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Silver modified magnetic carbon nanotubes composite as a selective solid phase extractor for preconcentration and determination of trace mercury ions in water solution

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A magnetic composite of silver/iron oxides/carbon nanotubes (Ag/Fe₃O₄/CNTs) was synthesized and used as an adsorbent for the preconcentration of mercury ions in water solutions at room temperature (25°C) in this study. The silver nanoparticles were supported on the magnetic CNTs. The modification enabled the composite had not only a high adsorption capacity for mercury ions (Hg²⁺) but also the magnetic isolation properties. A fast, sensitive, and simple method was successfully developed for the preconcentration and determination of trace amount of Hg²⁺ in water using the synthesized nanocomposite as adsorbent. The mercury concentration was determined by an atomic fluorescence spectrometer (AFS). The experimental conditions such as pH value, extraction temperature, extraction time, sample volume, eluent composition and concentration, sorbent amount, and coexisting ions were investigated for the optimization. A 500 mL of sample volume resulted in a preconcentration factor of 125. When a 200 mL of sample was employed, the limit of detection for Hg²⁺ was as low as 0.03 ng mL⁻¹ with relative standard deviation of 4.4% at 0.1 ng mL⁻¹ (*n* = 7). The ease of synthesis and separation, the good adsorption capacity, and the satisfactory recovery will possibly make the composite an attractive adsorbent for the preconcentration of ultratrace Hg²⁺ in waters.

Keywords: silver nanoparticles; magnetic carbon nanotubes; preconcentration; mercury; water solution

1. Introduction

The level of mercury in water can be elevated owing to the anthropogenic mercury emission. The mercury ions in the polluted water can be further transformed into the more toxic methyl mercury species by the action of aquatic organisms. Therefore, the level of Hg²⁺ in water should be kept under the permanently controlled conditions and be sensitively detected. Although, many instruments and methods have been developed for the sensitive determination of mercury [1], the analysis is still difficult and challenging when the level of mercury is low or the matrix is complex. Some pretreatment methods including solid phase extraction (SPE) [2–7], liquid–liquid microextraction (LLME) [8,9], cloud point extraction (CPE) [10,11] have been applied to remove interfering matrix components and preconcentrate Hg²⁺ before analysis by instruments [12]. Among the reported methods, SPE is regarded as the most effective preconcentration method for its simplicity, rapidity and ability with high concentration factors.

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Compared with the traditional SPE sorbents, the nanomaterials always have higher extraction efficiency owing to the larger surface area and shorter diffusion route during the extraction [13]. As a novel kind of nanomaterials, CNTs have been used as the effective sorbents for the preconcentration and removal of both organic pollutants and metal ions in water [14–18]. To further increase the adsorption capacity and selectivity of the adsorbents, CNTs can be modified by chemical treatment or used as supports for the synthesis of new nanocomposites [19–21]. The modified nanomaterials or composites have the advantages of high sorption capacity, large surface area and supported compounds [22]. The metallic oxides, complexing or chelating compounds have been reported to be supported onto CNTs and increased the adsorption capacity of CNTs to metal ions through physical loading or chemical binding [14,20,23,24].

Based on the amalgamation mechanism, the noble metals (especially gold) had been used as the adsorbents for mercury many years before [25–27]. A sorbent for mercury produced by amalgamation can be regenerated unlimited times theoretically. However, the pure noble metals are not suitable for the extraction and preconcentration of pollutants for their high density, low specific surface area, high cost, and difficulties in separation for recycling [28]. The problems mentioned above can be solved by supporting the noble metals on the nanomaterials, which have large surface area and high porosity. The high affinity of silver nanoparticles for mercury has been recently reported and applied to detect Hg^{2+} [29–31]. The mechanism is mainly based on both amalgam and nanoeffects or galvanic reaction [27,32]. The high affinity of silver nanoparticles for mercury makes it possible to enhance the selectivity and capacity of sorbents by silver nanoparticles modification. It has been reported that the sorbents such like active alumina decorated with silver nanoparticles were quite efficient for the capture of elemental mercury and the removal of mercuric ions in the contaminated waters [28,33].

