

Solid phase extraction and preconcentration of trace mercury(II) from aqueous solution using magnetic nanoparticles doped with 1,5-diphenylcarbazide

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Abstract A new method for solid-phase extraction and preconcentration of trace mercury(II) from aqueous solution was developed using 1,5-diphenylcarbazide doped magnetic Fe₃O₄ nanoparticles as extractant. The surface treatment did not result in the phase change of Fe₃O₄. Various factors which influenced the recovery of the analyte were investigated using model solutions and batch equilibrium technique. The maximum adsorption occurred at pH>6, and equilibrium was achieved within 5 min. Without filtration or centrifugation, these mercury loaded nanoparticles could be separated easily from the aqueous solution by simply applying an external magnetic field. At optimal conditions, the maximum adsorption capacity was 220 μmol g⁻¹. The mercury ions can be eluted from the composite magnetic particles using 0.5 mol L⁻¹ HNO₃ as a desorption reagent. The detection limit of the method (3σ) was 0.16 μg L⁻¹ for cold vapor atomic absorption spectrometry, and the relative standard deviation was 2.2%. The method was validated by the analysis of a certified reference material with the results being in agreement with those quoted by manufactures. The method was applied to the preconcentration and determination of trace inorganic mercury(II) in natural water and plant samples with satisfactory results.

Keywords Solid phase extraction · Hg(II) ·
1,5-Diphenylcarbazide · Magnetic nanoparticles

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Mercury ion and its organometallic species are considered to be highly toxic to the environment, especially the aquatic system. Metal-processing wastewater often contains a considerable amount of divalent mercury which can pose a severe threat to public health and environment if discharged without adequate treatment [1]. USEPA recommends that the levels of mercury in drinking water should be reduced to 0.002 mg·L⁻¹ [2]. Atomic absorption spectrometry (AAS) is the most widely used technique for such determinations because of simplicity and low running cost. However, this technique suffers from lack of sensitivity for the ultra-trace metal ions usually encountered in environmental samples. Therefore, selective preconcentration is becoming an essential treatment step before determination.

For this purpose, a variety of techniques have been founded for the separation and preconcentration of trace mercury(II) from aqueous samples. Among these methods, solid-phase extraction (SPE) is one of the most effective trace element preconcentration methods because of its simplicity, rapidity and ability to attain a high concentration factor [3]. An efficient solid-phase extractant should consist of a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with heavy metal ions [4]. So far, numerous substances have been applied as solid-phase extractants, such as XAD resins, activated carbon, silica gel, ion-exchange resins, chelating resins and various polymers. Using such solid-phase extraction materials, preconcentration of mercury has been described in off or on-line procedures with immobilizing reagents such as dithiocarbamate derivatives [5–7], cysteine [8], 4-(2-Pyridylazo)-Resorcinol [9], dithioacetal derivatives [10, 11] or aliphatic amines 2-thiophenecarboxaldehyde Schiff's bases [12], etc. Most of these methods have better sensitivity. However, the main

problems associated with these materials are time-consuming and high cost for their preparation and operating difficulties. Exploring new functional materials are still necessary because of complexities of real samples and analysis demand.

At present, nanometer material has become more and more important due to its special properties. Although investigations of the surface chemistry of highly dispersed oxides, e.g. TiO_2 , Al_2O_3 , ZrO_2 , SiO_2 and ZnO , indicated that these materials had very high adsorption capacity [13–17], separation of these particles from aqueous medium is difficult because of very small dimension and high dispersion.

