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Extraction and Determination of Heavy Metals Using Silver Coated Magnetic Nanoparticles and Flame Atomic Absorption Spectrometry

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Abstract

A rapid, simple and sensitive magnetic solid phase extraction (MSPE) method was developed for the pre-concentration and determination of copper and cadmium ions. In this study, modified Fe_3O_4@Ag nanoparticles were synthesized and then ligand 2-isonicotinoyl hydrazine carbodithiolate (ITHCDT) was bonded to silver due to the formation of covalent bond of S-Ag. In this method, copper and cadmium ions were absorbed on the sorbent and then eluted by 1 mL of HCl (2 mol L^{-1}) and measured by FAAS. Different effective parameters such as pH, eluent type and volume, amount of sorbent, sorption capacity, contact time were investigated and optimized. Relative standard deviation (RSD, n=7) under optimum condition for Cd (II) and Cu(II) was 1.23% and 1.67%, respectively. Limit of detection (LOD) of the method for cadmium and copper was 0.87 and 0.51 μg L^{-1}, respectively. The proposed method was successfully applied for the determination of trace amounts of copper and cadmium ions in water samples.

Keyword: *modified magnetic nanoparticles, cadmium, copper, flame atomic absorption spectrometry, water samples.*

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Introduction

Heavy metals are generally toxic, non-biodegradable and are retained by ecological systems. Therefore, heavy metal pollution is a serious concern to human health [1]. Cadmium (Cd) is classified as prevalent toxic metal even at very low concentration in the environment and has deleterious effects on organs, such as liver, kidneys and lungs [2]. Copper (Cu) is an essential element and has complex role in many body functions such as hemoglobin synthesis, normal function of the central nervous system and connective tissue development [3]. However, excessive intake of Cu would lead to its accumulation in liver cells and hemolytic crisis, neurologic disturbances and jaundice. Therefore, determination and removal of these heavy metals in environmental samples is very important. So far several techniques including flame atomic absorption spectrometry (FAAS) [2], electrothermal atomic absorption spectrometry (ETAAS) [4, 5], UV–Vis spectrophotometry [6, 7], voltammetry [8, 9], inductively coupled plasma-optical emission spectrometry (ICP–OES) [10, 11], and inductively coupled plasma-mass spectrometry (ICP–MS) [12] have been utilized for determination of cadmium and copper in a variety of matrices. FAAS has been widely applied for the determination of trace amounts of metal ions in different type of samples because it is inexpensive, simple, rapid and precise [13]. However, direct determination of metal ions at trace levels by FAAS is difficult in many cases. Therefore, a suitable sample preparation procedure is often necessary. Among the sample preparation procedures, solid-phase extraction (SPE) is particularly attractive because of its high pre-concentration factor, ease of operation, low consumption of organic solvents, fast phase separation and low cost [14-17]. In order to achieve high recovery and good selectivity in the SPE procedure, a suitable sorbent is required. Recently, applications of magnetic nanoparticles (MNPs) as adsorbing materials have been developed for extraction of metals at trace level from different samples. MNPs can be applied directly as the adsorbent material or as the core of the appropriate composites obtained using them with other nanoparticles [18] or chemical reagents [19–24]. When MNPs are used for solid phase extraction processes, these materials are quickly separated by a magnet without the need for centrifugation.

In this work, we synthesized a new sorbent for extraction and pre-concentration determination of trace amounts of cadmium and copper in water sample. The Fe_3O_4 magnetic nanoparticle was synthesized and covered with silver and then, ligand 2-isonicotinoyl hydrazine carbodithiolate (ITHCDT) was bonded to silver. Fe_3O_4@Ag@ITHCDT NPs was applied for extraction and pre-concentration of cadmium and copper. Vortex was used to facilitate desorption of the metal ions from the nanoparticles. The isolation of magnetic nanoparticles was carried out simply with an external powerful magnet. The levels of cadmium and copper were determined using flame atomic absorption spectrometry.

