

Thiophene Functionalized Magnetic Covalent Organic Frameworks for Selective Extraction of Trace Heavy Metals Followed by ICP-MS Detection

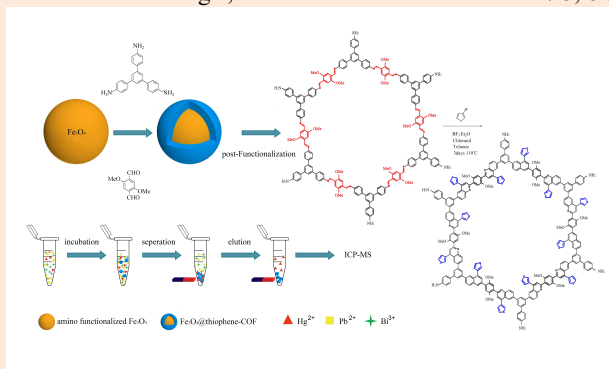
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ABSTRACT: Magnetic covalent organic frameworks (COFs) were prepared using aminated Fe_3O_4 nanoparticles as the magnetic core and 1,3,5-tris(4-aminophenyl)benzene (TPB) and 2,5-dimethoxyterephthalaldehyde (DMTA) as monomers. The resultant $\text{Fe}_3\text{O}_4@\text{TPB-DMTP-COF}$ was then post-modified with 3-ethynylthiophene through the “Aza D-A reaction”. The $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ composite showed a high Brunauer-Emmett-Teller surface area of $898 \text{ m}^2 \text{ g}^{-1}$, as well as a high content of S (5.27 wt.%). Trace mercury (Hg), lead (Pb), and bismuth (Bi) ions were extracted from environmental water samples, followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. Extraction conditions, such as extraction pH, sample volume, adsorbent amount, extraction/desorption time and elution volume, were optimized. Under the optimal conditions, the three heavy metal ions were extracted from 150 mL of aqueous solution within 20 min and eluted with $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ containing 8% cysteamine hydrochloride within 20 min. The method exhibited a high enrichment factor (188) and wide linear range of $3\text{--}5000 \text{ ng L}^{-1}$ for $\text{Hg}^{2+}/\text{Pb}^{2+}$ and $2\text{--}2000$ for Bi^{3+} , with the detection limits of 0.41 , 0.97 and 0.47 ng L^{-1} , respectively. Furthermore, the reproducibility of the method was evaluated, and the relative standard deviations of Hg^{2+} , Pb^{2+} and Bi^{3+} were found to be 7.5, 6.8 and 6.2% ($n = 7$, $c = 3 \text{ ng L}^{-1}$), respectively. The accuracy of this method was verified by analyzing certified reference materials in environmental water, including GSB 07-1185-2000 (202047), GSB 07-1185-2000 (201239) and BY 400143 (B2003113). The application potential of this method was further evaluated by analyzing real environmental water samples. Target Hg^{2+} and Pb^{2+} ions concentrations were found to be 4.91 and 62.5 ng L^{-1} , respectively, in the East Lake water sample and 10.2 and 103 ng L^{-1} , respectively, in the Yangtze River water sample. The recoveries of target three metal ions were found to be $86.1\text{--}104 \%$ in the two environmental water samples at three spiked concentration levels.



INTRODUCTION

The high toxicity, persistence and non-degradability of heavy metals have attracted increasing attention from researchers worldwide. The quantification of trace heavy metals in environmental samples is of great significance for environmental monitoring and health risk assessments. Sample pretreatment techniques are often necessary before instrumental analysis because of the complex environmental matrices and extremely

low contents of target metals in real samples.

Magnetic solid-phase extraction (MSPE), which has the advantage of easy phase separation under magnetic field assistance, has been demonstrated to be an excellent pretreatment technique for trace analysis.^{1,2} To remove complex matrices and enrich target analytes with fast adsorption and desorption dynamics, various functionalized materials have been composited with magnetic nanoparticles (MNPs). To date, two approaches are

commonly used to prepare functional magnetic composites. One is to selectively graft functional groups to target metals onto the surface of MNPs directly, and the other one is to use functional group-containing porous materials as the shell for the magnetic core. For example, in our previous study, trimethoxysilylpropanethiol was grafted onto MNPs to obtain sulfhydryl-functionalized sorbents.³ The resultant sorbent exhibited adsorption capacities of 45.2, 56.8, 83.8, and 70.4 mg g⁻¹ for Cd²⁺, Cu²⁺, Hg²⁺, and Pb²⁺, respectively, along with good stability. Chen *et al.*⁴ modified MNPs with oleic acid, loaded them with glycidyl methacrylate (GMA), and used ethanedithiol for click reactions. The synthesized magnetic porous polymer exhibited a sulfur content of 5.4% and was used for the preconcentration of heavy metals, with adsorption capacities of 64.2, 254, and 56.5 mg g⁻¹ for Cd²⁺, Hg²⁺, and Pb²⁺ ions, respectively. Ethanedithiol-modified MNPs with a sulfur content of 2.5% were used for the analysis of three Hg species,⁵ showing adsorption capacities of 141, 142, and 32.1 mg g⁻¹ for methyl mercury, ethyl mercury and phenyl mercury, respectively, and fast dynamics (adsorption and desorption within 2 min). However, this type of modification focuses on the outermost-layer surfaces of the MNPs, limiting the number of functional groups to a certain extent.

Porous materials with fast adsorption-desorption kinetics and good stability have been introduced for the preparation of magnetic sorbents.¹ Porous hybrid magnetic composites can be obtained by embedding or encapsulating MNPs in metal-organic frameworks (MOFs), or simply mixing the MOFs with MNPs, which have been demonstrated to be good candidates for solid-phase extraction.⁶ However, most MOFs are unstable under acidic conditions, which limits their preparation and application in trace heavy metal analysis.

Covalent organic frameworks (COFs) are a kind of new chemically stable material with controllable porous structures, large specific surface areas, and high porosities. They are used in catalysis, electronic devices, drug delivery, and gas separation and storage.⁷ They have also been demonstrated to have good applications in sample pretreatment.⁸ To satisfy the application requirements, COFs can be processed with appropriate post-modification and integrated with special functional groups (*e.g.*, amino, mercapto, and carboxyl). Functionalization of COFs enables them to exhibit unique properties.⁹ Based on the groups introduced into the COFs, their post-modification can be divided into alkenyl, alkynyl and sulfhydryl functionalization. Various strategies have been used to post-functionalize COFs.

