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Light-induced pH change and its application to solid phase extraction of trace heavy metals by high-magnetization $Fe_3O_4@SiO_2@TiO_2$ nanoparticles followed by inductively coupled plasma mass spectrometry detection

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ABSTRACT

We report here the preparation of high-magnetization $Fe_3O_4@SiO_2@TiO_2$ nanoparticles for solid phase extraction of trace amounts of Cd(II), Cr(III), Mn(II) and Cu(II) from environmental waters. The prepared nanoparticles were characterized by scanning electron micrograph (SEM) and transmission electron microscopy (TEM). The high-magnetization nanoparticles carrying the target metals could be easily and fast separated from the aqueous solution simply by applying an external magnetic field while no filtration or centrifugation was necessary. A light-induced hydroxide ion emitter, molecular malachite green carbinol base (MGCB) was applied to adjust pH value of solution for quantitative adsorption instead of the conventional used buffer. In the presence of UV light, MGCB gives out OH^- ions, and this leads to an increase in the pH value without the aid of buffer solution. Using high-magnetization $Fe_3O_4@SiO_2@TiO_2$ nanoparticles as the extraction material and the light-induced MGCB for pH adjustment, we developed an efficient and convenient two-step method for separation/preconcentration trace amounts of Cd(II), Cr(III), Mn(II) and Cu(II) in environmental water samples followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. The parameters affecting the extraction such as MGCB concentration, exposal time, sample volume, eluent condition, and interfering ions have been investigated in detail. Under the optimized conditions, the limits of detection for Cd(II), Cr(III), Mn(II) and Cu(II) were 4.0, 2.6, 1.6 and 2.3 ng L^{-1}, respectively, and the relative standard deviations (RSDs, $c = 1\ \mu g\ L^{-1}$, $n = 7$) were 3.6%, 4.5%, 4.0 and 4.1%, respectively. The proposed method has been validated using certified reference materials, and it has been successfully applied in the determination of trace Cd(II), Cr(III), Mn(II) and Cu(II) in environmental water samples.

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1. Introduction

Along with the development of science and technology, a lot of metals were used for different scientific and industrial purposes, and they are inevitably discharged into the environment. To evaluate the effects of these metals on environment, a very sensitive and reliable method is required to determine very low content of metals in the environmental samples [1].

Inductively coupled plasma mass spectrometry (ICP-MS) is considered to be the most appropriate technique for trace and ultra-trace elements analysis because of its very low limits of detection for most elements. However, it is not free of interference effects, specifically spectroscopic interference and matrix effects [2]. Spectroscopic interference in ICP-MS can be minimized using high-resolution (HR) ICP-MS and collision/reaction cell ICP-MS [3]. However, these techniques are costly and they still suffer from matrix effects when samples are analyzed directly. Therefore, a sample pretreatment step, which can separate the analytes from the matrix components and preconcentrate them before their measurement, is often mandatory [4].

Solid phase extraction (SPE) is an ideal technique for trace metals separation/preconcentration, and it possesses virtues such as simplicity, flexibility, easy of automation, and high enrichment factor. Since the adsorption materials play a very important role in SPE, much of the current research in SPE focuses on the development of new sorbents. To date, many novel adsorbents, such as nano materials [5], ion imprinted material [6], mesoporous materials [7], carbon nanotubes [8] and magnetic nanoparticles [9] have been employed in SPE.

Magnetic nanoparticles consisting of an iron oxide core and silica shell have attracted particular attention in the past few decades because of their unique physical and chemical properties, such as unique magnetic responsivity, low cytotoxicity, and chemically modifiable surface [10,11]. The core-shell magnetic silica

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nanoparticles have shown great potential in various fields, such as cell separation [12], magnetically assisted drug delivery [13], enzyme immobilization [14] and most recently magnetic solid phase extraction (MSPE) [15]. In our previous works, silica-coated magnetic nanoparticles (SCMNPs) immobilized with Bismuthiol II or γ-mercaptopropyl trimethoxysilane (γ-MPTMS) were synthesized and employed as an SPE adsorbent for separating and concentrating trace amounts of heavy metals from biological and environmental samples [9,16]. Besides core-shell structure $Fe_3O_4@SiO_2$ nanoparticles, core-shell structure $Fe_3O_4@TiO_2$ nanoparticles have also been prepared and applied for enrichment of phosphopeptides [17,18], and as a photocatalyst [19,20]. Our previous studies demonstrated that titania nanoparticles are good SPE adsorbent for extraction of trace metals due to their unique properties [21]. Therefore, it is reasonable that core-shell structure $Fe_3O_4@TiO_2$ nanoparticles should exhibit similar adsorption properties to the metals. However, to the best of our knowledge, no report on the use of $Fe_3O_4@TiO_2$ as SPE adsorbent for extraction of trace metals is appeared until present.

