

Supplemental information

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

Tiantong Guo, Beibei Chen, Man He*, Bin Hu

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, P R China

Text S1 Instrumentations

Text S2 Reagents and solutions

Text S3 Preparation of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-NH₂

Table S1 Working parameters of Agilent ICP-MS

Table S2 Pseudo-Second-Order Dynamics Model adsorption of Hg²⁺, Bi³⁺ and Pb²⁺

Table S3 Analytical results of Hg, Pb and Bi in CRMs of environmental Waters (mean±s.d., n=5)

Table S4 Comparison of the analytical performance of different adsorbents for metal ions

Fig. S1 Brunauer Emmett-Teller specific surface area and pore size investigation

Fig. S2 XRD characterization of the materials soaked under the three conditions

Fig. S3 Reuse times for the materials

Fig. S4 Effect of HNO₃ concentration on the recovery of Hg²⁺, Bi³⁺ and Pb²⁺. Conditions: concentration of each target analyte: 20 ng mL⁻¹; sample volume: 1 mL;

*Corresponding author: Fax: +86-27-68754067; Tel: +86-27-68752162; Email: heman@whu.edu.cn

pH = 6; adsorbent amount: 1 mg; adsorption time: 30 min; the concentration of cysteamine hydrochloride is 10% (m/V); elution volume: 1 mL; elution time: 30 min.

Fig. S5 Effect of cysteamine hydrochloride concentration on the recovery of Hg^{2+} , Bi^{3+} , and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL; pH = 6; adsorbent amount: 1 mg; adsorption time: 30 min; the concentration of HNO_3 is 0.1 mol L^{-1} ; elution volume: 1 mL; elution time: 30 min.

Fig. S6 Effect of elution volume on the recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL; pH=6; adsorbent amount: 20 mg; adsorption time: 30 min; elution time: 30 min.

Fig. S7 Effect of elution time on the recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL; pH=6; adsorbent amount: 20 mg; adsorption time: 30 min; elution volume: 0.8 mL.

Fig. S8 Effect of sample volume on the adsorption of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: Hg^{2+} , Bi^{3+} and Pb^{2+} each at 20 ng; pH = 6; adsorbent amount: 20 mg; adsorption time: 30 min; elution volume: 1 mL; elution time: 20 min.

Fig. S9 Effect of adsorbent amount on the adsorption of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: Hg^{2+} , Bi^{3+} and Pb^{2+} each at 20 ng; sample volume: 150 mL; pH=6; adsorption time: 30 min; elution volume: 1 mL; elution time: 5 min.

Fig. S10 Effect of adsorption time on the adsorption of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: Hg^{2+} , Bi^{3+} and Pb^{2+} each at 20 ng; sample volume: 150 mL; pH=6; adsorbent amount: 10 mg; elution volume: 1 mL; elution time: 5 min

Fig. S11 TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ (a), $\text{Fe}_3\text{O}_4@\text{thiophene-COF}$ (b)

Fig. S12 XPS data of S 2p for $\text{Fe}_3\text{O}_4@\text{COF-thiophene}$

Text S1 Instrumentations

HX-NC12 metal bath nitrogen evaporator (Wuhan Hengxin Century Technology Co., Ltd., China) was used for drying the prepared sorbents. X-ray photoelectron spectrometer (XPS) (Thermo Fisher, USA) was applied to detect elements on the surface of material with monochromatic Al-K α as an X-ray anode. PPMS-9 T vibrating sample magnetometer (VSM) (Quantum Design, USA) was used for magnetic strength characterization.

Text S2 Reagents

Ammonium acetate (CH₃COONH₄), NH₃·H₂O, C₂H₅OH, tetrahydrofuran, methanol, toluene, dioxane, mesitylene, acetic acid and isopropanol (all of analytical pure) were purchased from Sinopharm Chemical Reagent (Shanghai, China), along with HNO₃ of guaranteed reagent. Ferric chloride (FeCl₃·6H₂O), tetraethyl orthosilicate (TEOS), BF₃·OEt₂, l-cysteine hydrochloride, 1,3,5-tris(4-aminophenyl)benzene (TAPB) were purchased from Aladdin (Shanghai, China). Ferrous chloride (FeCl₂·4H₂O), 3-aminopropyl triethoxysilane (APTES), 2,5-dimethoxy-1,4-benzenedicarboxaldehyde (DMTA) were purchased from Macklin (Floor 2, Building 1, No. 68, Huatuo Road, Pudong New Area, Shanghai), 3-ethynylthiophene (97%) and chloranil (99%) were purchased from Energy Chemical (Shanghai, China), L-Cysteamine hydrochloride (97%) were purchased from Meryer (Shanghai, China). All the chemicals in this work were obtained commercially and used without further purification.