Experimental

Standards and Reagents

All chemicals were of analytical reagent grade. Ferrous chloride ($FeCl_2 \cdot 4H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), ammonia solution (25 wt. %), silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), methanol, ethanol, diethyl ether, carbon disulfide, nicotinic hydrazide potassium and potassium hydroxide, were supplied by Merck (Darmstadt, Germany). Nitric acid (HNO_3), 2-propanol, hydrochloric acid (HCl) and thiourea were used as eluent and were purchased from Merck (Darmstadt, Germany). Stock standard solutions (1000 mg L^{-1}) of Cu^{2+} and Cd^{2+} were prepared by dissolving their nitrate salts (Merck, Darmstadt, Germany) in double distilled water. Working solutions were prepared daily by diluting the stock solution with double-distilled water. The pH of sample solutions was adjusted with the aid of hydrochloric acid and ammonia.

Apparatus

A Shimadzu flame atomic absorption spectrophotometer (AA-680) equipped with a deuterium lamp for the background correction was used to measure Cd (II) and Cu (II) absorbance. A hollow cathode lamp from Hamamatsu, Photonic Co. Ltd, L233-series was employed as the radiation source at a wavelength of 328.8 and 327.4 nm for cadmium and copper, respectively. Investigation of surface modification of Fe_3O_4 nanoparticles was recorded by Fourier-transform infrared spectroscopy (FT-IR) in the range of 4000–400 cm^{-1} (PerkinElmer, USA). A pH meter (Metrohm Lab-827, Switzerland) was used for adjustment of pH solution. A vortex mixer (IKA Vortex Genius 3, Germany) was used to facilitate desorption of the analytes from the nanoparticles.

Synthesis of iron magnetic Fe_3O_4-MNPs

Iron magnetic nanoparticles (Fe_3O_4-MNPs) were prepared using the conventional co-precipitation method with minor modifications. Briefly, 5.2 g of $FeCl_3.6H_2O$ was dissolved in 2 mL of concentrated HCl and 10 mL water within a three neck flask. Under a nitrogen atmosphere, 2.0 g of $FeCl_2.4H_2O$ and 40 mL of water was added with vigorous stirring at 75°C. Then by adding 50 mL of NH_3 (2 mol L^{-1}) dropwise, the orange-red clear solution became a black suspension. The Fe_3O_4-MNPs were collected with a strong magnet, washed several times with distilled water and were suspended in 100 mL of water.

Synthesis of ligand

0.11 mole of potassium hydroxide was dissolved in 50 mL methanol, 0.07 mole of nicotinic hydrazide potassium was added and the mixture was immersed in an ice-bath and was stirred. Afterwards, 20 mL of carbon disulfide (0.11 mol) was added dropwise to suspension. Then suspension was removed from the ice bath and was stirred for 1 h at the room temperature. Finally, the obtained yellow powder was washed with 50 mL of diethyl ether and dried.

Preparation of ITHCDT-coated Fe_3O_4@Ag core@shell nanoparticles (Fe_3O_4@Ag@ ITHCDT NPs)

Firstly, 20 mL of diluted silver nitrate solution (0.064 mmol) was added to 70 mL suspension containing 1g Fe_3O_4 nanoparticles. The mixture was stirred for 5 min and 50 mL of 0.32 mmol $NaBH_4$ as a reductant agent were added drop by drop and was further stirred for 10 min. The color of the mixture changed from black to grayish green. The Fe_3O_4@Ag particles were collected by a permanent magnet and washed several times with distilled water to remove un-reacted materials. Afterwards, the obtained nanoparticles were suspended in ethanol for the next step.

In this step, 2 mL of a 1 mol L^{-1} ITHCDT solution were added to the suspension of Fe_3O_4@Ag NPs in ethanol (synthesized in previous step) and the mixture was stirred for 24h. Finally, Fe_3O_4@Ag@ ITHCDT NPs product were again separated with the help of a magnet and washed with distilled water several times and dried.