Xu *et al.*⁹ synthesized alkynyl group-functionalized COFs and then reacted them with chiral azide-containing groups. Using a similar strategy, Meri-Bofi *et al.*¹⁰ prepared COFs containing triazole and thiol groups by first synthesizing the precursor alkyne group [HC≡C]_{0.5}-TPB-DMTP-COF and then post-functionalizing the COFs with reagents containing azide and thiol groups. The

products were then used to remove Hg ions from environmental samples. Sun *et al.*¹¹ synthesized a COF precursor and used a monomer to introduce alkenyl groups into the products. An ethanedithiol-modified COF with a sulfur content of 20.9% was obtained, with an adsorption capacity of 1350 mg g⁻¹ for Hg ions. Yan *et al.*¹² first synthesized 2,5-divinylterephthalaldehyde, which was then reacted with 1,3,5-tris(4-aminophenyl)benzene to achieve COF alkenylation. The products were further functionalized to remove organic pollutants and nitrates. The same group¹³ synthesized a COF material through a one-step ester exchange reaction between 2,4,6-triformylphloroglucinol (Tp) and methacrylic anhydride (MA), and a monolithic column was synthesized based on the Schiff base reaction between Tp-MA and p-phenylenediamine for use as the stationary phase in high-performance liquid chromatography.¹⁴ Huang¹⁵ synthesized COFs containing mercaptomethyl groups for the removal of Hg from aqueous solutions, which exhibited significantly higher adsorption capacity than those of most porous materials (734 mg g⁻¹). An identical strategy was applied to directly synthesize COFs using monomers containing mercaptomethyl functional groups, and the product was used for the selective adsorption of Pb ions.¹⁶ The adsorption capacity of the material was 239 mg g⁻¹. Fu *et al.*¹⁷ used a covalent triazine framework combined with monomers containing aromatic sulfhydryl groups to synthesize a novel COF for the detection and removal of Hg from environmental samples. The adsorption capacity of the material was 658 mg g⁻¹.

Thiophene, as a functional group, can be grafted onto COF for adsorbing thiophilic metal ions. Subhra Jana *et al.*¹⁸ used thiophene as a polymer precursor to synthesize three polymer materials, Th-1, Th-2, and Th-3, of which the adsorption capacity of Th-2 for Hg²⁺ ions was 145 mg g⁻¹. Hamouz *et al.*¹⁹ used benzene mercaptan, thiophene and formaldehyde as raw materials for polymerization reactions and synthesized the polymer. Maity *et al.*²⁰ used a simple Schiff base condensation strategy to prepare a thiophene-chitosan 3D hydrogel with 2-thiophene formaldehyde. The removal efficiency of Hg reached 100%, and the preparation process was environmentally friendly. Abolhasani *et al.*²¹ used polythiophene to wrap ferromagnetic oxide supported on silica nanoparticles to extract Hg ions from seafood. As can be seen, the thiophene group exhibits high aromaticity and stability, and the synthesized materials can be recycled. The coordination constants of the complexes formed by thiophene groups and heavy metals are relatively large and stable, and thiophene groups have a strong tolerance to strong acid-base conditions.¹⁵

In this study, we prepared magnetic thiophene functionalized COFs (Fe₃O₄@COF-thiophene) by post-modification strategy and evaluated their adsorption performance. Specifically, the core-shell Fe₃O₄@COF precursor was prepared through a one-pot reaction of Fe₃O₄ MNPs, 1,3,5-tris(4-aminophenyl)benzene (TAPB), and 2,5-dimethoxyterephthalaldehyde (DMTA), followed by an “Aza D-A reaction” with 3-ethynylthiophene to

obtain Fe₃O₄@COF-thiophene composites. Three thiophilic metal ions (Pb²⁺, Hg²⁺ and Bi³⁺) were used as the target analytes, and the adsorption and desorption conditions were optimized. Based on this, an MSPE method combined with inductively coupled plasma mass spectrometry (ICP-MS) was proposed for the determination of Pb, Hg, and Bi in environmental water samples.

EXPERIMENTAL

Instrumentations. The instrument employed for detecting heavy metals (Hg²⁺, Bi³⁺, Pb²⁺) was a quadrupole (Q) ICP-MS (Agilent 7500a, Tokyo, Japan). The operational parameters for ICP-MS are listed in Table S1. Transmission electron microscopy (TEM) (JEM-2010, JEOL Ltd., Japan) was used to observe the surface morphologies of the prepared sorbents. N₂ isotherms were measured using an ASAP 2020 (Micromeritics, USA) surface area and pore size analyzer using a liquid nitrogen bath (77 K). Fourier transform infrared (FT-IR) spectra were recorded using an IS10 Thermo Spectrometer (Fisher Scientific, USA). The other instruments employed are listed in Supplementary Information (SI) as Text S1.

Reagents. Standard solutions of Hg²⁺, Pb²⁺, and Bi³⁺ (1000 mg L⁻¹) were prepared by dissolving HgCl₂ (Shanghai Chemical Reagent No.4 Factory), PbCl₂ (Tianjin Dengfeng Chemical Reagent Factory), and Bi(NO₃)₃ (Shanghai Chemical Reagent No.4 Factory) in 0.1 mol L⁻¹ nitric acid, respectively. The standard solution was obtained by stepwise dilution with 20 mmol L⁻¹ NH₄Ac-HAc solution. The ultrapure water used in the experiment was prepared using a Milli-Q Element system (18.2 MΩ·cm, Millipore, Molsheim, France), and the containers used were all disposable or used after soaking overnight in 1 mol L⁻¹ nitric acid solution. The other reagents are detailed in the Text S2.

Preparation of Fe₃O₄@thiophene-TPB-DMTP-COF

(1) Synthesis of Fe₃O₄@SiO₂-NH₂@COF. Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-NH₂ nanoparticles were prepared according to a previous study²² with a few modifications. Relevant details of the synthesis are included in Text S3.

Aminated Fe₃O₄ and 480 mg of DMTA were dispersed in 10 mL of dioxane and 10 mL of mesitylene, and sonicated in 10 mL of mesitylene for 10 min in a 100 mL round-bottomed flask. Aqueous solution (5.0 mL, 3 mol·L⁻¹ of acetic acid) was added dropwise as the catalyst, and 560 mg of TAPB was dispersed in 10 mL of dioxane and 10 mL of mesitylene. After letting it stand for 10 min, the mixture was allowed to react at room temperature for 2-3 days. The suspension was washed five times with methanol and dried at 60 °C in a vacuum oven for 12 h to obtain Fe₃O₄@TPB-DMTP-COF (approx. 1.08 g).