Another key step for a preconcentration and extraction method is the isolation of the solid adsorbent from the liquid phase. If the volume of polluted water is huge, a centrifugal separation will be inapplicable [13]. The application of a magnetic technology can solve this problem with the distinct advantage of magnetic isolation by an external magnetic field [13,21,22,34,35]. Different types of magnetic nanoparticles have been synthesized for the extraction and determination of both organic and inorganic pollutants [36,37]. CNTs were also used as the support for synthesis of magnetic sorbents and applied to preconcentrate or remove pollutants in waters [21,38].

Based on the high affinity of nanosilver particles for mercury and the large surface area of CNTs, it is very promising to explore a novel noble metal/carbon nanocomposite sorbents for mercury extraction or preconcentration. The aim can be achieved by incorporating the merits of noble metals and magnetic CNTs together in one composite. To the best of our knowledge, there is no publication about the preparation and application of magnetic CNTs composites loaded with nanosilver particles. In this study, the composite of $\text{Ag}/\text{Fe}_3\text{O}_4/\text{CNTs}$ was synthesized and used as a selective SPE sorbent to extract trace mercury in water samples for the first time. The major objective of this study was to develop a new magnetic solid phase extraction method for the preconcentration and determination of trace Hg^{2+} in water samples by the fabricated nanocomposite.

2. Experimental

2.1. Reagents and apparatus

All reagents used were of analytical grade or better. Deionized water was used to prepare all solutions. The stock solution of Hg^{2+} ($1000 \mu\text{g mL}^{-1}$) was obtained from National Institute of Metrology (Beijing, China). Working standard solutions were prepared daily by appropriate dilution of the stock solution with deionized water. 0.1 M HCl and 0.1 M NaOH were used to

adjust the sample pH in the range of 1–12. Acid solutions were prepared by dilution with deionized water from the concentrated acids. N, N-Dimethylformamide (DMF) and sodium borohydride (NaBH_4) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Silver nitrate (AgNO_3) was purchased from Tiangan Chemical Co. Ltd. Ammonium ferric sulfate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) and ferrous ammonium sulfate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Tianjin Tianda Chemical Works. Ammonium hydroxide (NH_4OH) was obtained from Tianjin Xintong Fine Chemical Co., Ltd. Sodium citric acid was purchased from Tianjin Fuchen Chemical Reagents Factory. CNTs were purchased from Shenzhen Nanotech Port Co. Ltd. The pipettes and vessels were kept in 10% nitric acid for at least 24 h and subsequently washed three times with de-ionized water before use. The measurements were performed with a cold vapour atomic fluorescence spectrometer (CVAFS) (Suzhou Instruments Co., Suzhou, China).

2.2. Synthesis of magnetic carbon nanotubes ($\text{Fe}_3\text{O}_4/\text{CNTs}$)

$\text{Fe}_3\text{O}_4/\text{CNTs}$ nanoparticles were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} ions in the presence of alkaline solution under hydrothermal treatment. Typically, 1.0 g of CNTs was oxidized by being refluxed in concentrated nitric acid for 1 h. Then, the modified CNTs were washed by deionized water and ethanol subsequently for cleaning. The cleaned CNTs were dried at 100°C for 4 h. 1.0 g of the purified CNTs was subsequently suspended in 200 mL of mixed solution containing 1.7 g $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 2.5 g $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. After that, 5.0 mL of 8 mol L^{-1} NH_4OH solution was added slowly in 10 min at a constant temperature of 50°C under nitrogen atmosphere with the aid of ultrasonic stirring. The pH of the mixture was controlled in the range of 11–12. The reaction was allowed to continue for 60 min. After the completion of the reaction, the suspension was allowed to cool at room temperature. The modified CNTs were isolated from the mixture by a permanent magnet and dried under vacuum at 55°C for 8 h.

2.3. Synthesis of $\text{Ag}/\text{Fe}_3\text{O}_4/\text{CNTs}$ nanocomposite

0.034 g of AgNO_3 and 0.1764 g of sodium citric acid were dissolved in 100 mL of deionized water in a beaker. The solution was then stirred using a magnetic blender and 2.0 mL of NaBH_4 solution (500 mmol/L) was added dropwisely within 5 min to obtain the silver stock solution. At the same time, 0.2 g of the magnetic CNTs was dispersed in 50 mL of DMF/ H_2O (1:1, v/v) solution and sonicated for 1 h. The dispersed solution containing magnetic CNTs was then added into the prepared silver stock solution. The mixture was then stirred for 12 h continuously to facilitate the silver in the solution to adsorb onto the surface of the magnetic CNTs. When the synthesis reaction completed, the nanosilver-loaded magnetic CNTs was vacuum filtered using a glass filter and washed by deionized water for at least three times. The prepared composite was dried at 55°C for 8 h in a vacuum oven and the synthesized adsorbent was ready for use.