Pre-concentration procedure

The magnetic solid phase extraction procedure was performed using batch experiment. The following steps were applied to extraction, pre-concentration and determination of the cadmium and copper:

40 mL solution containing Cd(II) and Cu(II) in the linear range was adjusted to pH 9 (using HCl and NH_3) and was transferred into a 50 mL conical tube. Then, 50 mg of the modified sorbent was added and the solution was fiercely vortexed for 2 min to facilitate adsorption of the metal ions onto the nanoparticles surface. The magnetic sorbent was separated from the suspension with an external magnet (3cm × 3cm × 3cm with 1.4T magnetic field) and the supernatant was completely decanted. Next, the adsorbed analytes were desorbed from the separated sorbent with 1 mL HCl (2 mol L^{-1}) as eluent by fierce vortex for 2 min. Finally, the eluate was separated from the sorbent by magnet again and was injected into the FAAS instrument for determination of cadmium and copper. The general process of magnetic solid phase extraction was presented in Figure 1.

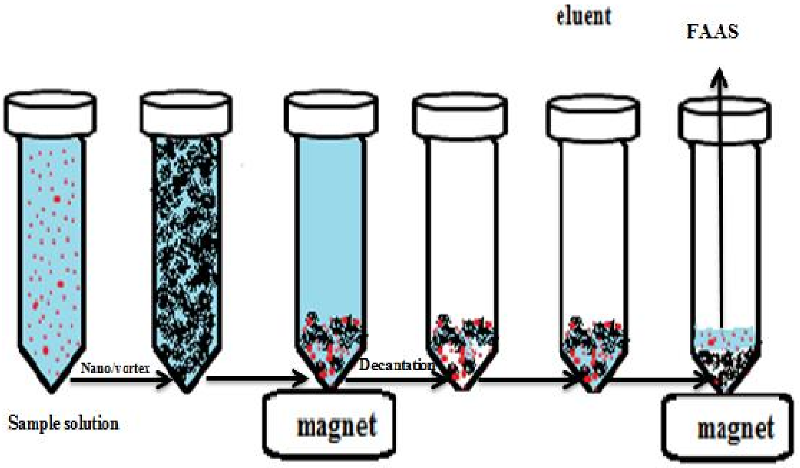

Figure1. The general process of magnetic solid phase extraction.

Sample preparation

Water samples were collected from different part of Arak, Iran (river water of Hossein Abad, mineral water of Sarband Mountain, tap water and well water of different part of the city). These water samples were filtered using 0.45 μm micropore membranes, adjusted to the pH of 9 and stored in glass containers at 4°C.

Result and discussion

Characterization of sorbent

The SEM images of the Fe_3O_4 and Fe_3O_4@Ag@ITHCDT NPs are shown in Figure 2a and b. As it is remarkable, minor changes on the surface of modified nanoparticles indicate that the nanoparticles have been modified with Ag and ITHCDT.

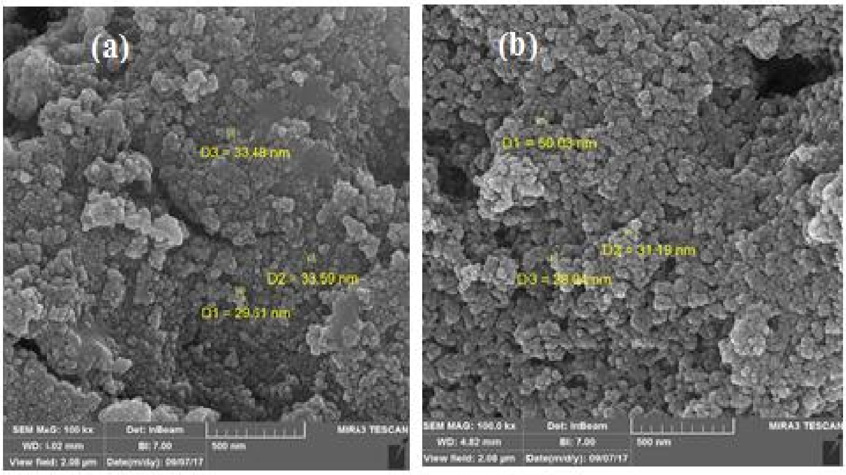

Figure 2. *SEM* images of (a) Fe_3O_4 and (b) Fe_3O_4@Ag@ITHCDT NPs.