(2) Synthesis of Fe₃O₄@COF-thiophene. Thiophene-functionalized magnetic COF was synthesized as previously described.²³ Fe₃O₄@TPB-DMTP-COF (200 mg), 3-ethynylthiophene (120 μL, 1 mmol), BF₃·OEt₂ (20 μL, 0.15 mmol), tetrachlorobenzoquinone (160 mg, 0.6 mmol), and 10 mL of toluene were added into a 20 mL-Pyrex tube. The tube was sealed and heated in an oil bath at 110 °C under a N₂ atmosphere. After three days, the mixture was cooled to room temperature, and the precipitate was separated by magnetic separation. The reaction mixture was washed with tetrahydrofuran (THF) and quenched with a saturated aqueous sodium bicarbonate solution (2 mL×3). Subsequently, the solid was washed with THF for 12 h in a Soxhlet extractor and dried under vacuum.

Magnetic Solid Phase Extraction procedure. The prepared Fe₃O₄@COF-thiophene (10 mg) was added to an NH₄Ac-HAc solution (pH = 6) containing a specific concentration of the target metal ions (Hg²⁺, Pb²⁺, and Bi³⁺), followed by stirring for 20 min. Then, Fe₃O₄@COF-thiophene was separated from the mixture by an applying a magnetic field. The material was then washed with ultrapure water and transferred to a 2-mL Eppendorf tube. Further, 0.8 mL of the desorbing agent (0.1 mol L⁻¹ HNO₃ + 8 % (m/v) Cysteamine hydrochloride) was added to the solution, followed by ultrasonication for 20 min. After magnetic separation, the desorbed solution was subjected to ICP-MS detection. A buffer system without target metal ions was used as the blank; analysis for each sample was repeated three times.

Adsorption efficiency and extraction recovery were used to evaluate the adsorption performance of Fe₃O₄@COF-thiophene.

$$\text{Adsorption efficiency} = \left(1 - \frac{C_a}{C_0}\right) \times 100\%$$

where C_a and C₀ are the concentration of analyte in the solution after adsorption and in the original solution, respectively.

$$\text{Extraction recovery} = \frac{C_f \times V_f}{C_0 \times V_0} \times 100\%$$

where V₀ and V_f are the volumes of the original and desorption solution, respectively; C₀ is the concentration of the analyte in the original solution; and C_f is the concentration of the analyte in the desorption solution.

Pretreatment of Certified Reference Materials and lake water samples. An external calibration method was used to quantify the target metal ions in real samples. Specifically, a series of standard solutions containing target metal ions was prepared and subjected to the proposed MSPE-ICP-MS method. A calibration curve was constructed by plotting the signal intensity of the metal ions of interest vs their corresponding concentration. The accuracy of this method was verified by analyzing GSB 07-1185-2000 (202047), GSB 07-1185-2000 (201239), and BY 400143 (B2003113)

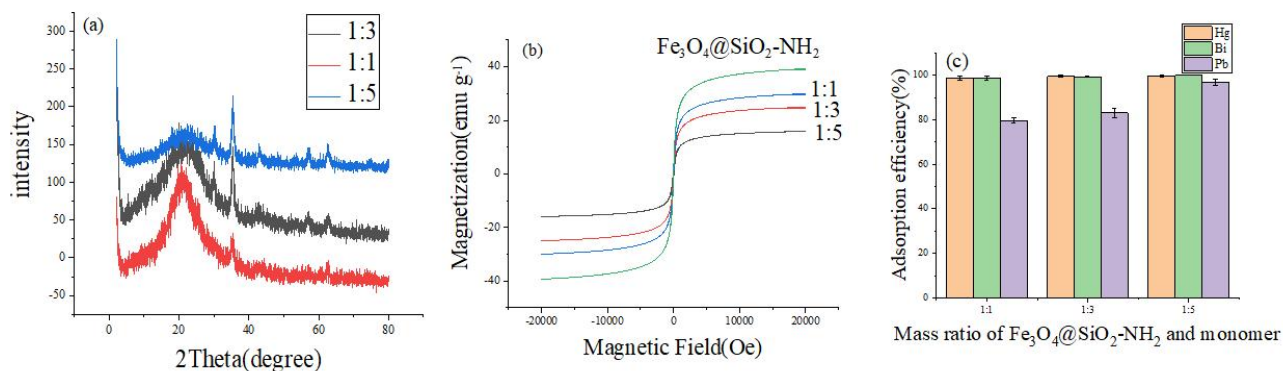


Fig. 1 (a) XRD spectra, (b) magnetic intensity, and (c) adsorption percentage of target metals on Fe₃O₄@COF-thiophene involving the mass ratios of Fe₃O₄@SiO₂-NH₂ to the monomer of 1:1, 1:3 and 1:5.

(environmental samples). Before analysis, the water samples were diluted 10 and 100 times with the aforementioned buffer (pH=6).

The East Lake water was collected from the East Lake outside Wuhan University, and the Yangtze River water was collected from Hanyangmen Wharf, on the shore of the Yangtze River. The collected fresh-water samples were kept overnight for the sedimentation of large particles and then filtered with 0.2-μm PTFE (polytetrafluoroethylene) membranes. Then, 1.0 mol L⁻¹ HNO₃ was added to prevent the metal ions from hydrolyzing. The pH of the sample was adjusted to 6 using 10 mol L⁻¹ HNO₃ and 10 mol L⁻¹ NaOH solutions before MSPE-ICP-MS analysis.

RESULTS AND DISCUSSION

Preparation and characterization of Fe₃O₄@COF-thiophene.

As binary composites, the two sorbent components played different roles. Specifically, Fe₃O₄ was used for magnetic separation with the aid of an external magnetic field, and COF-thiophene was used to selectively enrich target ions. The grafted COF determines the sulfur density in the composite to a great extent, which directly affects the adsorption performance of magnetic sorbents. Herein, the mass ratio of aminated Fe₃O₄ MNPs to COF monomers was optimized.

As shown in Fig. 1a, when the mass ratio of Fe₃O₄@SiO₂-NH₂ to the monomer was 1:1, the resultant Fe₃O₄@COF-thiophene exhibited a crystalline form. When the ratio was 1:3, mountain-shaped peaks corresponding to amorphous structures were observed. However, at a ratio of 1:5, the XRD pattern exhibited a main peak corresponding to the ideal crystal structure. Fe₃O₄@COF-thiophene, obtained at ratios of Fe₃O₄@SiO₂-NH₂ to the monomer of 1:1, 1:3, and 1:5, exhibited magnetic intensities of 29.1, 24.3, and 18.2 emu g⁻¹, respectively (Fig. 1b). All these

materials meet the requirements for magnetic separation. Using 1 mg of Fe₃O₄@COF-thiophene, quantitative adsorption of the three target metal ions was obtained at a mass ratio of Fe₃O₄-NH₂ to the monomer of 1:5 during synthesis (Fig. 1c). In the subsequent experiments, the mass ratio of Fe₃O₄-NH₂ to the monomer of 1:5 was fixed for the synthesis of Fe₃O₄@COF-thiophene.

