Electronic Supplementary Information

for

Preparation of functional magnetic porous organic polymer as sorbents for mercury speciation followed by HPLC-ICP-MS analysis

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Text S1-S3

Figure S1-S7

Table S1-S5

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Text S1. Reagents and Instrumentation

$FeCl_3·6H_2O$ (Aladdin Industrial Corporation, Shanghai, China), benzidine (BD) (Saen Chemical Technical Co., Ltd., Shanghai, China), methacrylic anhydride (MA) (Aladdin Industrial Corporation, Shanghai, China), 2,4,6-triformylphloroglucinol (Tp) (Bide Pharmatech Co., Ltd., Shanghai, China), 1,2-ethanedithiol (Shanghai Macklin Biochemical Co., Ltd. Shanghai, China) were employed to prepare the sorbent. L-Cysteine (J&K Chemicals, Beijing, China), $(NH_4)_2HPO_4$ (Shanghai Reagent, Shanghai, China) and triethylamine (Aladdin Industrial Corporation, Shanghai, China) were applied to prepare the mobile phase. 2, 2'-azobis(2-methylpropionitrile) (AIBN) was obtained from Aladdin (Shanghai, China). $HgCl_2$ was purchased from Shanghai Reagent Factory (Shanghai, China), and other three mercury species of MeHgCl, EtHgCl and PhHgCl were obtained from Alfa Aesar (Tianjin, China).

All the other reagents used were analytically pure reagents. All the aqueous solutions were prepared by high-purity deionized Milli-Q water (18.2 MΩ cm, Millipore, Molsheim, France). All the glassware could be used until they were soaked over 24 h in 20 % (v/v) nitric acid and washed with purity deionized water.

The prepared Fe_3O_4@BD-TpMA-S-SH MOPs was characterized by NEXUS 870 Fourier transform infrared spectroscopy (FT-IR) (Thermo, Madison, USA), JEM-2010 transmission electron microscope (TEM) (JEOL, Tokyo, Japan), X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, Thermo Fisher, USA) and accelerated surface area and porosimetry system (ASAP2020, Micromeritics, USA). A Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd. Shanghai, China) was used to control the pH values. The nanoparticles were dispersed in solution by A KQ5200DE model water bath ultrasonicator (Shumei Instrument Factory, Kunshan, China). The magnetic separation was realized by an Nd-Fe-B magnet (8.0 cm×6.0 cm×1.6 cm).

Text S2. Preparation of Fe_3O_4 MNPs

The Fe_3O_4 MNPs were prepared through a modified solvothermal reaction. [1] Briefly, 3.25 g $FeCl_3·6H_2O$, 1.30 g trisodium citrate and 6.00 g NaAc were dissolved in 100 mL ethylene glycol. A homogeneous solution was obtained with vigorously stirring at 100 ℃ under nitrogen gas for 1 h, then transferred to a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 ℃ for 12 h. After cooled to room temperature, the product was washed with high purity deionized water and ethanol for several times, and then dried at 50 °C for further use.

Text S3. Optimization of MSPE Conditions

Effect of pH

The effect of sample pH in the range of 2-8 on the adsorption of target mercury species on Fe_3O_4@TpBD-MA-S-SH MOPs was investigated, and the results are shown in Fig. S3(a). It can be seen that four target mercury species can be completely adsorbed (adsorption efficiency higher than 95%) on the MOPs in the entire studied pH range, indicating a good adsorption performance in a wide range of sample pH. To avoid hydrolysis of Hg^{2+} in neutral or alkaline solution, sample pH was adjusted to pH 4 in the following experiments.

Effect of Eluent and Its Concentration

According to our previous works, [2, 3] thiourea prepared in diluted nitric acid was used as eluent to elute target mercury species retained on the MOPs. The effect of concentration of nitric acid in the range of 0-1.0 mol L^{-1} (with 4% (m/v) thiourea) and thiourea in the range of 1-5% (m/v) (with 0.5 mol L^{-1} nitric acid) on the recovery of target mercury species was investigated. The results demonstrate that four target mercury species can be quantitatively recovered (recovery > 80%) when the concentration of nitric acid and thiourea was higher than 0.3 mol L^{-1} (Fig. S3(b)) and 3% (m/v) (Fig. S3(c)), respectively. Finally, 0.5 mol L^{-1} nitric acid and 4% (m/v) thiourea solution was used as the eluent.