The FT-IR spectra of Fe_3O_4-MNPs and Fe_3O_4@Ag@ITHCDT NPs are shown in Figure 3. The absorption peaks that observed at 570 cm^{-1} (Fe–O) and 3390 cm^{-1} (O–H) in the FT-IR spectra of Fe_3O_4 NPs confirmed the successful synthesis of Fe_3O_4 nanoparticles. On the other hand, the peaks observed at 1270 cm^{-1} (C=S), 1486 cm^{-1} (C=C), 1720 cm^{-1} (C=O) and 2900 cm^{-1} (C-H) in the spectrum of Fe_3O_4@Ag@ITHCDT indicated the successful modification of Fe_3O_4 with ITHCDT agent.

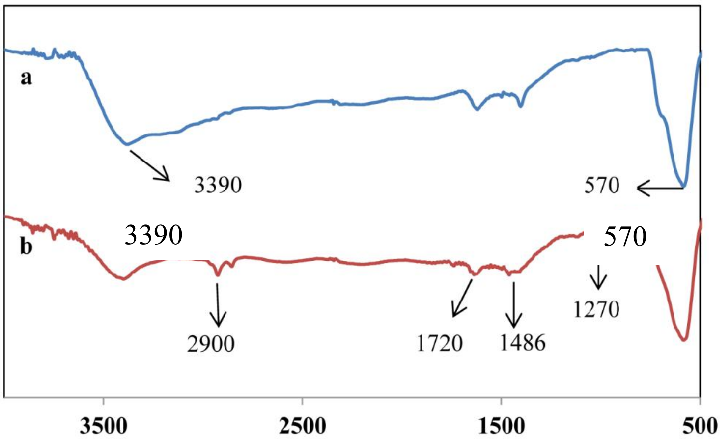

Figure 3.FT-IR spectra of (a) Fe_3O_4 and (b) Fe_3O_4@Ag@ITHCDT NPs.

Energy dispersive X-ray (EDS) analysis was done to study the elemental composition of the sorbent. The EDS analysis of the Fe_3O_4@Ag@ITHCDT NPs is presented in Table 1. As can be seen the Fe_3O_4@Ag@ITHCDT nanoparticles has the following composition: Fe (51.49%), O (39.71), C (5.00%), S (1.93), N (1.51%), and Ag (0.09).

Table 1. EDS analysis of the sorbent.

Element	**Fe_3O_4@Ag@ITHCDT NPs (W %)**
C	5.00
N	1.51
O	39.71
S	1.93
Ag	0.09
Cl	0.17
Fe	51.49
K	0.1
Total	100.00

Optimization of the preconcentration procedure

Several parameters such as volume and type of eluent, pH of solution, amount of sorbent, adsorption and desorption times can affect extraction efficiency. These parameters were investigated and optimized to achieve the best extraction efficiency of analytes.

Selection of sample pH

It is known that in the extraction of metal ions, the extraction efficiencies of metal complex are closely related to the pH of sample solution. Thus, the effect of sample pH was studied in the range of 2–10. Figure 4 shows the dependence of extraction efficiency of Cd (II) and Cu (II) on the sample pH. As can be seen, the quantitative adsorption of Cd (II) increases with the increase of pH up to 9, and then more or less remains constant. Also, maximum adsorption of copper occurred over the pH 9. Therefore, pH 9 was chosen for all subsequent experiments.

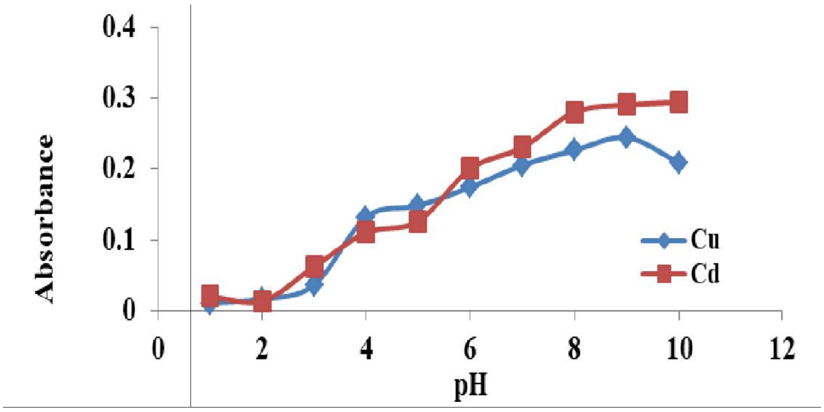

Figure 4. Effect of pH on the extraction efficiency (40 mL of sample solution containing100μg $L^{-1}$of each ion; 25 mg of Fe_3O_4@Ag@ITHCDT NPs; extraction time 10 min; 2 mL of HCl (2 mol L^{-1}) as eluent; desorption time 2 min).