In this study, a new method combining nanoparticle adsorption with magnetic separation has been developed and applied for the SPE and preconcentration of mercury ions. Functional magnetic nanoparticles were chosen for new sorbents by considering the main advantages: (1) magnetic nanoparticles can be produced in large quantity using simple method; (2) it can be expected that the adsorption capacity is higher by considering the larger surface area; and (3) these particles are superparamagnetic, that means metal-loaded sorbent can be easily separated from the treated water via an external magnetic field. Magnetic nanoparticles have been successfully applied to separate some proteins, organic compounds and metal ions [18–20]. Hu et al. employed magnetic Fe_2O_3 nanoparticles as sorbent for the removal and recovery of Cr(VI) from wastewater. The adsorption capacity was found to be very high [21]. Fe_3O_4 modified by mercaptopropyltrimethoxysilane or gum arabic were explored for preconcentration of some heavy metal ions and tellurium [22–24]. Cyanex 272 was used to prepare magnetic alginate doped microcapsules for nickel adsorption [25]. And poly(1-vinylimidazole)-grafted magnetic nano-sorbent was also synthesized and used to separate copper ions [26]. Our study adopted doping method to prepare functional magnetic material. 1,5-diphenylcarbazine (DPC) was chosen as doping reagent because of its favorable coordination capacity and selectivity for mercury(II). It is concluded from the extraction data that the new sorbent is a promising material for the solid-phase extraction and preconcentration of mercury.

Experimental

Instruments and apparatus

TSM-680LA scanning electron micrograph (SEM, JEOL, Japan) was used to examine the dimension of synthesized materials. The structure of synthesized materials was determined by an X-ray diffractometer (XRD) (D/max-

2550/pc) at ambient temperature. The instrument was equipped with a copper anode generating $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra ($4000\text{--}400 \text{ cm}^{-1}$) in KBr were recorded using Nicolet Nexus 670 FT-IR spectrometer (Nicolet, USA). A model pH-10C digital pH meter (Xiaoshan Instrument Factory, China) was used for the pH adjustments. Mercury was determined by cold vapor atomic absorption spectrometry (CVAAS) with a Perkin-Elmer AA-6800 atomic absorption spectrometer. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected for Hg was 253.6 nm.

Chemicals and reagents

Unless otherwise stated, all water are $18 \text{ M}\Omega \text{ cm}$ pure water purified with a Milli-Q system (Millipore, USA), all reagents used were of analytical grade, and all solutions were prepared with pure water.

Tetraethoxysilane (TEOS) 98.5%, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1,5-diphenylcarbazine (DPC, Shanghai, China, <http://www.reagent.com.cn/>) were used in sorbent preparation. Standard stock solution of Hg(II) (1 mg mL^{-1}) was prepared by carefully dissolving spectral pure grade chemicals HgCl_2 (Shanghai, China, <http://www.reagent.com.cn/>) in 1.0% (v/v) HNO_3 and further diluted prior to use. The Hg(II) concentration in the working solutions was $2 \mu\text{g mL}^{-1}$ unless otherwise stated. Standard stock solutions of other ions (1 mg mL^{-1}) were prepared according to standard method and further diluting daily prior to use as well. The certified water reference material (GBW 08603) was provided by National Research Center for Certified Reference Materials (Beijing, China, http://www.nrcrm.org.cn/eng/index_en.asp).

Synthesis of magnetic Fe_3O_4 nanoparticles

In the laboratory, DPC doped magnetic Fe_3O_4 nanoparticles were prepared by conventional co-precipitation and sol-gel method with minor modifications from ref. [27, 28].

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8.10 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.80 g) were dissolved in 100 mL purified water under nitrogen gas with vigorous stirring. Then, 2 g of polyethylene glycol (PEG, *Mr*: 1000) dissolved in 15 mL water was added. With nitrogen gas protection, $1.5 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O}$ solution was dropwise added until the system pH reached 12. The color of bulk solution changed to black immediately. The obtained precipitate was isolated by an external magnetic field with the supernate decanted. To obtain the pure and neutral products, synthesized materials were rinsed with water three times. The washed magnetic carries were stored in 100 mL water and named as NF for subsequent experiments.

Pre-polymerization of TEOS

To a test tube added TEOS (5 mL) and ethanol (10 mL). Then added 0.15 mL HCl (36%) and 0.4 mL water, and placed in a beaker of water which was maintained at 50 °C. After 1 h, 0.1 g DPC was added. The mixture was continuously stirred for 2 h. A transparent solution was obtained and named as PTEOS.