Text S3 Preparation of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-NH₂

Fe₃O₄@SiO₂ was prepared by a coprecipitation method [21]. Specifically, 11.68 g of ferric chloride and 4.30 g of ferrous chloride were dissolved in 200 mL of high-purity water, and stirred under a nitrogen atmosphere. When the temperature reached 85 °C, 25 mL of 30% NH₃·H₂O was added to it and the mixture was stirred for 30 min. After cooling down to room temperature, the obtained materials were washed several times with water and ethanol, respectively. Half of the prepared materials were mixed with 160 mL of ethanol and 40 mL of water. In order to activate the MNPs, 5 mL of NH₃·H₂O was added dropwise to the flask, followed by addition of 6 mL of TEOS. The mixture was stirred overnight at room temperature. The prepared Fe₃O₄@SiO₂ (appr. 4 g) were washed for 3 times with water and ethanol, respectively, and stored in ethanol.

Then, 1g of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were dispersed in a three-necked flask containing 120 mL isopropanol, and ultrasonicated for 30 min, followed by addition of 3 mL APTES under argon protection. The mixture was heated up to 70 °C and maintained for 4-5 h, the obtained product was washed several times with high-purity water and ethanol to obtain aminated magnetic nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$).

Table S1 Operating conditions of ICP-MS

ICP-MS plasma	
Rf power	1150 w
Plasma gas (Ar)flow rate	14 L min ⁻¹
Auxiliary gas (Ar)flow rate	0.88 L min ⁻¹
Carrier gas (Ar)flow rate	1.08 L min ⁻¹
Sampling depth	7.0 mm
Sample/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Data acquisition	Time resolved
Scanning mode	Peaking-hopping
Dwell time	100ms
Integration mode	Peak area
Points per spectral peak	3
Isotopes	²⁰² Hg, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi
Nebulizer	Babington
Spray chambers	Scott

Table S2 pseudo-second order kinetic and pseudo-first-order kinetic model constants
for adsorption of Hg²⁺, Bi³⁺ and Pb²⁺

metal ion	pseudo-second order kinetic model			Pseudo-first-order kinetic model		
	q _e (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	r ²	q _e (mg g ⁻¹)	K ₁	r ²
Hg ²⁺	4.763	0.04365	0.9983	3.856	1.939	0.9730
Bi ³⁺	4.800	0.4517	0.9992	55	4.144	0.9758
Pb ²⁺	2.322	11.18	0.9999	2.391	6.123	0.9777

Table S3 Analytical results of Hg, Pb and Bi in CRMs of environmental Waters
(mean \pm s.d., n=5)

CRMs	Elements	Found ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)	T-test ^a
GSB 07-1185-2000(202047)	Hg	12.1 \pm 0.2	12.5 \pm 0.4	2.24
GSB 07-1185-2000(201239)	Pb	20.0 \pm 0.6	20.1 \pm 1.3	0.17
BY 400143(B2003113)	Bi	49.2 \pm 0.4	49.4 \pm 0.9	0.49

^a At 0.05, 4=2.78.

Table S4 Comparison of the analytical performance of different adsorbents for metal ions

Sorbents	Analytical method	LOD (ng·L ⁻¹)				EFs	Adsorption / Elution time (min)	Ref.
		Cd	Hg	Pb	Bi			
Carbon-coated Fe ₃ O ₄	MSPE-ICP-MS	55	-	110	-	37.5	10/5	[24]
Fe ₃ O ₄ -GO@SiO ₂	MSPE-ICP-MS	3.8	-	3.6	-	10	6/3	[25]
Al ₂ O ₃ -PB ^a -AC ^b	SPE-ICP-MS	0.1	-	5	-	16.7	50/3	[26]
PPy/CNT/phen coated fiber	DI-SPME-ICP-MS	27	-	22	-	10	60/60	[27]
Fe ₃ O ₄ @SiO ₂ @γ-MPTMS ^c	MSPE-ICP-MS	0.0	0.1	0.0	-	400	10/5	[28]
		2		6				
DDTC-1-dodecanol/p-xylene solvent mixture	SFODME-ETV-ICP-MS	2	4.1	17	4.1	142-34	20/-	[29]
						2		
Fe ₃ O ₄ @SiO ₂ @PAR ^d	MSPE-ICP-MS	0.8	-	4.1	-	30	5/10	[30]
Fe ₃ O ₄ @SiO ₂ @GMA-S-SH MPPs-SH	MSPE-ICP-MS	0.2	0.8	2.9	-	150	10/5	[31]
		1						
MGO@SiO ₂ -APTES-IL	MSPE-ICP-MS	3.7	-	2.4	-	-	6.3/6.6	[32]
		5		2				
MNPC	MSPE-ICP-MS	0.4	-	3.1	-	100	5/2	[33]
		9						
Fe ₃ O ₄ @COF-thiophene	MSPE-ICP-MS	-	0.4	0.9	0.4	188	20/20	This work
			1	7	7			

^aPB: Polybrene^bAC: Alizarin Complexone^cMPTMS: γ-mercaptopropyltrimethoxysilane^dPAR: 4-(2-pyridylazo)resorcinol