Effect of Eluent Volume and Elution Time

Fixing 0.5 mol L^{-1} nitric acid and 4% (m/v) thiourea solution as the eluent, the effect of eluent volume ranged from 0.2 to 2.0 mL on the recovery of target mercury species was investigated. The results shown in Fig. S3(d) indicate quantitative recovery of four target mercury species could be obtained when the eluent volume was equal to or higher than 0.5 mL. A lower eluent volume would lead to a higher enrichment factor (EF), therefore, 0.5 mL was chosen as the eluent volume.

The effect of elution time on the recovery of target mercury species was also studied. Four target mercury species adsorbed on the MOPs was subjected to ultrasonic elution for 1, 2, 3, 5, 10 min, respectively, and the recoveries are displayed in Fig. S4(a). It can be seen that the recoveries were higher than 80% in the whole tested range, indicating fast desorption dynamics. For subsequent experiment, elution time was selected as 2 min.

Effect of Sample Volume

Keep the amount of Hg^{2+}, $MeHg^+$, $EtHg^+$ and $PhHg^+$ as 10 ng in sample solution, and the effect of sample volume in the range of 10-250 mL on the recovery of target mercury species was studied. It was found in Fig. S4(b) that quantitative recovery of four target mercury species could be obtained when sample volume was in the range of 10-200 mL. When sample volume was 250 mL, the recovery of $PhHg^+$ was slightly lower than 80%. To maintain good recoveries of mercury species, 200 mL sample solution was used for MSPE. With the eluent volume of 0.5 mL, the theoretical EF of the method is 400-fold.

Effect of MOPs Amount

The effect of the amount of MOPs on the recovery of target mercury species was investigated in the range of 1-15 mg, and the results are shown in Fig. S4(c). The recoveries of mercury species increased with increasing the MOPs amount from 1 to 5 mg, and then remained constantly (> 80%) with further increasing the MOPs amount to 15 mg. To guarantee quantitative adsorption of target mercury species, 7 mg MOPs was used as MSPE sorbent.

Effect of MOPs Adsorption Time

The effect of adsorption time (2, 3, 5, 10 min) on the recovery of target mercury species was studied. From Fig. S4(d), it can be seen that the recoveries of four mercury species increased when the adsorption time increased from 1 to 5 min, and then levelled off. Four target mercury species can be quantitatively recovered within 5 min, indicating a good adsorption dynamic. In the following experiments, adsorption time was chosen as 5 min.

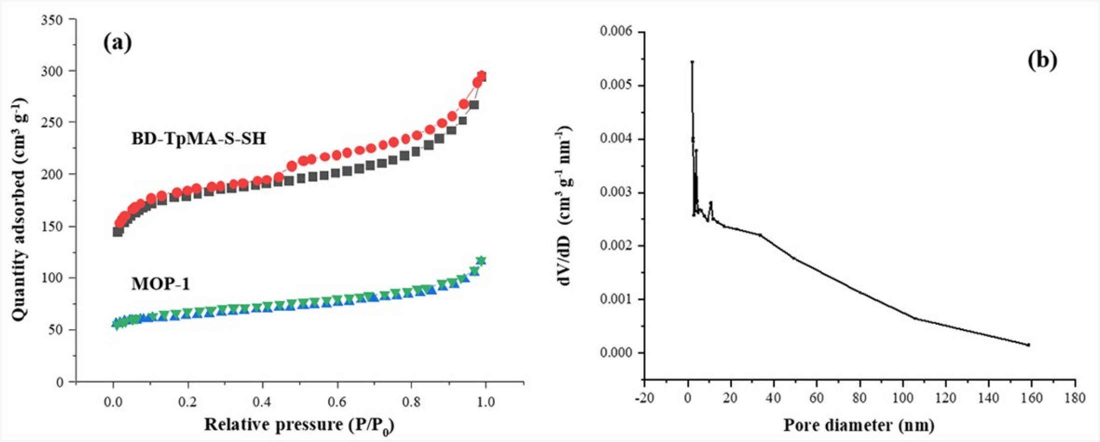

Figure S1 N_2 adsorption/desorption isotherms of BD-TpMA-S-SH and MOP-1 (a) and pore size distribution of MOP-1 (b).