Characterization of prepared sorbents. FT-IR spectroscopy was used to characterize Fe₃O₄@TPB-DMTP-COF and Fe₃O₄@COF-thiophene, and the results are shown in Fig. 2a. In the FT-IR spectrum of the TAPB monomer, vibrational absorption peaks corresponding to the amino groups were observed at 3432, 3215, and 3358 cm⁻¹. These peaks disappeared in the FT-IR spectrum of Fe₃O₄@TPB-DMTP-COF, indicating the completion of the reaction. In the spectrum of Fe₃O₄@COF-thiophene, the vibration absorption peak corresponding to the aldehyde group at 1678 cm⁻¹ disappeared and the vibration absorption peak corresponding to C=N at 1614 cm⁻¹ appeared, proving that the aldehyde-amine condensation reaction was successful. The vibration absorption peak corresponding to the C-S-C bond appeared at 1050 cm⁻¹, indicating that the thiophene ring was grafted onto the COF material and that the post-functionalization reaction was successful.

As shown in Fig. 2b, the XRD pattern of the synthesized precursor magnetic material shows peaks at 2.81°, 4.81°, 5.56°, 7.40° and 9.68°, which correspond to the (100), (110), (200), (210), and (210) crystal planes, respectively. The diffraction peaks of (220), (220), (311), (400), (422), (551), and (440) corresponding to the aminated MNPs indicate that the material exhibits magnetic properties. After modification, the thiophene-functionalized material was characterized, and the position of the main peak did not change significantly.

As shown in Fig. 2c, the saturation points of Fe₃O₄@SiO₂-NH₂ and Fe₃O₄@COF-thiophene were 39.3 and 15.9 emu g⁻¹,

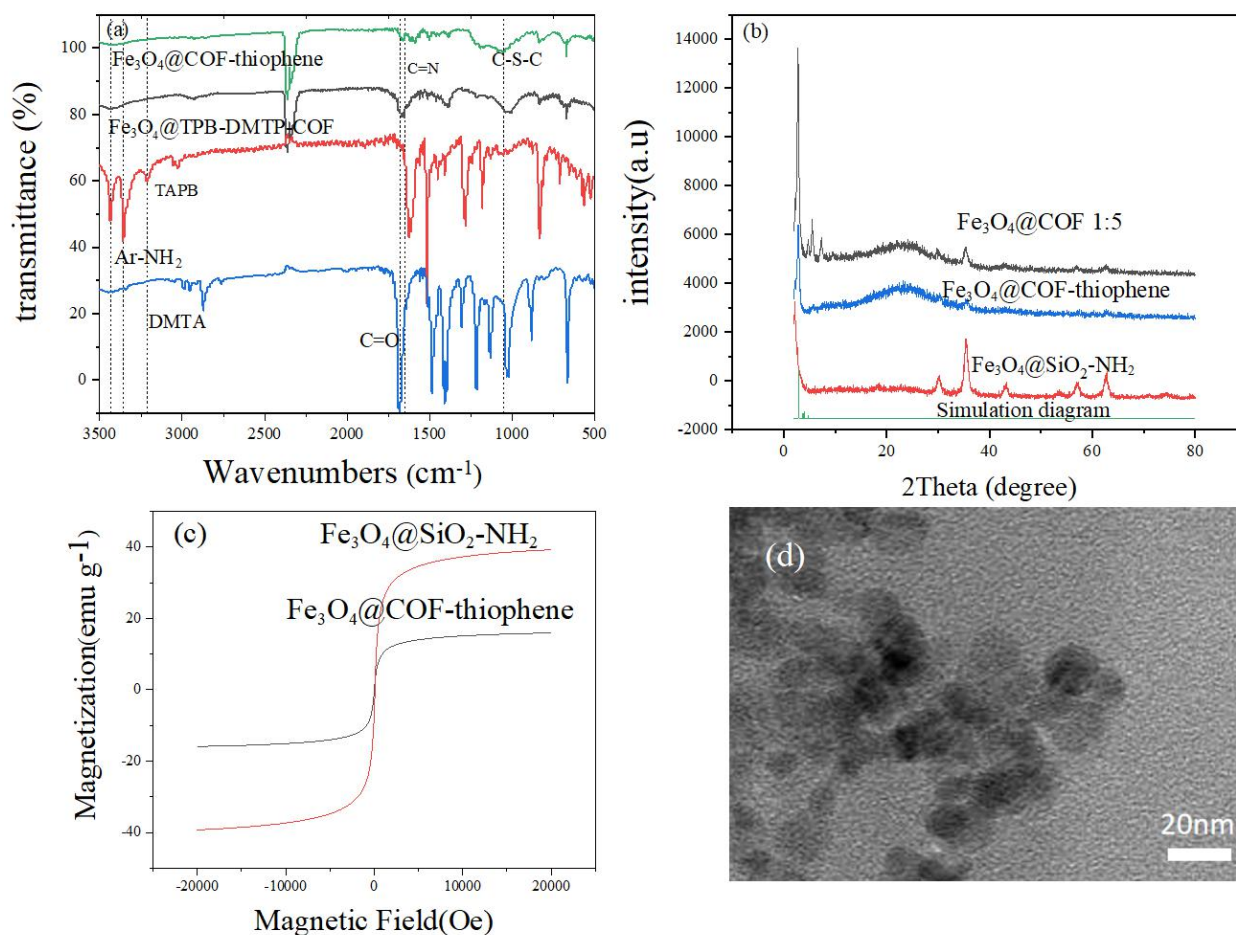


Fig. 2 (a) FT-IR of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$, $\text{Fe}_3\text{O}_4@\text{TPB-DMTP-COF}$, TAPB, and DMTA, (b) XRD pattern of $\text{Fe}_3\text{O}_4@\text{COF}$ 1:5, $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{NH}_2$; (c) simulation diagram by vibrating sample magnetometer (VSM) analysis of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2-\text{NH}_2$; and (d) TEM characterization of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$.

respectively. After the material combined with the MNPs, their magnetic strength decreased; however, it was still greater than 10 emu g^{-1} and could meet the requirements of magnetic separation with relatively high separation rate.