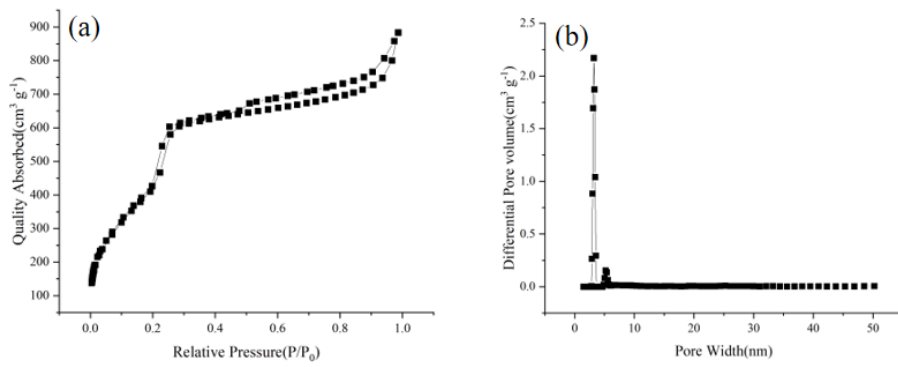


Fig. S1 Nitrogen adsorption and desorption curve and pore size distribution of $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene

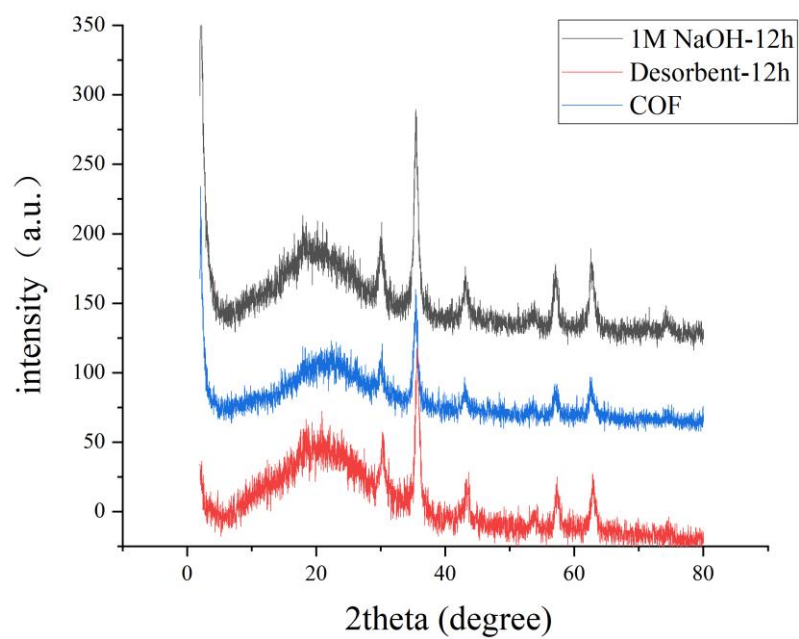


Fig. S2 XRD characterization of Fe₃O₄@COF-thiophene after soaking in different media

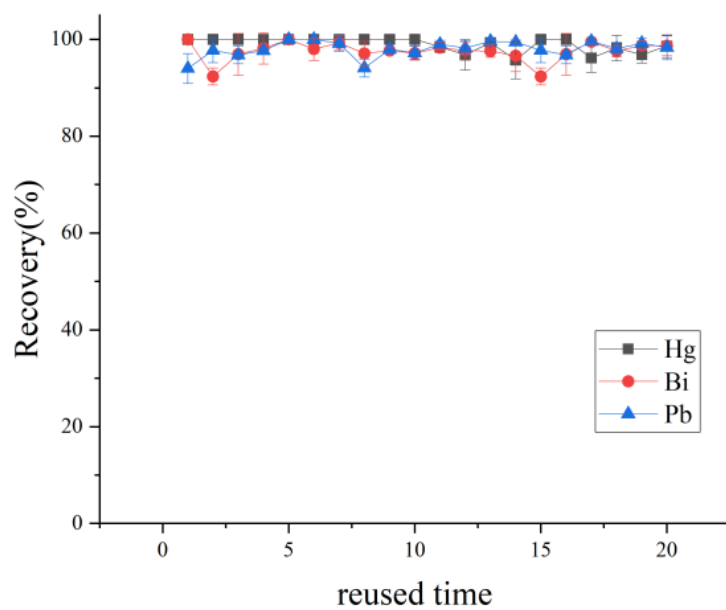


Fig. S3 Effect of reuse times on the recovery of target metal ions on $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene

