42-48	[25]
Spectrophotometry	LLE	10-400	2.0-4.0	2.0	5	[26]
FAAS	CPE[c]	-	0.3	1.8	69	[27]
FAAS	DLLME	1-600	0.5	1.4	-	[28]
FAAS	CPE	5-200	0.94	< 3	-	[29]
FAAS	SPE	-	2.5	3.3	-	[30]
FAAS	SPE	5-800	2.16	3	25	This study

[a]Dispersive liquid liquid microextraction. [b]Solid phase extraction. [c]Cloud point extraction.

coefficient of 0.998. The limit of detection and limit of quantification were found to be 2.16 μg l^{-1} and 6.51 μg l^{-1}, respectively. The relative standard deviation (RSD) for ten replicate measurements of 100.0 μg l^{-1} of Cu(II) was 3%. The enrichment was found to be 23. A comparison of the analytical performance obtained by this method with those of other approaches reported in literatures for copper extraction from real samples is shown in Table 2. It is therefore believed that 8-HQ/GO has a potential to use as a SPE adsorbent. On the other hand, the low cost and simplicity as well as its high selectivity for copper ions made it a suitable quantitative determination method. The method was successfully applied to the determination of the trace of the copper in black tea, rice and red pepper. To verify the accuracy of the proposed procedure, the method was used to determine the content of Cu in the National Standard Reference Material for Rock sample (J$_{B-3}$) after an appropriate dilution. The results for this test (Table 3), using t-test at 95% confidence interval, did not show any significant statistical difference between the obtained results.

Real Samples Analysis

The proposed method was applied to determine Cu(II) ions in black tea, rice and red pepper samples. The results, along with the recovery for the spiked samples are given in Table 4. The recoveries for the addition of Cu(II) to all the samples were in the range of 92-94.6%, which indicates the capability of the system in the determination of Cu(II) in real samples with different matrices.

CONCLUSIONS

In this study, the 8-HQ/GO nanocomposite as a new adsorbent was successfully synthesized and applied in SPE procedure for extraction, preconcentration and determination of copper. The synthesized adsorbent was characterized by FT-IR and SEM techniques. The proposed system for copper was used for 5 subsequent preconcentration cycles without any loss on the adsorption performance of nanocomposite throughout the work. The proposed procedure was compared with that in the similar works. The detection limit and enrichment obtained by the

Table 3. Analytical Results of Cu(II) Determination in Standard Reference Material with the SPE-FAAS Method (n = 3)

Sample	Concentration	Found	Recovery
	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$)	
JB-3	199.00 ± 2.51	206.40 ± 35.34	103.7

Table 4. Analytical Results for Determination of Cu(II) in Real Samples

Sample	Added Cu^{2+}	Founded Cu^{2+}	Relative recovery
	($\mu g\ g^{-1}$)	($\mu g\ g^{-1}$) $\pm$ RSD (%)	(%)
Black tea	0	109.08 ± 0.03	-
	200	303.15 ± 0.02	94.6
Rice	0	2.36 ± 0.05	-
	10	12.18 ± 0.02	92.4
Red pepper	0	0.50 ± 0.01	-
	1	1.46 ± 0.03	92.0

present method are comparable to those reported methods. Generally, the method provides a convenient, effective, low cost and sensitive method for preconcentration of Cu(II) from samples such as food samples.

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