The morphology and particle size of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ were characterized by TEM. As shown in Fig. 2d, the material exhibited a core-shell structure with a particle size of approx. 18 nm, and the thickness of the COF shell layer was approx. 2 nm. The porosity of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ was studied using nitrogen adsorption isotherms at 77 K. The adsorption curve is a typical type IV isotherm, which is characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface area and pore volume were estimated to be 898 $\text{m}^2 \text{g}^{-1}$ and 1.36 $\text{cm}^3 \text{g}^{-1}$, respectively. The pore size distribution was calculated using the nonlocal density functional theory (NLDFT) method, and a pore size of 1.50 nm was observed for $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ (Fig. S1).

X-ray photoelectron spectroscopy (XPS) was used for semi-

Table 1. Determination of elemental content of materials by XPS semi-quantitative method

Element	Atomic %	Weight%	Weight% ^a	Weight% ^b	Weight% ^c
C1s	55.9	43.3	-	89.3	-
O1s	25.7	26.6	-	4.3	-
N1s	5.31	4.8	-	-	-
S2p	2.55	5.27	2.8	5.4	2.5
Si2p	9.96	18	-	0.7	-
Fe2p	0.57	2.06	-	0.3	-

^a Mercaptopropyltrimethoxysilane-silica-coated magnetic nanoparticles³

^b Magnetic porous polymer-SH ($\text{Fe}_3\text{O}_4@\text{SiO}_2@$ polyethylene dimethacrylate-co-glycidyl methacrylate)⁴

^c Glycidyl methacrylate-S-SH magnetic nanoparticles⁵

quantification of the elements in $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$, and the results are listed in Table 1. The content of sulfur in the prepared $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ was 5.27% (wt.), which is a high level among reported sulphur-functionalized sorbents.

Stability of $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$. The prepared $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$ was subjected to XRD characterization before and after soaking in 0.1 mol L^{-1} nitric acid containing 8 % (m/v) cysteamine hydrochloride (the eluent used in MSPE) or 1

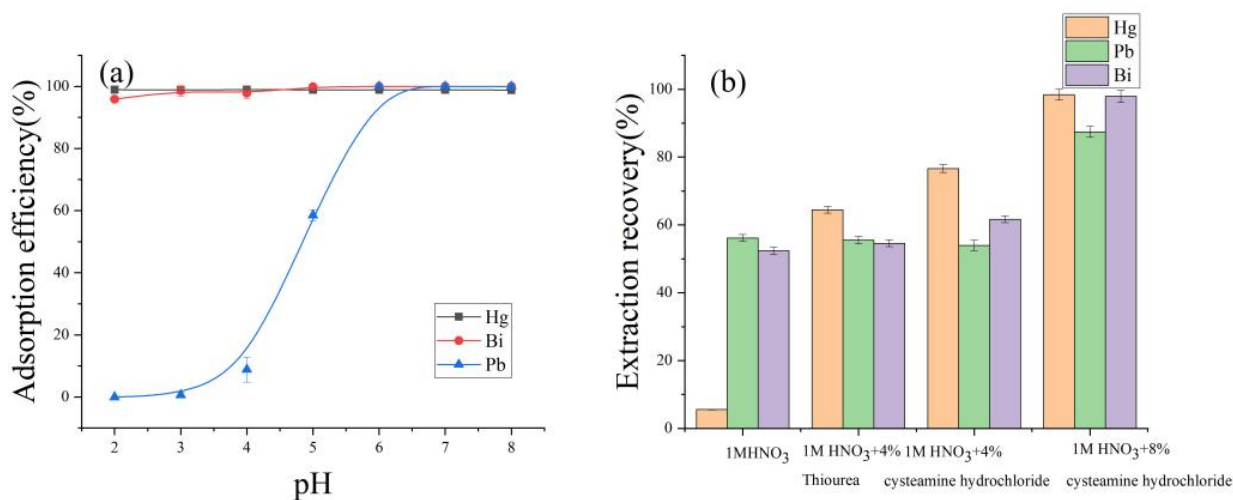


Fig. 3 (a) Adsorption efficiency of target metal ions (Hg^{2+} , Pb^{2+} and Bi^{3+} , each at $20 \text{ ng}\cdot\text{mL}^{-1}$) with respect to pH by $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene under following conditions: sample volume: 1 mL, adsorbent amount: 2 mg; adsorption time: 30 min. (b) Recovery of three metal ions under different desorbents (Hg^{2+} , Pb^{2+} and Bi^{3+} , each at $20 \text{ ng}\cdot\text{mL}^{-1}$) and conditions were follows: sample volume: 1 mL; adsorbent amount: 1 mg; adsorption time: 30 min; elution volume: 1 mL; elution time: 30 min. Error bar represents the standard deviation of the results ($n = 3$).

mol L^{-1} NaOH for 12 h. The position of the main peak of $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene hardly varied after soaking in the eluent (Fig. S2), but the peak strength decreased to a certain extent. However, neither the position nor strength of the main peak of $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene varied after soaking in 1 mol L^{-1} NaOH for 12 h. The results indicate that the acidic medium had a destructive effect on the prepared $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene, which exhibited high alkali resistance.

The reusability of the prepared $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene was investigated through repeated adsorption and desorption experiments. Figure S3 shows that target metal ions could still be quantitatively recovered using $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene even after 20 cycles of adsorption and desorption. This indicates that the prepared $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene can be reused at least 20 times.

Optimization of MSPE conditions. Extraction conditions, such as sample volume, adsorbent amount and extraction time were optimized.

(1) Effect of pH on adsorption. The adsorption behavior of the three target metal ions on $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene was studied in the pH range of 2–8, and the results are shown in Fig. 3a. In the pH range of 2–8, the adsorption efficiencies of both Hg^{2+} and Bi^{3+} ions were close to 100%; however, for the adsorption of Pb^{2+} ions, a higher pH solution was required. A possible reason for this is that Hg^{2+} and Bi^{3+} are two types of soft acids, the sulfur atoms are soft bases, and the coordination between them is strong. When the pH of the solution was increased to 6, Pb^{2+} ions were quantitatively adsorbed. Hydrogen ions were assumed to compete with lead ions for sulfur-active sites at lower pH, which weakened the interaction between the material and Pb^{2+} ions. In subsequent experiments,

pH 6 was adopted to achieve simultaneous adsorption of the three metal ions. Figure 3b shows the effect of the eluent on the recoveries of three metal ions of interest. The recoveries of target metals obtained using cysteamine hydrochloride-containing eluents were significantly better than those obtained using other eluents. Therefore, cysteamine hydrochloride and HNO_3 were selected as the eluents for subsequent experiments.

