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.

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.

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 $Cd(NO_3)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and

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

$Mn(NO_3)_2 \cdot 6H_2O$ (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. $FeCl_3 \cdot 6H_2O$, 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.