In traditional SPE procedures for trace metals, pH plays an important role in preconcentration step. Acid and base are used to adjust pH value of sample solution. Sometimes, such procedures are both time consuming and labor taking. Additionally, the blanks of metal ions resulting from the buffer are also an unnegligible problem. Molecular malachite green carbinol base (MGCB) is a light-induced hydroxide ion emitter. In the presence of 302 nm UV light, MGCB gives out OH^- ions, as well as showing an obvious color change, and this leads to an increase in the pH value [22,23]. In the most pronounced case, the pH was increased from 5.4 to 10.0 by irradiation within 3 min. And after removal of the light, the pH returned to the initial value after 15 min in the dark [23]. With the aid of MGCB and UV light, the pH value could be controlled without adding acid or base.

In this study, $Fe_3O_4@SiO_2@TiO_2$ nanoparticles were synthesized and employed as an SPE adsorbent for separating and concentrating trace amounts of Cd(II), Cr(III), Mn(II) and Cu(II) from environmental samples prior to their determination by ICP-MS. To facilitate the extraction operation, the light-induced hydroxide ion emitter (MGCB) was applied to adjust pH value of solution for quantitative adsorption. The factors affecting the extraction were investigated in detail, and the applicability of the method was evaluated by the analysis of trace metals in environmental waters.

2. Experimental

2.1. Instruments and apparatus

Determination of the target analytes was carried out on a quadrupole (Q) ICP-MS (Agilent 7500a, Tokyo, Japan) equipped with a Babington nebulizer. The operating conditions used in this work are summarized in Table 1. The scanning electron micrograph (SEM) was obtained using an X-650 scanning electron microscope (Hitachi, Tokyo, Japan) at an acceleration voltage of 25 kV. The prepared $Fe_3O_4@SiO_2@TiO_2$ nanoparticles were also characterized by a JEM-100CXII electron microscope (JEOL, Tokyo, Japan). A SY1200 model Ultrasonicator (Shengyuan Instrument Factory, Shanghai, China) was used to disperse the nanoparticles solution. An Nd–Fe–B magnet (8.0 mm × 6.0 mm × 1.6 mm) was used for magnetic separation.

Table 1
Operating parameters of ICP-MS with a Babington nebulizer.

ICP-MS	Parameters
RF power	1200 W
RF matching	1.6 V
Outer gas flow rate	15 L min^{-1}
Intermediate gas flow rate	0.7 L min^{-1}
Nebulizer gas flow rate	0.5 L min^{-1}
Nebulizer pump	0.05 rps
Sampling depth	5.8 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	10–20 ms
Integration mode	Peak area
Points per spectral peak	1
Isotopes	^{53}Cr ^{55}Mn ^{63}Cu ^{111}Cd

2.2. Standard solutions and reagents

The stock solutions (1 g L^{-1} of Cd(II), Cr(III), Cu(II) and Mn(II)) were prepared by dissolving appropriate amounts of $Cd(NO_3)_2·4H_2O$, $Cr(NO_3)_3·9H_2O$, $Cu(NO_3)_2·3H_2O$ and $Mn(NO_3)_2·6H_2O$ (Shanghai Reagent Factory, Shanghai, China) in high purity deionized water, respectively. HNO_3 was added to their stock solution to prevent hydrolysis. Calibration solutions and test solutions were prepared by serial dilution of their stock solutions. MGCB was purchased from Hong Jin Trading Co., LTD, Qing Dao, China; tetraethoxysilane (TEOS) were obtained from Wuhan University Chemical Factory, Wuhan, China. $FeCl_3·6H_2O$, sodium acetate and tetrabutyl titanate were purchased from Shanghai First Reagent Factory, Shanghai, China. Ultra pure grade of HNO_3 was further purified by sub-boiling distillation prior to use. All other chemicals were of analytical reagent grade. All stock standard solutions were stored in polyethylene bottles in refrigerator held at 4 °C. All glassware were kept in 10% nitric acid for at least 24 h and washed three times with high purity deionized water before use. The high purity deionized water (18.2 MΩ cm) obtained from a Labconco system (Kansas City, MO, USA) was used throughout this work. The pH of the solution was adjusted to 0–2, 2–8, and 8–9 by HNO_3, Na_2HPO_4/citric acid and NH_4Cl/NH_4OH, respectively.