Preparation of DPC doped nanomagnetic sorbent

The magnetic suspension prepared above (25 mL) was placed in a beaker. The supernate was removed by an external magnetic field. The particles were washed with ethanol two times and then dispersed in ethanol (100 mL). PTEOS prepared as described above and 3 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) was added in sequence with continuous stirring. The system changed to black colloidal solution immediately. After 2 h, the mixture was dried under vacuum at 60 °C. Functional magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2$ composite material was obtained and named as DPC-NF-SiO₂.

In the same way without DPC addition, control material was also prepared and named as NF-SiO₂. The synthesized functional sorbents were then characterized before their applications.

Batch procedure

Before using, the dry sorbent powder was soaked in water for 12 h to leach the undoped reagent. After that, the material was oven dried at 60 °C. Batch adsorption studies were performed by mixing 0.1 g DPC-NF-SiO₂ with 50 mL of $2 \mu\text{g mL}^{-1}$ Hg(II) standard or sample solution in a stopper conical flask. HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}) solutions were used for pH adjustment. The mixture was shaken for 30 min to facilitate adsorption of the metal ions onto the sorbents. All adsorption experiments were carried out at pH 6–8 and room temperature except stated otherwise. Desorption was performed by mixing Hg-loaded sorbents with 5 mL 0.5 mol L^{-1} of HNO_3 . After equilibrium, the sorbent was separated via an external magnetic field and the supernate was collected for metal concentration measurement.

Kinetic experiments

The kinetic study was performed by following process. A series of conical flasks, each containing the same amount of Hg(II) solution, were used for each kinetic run. The moment when the sorbent was introduced into the flasks was taken as the time zero of the experiments. At various time intervals, one of the flasks was quickly placed on an external magnetic field. The sorbents were rapidly gathered

on the vessel bottom and the supernate was collected for metal concentration measurements. And a plot of amount of metal ions retained on the sorbent as a function of time was drawn.

Adsorption capacity

0.1 g of magnetic composite sorbents was equilibrated with $20 \mu\text{g mL}^{-1}$ of various volumes of Hg(II) solutions at pH 7 for 10 min. The loading sorbents were collected via an external magnetic field, the concentrations of Hg(II) in solution were measured and the adsorption capacity was calculated.

Sample preparation

Tap water samples were taken from our research laboratory without pretreatment. The surface river water samples were collected from Yellow River, Lanzhou, China. To oxidize organic matter such as humic acid, the samples were digested by an oxidizing UV photolysis in the presence of 1% H_2O_2 using a low pressure Hg-lamp which was integrated into a closed quartz vessel [29, 30]. Then the samples were immediately acidified to pH 1.0 with hydrochloric acid, filtered through a Millipore cellulose membrane (pore size $0.45 \mu\text{m}$) and stored in pre-cleaned polyethylene bottles. Analyses were performed with the least possible delay.

Vegetable samples were obtained from Anning village, Lanzhou, China. The digested method was performed according to the previous procedure [31]. After digestion, each sample solution was determined by batch procedure.

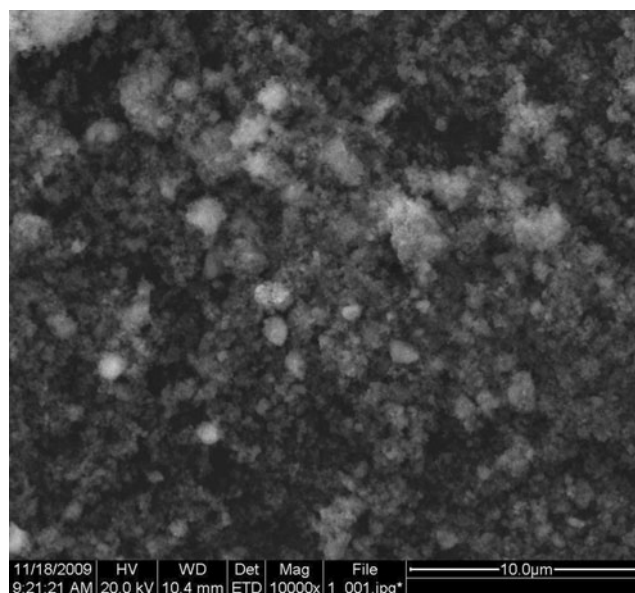
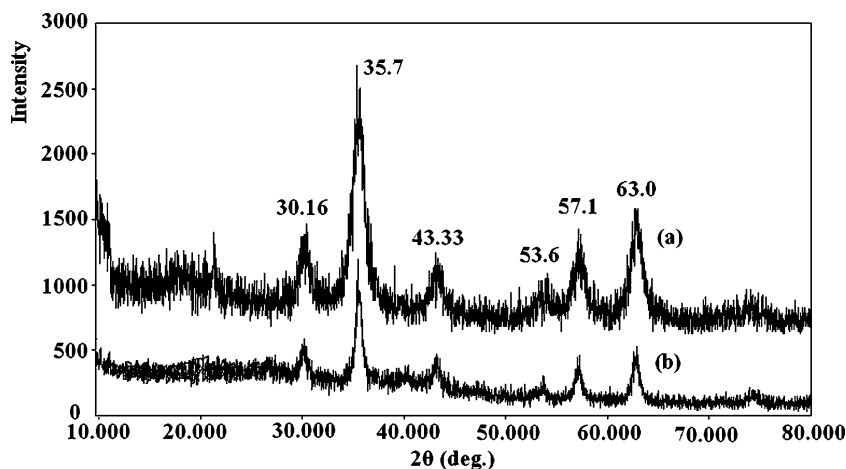