2.4. Characterization methods

The morphology of the synthesized nanocomposite was characterized by scanning electron microscopy (SEM), energy dispersive spectrum (EDS) analysis using a Zeiss Supra55 microscope (Carl zeiss, Supra55, Germany), and a transmission electron microscope (TEM, Hitachi H-7500, Japan) equipped with a tungsten cathode. The structure of the nanocomposites was analyzed by X-ray powder diffraction (XRD) pattern recorded on a D/max 2550 X-ray Diffractometer (D8 Advance, Bruker, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$) in

steps of $0.05^{\circ}(20) \text{ min}^{-1}$ from 15° to 85° . The magnetic properties of the composites were monitored by a vibrating sample magnetometer (VSM) (Wuke photoelectric technology Co, Beijing).

2.5. Preconcentration and determination of Hg^{2+}

The preconcentration experiments of Hg^{2+} were performed according to the batch method. The conical beakers containing 10 mg of $\text{Ag}/\text{Fe}_3\text{O}_4/\text{CNTs}$ and 50 mL of mercury solution with the initial pH value at 3.0 were placed in a constant temperature bath oscillator to vibrate at room temperature (25°C). After a period of time ($>20 \text{ min}$), the adsorbent was separated from the solutions using a permanent magnet. The adsorbed analyte was eluted by 4.0 mL of eluent containing 10% (v/v) HCl and 60 μL saturated dithizone ethanol solution. The concentration of mercury in the eluent was directly determined by AFS. The high voltage of AFS was set at 400 V after optimization for the good ratio between noise and signal. The high purified nitrogen ($>99.99\%$) was used as both carrier gas (200 mL/min) and assistant gas (500 mL/min). The 253.7 nm mercury wavelength was used for the detection of mercury. 0.4 mL of acidic solution of tin (II) chloride (10%, m/v) was used as reducing agent. The sample volume for injection was 1.0 mL.

River water samples, lake water samples and tap water samples were collected in Baoding city, where the authors accommodated. The water samples were filtered through filter paper and adjusted to pH 3.0 before analysis. The preconcentration experiments were conducted by adding 10 mg of the composite into 100 mL of water sample in a beaker. The separation of adsorbent from water was achieved by the application of magnetic field after the preconcentration. The mercury adsorbed by the sorbent was eluted by the elution and then the concentration of mercury in the eluent was measured by AFS.

Adequate amounts (0.1 g) of certified reference material (GBW07310, stream sediment) were weighted into a PTFE container (30 mL) in triplicate. 10 mL of aqua regia was then added. The samples were decomposed in oven at 75°C for 6 h. After digestion, the residue was diluted to 100 mL by deionized water. The pH was adjusted to 3.0 before analysis. Then, the extraction procedure mentioned above was applied for the preconcentration of mercury in the solution.

3. Results and discussion

3.1. Characterization of synthesized nanocomposite

Characterization of the nanocomposite was performed by SEM, EDS, TEM, VSM and XRD. The surface characteristics of prepared composite were investigated by SEM and TEM. The SEM and TEM images are shown in Figure 1(a) and 1(b). The characterization results of TEM revealed that the silver particles with the crystal sizes of 20–30 nm were synthesized. The spherical particles of silver aggregated together and attached onto the surface of nanotubes.

The morphology of nanocomposite indicated that CNTs provide large surface area and ideal supporter for the dispersing of nanosilver particles. Based on the images of SEM and TEM, it was observed that the solid particles were successfully coated on the surface of CNTs. The results of EDS (Figure S1) and XRD analysis (Figure 2) revealed that the solid particles contained abundant Fe_3O_4 and elementary silver. The size of Fe_3O_4 from TEM and peak broadening in XRD was calculated 22.5 nm by Debye-Scherrer equation. The VSM analysis results demonstrated that the paramagnetism of the composite was strong (30 emu/g) and could be easily isolated by external magnetic field (Figure 3). The nanosilver dispersed onto magnetic CNTs and the porous structure of magnetic CNTs make the composite with high extraction capacity for Hg^{2+} . EDS and XRD spectra for the composite displayed C, Fe, and Ag peaks and the weight ratios were: C, 61.13%; O, 20.49%, Fe, 11.45%, Ag, 6.93% (Figure S1).