2.3. Synthesis of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles sorbent

The magnetic Fe_3O_4 particles were prepared through a solvothermal reaction as described in reference [11]. 0.20 g of prepared Fe_3O_4 particles was treated with 0.1 mol L^{-1} HCl aqueous solution by ultrasonication. After the treatment for 3 min, the magnetite particles were separated and washed with high purity deionized water, and then homogeneously dispersed in the mixture of ethanol (100 mL), deionized water (20 mL) and concentrated ammonia aqueous solution (1.0 mL), followed by the addition of 0.2 mL TEOS. After stirring at room temperature for 6 h, the $Fe_3O_4@SiO_2$ nanoparticles were separated and washed with ethanol and water.

Synthesis of $Fe_3O_4@SiO_2@TiO_2$ core-shell nanoparticles was similar to Ref. [18] with minor modification. Tetrabutyltitanate (2 mL) was dissolved in ethanol (50 mL) to form a clear solution. $Fe_3O_4@SiO_2$ magnetic nanoparticles (200 mg) were then dispersed in the freshly prepared solution with the aid of ultrasonication for 5 min. 1 mL 1:5 (v/v) mixture of water and ethanol was added dropwise to the suspension of $Fe_3O_4@SiO_2$ magnetic nanoparticles with vigorous magnetic stirring over a period of approximately 10 min.

Thereafter, the suspension was stirred for a further 1 h before separation and washing with ethanol. After five cycles of separation/washing/redispersion with ethanol, the $Fe_3O_4@SiO_2@TiO_2$ obtained was oven-dried and calcined at 500 °C in nitrogen.

2.4. General procedure for preconcentration/separation

Certain amount of MGCB was dissolved in the test solutions containing 20 μg L^{-1} Cd(II), Cr(III), Mn(II) and Cu(II). The solution was exposed to UV light for several minutes. 40 mg of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles was added into solutions and the mixtures were dispersed by ultrasonication. The nanoparticles were then magnetically separated, washed by high purity deionized water and then magnetically separated again. HNO_3 was used for elution of the retained metal ions. After desorption, the nanoparticles were again magnetically separated and the eluent was introduced to ICP-MS for subsequent determination. High purity deionized water was employed as the blank solution and was subjected to the same procedure.

2.5. Sample preparation

Certified reference materials of GSBZ 50009-88 was employed for testing the accuracy of the proposed method. In addition, corresponding real samples, lake water (East Lake, Wuhan, China) and tap water were analyzed. Details of the sample preparation are as follows.

Lake water (pH 6.8) was sampled from the central part of East Lake, Wuhan, China; tap water (pH 7.3) was collected from our lab. Immediately after sampling, all water samples were filtered through a 0.45 μm membrane (Tianjing Jinteng Instrument Factory, Tianjin, China) and stored in precleaned polypropylene bottles in a refrigerator at 4 °C until analysis.

The environmental water reference materials ERMs, GSBZ 50009-88 was provided by the Institute for Reference Materials of Sepa, Beijing, China. Prior to use, the ampoule was broken carefully at the neck and 10 mL of the sample was pipetted into 250 mL volumetric flask and brought to volume using high purity deionized water according to the instructions by the supplier. The sample was further diluted and adjusted to desired pH for analysis. The blank samples were also prepared by the same procedure described above except that no analytes were added.

3. Results and discussion

3.1. Characterization of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles

The $Fe_3O_4@SiO_2@TiO_2$ magnetic nanoparticles were characterized by transmission electron microscopy (TEM). As shown in Fig. 1, the light color of TiO_2 is on the surface of black Fe_3O_4 core, and the average diameter of the $Fe_3O_4@SiO_2@TiO_2$ nanoparticles was estimated to be about 22 nm.

Fig. 2 was the SEM images of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles. As could be seen, the $Fe_3O_4@SiO_2@TiO_2$ nanoparticles are porous, which could offer high surface area.

Surface area and pore size analysis of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles were carried out by ASAP 2020 accelerated surface area and porosimetry analyzer, and the results indicated that BET surface area was 157.07 $m^2\,g^{-1}$ and BJH adsorption average pore width (4 V/A) was 3.53 nm.