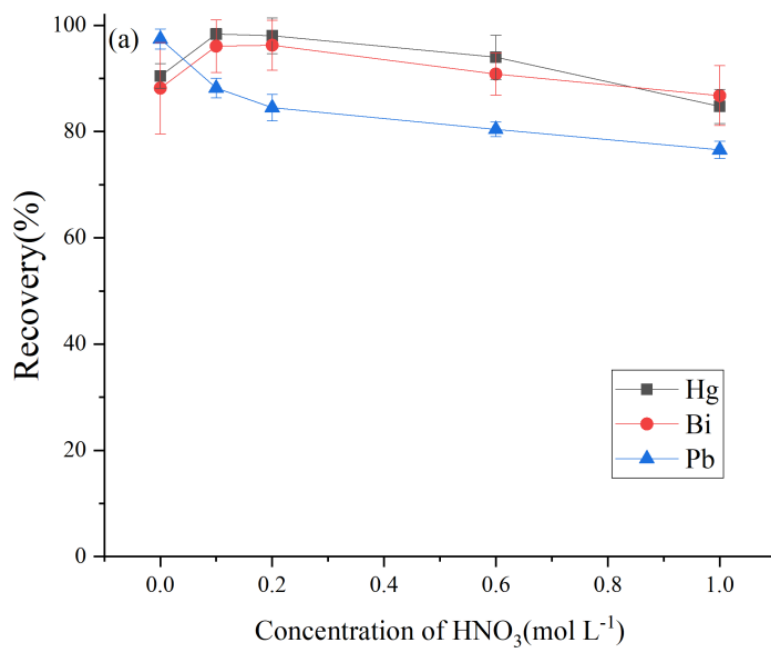


Fig. S4 Effect of HNO₃ concentration on the recovery of Hg²⁺, Bi³⁺ and Pb²⁺.

Conditions: concentration of each target analyte: 20 ng mL⁻¹; sample volume: 1 mL; pH=6; adsorbent amount: 1 mg; adsorption time: 30 min; the concentration of cysteamine hydrochloride is 10% (m/V); elution volume: 1 mL; elution time: 30 min.

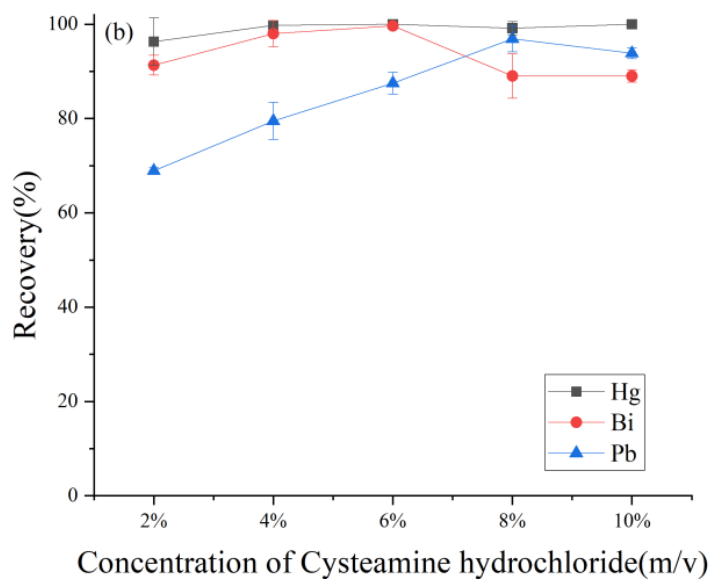


Fig. S5 Effect of cysteamine hydrochloride concentration on the recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL ; $\text{pH}=6$; adsorbent amount: 1 mg ; adsorption time: 30 min ; the concentration of HNO_3 : 0.1 mol L^{-1} ; elution volume: 1 mL ; elution time: 30 min .

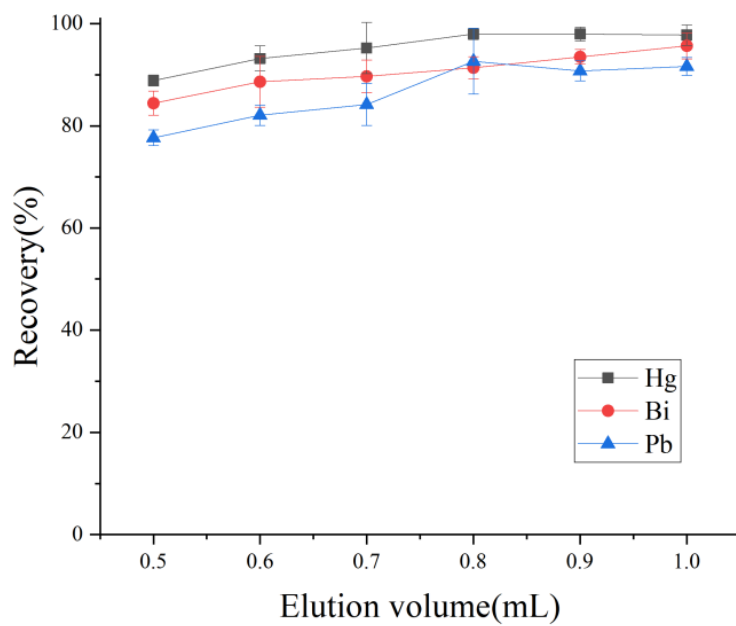


Fig. S6 Effect of elution volume on the recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL; $\text{pH}=6$; adsorbent amount: 20 mg; adsorption time: 30 min; elution time: 30 min.