Figure 1. SEM (a) and TEM (b) images of Ag/Fe₃O₄/CNTs composite.

Figure 2. XRD patterns of Ag/Fe₃O₄/CNTs composite.

3.2. Enhancement of adsorption capacity by silver modification

The batch extraction experiments were conducted with both the unmodified magnetic CNTs and the silver modified CNTs under the optimized experimental conditions. The composite was labeled according to the mass ratio of Ag (calculated by the molecular weight of AgNO₃) to CNTs or Fe (calculated by the molecular weight of (NH₄)₂Fe(SO₄)₂ · 6H₂O and NH₄Fe(SO₄)₂ · 12H₂O) to CNTs used as the substrates in the synthesis reaction. The composites loaded with the same amount of Ag and the different amounts of Fe were labelled as 10%Ag/35%Fe/CNTs, 10%Ag/25%Fe/CNTs, and 10%Ag/10%Fe/CNTs. The composite which was not modified by Fe₃O₄ was labelled as 10%Ag/CNTs. The composites loaded with the same amount of Fe but the different amounts of Ag were labelled as 5%Ag/35%Fe/CNTs and 1%Ag/35%Fe/CNTs. The magnetic CNTs without silver modification was labeled as 35%Fe/CNTs.

Figure 3. Magnetization characteristics of synthesized Ag/Fe₃O₄/CNTs composite (a) and magnetic separation (b: before magnetic separation; c: after magnetic separation).

The adsorbents (0.01 g) containing the different amounts of silver and iron were used to remove Hg²⁺ in 40 mL of water solution at pH 3 at room temperature. After extraction, the residual mercury in the solution was determined by AFS. The removal efficiencies were calculated by comparing the initial concentration and the residual concentration of mercury before and after extraction. The results are shown in Table 1. The results illustrated that Ag/Fe₃O₄/CNTs composite showed much higher extraction efficiency than those of Fe₃O₄/CNTs and CNTs. The extraction efficiencies of the magnetic composites were greatly improved by silver modification.

The contents of Fe and Ag in the composites were also determined by atomic absorption spectrometer (AAS). The results were listed in Table S1. The effects of Fe and Ag contents in the composites on the extraction were also investigated in our experiment. From the results, it can be concluded that higher content of Ag benefitted the extraction procedure. For the composites with the same amount of silver, the contents of iron in the composites did not affect the extraction efficiency obviously. The results explained that the silver component played a key role for the extraction of Hg²⁺ in water. Kumar and his co-workers had reported that Hg²⁺ ions could be quantitatively adsorbed in the silver nanoparticles embedded cation-exchange

Table 1. Enhancement of adsorption efficiency by silver modification.

Composites	Adsorption efficiency/%
10%Ag/35%Fe/CNTs	98.3
10%Ag/25%Fe/CNTs	97.6
10%Ag/10%Fe/CNTs	98.4
10%Ag/CNTs	98.2
5%Ag/35%Fe/CNTs	93.6
1%Ag/35%Fe/CNTs	90.2
35%Fe/CNTs	42.5
CNTs	59.4

membrane by galvanic reaction [32]. Here, the enhancement of Hg^{2+} adsorption capacity was also probably attributable to the galvanic reaction between Hg^{2+} and silver nanoparticles on the surface of or embedded in the CNTs bulk.

3.3. Optimization of extraction procedure

3.3.1. pH effect

As the acidity of the solution plays an important role in adsorption extraction procedure [33], the potential effects of pH were studied in the range of 1–12 (Figure 4). The pH was adjusted by either diluted nitric acid or sodium hydroxide solution. The results revealed that a quantitative recovery was found for Hg^{2+} at the pH range of 2–4. In the end, pH of 3 was selected for subsequent experiment. At pH greater than 8, preconcentration of mercury decreased probably attributable to precipitation of mercury as mercury hydroxide.