3.2. Effect of pH

The effect of pH on the retention of Cd(II), Cr(III), Mn(II) and Cu(II) on $Fe_3O_4@SiO_2@TiO_2$ nanoparticles was investigated according to the general procedure with aid of buffer solutions (because the pH value below 8 could not be precisely controlled by MGCB). 50 mL of solutions with target metals concentration of 20 μg L^{-1} were prepared separately and pH values of sample solutions were adjusted to a range of 0–9 with buffer solution. 40 mg $Fe_3O_4@SiO_2@TiO_2$ nanoparticles was then added into the above solutions and the mixtures were dispersed by ultrasonication. After magnetic separation, the supernatants were measured by ICP-MS as described in the recommended procedure. Fig. 3 was the effect of pH on the adsorption percentage of Cd(II), Cr(III), Mn(II) and Cu(II). As could be seen, there was no adsorption when the pH value was below 1. The absorption percentage for Cd(II), Cr(III), Mn(II) and Cu(II) was increased with the increase of pH from 2.0 to 8.0 and quantitative adsorption was obtained in the pH range 8–9. In this work, pH higher than 8 was selected for determination of Cd(II), Cr(III), Mn(II) and Cu(II). It should be pointed out that the pH value of environmental waters were around 7, and without addition of MGCB for the increase of pH value, quantitative adsorption is not feasible.

The above experimental results could be explained by the same mechanism as described in Ref. [22]. Briefly, the surface of titanium dioxide is bond of terminal —OH and bridged —OH. When the pH value is higher than the IEP of titania (6.2), the —OH groups were

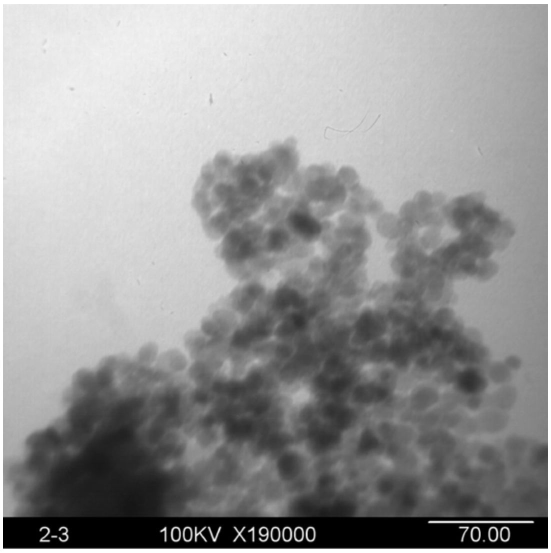

Fig. 1. TEM of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles.

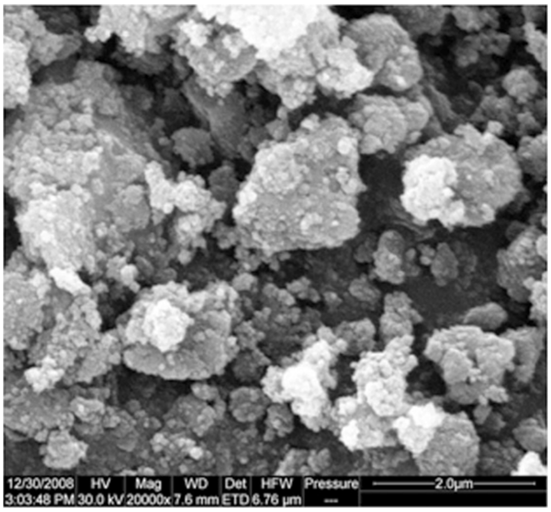

Fig. 2. SEM of $Fe_3O_4@SiO_2@TiO_2$ nanoparticles.

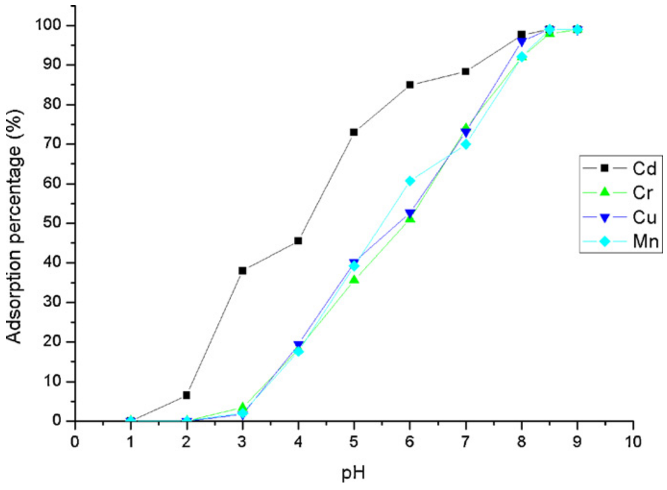

Fig. 3. Effect of pH on the adsorption percentage (%) of Cd(II), Cr(III), Mn(II) and Cu(II). Concentration of target analytes: 20 ng L^{-1}; Fe_3O_4@SiO_2@TiO_2 nanoparticles: 40 mg; sample volume: 50 mL; ultrasonication time: 3 min; sediment time: 1 min.

negatively charged. As a result, metal ions which exist as cations could be adsorbed onto titanium dioxide.