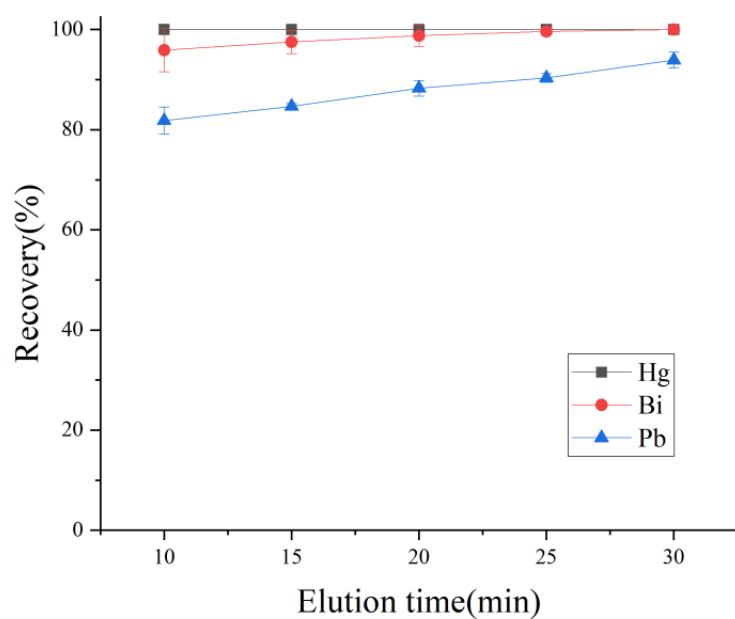


Fig. S7 Effect of elution time on the recovery of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: concentration of each target analyte: 20 ng mL^{-1} ; sample volume: 1 mL; pH=6; adsorbent amount: 20 mg; adsorption time: 30 min; elution volume: 0.8 mL.

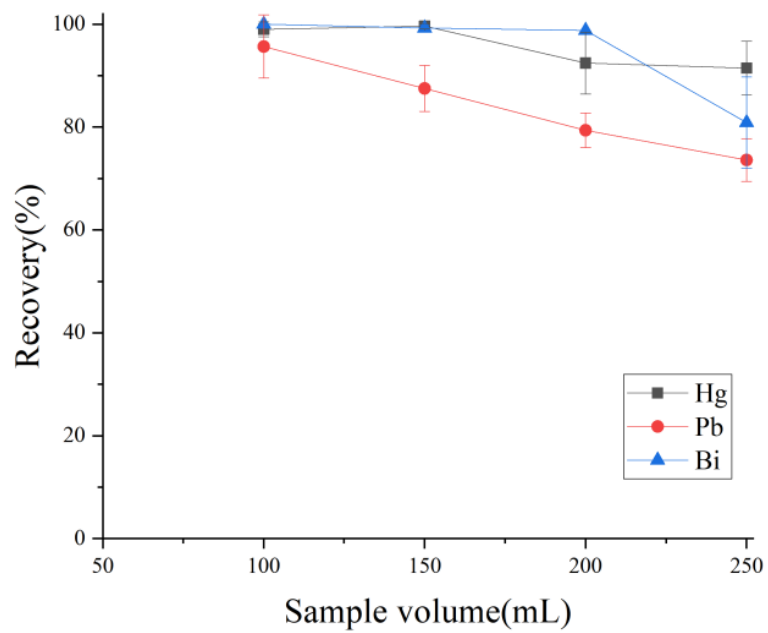


Fig. S8 Effect of sample volume on the adsorption of Hg^{2+} , Bi^{3+} and Pb^{2+} . Conditions: Hg^{2+} , Bi^{3+} and Pb^{2+} , each at 20 ng; pH=6; adsorbent amount: 20 mg; adsorption time: 30 min; elution volume: 1 mL; elution time: 20 min.