3.3.2. Amount of nanocomposite sorbent

The optimal amount of the composite for the quantitative extraction of Hg^{2+} from 50 mL of aqueous sample was investigated. Different amounts of the composites from 5 mg to 25 mg were employed in our experiment. The results revealed that with 10 mg of the composite or more, the extraction of Hg^{2+} was quantitative, whereas the use of less amount of the composite resulted in considerable decrease in the extraction efficiency. From our results, the amounts

Figure 4. Effect of sample pH on extraction of Hg^{2+} .

higher than 10 mg would not obviously increase the extraction efficiency. Therefore 10 mg of the composite was used for subsequent work.

3.3.3. Extraction time

The equilibration time can affect the extraction efficiency during the extraction procedure. The extraction efficiency increased with the extraction time from 5 min to 20 min. After 20 min, the extraction efficiency reached the maximum value and kept constant. So, the extraction time of 20 min was applied as the optimum.

3.3.4. Extraction temperature

The temperature in the range of 25–70°C was investigated in order to check the potential effects of temperature on the extraction. From our results, the quantitative extraction can be achieved in the temperature range of 25 to 50°C. When the temperature is higher than 50 °C, the extraction efficiency decreased. Therefore, 25°C was selected as the optimization for the following experiments.

3.3.5. Effects of sample volume

The effect of the sample volume on the adsorption of Hg^{2+} was tested in our experiment. The breakthrough volume of sample solution was tested by processing 100 ng of Hg^{2+} in different volumes in the range of 50–500 mL. The preconcentration was conducted under the optimized conditions. It was found that the quantitative adsorptions of Hg^{2+} were obtained for sample volumes up to 500 mL. When the volume was higher than 500 mL, the adsorption efficiency decreased. Consequently, an enrichment factor of 125 was determined based on the final elution volume (4 mL) and breakthrough volume (500 mL). In this work, 50 mL of sample solution was adopted for the experimental optimization and 200 mL for the preconcentration of analytes from water sample for convenience.

3.4. Elution of adsorbed mercury and optimization of desorption conditions

In order to choose a proper eluent for the quantitative recovery of retained mercury ions onto the sorbent after extraction, nitric acid, hydrochloric acid, acetic acid, oxalic acid, formic acid were tested as the elution for mercury washing in our experiment. The use of a ligand such as dithizone, diethyldithiocarbamate (DDTC), sodium thiosulphate favoured the elution of the metal ions in acidic media according to our experiments. The ligands and mercury ions could possibly form complexes, which facilitated the elution to strip the analytes from the sorbent. The

Table 2. Recovery of mercury from the sorbent using different eluent agent^a.

Elution	Recovery	Elution	Recovery (%)
50% (v/v) CH_3COOH	1.2%	10% (v/v) HCl + 0.6%DDTC	62.3
50%(v/v) HCOOH	2.7%	10% (v/v) HCl + 0.1M $\text{Na}_2\text{S}_2\text{O}_3$	5.6
0.5M $\text{H}_2\text{C}_2\text{O}_4$	2.5%	10% (v/v) HCl + dithizone	98.9
5% (v/v) HCl	52.6%	50% (v/v) HNO_3	100

^a0.1 ng mL^{-1} Hg^{2+} , 50 mL of sample solution, pH 3.0 for preconcentration.

results are summarized in Table 2 and revealed that a mixed solution of HCl and dithizone provided higher recovery of mercury from the magnetic composite. Furthermore, the concentrations of HCl and dithizone in the elution were also optimized for the maximum recovery of Hg^{2+} . The final results indicated that the mixture solution of 10% HCl and 60 μL of dithizone saturation solution in ethanol were sufficient for quantitative stripping of retained mercury (98.9%). Quantitative recovery of mercury ions was also obtained with the concentration of 50% (v/v) HNO_3 . However, the composite would be destroyed for the high acidity and could not be regenerated. Therefore, the mixture of 10% HCl (v/v) and dithizone was chosen for elution. The effect of elution volume on desorption of mercury from the sorbent was also investigated. The minimum volume of a mixed solution of HCl and dithizone was 4 mL for a quantitative recovery of adsorbed mercury on nanocomposite. However, we need clarify here that there should be a small loss of Ag during elution with HCl + dithizone mixed solution for each cycle.

The effects of elution temperature on desorption was investigated. The recovery increased with the temperature increasing from 20°C to 40°C and then kept constant until 70°C. In order to achieve the maximum desorption efficiency, 50°C was selected as the optimum with the recovery of almost 100%. The elution time was also investigated in our experiment. The results indicated that 40 min was needed for the total elution of adsorbed mercury from the sorbent.