3.3. *The optimization of exposal time and MGCB concentration*

The relation of exposal time and pH value was investigated with exposal time changing from 1 min to 15 min. The experimental results indicated that after 3 min UV light (302 nm) irradiation, pH value reached around 9 and longer irradiation would not increase the pH. Hence, the exposal time was selected as 4 min in further experiments.

The MGCB concentration was also studied. The results showed that when the concentration of MGCB was higher than 1 mmol L^{-1}, after 4 min UV light irradiation, the pH value of test solution could increase to 9. Thus, 1 mmol L^{-1} MGCB was applied in the whole experiment.

3.4. *The optimization of eluent concentration*

From Fig. 3, it could be concluded that the adsorption of the target metals was decreased at low pH value, therefore, acid was chosen to elute the adsorbed metals. HNO_3 is a recommended acid for ICP-MS, for this reason, various concentrations of HNO_3 were studied independently for desorption of adsorbed target metals. With the elution volume and elution time fixed as 0.5 mL and 1 min, respectively, the experimental results in Fig. 4 indicated that 0.5 mol L^{-1} HNO_3 was sufficient for quantitatively elution of Cd(II), Cr(III), Mn(II) and Cu(II) from the magnetic nanoparticles. Therefore, 0.5 mol L^{-1} HNO_3 was chosen as eluent in subsequent experiments.

3.5. *Elution volume and time*

The effect of elution volume for quantitative elution of the studied Cd(II), Cr(III), Mn(II) and Cu(II) by 0.5 mol L^{-1} HNO_3 was investigated. It was found that 0.5 mL of 0.5 mol L^{-1} HNO_3 was sufficient to recover all the studied metals quantitatively.

With 0.5 mL of 0.5 mol L^{-1} HNO_3 as eluent, the effect of elution time on the recovery of Cd(II), Cr(III), Mn(II) and Cu(II) was investigated. The experimental results indicated that all the target metals could be recovered quantitatively in 1 min. Consequently, the elution time of 1 min was selected for quantitative recovery of target analytes in the subsequent experiments.

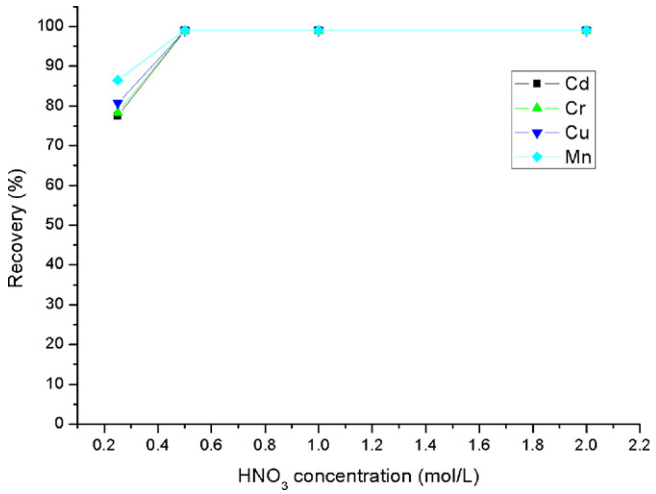

Fig. 4. Effect of HNO_3 concentration on the recovery (%) of Cd(II), Cr(III), Mn(II) and Cu(II). Concentration of target analytes: 20 ng L^{-1}; Fe_3O_4@SiO_2@TiO_2 nanoparticles: 40 mg; MGCB concentration: 1 mmol L^{-1}; irradiation time: 4 min; sample volume: 50 mL; ultrasonication time: 3 min; sediment time: 1 min; elution volume: 0.5 mL; elution time: 1 min.

3.6. *Sampling time and sample volume*

The sampling time should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. To study the effect of sampling time, 50 mL sample solution containing 20 ng L^{-1} target analytes, 1 mmol L^{-1} MGCB and 40 mg Fe_3O_4@SiO_2@TiO_2 nanoparticles was irradiated under the UV light (302 nm) for 4 min, and then ultrasonicated for several minutes. It was found that, with the aid of ultrasonication, Cd(II), Cr(III), Mn(II) and Cu(II) could be quantitatively adsorbed in 3 min. In this work, 3 min was selected for quantitative adsorption.