Selection of eluent type and volume

To find the best eluent to desorb the metal ions from the sorbent, several solvents (nitric acid, hydrochloric acid, thiourea and 2-propanol) were examined. The results showed that hydrochloric acid (HCl) give much higher elution efficiency than other eluents. Next, different concentration of HCl (0.25, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 mol L^{-1}) were examined. The results demonstrated that maximum adsorption for all studied metal ions could be obtained at concentration of 2 mol L^{-1}. So, HCl (2 mol L^{-1}) was used for all subsequent experiments (Figure 5).

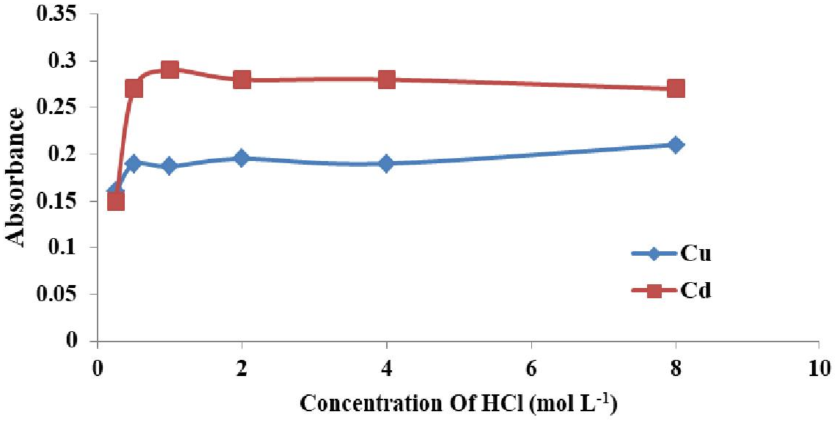

Figure 5. Effect of HCl concentration (mol L^{-1}) on extraction efficiency (40 mL of sample solution containing100µg L^{-1}of each ion; 25 mg of Fe_3O_4@Ag@ITHCDT NPs; extraction time 10 min; 2 mL of HCl as eluent; desorption time 2 min).

The effect of elution volume for quantitative elution of the metal ions was also evaluated by changing the eluent volume in the range of 0.5–4 mL. Based on the results obtained from Figure 6, minimum volume for quantitative elution of the retained ion metals was found to be 1 mL. Hence, the eluent volume of 1 mL was chosen for the next steps.

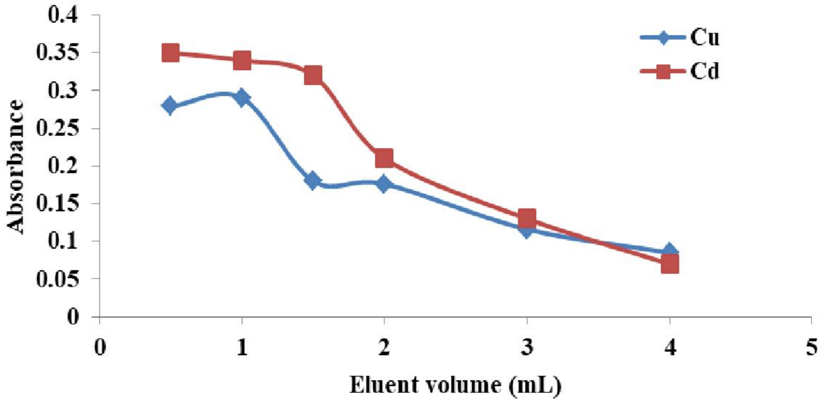

Figure 6. Effect of HCl volume (2 mol L^{-1}) on extraction efficiency (40 mL of sample solution containing100µg L^{-1}of each ion; 25 mg of Fe_3O_4@Ag@ITHCDT NPs; extraction time 10 min; HCl (2 mol L^{-1}) as eluent; desorption time 2 min).