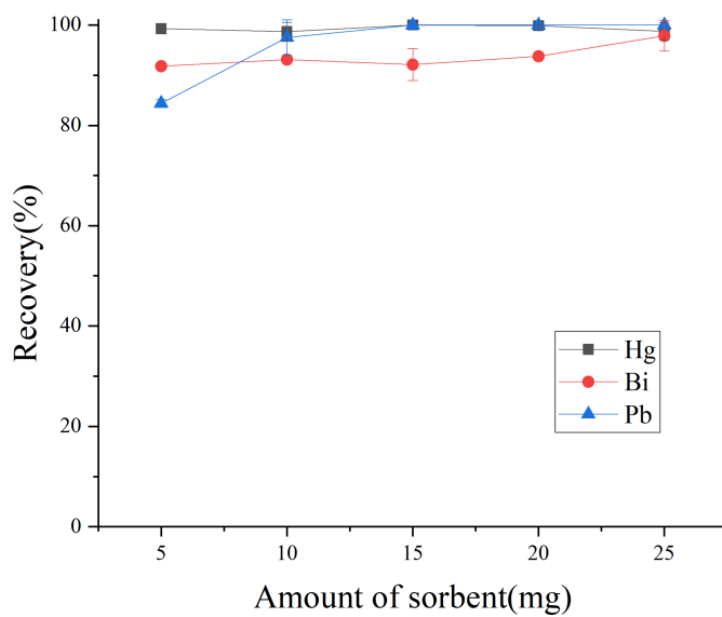


Fig. S9 Effect of adsorbent amount on the adsorption of Hg^{2+} , Bi^{3+} and Pb^{2+} .
Conditions: Hg^{2+} , Bi^{3+} , and Pb^{2+} , each at 20 ng; sample volume: 150 mL; pH=6;
adsorption time: 30 min; elution volume: 1 mL; elution time: 5 min.

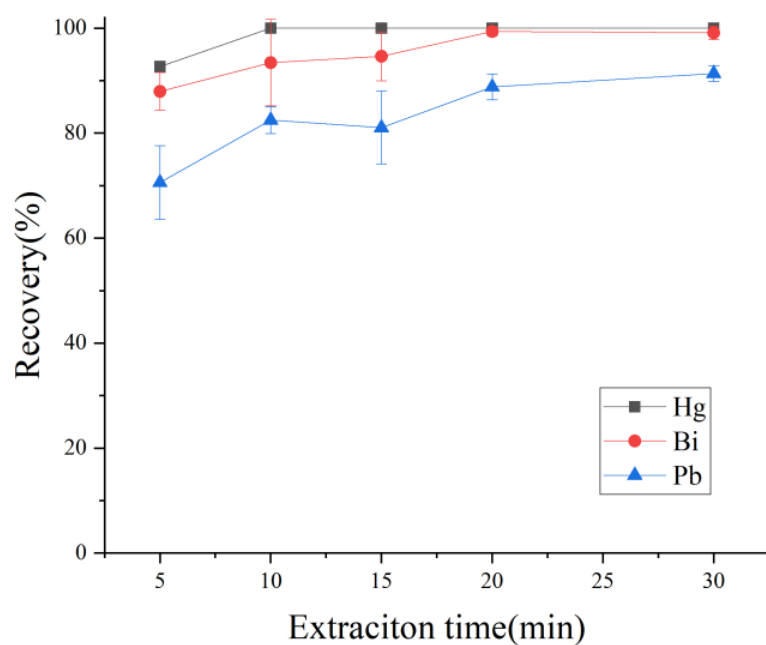
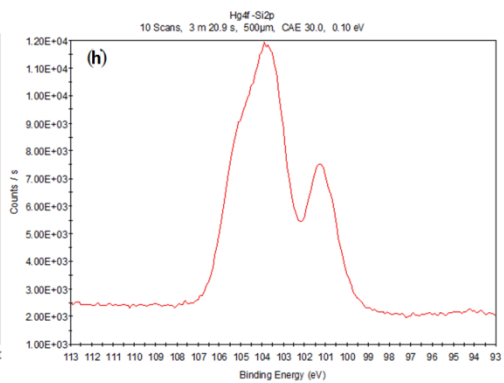
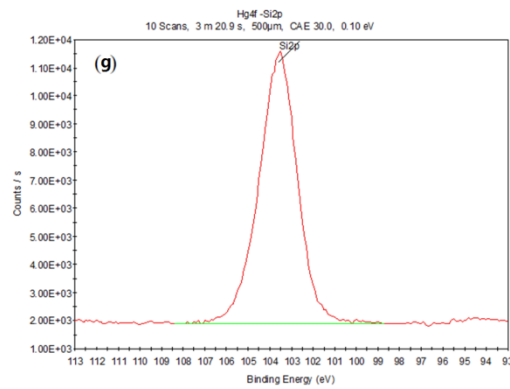
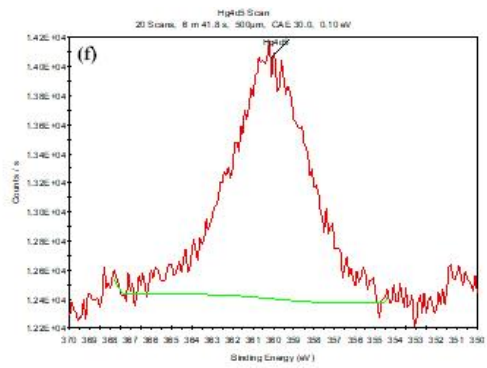
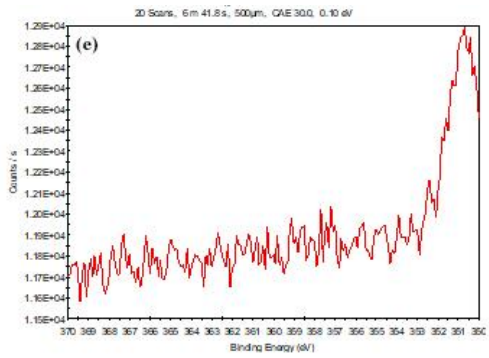
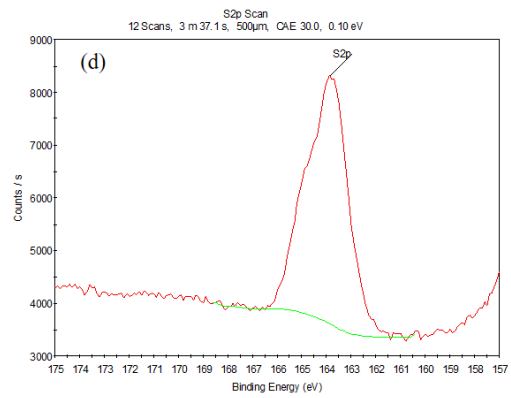
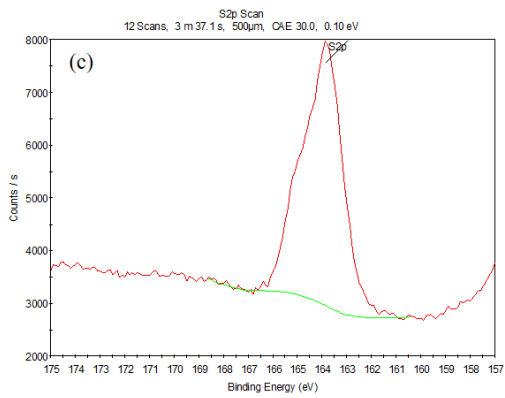
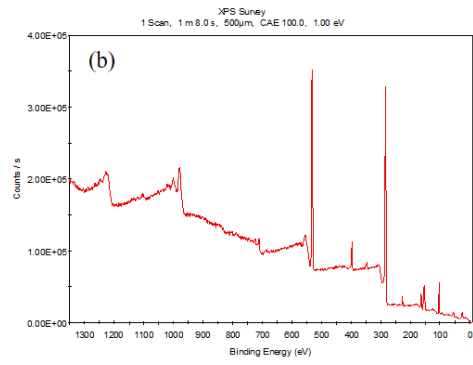
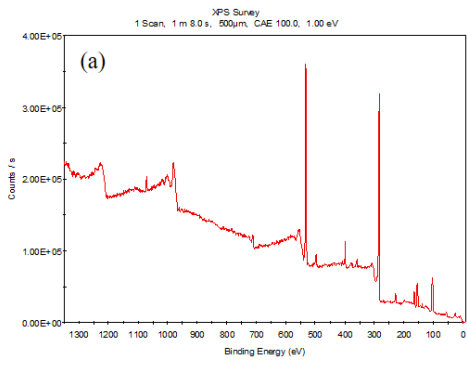