Fig. 1 SEM image of synthesized magnetic nanoparticles (DPC-NF-SiO₂)

Fig. 2 XRD patterns of magnetic particles (a) blank Fe_3O_4 and (b) functional sorbent



Results and discussion

Characterization of sorbent

The SEM image as shown in Fig. 1 revealed that DPC-NF-SiO₂ synthesized in this study was spherical particles with average diameter of around 60–80 nm. The identity and purity of the magnetic nanoparticles were verified by XRD (Fig. 2), with the XRD peaks of the nanocrystallite matching well with standard Fe_3O_4 and without other crystalline phases detected, according to the database in JCPDS file (PCPDFWIN v.2.02, PDF no.85–1436). The XRD analysis of DPC-NF-SiO₂ also indicated six characteristic peaks at same positions, revealing the coating and doping process did not result in the phase change of Fe_3O_4 .

The FT-IR spectra of NF, NF-SiO₂, and DPC-NF-SiO₂ were shown in Fig. 3. It can be seen that the characteristic peak of magnetic Fe_3O_4 appeared at 587 cm^{-1} . This band was shifted to high wavenumber compared to the Fe-O bond peak of bulk magnetite at 570 cm^{-1} due to nanoparticle size [32]. The characteristic absorption peaks of Si-O in DPC-NF-SiO₂ and NF-SiO₂ spectra occurred at 1,630, 1,080, 800 and 460 cm^{-1} due to the introduction of SiO₂ inorganic coating layers. Moreover, some peaks around 1,721, 1,486, 1,442 and 1,401 cm^{-1} also occurred in DPC-NF-SiO₂ spectra which could be assigned as features of carbonyl band, benzene cycle and amine in the DPC molecules. The above experimental results suggested that DPC had been successively doped into the composite magnetic nanoparticles.

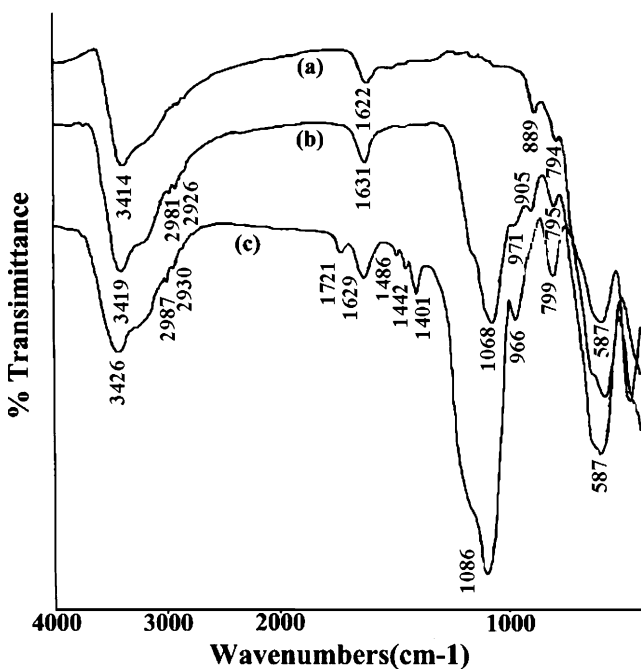


Fig. 3 FT-IR of NF(a), NF-SiO₂(b), DPC-NF-SiO₂(c)