Effect of sorbent amount

In order to investigate the effect of sorbent quantity on the extraction efficiency of metal ions, different amounts of sorbent in the range of 10–60 mg were added to the solution and results are shown in Figure 7. Based on Figure 7, 50 mg of the sorbent sufficed for maximum absorption. Thus, 50 mg of sorbent was selected for all experiments.

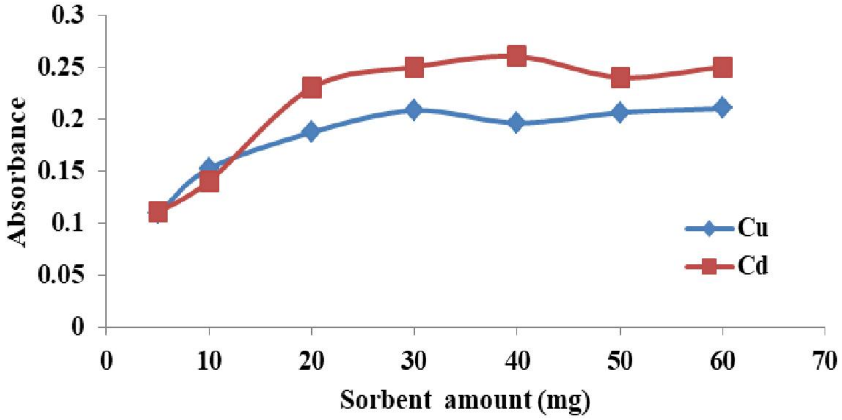

Figure 7. Effect of sorbent amount on extraction efficiency (40 mL of sample solution containing 100 µg L^{-1} of each ion; extraction time 10 min; 1 mL of HCl (2 mol L^{-1}) as eluent; desorption time 2 min).

Effect of extraction and desorption time

In order to minimize the extraction time and desorption time of metal ions, vortex was used. So, vortex time was investigated and optimized. The experimental results showed that the maximum adsorption was achieved when the vortex time was about 2 min for extraction and desorption process (Figure 8 and Figure 9). Therefore, 2 minute was selected as the vortex time.

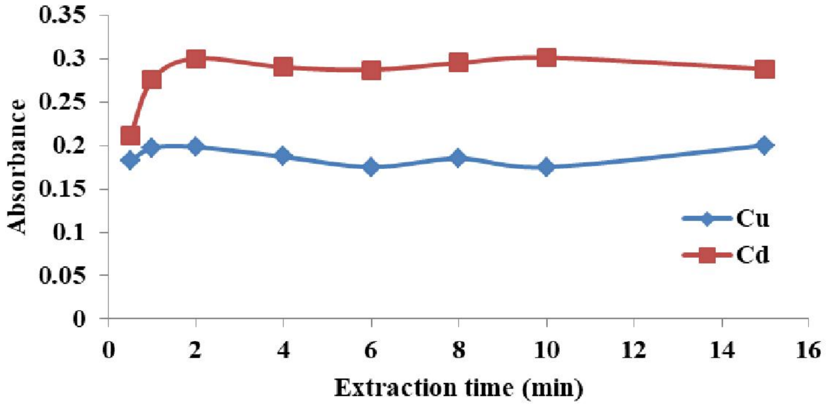

Figure 8. Effect of extraction time on extraction efficiency (40 mL of sample solution containing100µg $L^{-1}$of each ion; 50 mg of Fe_3O_4@Ag@ITHCDT NPs; 1 mL of HCl (2 mol L^{-1}) as eluent; desorption time 2 min).