In order to investigate the effect of sample volume on the extraction, the sample solutions of 5, 20, 50, 100 and 200 mL containing Cd(II), Cr(III), Mn(II) and Cu(II) were prepared and then operated according to the general procedure. As could be seen from Fig. 5, the target metals could still be quantitatively recovered when sample volumes were 100 mL. Therefore, a sample volume of 50 mL and

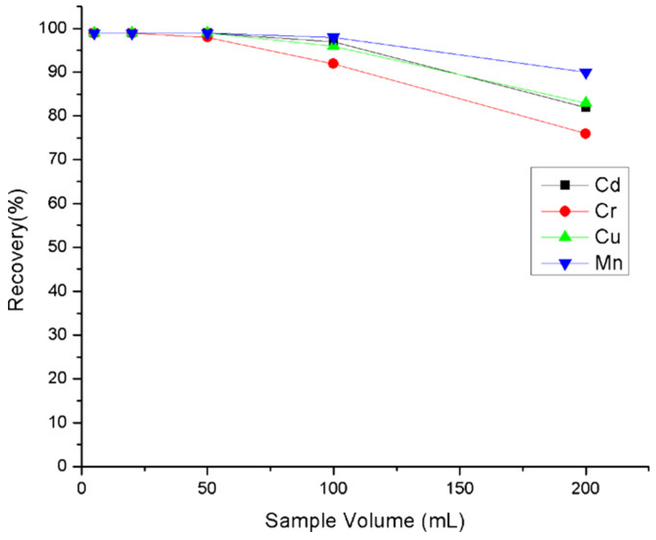

Fig. 5. Effect of sample volume on the recovery (%) of Cd(II), Cr(III), Mn(II) and Cu(II). Fe_3O_4@SiO_2@TiO_2 nanoparticles: 40 mg; MGCB concentration: 1 mmol L^{-1}; irradiation time: 4 min; ultrasonication time: 3 min; sediment time: 1 min; HNO_3 concentration: 0.5 mol L^{-1}; elution volume: 0.5 mL; elution time: 1 min.

an elution volume of 0.5 mL were used, so that an enrichment factor of 100 was obtained in this work.

3.7. Effect of sediment time

Conventional SPE usually requires filtration or centrifugation to separate the sorbent from aqueous solutions, which is time-consuming. In this study, the sorbent could be separated readily from the sample solution by applying an external magnetic field, due to the fast magnetic responsivity. The effect of sediment time on the recovery of metal ions was investigated, and no significant effect was observed when the sediment time was greater than 30 s. Hence, the sediment time of 1 min was used in subsequent experiments.

3.8. Effect of coexisting ions

The effects of common coexisting ions on the extraction and subsequent determination were investigated. In these experiments, sample solutions containing 20 μg L^{-1} of Cd(II), Cr(III), Mn(II) and Cu(II) and the added interfering ions were treated according to the general procedure described above. The tolerance of the coexisting ions was defined as the largest amount making the recovery of the studied elements less than 90%. The analytical results show that the presence of 5 g L^{-1} K$^+$ and Na$^+$, 2 g L^{-1} Ca^{2+} and Mg^{2+}, 0.05 g L^{-1} Zn^{2+}, 8 g L^{-1} Cl$^-$, 5 g L^{-1} NO$_3{}^{2-}$ and 2 g L^{-1} SO$_4{}^{2-}$ has no obvious influence on the extraction and determination of all target elements under the selected conditions, indicating that Fe_3O_4@SiO_2@TiO_2 nanoparticles as the sorbent has a good selectivity for target metals and is suitable for the analysis of samples with complicated matrix.

3.9. Adsorption capacities of magnetic Fe_3O_4@SiO_2@TiO_2 nanoparticles for Cd(II), Cr(III), Mn(II) and Cu(II)

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. The method used in capacity study was adapted from that recommended by Maquieira et al. [24]. Briefly, 50 mL sample solutions containing target analytes with a series of concentration were preconcentrated and eluted. Evaluation of adsorption capacity was made from a breakthrough curve by plotting the total metal concentration vs the adsorbed metal concentration. The adsorption capacities of Fe_3O_4@SiO_2@TiO_2 magnetic nanoparticles for Cd(II), Cr(III), Mn(II) and Cu(II) were found to be 59.3, 27.8, 15.4 and 33.2 mg g^{-1}, respectively.