3.5. Dissolution of Fe_3O_4 at the lower pH

The extraction was conducted under acidic conditions (pH 2.0–4.0). Fe_3O_4 can be dissolved in the acidic solution. In order to check whether the dissolution of Fe_3O_4 affects the extraction efficiency, the adsorbents were put into the acidic solutions and stirred for 60 min. After that, the iron concentration in it was determined by an atomic absorption spectrometer. As the optimized pH for the extraction procedure was 2.0–4.0, and the optimized elution was 10% (v/v) HCl with dithizone, the dissolution experiments were conducted at pH 2 and in 10% (v/v) HCl solutions, respectively. The analytical results (Table S2) demonstrated that 5.2% of the total Fe was dissolved at pH 2 during the extraction. However, more Fe was dissolved in 10% HCl (about 27.2% of the total Fe) during the elution for the first usage of the composite. But only a little amount of Fe (about 0.25–0.15% of the total Fe) was dissolved during the following reuses, which enabled the composite kept strong magnetic abilities for reuse.

3.6. Reusability of nanocomposite

In order to test the recycling of the nanocomposite sorbents, the desorbed sorbent was rinsed with 20 mL deionized water for 5 min before application in the next time. The concentrations of Ag in elution were also determined by AAS after washing. The loss of Ag was negligible (<0.01%) during the course. Because the adsorption was mainly generated by Ag loaded on CNTs and the amount of Ag in the composite was kept constant, there was no obvious decrease or increase for the recoveries of analytes after five times of recycling. The results indicated that the sorbent was reusable at least five cycles without obvious mercury carryover during extraction procedure.

3.7. Interference effects

In order to demonstrate the selectivity of the developed method for the determination of Hg^{2+} , the effect of coexisting ions including both cations and anions was investigated. The solutions containing mercury ions (0.1 ng mL^{-1}) was applied. The results showed that up to 1000 to 10^5 times higher concentrations of the coexisting ions had no interferences with the determination of mercury. The results demonstrated that the method had a good tolerance to coexisting ions

Table 3. Influence of coexisting ions on preconcentration and determination of Hg^{2+} ^a.

Ions	Ion to analyte ratio (mass)	Recovery (%)
K^+	10^5	94.2 ± 6.8^b
Na^+	10^5	97.3 ± 4.5
Ca^{2+}	10^4	104.8 ± 2.3
Mg^{2+}	10^4	95.2 ± 10.5
Cu^{2+}	1000	101.6 ± 0.5
Zn^{2+}	1000	91.0 ± 4.5
Ba^{2+}	1000	103.7 ± 6.0
Fe^{2+}	1000	95.2 ± 3.0
Fe^{3+}	1000	92.0 ± 1.5
Pb^{2+}	1000	103.7 ± 0.7
Ni^{2+}	1000	105.8 ± 7.5
Mn^{2+}	1000	97.3 ± 0.8
Al^{3+}	1000	112.1 ± 0.1
Co^{2+}	1000	103.8 ± 3.4
Cd^{2+}	1000	96.5 ± 5.2
Cl^-	10^5	93.4 ± 5.5
F^-	10^5	101.4 ± 1.7
NO_3^-	10^4	95.4 ± 4.6
CO_3^{2-}	10^4	94.1 ± 6.9
HCO_3^-	10^4	90.4 ± 2.6
SO_4^{2-}	10^4	96.9 ± 5.2

^aPreconcentration step: 50 mL of $0.1 \text{ ng mL}^{-1} \text{ Hg}^{2+}$, pH 3.0, 0.01 g of sorbent, 20 min of extraction time at 25°C .^bMean $\pm$ standard deviation ($n = 3$).

(Table 3). The recoveries more than 100% in Table 3 were probably caused by the added reagent with the impurities containing mercury.

3.8. Analytical performance

The analytical merits of the present method were evaluated under the optimal experimental conditions (Table 4). The limit of detection (LOD) of the method defined as three times the standard deviation of the blank (3δ) was 0.03 ng mL^{-1} for 200 mL sample volume. The relative standard deviation ($n = 7$) at 0.1 ng mL^{-1} of Hg^{2+} was 4.4%.

3.9. Application

In order to test the applicability of the developed method, the proposed procedure was applied to the determination of Hg^{2+} in tap water, lake water, river water, and the certified reference material GBW07310 (stream sediment). The certified value and found value in GBW07310 by

Table 4. Analytical characteristics of the method.