Effect of pH

Effect of different pH on Hg(II) uptake was tested as showed in Fig. 4. It can be seen that the adsorption behavior of metal ions was sensitive to pH changes. In the case of control sorbent NF-SiO₂, the adsorption was un conspicuous. While in the case of DPC-NF-SiO₂, below pH 4, the protonated ligand sites had no reactivity to the positively charged

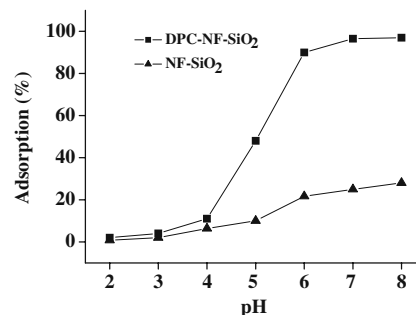


Fig. 4 Effect of pH on Hg(II) adsorption on DPC-NF-SiO₂ and NF-SiO₂

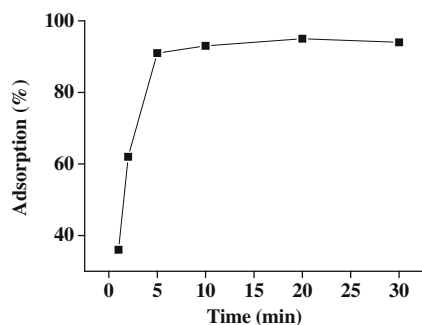


Fig. 5 Kinetics of Hg(II) adsorption on DPC-NF-SiO₂

mercuric ions; with the pH increasing, adsorption greatly increased and attained quantitative extraction (>95%) at pH about 6–8. In consideration of hydrolysis, pH above 8.0 was not tested. So pH 6–8 was selected as the adsorption acidity for subsequent experiments.

The adsorption action of DPC doped magnetic nanoparticles might be due to following two reasons: (1) adsorption by the surface silica, i.e., ion exchange with silanol groups (-SiOH) and/or by -SiO on the surface of silica; (2) adsorption by the entrapped reagent, i.e., complexation of Hg(II) with DPC entrapped in silica shell. The obvious difference between doped and control sorbents clearly indicated that the adsorption of Hg(II) using present magnetic nanoparticles mainly attributed to the entrapped DPC (Fig. 4). Ion exchange with silanol groups and/or -SiO on the surface of silica played a very minor role.

Kinetic experiments

Figure 5 showed an equilibration time of adsorption. It was clear that adsorption was very rapid initially and gradually became slower with lapse of time. About 95% of total Hg(II) was adsorbed within the first 5 min. And the time ($t_{1/2}$) of 50% adsorption was less than 2 min. The adsorption rate was very fast comparing with traditional sol-gel silica materials [28]. Two factors could be used to explain the obtained results. One was that DPC had favorable coordination capacity and selectivity for Hg(II). The other owed to the silica inorganic layer coated on the magnetic nanoparticles. As reported earlier [10], the surface of silica contained abundant free sites which could react with some

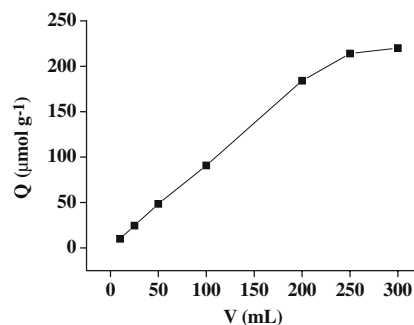


Fig. 6 The maximum adsorption quantity of Hg²⁺ on DPC-NF-SiO₂

metal ions. However, the active sites near the surface would decrease with the lapse of time. In this case, metal ions had to diffuse into the silica through the interconnected three-dimensional network of pores and channels before they reacted with the entrapped reagent molecules and were retained inside the silica. In this study, instead of whole wrapping, DPC molecules were doped in a layer of silica polymer which coated on the surface of magnetic Fe₃O₄ particles. So, the target ions could easily reach the function sites and then were trapped by the sorbent.