3.10. Method validation and applications

Under the optimized experimental conditions, the analytical performance of the method was evaluated. According to the IUPAC definition, the limits of detection (LODs) of the method, defined as three times the standard deviation of blank signal intensity (3σ), were found to be 4.0, 2.6, 1.6 and 2.3 ng L^{-1} for Cd(II), Cr(III), Mn(II) and Cu(II), respectively. The precision (RSDs) for 7 replicate determinations of 1 μg L^{-1} of Cd(II), Cr(III), Mn(II) and Cu(II) were 3.6%, 4.5%, 4.0% and 4.1%, respectively. Table 2 is the comparison of LODs of this work with other literature works on the determination of the same elements [25–31]. As could be seen, the LODs obtained by this work are the lowest one for almost all the target metals except that reported in Ref. [29].

The regeneration is one of the key factors in evaluating the performance of the sorbent. In the eluting agent of 0.5 mol L^{-1} HNO_3, the double coated core-shell structure protect the iron core from erosion and endowed the sorbent more than 50 reused times, which indicates that the material has good stability under acidic conditions. Compared to single coated magnetic nanoparticles which could be used 10 times, the reuse time was greatly prolonged.

Table 2
Comparison of limits of detection (ng L^{-1}) for Cd(II), Cr(III), Mn(II) and Cu(II) obtained by the proposed method with other analytical methods.

Analytical technique	Cd(II)	Cr(III)	Mn(II)	Cu(II)	Ref.
Fe_3O_4@SiO_2@TiO_2 magnetic SPE–ICP-MS	4.0	2.6	1.6	2.3	This work
Sol–gel zirconia coating CME–ICP-MS	4.5	9.9		17.9	[24]
8-Hydroxyquinoline immobilized polyacrylonitrile fiber SPE–ICP-MS	6.1	–	121.5	9.8	[25]
On-line solid-phase chelation-FI–ICP-MS	240	530	4		[26]
APTES-silica hybrid monolithic CME–ICP-MS	1.2	–	6.2	6.3	[27]
On-line SPE–ICP-MS	0.79	1.2	–	2.5	[28]
On-line SPE–ICP-MS	5	–	–	31	[29]
TiO_2 hollow fiber FI–SPMME-ICP-MS	2				[30]

CME: capillary microextraction; FI: flow injection.

Table 3
Analytical results of Cd, Cr and Cu in certified reference materials of GSBZ 50009-88 (mean ± s.d., $n = 3$).

Sample	Element	Certified value	Determined value
GSBZ 50009-88 (μg mL^{-1})	Cu	1.49 ± 0.04	1.44 ± 0.04
	Cr	1.49 ± 0.06	1.50 ± 0.04
	Cd	0.105 ± 0.004	0.102 ± 0.002

To evaluate the accuracy of the developed method, certified reference materials of GSBZ 50009-88 environmental water was analyzed, and the analytical results are shown in Table 3. As can be seen, the determined values are in good agreement with the certified ones.

The proposed method was also applied to the analysis of East Lake water and tap water. The analytical results, along with the recovery for the spiked samples, are given in Table 4. As can be seen, recoveries for the target analytes ranged from 94.5% to 109%.

Table 4
Analytical results of Cd, Cr, Cu and Mn in East Lake water and tap water (mean ± s.d., $n = 3$).

Sample	Element	Added	Found	Recovery %
Tap water (ng mL^{-1})	Cd	0	0.22 ± 0.01	–
		1	1.24 ± 0.03	102
	Cr	0	1.13 ± 0.04	–
		1	2.18 ± 0.06	105
	Cu	0	0.38 ± 0.03	–
		1	1.37 ± 0.02	101
	Mn	0	0.66 ± 0.02	–
		1	1.75 ± 0.05	109
East Lake (ng mL^{-1})	Cd	0	1.18 ± 0.03	–
		2	3.09 ± 0.05	95.5
	Cr	0	2.86 ± 0.04	–
		2	4.75 ± 0.11	94.5
	Cu	0	4.35 ± 0.11	–
		2	6.19 ± 0.21	92.0
	Mn	0	2.60 ± 0.04	–
		2	4.50 ± 0.06	95

4. Conclusions

$Fe_3O_4@SiO_2@TiO_2$ magnetic nanoparticles have been prepared and applied for solid phase extraction of trace amounts of Cd(II), Cr(III), Mn(II) and Cu(II) followed by ICP-MS detection. A light-induced hydroxide ion emitter, MGCB was employed to adjust pH value of sample solution for quantitative adsorption. The prepared material had fast magnetic responsivity, high adsorptive capacities and rapid sorption/desorption kinetics for Cd(II), Cr(III), Mn(II) and Cu(II). Compared with established methods, the method described here bring forward a new way to control sample pH, in addition, it has a high enrichment factor and very low LODs, and is suitable for rapid adsorption of Cd(II), Cr(III), Mn(II) and Cu(II) from large volumes of sample solution.