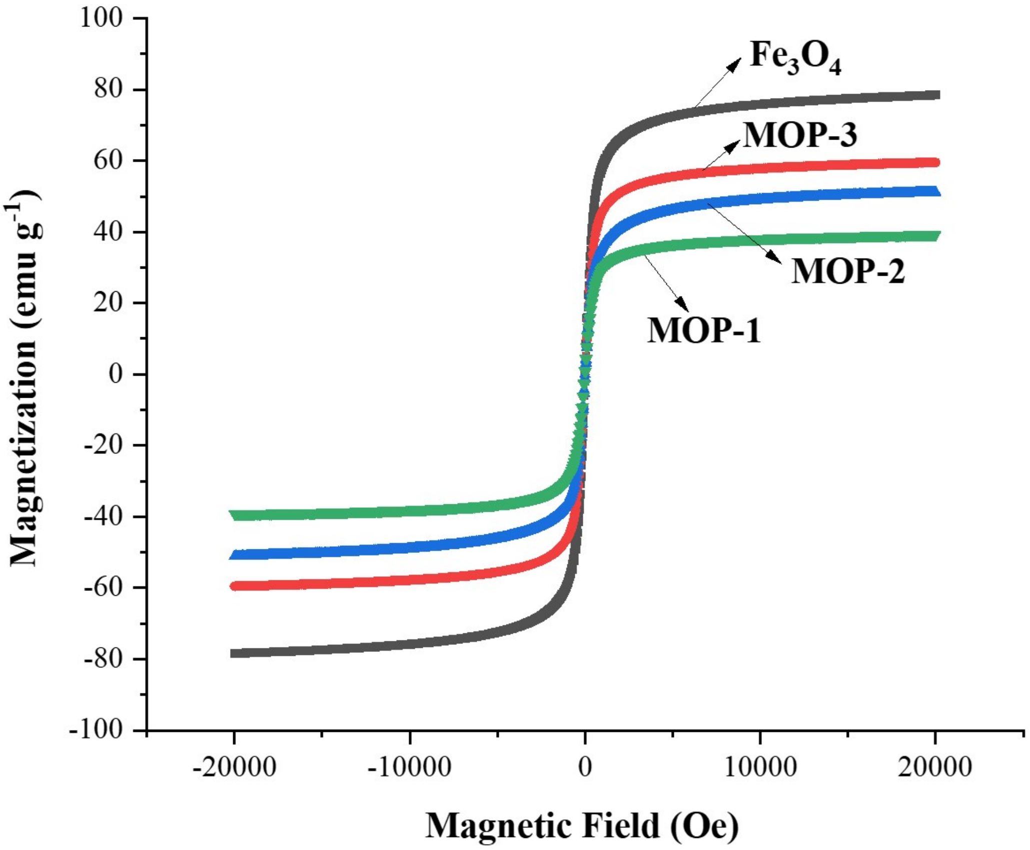

Figure S2 VSM magnetization curves of Fe_3O_4@BD-TpMA-S-SH MOPs.