Elution characteristic

Since the protonation of the amine groups under strong acid conditions, the coordination interaction of chelated Hg(II) ions could be easily disrupted and subsequently Hg(II) ions were released from loaded sorbents into desorption medium. So, elution of Hg(II) was carried out by using various concentrations of HCl or HNO₃ solutions as desorption reagent. The results showed in Table 1 revealed that HNO₃ was better than HCl. And 2 mL of 0.5 mol L⁻¹ HNO₃ solution was sufficient for 95% recovery.

Adsorption capacity and preconcentration factor

In order to avoid hydrolysis of high concentration of Hg(II) at pH >7, the adsorption capacity of the new sorbent was carried out by retaining concentration of Hg(II) and amount of sorbent constant and gradually increasing solution volume. As can be seen in Fig. 6, the maximum adsorption quantity of Hg²⁺ on DPC-NF-SiO₂ was 220 μmol g⁻¹, and

Table 1 Effect of concentration and volume of desorption reagent on recovery of Hg(II)

Concentration of elution (mol L ⁻¹)		0.05	0.1	0.2	0.5	1.0
Recovery (%)	HCl	60.7±2.2	63.0±3.5	76.5±2.6	85.3±1.2	95.6±0.8
	HNO ₃	68.4±1.8	79.5±1.4	88.2±2.4	97.5±1.1	98.8±0.6
Volume of elution (mL, HNO ₃)		0.5	1	2	4	5
Recovery (%)		63.4±4.2	89.8±2.3	97.6±1.5	98.3±1.3	97.5±0.5

Table 2 Analytical results of real samples ($n=3$)

Samples	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
GBW08603	2.0 ^a	1.95±0.24	97.5
	5.0 ^a	4.98±0.32	99.6
River water	0.0	0.68±0.14	
	2.0	2.65±0.28	98.5
Tap water	5.0	5.54±0.46	97.2
	0.0	unfound	
	2.0	1.98±0.32	99.0
Balsam pear leaves	5.0	5.02±0.64	100
	Added ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	Recovery (%)
	0.0	0.36±0.07	
	0.5	0.84±0.18	96.0
	1.0	1.33±0.33	97.0

^a Reference value. The certified sample solution was accurately diluted to 2 and 5 $\mu\text{g L}^{-1}$, respectively

over 95% of Hg(II) in solution was directly adsorbed when the testing volume less than 200 mL. So the preconcentration factor was 100 since the final elution volume was 2 mL.

Effect of potentially interfering ions

The effect of common electrolytes on the adsorption of Hg(II) was studied. The reported tolerance limit is defined as the ion concentration causing a relative error $<\pm 5\%$. The testing results showed that 1000-fold K^+ , Na^+ , Cl^- , NO_3^- , HCO_3^- and 400-fold Ca^{2+} and Mg^{2+} did not interfere with adsorption of Hg(II), indicating that the present functional sorbent can be suitably used in high electrolytes solution.

In order to further check the selectivity of the method, solutions containing Hg(II) and other metal ions such as Cu (II), Zn(II) or Cd(II), were prepared and analyzed. Studies with 2.0 $\mu\text{g L}^{-1}$ of Hg(II) showed that 50 $\mu\text{g L}^{-1}$ of Cu(II), Zn(II) or Cd(II) did not interfere with Hg(II) determination by CVAAS after the SPE and batch procedure.

Regeneration of sorbent

To test the stability and potential recyclability of new composite material, several loading and elution operations cycles were carried out. The operating capacity was calculated from the loading and elution tests. For each cycle, 100 mL of 40 $\mu\text{g mL}^{-1}$ Hg(II) solution was treated by 0.1 g of composite nanoparticles for 10 min and then desorbed with 5 mL of 0.5 mol L^{-1} HNO_3 for 5 min. After each cycle of adsorption-elution, the composite nanoparticles were washed thoroughly with ultrapure water to neutrality and reconditioned for adsorption in the succeeding cycle.