Acknowledgments

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References

[1] J. Yin, Z.C. Jiang, G. Chang, B. Hu, Anal. Chim. Acta 540 (2000) 333.
[2] L. Yang, R.E. Sturgeon, D. Prince, S. Gabos, J. Anal. At. Spectrom. 17 (2002) 1300.
[3] E. McCurdy, G. Woods, J. Anal. At. Spectrom. 19 (2002) 607.
[4] B. Hu, F. Zheng, Anal. Chim. Acta 605 (2007) 1.
[5] X.L. Pu, Z.C. Jiang, B. Hu, H.B. Wang, J. Anal. At. Spectrom. 19 (2004) 984.
[6] T.P. Rao, S. Daniel, J.M. Gladis, Trends Anal. Chem. 23 (2004) 28.
[7] X. Feng, G.E. Fryxell, L.Q. Wang, A.Y. Kim, J. Liu, Science 276 (1997) 923.
[8] M. Valcarcel, S. Cardenas, B.M. Simonet, Y. Moliner-Martinez, R. Lucena, Trends Anal. Chem. 27 (2008) 34.
[9] C.Z. Huang, B. Hu, Spectrochim. Acta Part B 63 (2008) 437.
[10] C.H. Deng, X.Q. Xu, M.X. Gao, W.J. Yu, P.Y. Yang, X.M. Zhang, Adv. Mater. 18 (2006) 3289.
[11] C. Deng, Y. Deng, D. Qi, X. Zhang, D. Zhao, J. Am. Chem. Soc. 130 (2008) 28.
[12] Y.H. Deng, C.H. Deng, D. Yang, C.C. Wang, S.K. Fu, X.M. Zhang, Chem. Commun. (44) (2005) 5548.
[13] S.K. Fu, Y.H. Deng, C.C. Wang, X.Z. Shen, W.L. Yang, L. An, H. Gao, Chem. Eur. J. 11 (2005) 6006.
[14] A. Guiseppi-Elie, N.F. Sheppard, S. Brahim, D. Narinesingh, Biotechnol. Bioeng. 75 (2001) 475.
[15] C.Y. Chen, C.L. Chiang, P.C. Huang, Sep. Purif. Technol. 50 (2006) 15.
[16] J.S. Suleiman, B. Hu, H.Y. Peng, C.Z. Huang, Talanta 77 (2008) 1579.
[17] Y.C. Chen, C.T. Chen, Anal. Chem. 77 (2005) 5912.
[18] C.H. Deng, Y. Li, X.Q. Xu, D.W. Qi, P.Y. Yang, X.M. Zhang, J. Proteome Res. 7 (2008) 2526.
[19] D. Beydoun, R. Amal, Mater. Sci. Eng. B-Solid 94 (2002) 71.
[20] D.G. Fu, J.J. Xu, Y.H. Ao, C.W. Yuan, J. Phys. Chem. Solids 69 (2008) 1980.
[21] B. Hu, C.Z. Huang, Z.C. Jiang, Talanta 73 (2007) 274.
[22] D.S. Liu, H.J. Liu, Y. Xu, F.Y. Li, Y. Yang, W.X. Wang, Y.L. Song, Angew. Chem. Int. Ed. 46 (2007) 2515.
[23] M. Irie, J. Am. Chem. Soc. 105 (1983) 2078.
[24] A. Maquieira, H.A.M. Elmahadi, R. Puchades, Anal. Chem. 66 (1994) 3632.
[25] Y.W. Wu, B. Hu, Z.C. Jiang, Y.Q. Feng, P. Lu, B.Y.Z. Li, Rapid Commun. Mass Spectrom. 20 (2006) 3527.
[26] B. Wen, X. Shan, Anal. Bioanal. Chem. 374 (2002) 948.
[27] E.V. Alonso, I.S. Trujillo, M.T.S. Cordero, J.M.C. Pavon, A.G. de Torres, J. Anal. At. Spectrom. 25 (2010) 1063.
[28] L. Zhang, B.B. Chen, H.Y. Peng, M. He, B. Hu, J. Sep. Sci. 34 (2011) 2247.
[29] J. Wang, X. Ma, G. Fang, M. Pan, X. Ye, S. Wang, J. Hazard. Mater. 186 (2011) 1985.
[30] T.T. Shih, W.Y. Tseng, K.H. Tsai, W.Y. Chen, M.W. Tsai, Y.C. Sun, Microchem. J. 99 (2011) 260.
[31] C.Z. Huang, B. Hu, Analyst 136 (2011) 1425.