(2) Eluent and its concentration. The effect of eluent composition on the extraction recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} was investigated. Initially, the concentration of cysteamine hydrochloride was fixed at 10 % (m/v), and the concentration of nitric acid was varied from 0.0 to 1.0 mol $\cdot\text{L}^{-1}$. As shown in Fig. S4, when the nitric acid concentration was less than 0.2 mol $\cdot\text{L}^{-1}$, the recoveries of three metals were all higher than 85%. Next, the concentration of nitric acid was fixed at 0.1 mol $\cdot\text{L}^{-1}$, and the effect of cysteamine hydrochloride concentration in the eluent was investigated in the range of 2–10% (m/v). Figure S5 indicates that the three target metal ions were quantitatively recovered when the concentration of cysteamine hydrochloride was in the range of 6–10% (m/v). In subsequent experiments, 0.1 mol $\cdot\text{L}^{-1}$ nitric acid containing 8% (m/v) cysteamine hydrochloride was used for the desorption of target metal ions from $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene.

(3) Elution volume and duration. A smaller desorption volume results in higher enrichment factor. By using the eluent of 0.1 mol $\cdot\text{L}^{-1}$ nitric acid containing 8% (m/v) cysteamine hydrochloride, the desorption volume was investigated in the range of 0.5–1.0 mL. The extraction recovery of metal ions is shown in Fig. S6. When the desorption volume was greater than 0.7 mL, the three target metal ions were quantitatively recovered. Therefore, a desorption volume of 0.8 mL was used in the following experiments.

Subsequently, the desorption duration was optimized. Under the optimized conditions, the extraction recovery of metal ions was investigated by varying the desorption time in the range of 10–30 min. As shown in Fig. S7, quantitative recovery of the three target metal ions was achieved within 20 min. Therefore, the desorption duration was fixed at 20 min for the subsequent experiments.

(4) Sample volume, adsorbent amount, and extraction time.

The sample volume directly determines the enrichment factor of the proposed method, which is closely related to the detection limit. The larger the sample volume, the higher the enrichment factor, and the lower the detection limit of the method. To obtain a lower detection limit for this method, the extraction recovery of the three elements was investigated by varying the sample volume in the range of 100–250 mL. The results presented in Fig. S8 reveal that as the sample volume increased, the extraction recovery of the three elements decreased. To ensure an extraction recovery of the three metals of more than 85%, 150 mL of sample was selected for subsequent experiments. By fixing the sample volume at 150 mL, the extraction recovery of the target metal ions was investigated by varying the material dosage from 5 to 25 mg. The results (Fig. S9) revealed that as the amount of material increased, the extraction recovery of the target metal ions in the desorption solution increased. Quantitative recovery was achieved when the amount of material was greater than or equal to 10 mg. Therefore, the quantity of material was fixed at 10 mg for subsequent experiments.

Subsequently, the extraction duration was optimized in the range of 5–30 min with a sample volume of 150 mL, the magnetic sorbents dosage of 10 mg, and absolute amounts of the three target metal ions of 20 ng. As shown in Fig. S10, when the extraction duration was > 20 min, quantitative recovery of target metal ions was achieved. Therefore, the optimal extraction time was determined to be 20 min.

The final optimized conditions are as follows: the sample volume is 150 mL, material dosage is 10 mg, the extraction time is 20 min, desorption time is 20 min and desorption volume is 0.8 mL; the extraction medium pH is adjusted to 6, and desorption solvent is 0.1 mol·L⁻¹ nitric acid containing 8% (m/v) cysteamine hydrochloride.

Interference of coexisting ions. The matrix in environmental water samples is complex, and the commonly co-existing anions and cations often interfere with the extraction process. To investigate the efficiency of the method, in the presence of interference from common anions and cations, the extraction recovery of target metal ions was investigated under the optimized conditions, keeping the total amount of each target metal ion fixed at 20 ng, and adding different concentrations of common anions and cations. When the extraction recoveries of Hg²⁺, Bi³⁺ and Pb²⁺ were between 85 and 115%, the interference of these coexisting

Table 2. Tolerance limit of interfering ions

Coexisting ions	Tolerance limits of ions (mg L ⁻¹)	Concentration of common ions in natural water (mg L ⁻¹)	Recovery of Hg ²⁺ (%)	Recovery of Pb ²⁺ (%)	Recovery of Bi ³⁺ (%)
Na ⁺	9000	1.8–31.3	88.1±7.8	87.9±0.2	89.6±1.7
K ⁺	9000	0.8–28.5	87.7±1.7	86.3±1.6	87.4±4.9
Ca ²⁺	6000	4.7–80.7	119±21	103±13	92.6±4.0
Mg ²⁺	6000	1.6–27.3	106±8	88.6±0.7	96.4±3.0
Al ³⁺	15	-	91.0±10.4	92.0±14.1	103±3
Zn ²⁺	100	2	109±14	108±8	105±4
Fe ³⁺	100	0.3	111±15	113±1	89.9±0.8
Cu ²⁺	15	1	101±1	95.6±0.7	101±1
Cd ²⁺	50	-	104±1	93±3	102±1
NO ₃ ⁻	12000	10	101±1	109±16	96.7±5.7
Cl ⁻	12000	1.1–42.8	88.1±7.8	87.9±0.2	89.6±1.7

ions were ignored. The results are presented in Table 2. When 9,000 mg L⁻¹ of Na⁺ and K⁺, 6000 mg L⁻¹ of Ca²⁺ and Mg²⁺, 5000 mg L⁻¹ of SO₄²⁻, 12,000 mg L⁻¹ of NO₃⁻ and Cl⁻, 15 mg L⁻¹ of Al³⁺ and Cu²⁺, 100 mg L⁻¹ of Fe³⁺, 1 mg L⁻¹ of Cu²⁺, and 50 mg L⁻¹ of Cd²⁺ coexisted with the target metal ions, Cd²⁺, Hg²⁺ and Pb²⁺ could be still quantitatively recovered. This shows that the method exhibits a good efficiency against common coexisting ions and can be used for the determination of Hg²⁺, Bi³⁺ and Pb²⁺ ions in complex environmental samples.