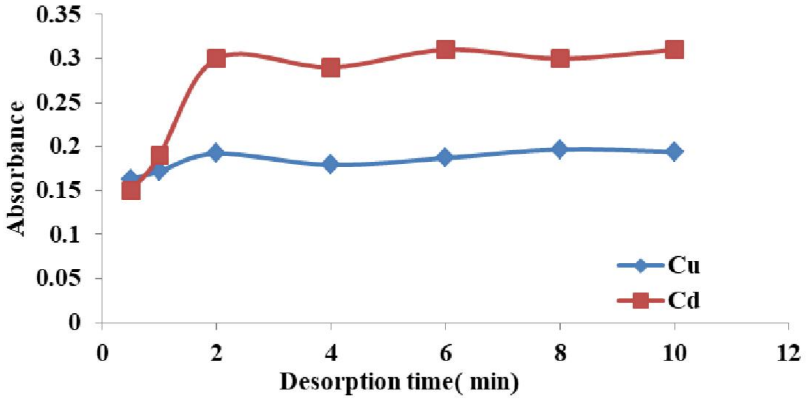

Figure 9. Effect of desorption time on extraction efficiency (40 mL of sample solution containing100μg $L^{-1}$of each ion; 50 mg of Fe_3O_4@Ag@ITHCDT NPs;extraction time, 2 min; 1 mL of HCl (2 mol L^{-1}) as eluent).

Adsorption capacity and reusability of the sorbent

The adsorption capacity can define how much sorbent is required for quantitative extraction of a certain amount of metal ions from the solution. The maximum capacity of Fe_3O_4@Ag@ITHCDT nanoparticle for cadmium and copper was investigated. The adsorption capacity of the sorbent was carried out by 50 mg of Fe_3O_4@Ag@ITHCDT NPs and certain volume of solution containing various concentrations of metal ions. The maximum adsorption capacity of Fe_3O_4@Ag@ITHCDT NPs was found to be 12.38 and 12.43 mg g^{-1} for cadmium and copper, respectively. Reusability is an important factor for evaluation of sorbent. The reusability of the synthesized nanoparticles was tested after several loading and elution steps. The results indicated that the sorbent could be applied for SPE repeatedly at least for 7 times without loss of analytical performance.

Kinetic studies

Adsorption kinetics of Cd(II) and Cu(II) using the Fe_3O_4@Ag@ITHCDT NPs was examined. The experimental results showed that the magnetic solid phase extraction process was very fast. When the extraction time and desorption time was about 2 min, the target analytes could be quantitatively extracted. The fast adsorption kinetics of synthesized nanoparticles was a clear advantage for its application in magnetic solid phase extraction.

Interferences study

In order to evaluate the selectivity of the developed method for determination of Cd(II) and Cu(II) at trace levels, the effects of foreign ions on the analytical signals of Cd(II) and Cu(II) were studied.

For this purpose, various amounts of foreign ions were added to 40 mL of the standard solutions containing 100 µg L^{-1} Cu (II) and Cd (II), and then the recommended extraction procedure was performed and the results are given in Table 2**.** The results showed that at these levels of concentrations, there aren't any significant interfere.

Table 2. Tolerance limits of foreign ions for the determination of cadmium and copper (100 µg L^{-1}).

Foreign ion added	**Tolerance limits (µg L^{-1})**	
	Cd	**Cu**
Pd^{2+}	100	100
Pb^{2+}	1000	1000
Ag^{+}	1000	1000
Zn^{2+}	1000	1000
Mn^{2+}	1000	1000
Co^{2+}	1000	1000
Hg^{2+}	1000	1000
Cr^{3+}	1000	1000

Analytical performance

Under the optimum conditions, the analytical characteristics of the MSPE procedure, such as limit of detection, reproducibility and enrichment factor were investigated and the results are summarized in Table 3. The limit of detection (LOD) was determined based on $3S_b/m$ where, S_b is the standard deviation for seven blank measurements and m is the slope of the calibration curve, were 0.87 and 0.51 µg L^{-1} for Cd(II) and Cu(II), respectively. The calibration curve was linear in the range of 5–700 and 2–1000 µg L^{-1}, with the r^2 value of 0.9991 and 0.9997 for Cd (II) and Cu(II), respectively. The precision of the method was evaluated by the relative standard deviation (RSD) based on analysis of seven replicates containing 100 µg L^{-1} of Cd(II) and Cu(II). The preconcentration factor for the proposed method for was calculated by the ratio of the sample volume (40 mL containing 100 µg L^{-1} of Cd(II) and Cu(II)) to the final volume (1 mL). So, the preconcentration factor was 40 for 40 mL of sample solution.