Element conditions	Concentration range (ng mL^{-1})	Regression equation	R^2	LOD (ng mL^{-1}) ^a	RSD(%)
Hg without SPE	1.0–50	$Y = 24.08C + 0.3318$	0.998	0.5	2.4
Hg with SPE ^b	0.1–5.0	$Y = 1080.9C - 21.626$	0.994	0.03	4.4

^aLOD means limit of detection (3δ); ^bSample volume was 200 mL.

Table 5. Determination of Hg^{2+} in real and spiked water samples (ng mL^{-1} , $n = 3$, 200 mL).

Sample	Measured ^a	Spiked	Found ^a	Recovery ^b (%)
Tap water	0.31 ± 0.03	0.4	0.67 ± 0.02	90
Lake water	0.09 ± 0.01	0.1	0.21 ± 0.02	120
River water	0.70 ± 0.04	0.5	1.12 ± 0.03	84

^aMean $\pm$ standard deviation; ^b $100 \times [(\text{found-measured})/\text{spiked}]$.

the presented method were $280 \pm 30 \text{ ng g}^{-1}$ and $261 \pm 7 \text{ ng g}^{-1}$, respectively. The recovery was 93.2%. The agreement between the obtained result and the certified value indicated that the established method was reliable and capable for real sample analysis. The analytical results of water samples are shown in Table 5. The reliability of the method was further checked by spiking and recovery experiments. The results show that the recovery is quantitative and indicates that the method is applicable to the determination of mercury in real water samples. The recovery for the spiked lake water sample was 120% in Table 5 because the concentration of mercury in the sample was so low that the reasonable measurement deviation was probably magnified when the recovery was calculated. As we know, a broader band would be acceptable for recovery calculation when the concentration of analyte was much lower.

3.10. Comparison with other methods

The developed method for the determination of mercury in this paper was compared with the other reported methods for Hg^{2+} preconcentration (Table S3). The preconcentration method developed in our experiment showed a comparatively low detection limit and high enrichment factor. In addition, the present method has the advantages of magnetic separation, which will facilitate the treatment of sample with large volume and minimize the secondary pollution.

4. Conclusion

The preconcentration and determination of trace amounts of Hg^{2+} in water samples using the synthesized nanocomposites was described in this study. The nanocomposite was composed with nanosilver, Fe_3O_4 and CNTs. The new adsorbent was prepared easily and at low cost. The developed method has the merits of easy and fast separation with high enrichment factor. The results demonstrated that nanosilver played a very important role in enhancement of adsorption capacity and the nanocomposite is very suitable for the rapid preconcentration/separation of mercury ions from large volume of water samples.

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References

- [1] K. Leopold, M. Foulkes and P.J. Worsfold, Trends Anal. Chem. **28**, 426 (2009).
- [2] E.M. Soliman, M.B. Saleh and S.A. Ahmed, Talanta **69**, 55 (2006).