Adsorption mechanism and kinetics. As shown in Fig. 4, after the adsorption of Hg²⁺ and Pb²⁺, the element S produced a peak shift of 0.5 eV and 0.24 eV, respectively. Similarly, after the adsorption of Bi³⁺, S 2p_{1/2} produced a peak shift of 0.12 eV, and S 2p_{3/2} produced a peak displacement of 0.18 eV. These results indicate that the adsorption process could mainly be attributed to S in the prepared Fe₃O₄@COF-thiophene.

Variations in the XPS characteristics of Fe₃O₄@COF-thiophene before and after adsorption of target ions were studied (Fig. S11). Herein, Hg ions are used as representatives for discussion. When Hg ions were adsorbed, the peaks shifted in the positive direction by 0.5 eV, indicating that S played a crucial role in the adsorption process. This reflected the higher functionalization efficiency of the Aza D-A reaction. Furthermore, the adsorption of the material was observed by characterizing mercury before and after adsorption. After Hg adsorption, a characteristic peak corresponding to 4f electrons was observed. XPS analysis indicated that the adsorption mechanism of the material was mainly due to the coordination effect of thiophene sulfur on the metal ion.

Investigation of pseudo-second-order dynamics model. To determine the adsorption kinetics of Hg²⁺, Bi³⁺ and Pb²⁺, a series of standard solutions containing these ions were prepared and subjected to MSPE under optimal conditions (pH 6, shaking for 12 h). The initial and final concentration were determined to establish the kinetic models.

First, a pseudo-first-order kinetic model was used to evaluate the adsorption behavior of the material, and ln(q_e-q_i) was used to

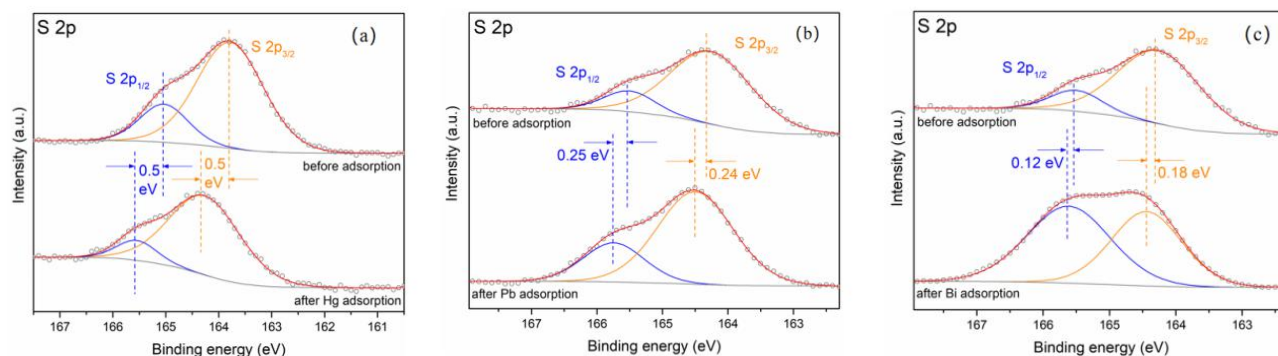


Fig. 4 (a) Displacement of S before and after Hg²⁺ adsorption (b) Displacement of S before and after Pb²⁺ adsorption (c) Displacement of S before and after Bi³⁺ adsorption.

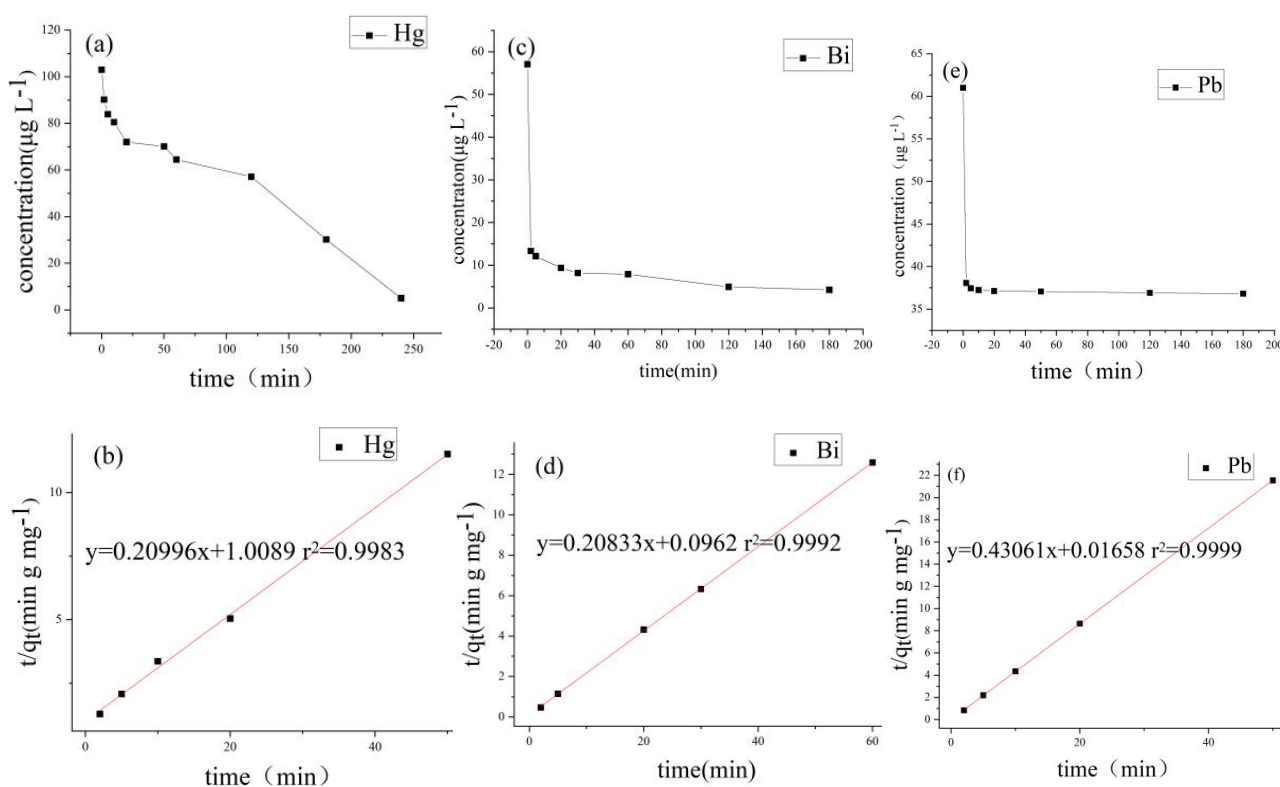


Fig. 5 Ion concentration vs time graph (a, c and e for Hg, Bi and Pb) and linear regression by fitting the equilibrium adsorption data with pseudo-second-order adsorption model (b, d and f for Hg, Bi and Pb).

plot t .