The present sorbent was relatively stable up to at least 8 adsorption-elution cycles without obviously decrease in the recoveries. The sorbent was conserved for more 6 months and the physical and chemical characteristics had no evident change.

Analytical accuracy and precision

Under the selected conditions, eleven portions of 10 $\mu\text{g L}^{-1}$ Hg(II) standard solutions (100 mL) were treated and analyzed simultaneously following the batch procedure. The relative standard deviations (RSD) of the method was 2.2%, indicating that the method had good precision for the analysis of trace Hg(II) in solution samples. The detection limit (3σ), defined as by IUPAC, was found to be 0.16 ng mL^{-1} for 200 mL sample.

Table 3 Figures of merit of comparable methods for determination of Hg(II) by solid-phase extraction

Methods/reagent(s) used	pH	Capacity (mmol g^{-1})	Equilibrium (min)	LOD ($\mu\text{g L}^{-1}$)	PF	Ref.
Nanometer SiO_2 / PAR	4	0.276	2	0.43	50	[9]
DPC doped sol-gel silica	6	0.028	30			[28]
Silica gel-loaded/ dithizone	5–6	0.12–0.2	30		200	[10]
XAD/ bis(<i>o</i> -aminophenyl- thio)ethane	5	0.38	12 (50% uptake)	0.09		[33]
XAD-2/2-aminoacetylthio- phenol	3.5–7	0.24	40	0.23	300	[34]
PS-DVB/ imidazolyl azo groups	4–6	0.62	45 (50% uptake)			[35]
Polyaniline	5	0.50	2	0.05	120	[36]
Hg(II)-imprinted copolymer	8	0.205	60	0.05	200	[37]
Hg(II)-imprinted hybrid sorbent	6.5	0.197	5	0.06		[38]
Silica gel/ dithiocarbamate derivatives	1M NaOAC	0.6–0.92	10			[5]
DPC-doping magnetic nanoparticles	6–8	0.22	5	0.16	100	This work

Hg(II) determination in real samples

The developed method was validated by analysis of a standard reference material containing $10.0 \mu\text{g L}^{-1}$ Hg(II) (GBW 08603, water) by recommended procedure. Hg(II) standard solutions were accurately diluted to 2 and $5 \mu\text{g L}^{-1}$, respectively. The analytical results (Table 2) for the standard material were in good agreement with the reference values. Moreover, the prepared DPC-NF-SiO₂ composite nanoparticles were applied for preconcentration and determination of trace Hg(II) in two natural water samples and vegetable sample by the recovery test method. 0.1 g of DPC-NF-SiO₂ was added into 200 mL of treated samples, and then eluted with HNO₃ solution. As shown in Table 2, the recoveries of Hg(II) were in range of 96–100%. The obtained results implied the suitability of present magnetic nanoparticles for selective solid-phase extraction and preconcentration of trace Hg(II) from real samples.

Comparison with alternative materials

Although sorbents reported in the literatures for SPE and preconcentration of mercury as shown in Table 3 could effectively achieve mercury determination, there is scope for improvement. The functional magnetic composite material in this work showed fast exchange kinetics, regenerability and reasonable selectivity for mercury ions. The LOD and preconcentration factor (PF) of this method are also comparable. In addition, the adsorption acidity is nearly close to natural water. So, Low cost, rapid and simple preparation and especially easy separation from matrix solution are other obvious advantages comparing with other methods.

Conclusions

From this studied work we can see that the composite magnetic nanoparticles are not only a good natural sorbent for mercury with near neutral condition, but also it can be easily separated from matrix solution via an external magnetic field. Hg(II) can be recovered with acids at low acidity and the sorbent can be used repeatedly. Therefore, the method is very simple, low cost and eco-friendly to nature. The developed method was successfully applied to the analysis of trace inorganic mercury(II) in certified and real samples with satisfactory results. It is also very interesting to study the adsorption of other metal ions and semi-metals such as arsenic which is known to easily accumulate in biomass. Work in these directions is under investigation in our laboratory.

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