Fig. S10 Effect of adsorption time on the adsorption of Hg^{2+} , Bi^{3+} , and Pb^{2+} .

Conditions: Hg^{2+} , Bi^{3+} and Pb^{2+} , each at 20 ng; sample volume: 150 mL; pH=6;

adsorbent amount: 10 mg; elution volume: 1 mL; elution time: 5 min.



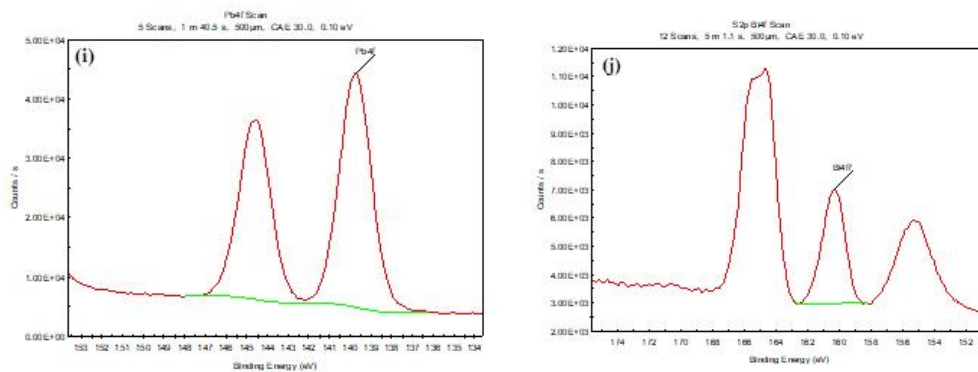


Fig. S11 XPS spectra of Fe₃O₄@COF-thiophene before and after adsorption of Hg, Pb and Bi