- [3] Y. Zhai, S. Duan, Q. He, X. Yang and Q. Han, *Microchim. Acta* **169**, 353 (2010).
- [4] F. Mohammad, Y. Yadollah and R. Mohammad, *Talanta* **81**, 831 (2010).
- [5] N. Pourreza and K. Ghanemi, *J. Hazard. Mater.* **161**, 982 (2009).
- [6] W. Qu, Y. Zhai, S. Meng, Y. Fan and Q. Zhao, *Microchim. Acta* **163**, 277 (2008).
- [7] E. Zolfonoun, A. Rouhollahi and A. Semnani, *Int. J. Environ. Anal. Chem.* **88**, 327 (2008).
- [8] Z. Li, Q. Wei, R. Yuan, X. Zhou, H. Liu, H. Shan and Q. Song, *Talanta* **71**, 68 (2007).
- [9] I. Lopez-Garcia, R.E. Rivas and M. Hernandez-Cordoba, *Anal. Bioanal. Chem.* **396**, 3097 (2010).
- [10] C.G. Yuan, K. Lin and A. Chang, *Microchim. Acta* **171**, 313 (2010).
- [11] A. Afkhami, T. Madrakian and H. Siampour, *Int. J. Environ. Anal. Chem.* **86**, 1165 (2006).
- [12] H. Ashkenani, S. Dadfarnia, A.M.H. Shabani, A.A. Jaffari, A. Behjat and J. Hazard, *Mater.* **161**, 276 (2009).
- [13] A. Mehdinia, F. Roohi and A. Jabbari, *J. Chromatogr. A* **1218**, 4269 (2011).
- [14] X. Peng, Z. Luan, Z. Di, Z. Zhang and C. Zhu, *Carbon* **43**, 855 (2005).
- [15] B. Tawabini, S. Al-Khaldi, M. Atieh and M. Khaled, *Water Sci. Technol.* **61**, 591 (2010).
- [16] X.H. Shang, *Atom. Spectrosc.* **28**, 35 (2007).
- [17] Y.Q. Cai, Y.E. Cai, S.F. Mou and Y.Q. Lu, *J. Chromatogr. A* **1081**, 245 (2005).
- [18] C.G. Yuan, Y. Zhang, S. Wang and A. Chang, *Microchim. Acta* **173**, 361 (2011).
- [19] Y.H. Li, S. Wang, A. Cao, D. Zhao, X. Zhang, C. Xu, Z. Luan, D. Ruan, J. Liang, D. Wu and B. Wei, *Chem. Phys. Lett.* **350**, 412 (2001).
- [20] X. Peng, J. Ding, Z. Di, Y. Li, Z. Luan and B. Tian, *Mater. Lett.* **59**, 399 (2005).
- [21] V.K. Gupta, S. Agarwal and T.A. Saleh, *Water Res.* **45**, 2207 (2011).
- [22] C. Chen, J. Hu, D. Shao, J. Li and X. Wang, *J. Hazard. Mater.* **164**, 923 (2009).
- [23] V.K. Gupta, S. Agarwal and T.A. Saleh, *J. Hazard. Mater.* **185**, 17 (2011).
- [24] D.T. Nguyen, L.D. Tran, H.L. Nguyen, B.H. Nguyen and N.V. Hieu, *Talanta* **85**, 2445 (2011).
- [25] Z.Q. Tan, J.F. Liu, R. Liu, Y.G. Yin and G.B. Jiang, *Chem. Commun.* **45**, 7030 (2009).
- [26] A.P. Fan, Y. Ling, C.W. Lau and J.Z. Lu, *Talanta* **82**, 687 (2010).
- [27] A. Zierhut, K. Leopold, L. Harwardt and M. Schuster, *Talanta* **81**, 1529 (2010).
- [28] G. Luo, H. Yao, M. Xu, X. Cui, W. Chen, R. Gupta and Z. Xu, *Energy Fuels*, **24**, 419 (2010).
- [29] X.C. Jiang, S.X. Xiong, C.Y. Chen, W.M. Chen and A.B. Yu, *J. Nanopart. Res.* **13**, 5087 (2011).
- [30] L. Deng, Z.X. Zhou, J. Li, T. Li and S.J. Dong, *Chem. Comm.* **47**, 11065 (2011).
- [31] C.F. Jiang, Z.P. Guan, S.Y.R. Lim, L. Polavarapu and Q.H. Xu, *Nanoscale* **3**, 3316 (2011).
- [32] R. Kumar, A.K. Pandey, S. Das, S. Dhara, N.L. Misra, R. Shukla, A.K. Tyagi, S.V. Ramagiri, J.R. Bellare and A. Goswami, *Chem. Comm.* **46**, 6371 (2010).
- [33] E. Sumesh, M.S. Bootharaju, T. Anshup and J. Pradeep, *Hazard. Mater.* **189**, 450 (2011).
- [34] J. Meng, C. Shi, B. Wei, W. Yu, C. Deng and X. Zhang, *J. Chromatogr. A* **1218**, 2841 (2011).
- [35] J.F. Liu, Z.S. Zhao and G.B. Jiang, *Environ. Sci. Technol.* **42**, 6949 (2008).
- [36] K. Aguilar-Arteaga, J.A. Rodriguez and E. Barrado, *Anal. Chim. Acta* **674**, 157 (2010).
- [37] L. Chen, T. Wang and J. Tong, *Trends Anal. Chem.* **30**, 1095 (2011).
- [38] J.L. Gong, B. Wang, G.M. Zeng, C.P. Yang, C.G. Niu, Q.Y. Niu, W.J. Zhou and Y. Liang, *J. Hazard. Mater.* **164**, 1517 (2009).