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

As depicted at Fig. S12, the linearity of the three simulated images is poor, indicating that the adsorption behavior of the material does not conform to the pseudo-first-order kinetic model.

Therefore, the pseudo-second-order adsorption kinetic model was used to investigate the adsorption behavior of the ions, and

' t/q_t ' was used for plotting ' t '. The equation for the second-order adsorption model is presented below and plotted in Fig. 5.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

In this equation, k_2 (g mg⁻¹.min⁻¹) is the pseudo-second-order rate constant of adsorption; q_t (mg.g⁻¹) is the number of ions adsorbed at time t (min), and q_e (mg.g⁻¹) is the number of ions adsorbed at equilibrium. The initial adsorption rate h ($k_2 q_e^2$) has

Table 3. Determination of elemental content of materials by XPS semi-quantitative method

Target ion	LOD (ng L ⁻¹)	EFs	RSD intra-assays (% , n = 7)	Linear equation (ng L ⁻¹)	R ²	Linear range (ng L ⁻¹)
Hg ²⁺	0.41	188	7.5 ^a	y=753x+7629	0.9999	3-5000
Pb ²⁺	0.97	188	6.8 ^a	y=1721x+17936	0.9993	3-5000
Bi ³⁺	0.47	188	6.2 ^a	y=3390x+6850	0.9992	2-2000

^a c = 3 ng L⁻¹.

Table 4. Analytical results for CRMs of Environmental Waters (mean ± s.d., n = 5)

CRMs	Elements	Found (µg·L ⁻¹)	Certified value (µg L ⁻¹)	T-test ^a
GSB 07-1185-2000(202047)	Hg	12.1±0.2	12.5±0.4	2.24
GSB 07-1185-2000(201239)	Pb	20.0±0.6	20.1±1.3	0.17
BY 400143(B2003113)	Bi	49.2±0.4	49.4±0.9	0.49

^a c = 3 ng L⁻¹.

Table 5. Determination of Hg, Pb, and Bi in environmental water samples (mean ± s.d, n = 3)

Sample	Added (ng·L ⁻¹)			Found (ng·L ⁻¹)			Recovery (%)		
	Hg ²⁺	Pb ²⁺	Bi ³⁺	Hg ²⁺	Pb ²⁺	Bi ³⁺	Hg ²⁺	Pb ²⁺	Bi ³⁺
East Lake	0	0	0	4.91±0.45	62.5±0.9	N.D.	-	-	-
	5	50	5	9.86±0.05	102±2	4.92±0.11	99.5	90.5	98.4
	50	200	50	53.9±2.1	226±4	48.2±1.8	98.0	86.1	96.4
	200	1000	200	183±10	919±32	205±8	89.1	86.5	103
Yangtze River	0	0	0	10.2±0.7	103±8	0	-	-	-
	10	100	5	20.4±1.2	210±6	5.10±0.16	101	103	102
	50	200	50	60.4±0.3	298±13	52.0±0.1	100	98.3	104
	200	1000	200	207±4	1130±32	204±11	98.3	102	102

N.D.: not detected

been widely used to evaluate the adsorption rates. The relationship was linear, indicating that the model conformed to pseudo-second-order adsorption, and that the process was chemical adsorption (Table S2).

Analytical performance. The analytical performance of this method was investigated under optimized experimental conditions. The detection limits of Hg²⁺, Pb²⁺, and Bi³⁺ ions were 0.41, 0.97 and 0.47 ng·L⁻¹, respectively. The enrichment factor of this method was as high as 188 times, and the linear range was 3-5000 ng·L⁻¹ for Hg²⁺/Pb²⁺, and 2-2000 ng·L⁻¹ for Bi³⁺, which meets the enrichment and detection limits of heavy metals in real environmental water samples. As shown in Table 3, the precision of the method was high, and the relative standard deviations for Hg²⁺, Pb²⁺ and Bi³⁺ were 7.5, 6.8 and 6.2% (RSD, n = 7, c_{Hg}, Pb, Bi = 3 ng L⁻¹), respectively.

A comparison of the method developed in this study with other reported methods is shown in Table S4. It shows that the detection limit of this method is lower and the enrichment factor is higher than those of previously reported methods.²⁴⁻³² However, the detection limit was comparable to that of this method.^{4, 29-32} The extraction kinetics of this method were better than those reported in Ref. 27. In comparison, the enrichment factor of this method is higher than that of the method in Ref. 4. Although the extraction kinetics of the method developed in this study were slower than those of some previously developed,^{28,31} the enrichment factor of

the current method was higher than that of these methods. In general, the method developed in this study has the advantages of a high enrichment factor, low detection limits, and high adsorption and desorption kinetics.

Environmental waters CRMs. Certified reference materials, including GSB 07-1185-2000 (202047), GSB 07-1185-2000 (201239), and BY 400143 (B2003113), were used in the proposed method. The results are summarized in Table 4. The t-test calculated t-values were all less than 2.78, indicating no significant difference between the determined and certified values and demonstrating the good accuracy of the method.

Analysis of environmental water. This method was applied to the analysis of environmental water samples, and the contents of the three heavy metal ions in the East Lake and Yangtze River waters were found to be lower than the national standard limits (Hg: 0.001 mg L⁻¹, Pb: 0.010 mg L⁻¹). The concentration of Hg²⁺ was lower than 15 ng L⁻¹ and that of Pb²⁺ was lower than 150 ng L⁻¹. In these water samples, Bi³⁺ was not detected. To further verify the accuracy of the method, recovery tests were performed at three concentrations (5, 50 and 200 ng L⁻¹). As shown in Table 5, the recovery was between 86.1 and 104 %, which indicates the high reliability of the method. Therefore, this method can be applied for the analysis of the three heavy metals in environmental water samples.

CONCLUSION

In this study, a magnetic thiophene-modified COF composite was prepared using a simple synthetic method. The prepared $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene exhibited high stability, good magnetic properties, and good extraction performances for Hg^{2+} , Bi^{3+} , and Pb^{2+} . A method based on MSPE and ICP-MS was developed to detect three target metal ions in environmental water samples. Compared with other methods, this method exhibited a large enrichment factor (188), low detection limit, wide linear range, and strong anti-interference ability. This method was successfully applied for the detection of trace metal ions in the East Lake and Yangtze River water samples.

ASSOCIATED CONTENT

The supporting information (Figs. S1–S12, Tables S1–S3, and Texts S1–S3) is available at www.at-spectrosc.com/as/home.

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Notes

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