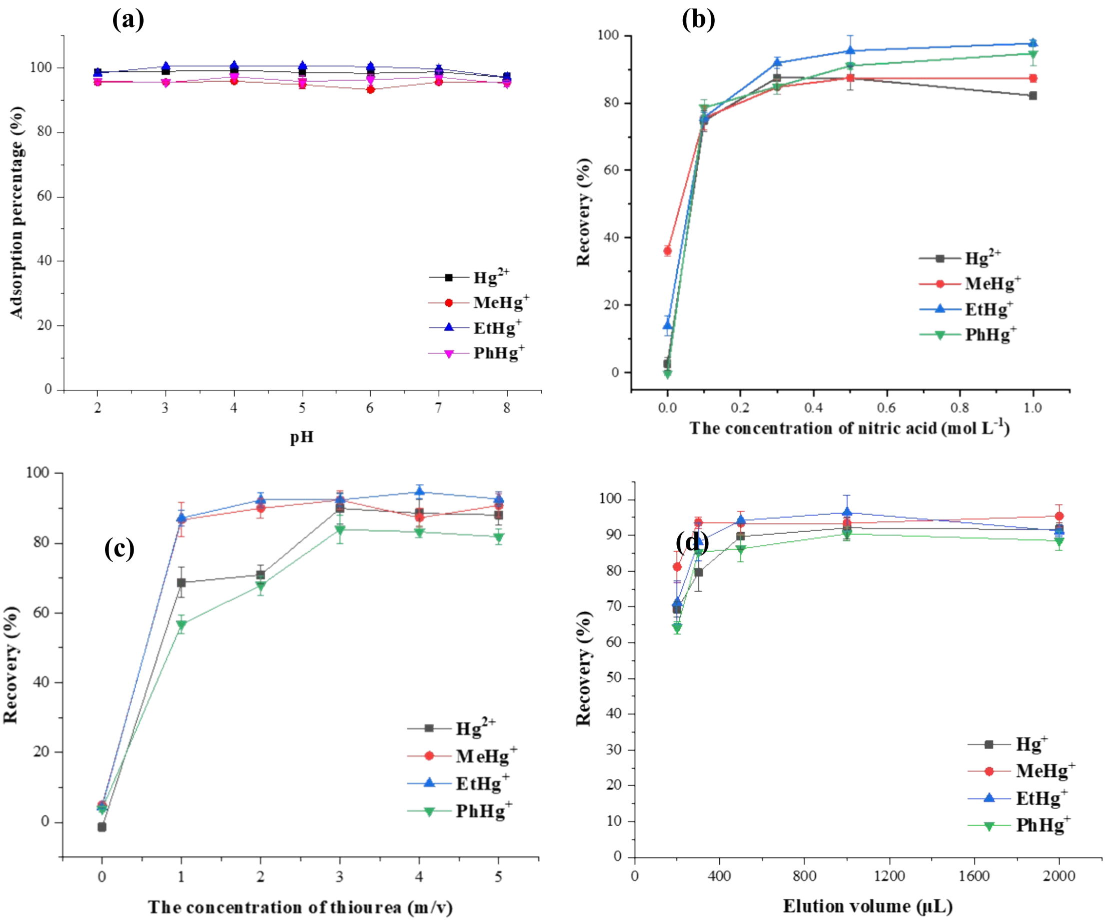

Figure S3 The effect of sample pH on the adsorption efficiency of target mercury species (a), and the effect of the concentration of nitric acid (b) and thiourea (c) in the eluent, and the elution volume (d) on the recovery of target mercury species. Conditions: sample volume: 100 mL, MOPs amount: 10 mg, adsorption time: 15 min, eluent time: 2 min.