Table 3. Analytical characteristics of the proposed method.

Parameters	Cd	Cu
Linear dynamic range (μg L^{-1})	5-700	2-1000
Correlation coefficient (r^2)	0.9991	0.9997
RSD (%) (n=7,C=100 μg L^{-1})	1.23	1.67
Limit of detection (LOD) (μg L^{-1}, n=7)	0.87	0.51
Pre-concentration Factor	40	40

A comparison between dynamic linear range, LOD, and RSD for the proposed method and some of the published methods for determination of trace Cd (II) and Cu(II) in environmental water samples is summarized in Table 4. In these methods, SPE for sample separation and preconcentration coupled with FAAS determination was employed. However, the sorbents applied for SPE are different. According to Table 4, the new sorbent is a powerful alternative to other sorbents for extraction and determination of trace amounts of Cd (II) and Cu(II) in water samples.

Table 4. Comparison with other previously reported techniques.

Sorbent	Linear range (μg L^{-1})		LOD (μg L^{-1})		RSD (%)		Reference
	Cd	Cu	Cd	Cu	Cd	Cu	
(MGO-DVB-VA)[1]	-	-	0.37	2.34	3.1	1.7	[25]
Diaminobenzidine-coated silica gel	0.1–10	0.5–100	4	10	1.64	2.29	[26]
Fe_3O_4@SiO_2@alizarin complexone	1.0-100	1.0-100	0.12	0.18	2.3	2.4	[27]
mag-MoS_2-Fe_3O_4[2] nanocomposite	-	-	-	1.8	-	1.5	[28]
Graphite oxide	-	-	-	1.25	-	2	[29]
Phosphorus-containing polymeric	-	-	1.1	-	4.6	-	[30]
Fe_3O_4@Ag@ITHCDT	5–700	2-100	0.87	0.51	1.23	1.67	This work

[1] Magnetic allylamine modified graphene oxide-poly (vinyl acetate-co-divinylbenzene)

[2] Magnetic molybdenum disulfide

Application of the proposed method to real samples

In order to investigate the accuracy and applicability of the proposed method for determination of trace amounts of Cd(II) and Cu(II), based on MSPE using the new nanoparticles sorbent coupled with FAAS determination, real environmental water samples were analyzed and the results are given in Table 5. As can be seen, the recoveries for the addition of different concentrations of metal ions were in the range 97.58-106.52%, which indicated that the matrices of the samples have little effect on the proposed method for determination of metal ions.

Table 5. Analytical results of Cd(II) and Cu(II) in environmental water samples.

Sample	Cd added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)	Cu added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Tap water	0	N.D[b]	-	0	N.D	-
	50	46.87	93.74	50	52.56	105.12
	100	91.98	91.98	100	106.52	106.52
Well water	0	N.D	-	0	N.D	-
	50	49.84	99.68	50	48.79	97.58
	100	105.36	105.36	100	104.65	104.56
Mineral water	0	N.D	-	0	N.D	-
	50	48.14	96.28	50	49.98	99.96
	100	103.45	103.45	100	103.74	103.74
River water	0	N.D	-	0	N.D	-
	50	47.61	95.22	50	51.29	102.58
	100	104.34	104.34	100	98.76	98.76

Conclusion

In this study, Fe_3O_4@Ag@ITHCDT NPs were successfully synthesized as a new novel sorbent and were used in SPE procedure for extraction, pre-concentration, and determination of cadmium and copper. The prepared sorbent was characterized using SEM, FT-IR and EDS techniques. The new sorbent indicates high adsorption capacity, good extraction performance, acceptable stability and repeatability. Other advantages of proposed method are low time consumption due to rapid separation of the sorbent by a strong magnetic field and high surface area, simple, fast, and inexpensive synthesis method; high sensitivity, and precision and accuracy in pre-concentration and determination of metal ions in environmental water samples.

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