- (a) XPS spectra of Fe₃O₄@COF-thiophene before adsorption
- (b) XPS spectra of Fe₃O₄@COF-thiophene after adsorption
- (c) S absorption peak of Fe₃O₄@COF-thiophene before adsorption
- (d) S absorption peak of Fe₃O₄@COF-thiophene after adsorption
- (e) Hg absorption peak of Fe₃O₄@COF-thiophene before adsorption
- (f) Hg absorption peak of Fe₃O₄@COF-thiophene after adsorption
- (g) Hg-Si absorption peak of Fe₃O₄@COF-thiophene before adsorption
- (h) Hg-Si absorption peak of Fe₃O₄@COF-thiophene after adsorption
- (i) Pb absorption peak of Fe₃O₄@COF-thiophene before adsorption
- (j) Bi absorption peak of Fe₃O₄@COF-thiophene after adsorption

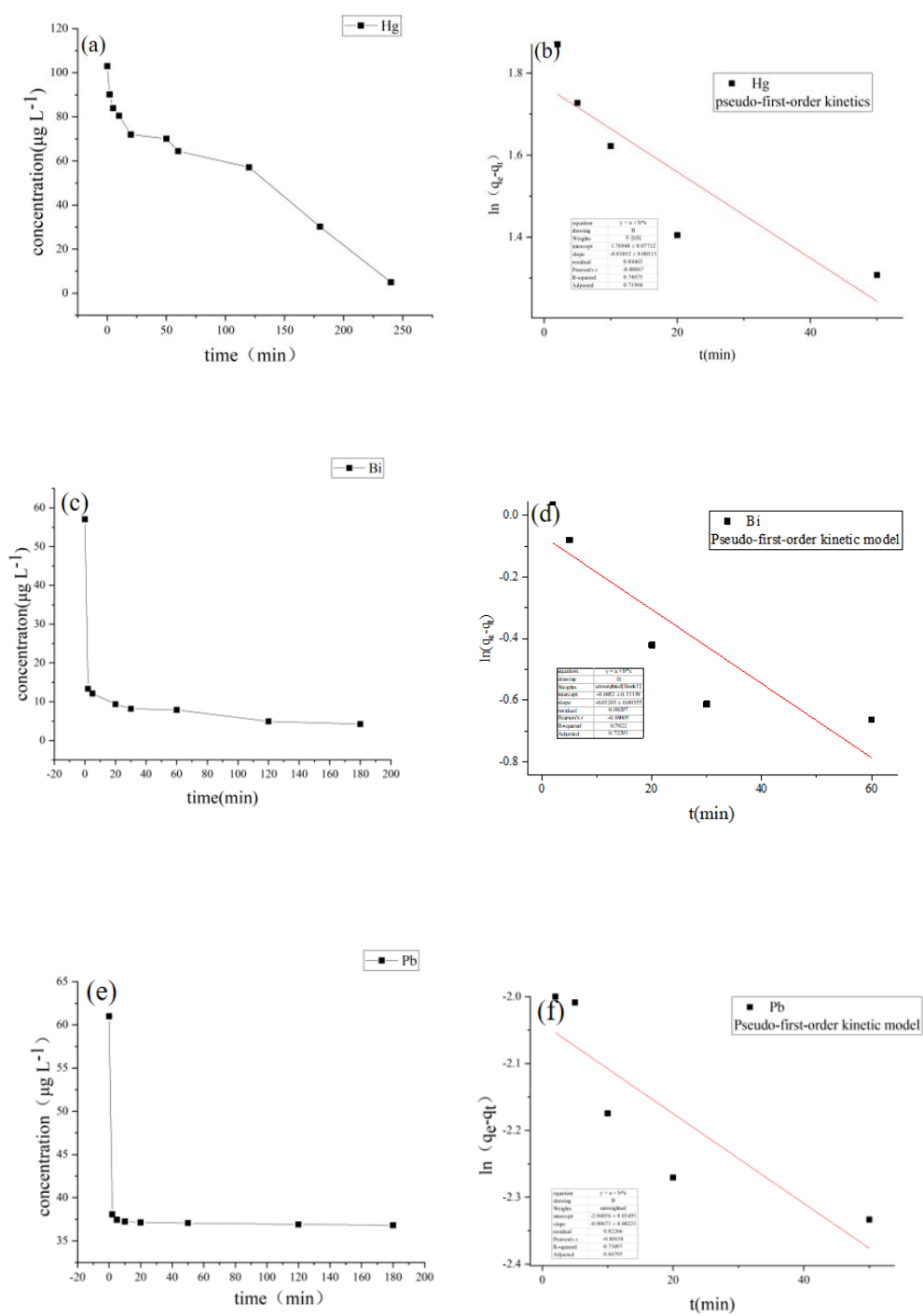


Fig. S12 Pseudo-first-order kinetics simulation for three metal ions on $\text{Fe}_3\text{O}_4@\text{COF}$ -thiophene