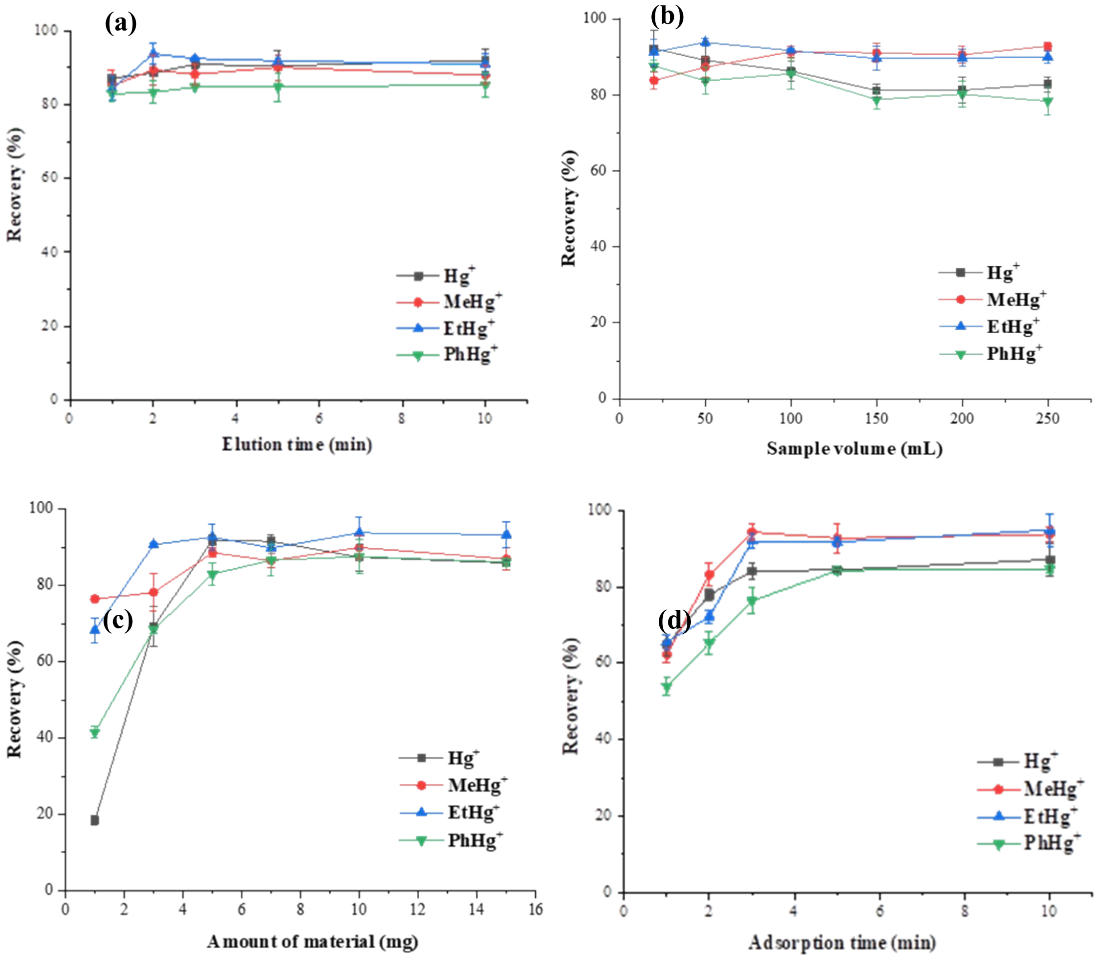

Figure S4 The effect of elution time (a), sample volume (b), MOPs amount (c) and adsorption time (d) on the recovery of target mercury species. Conditions: sample pH: 4, eluent: 0.5 mol L^{-1} nitric acid and 4 % (m/v) thiourea elution, eluent volume: 0.5 mL, elution time: 2 min.

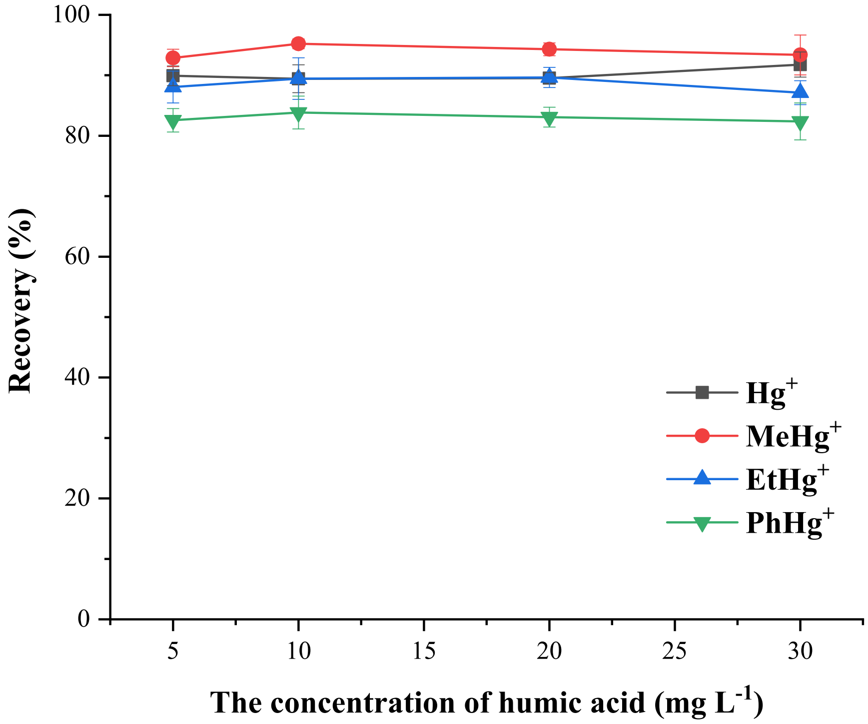

Figure S5 The effect of humic acid concentration on the recovery of four mercury species. Conditions: sample pH: 4, sample volume: 200 mL, MOPs amount: 7 mg, adsorption time: 5 min, eluent: 0.5 mol L^{-1} nitric acid and 4% (m/v) thiourea solution, eluent volume: 0.5 mL, elution time: 2 min.

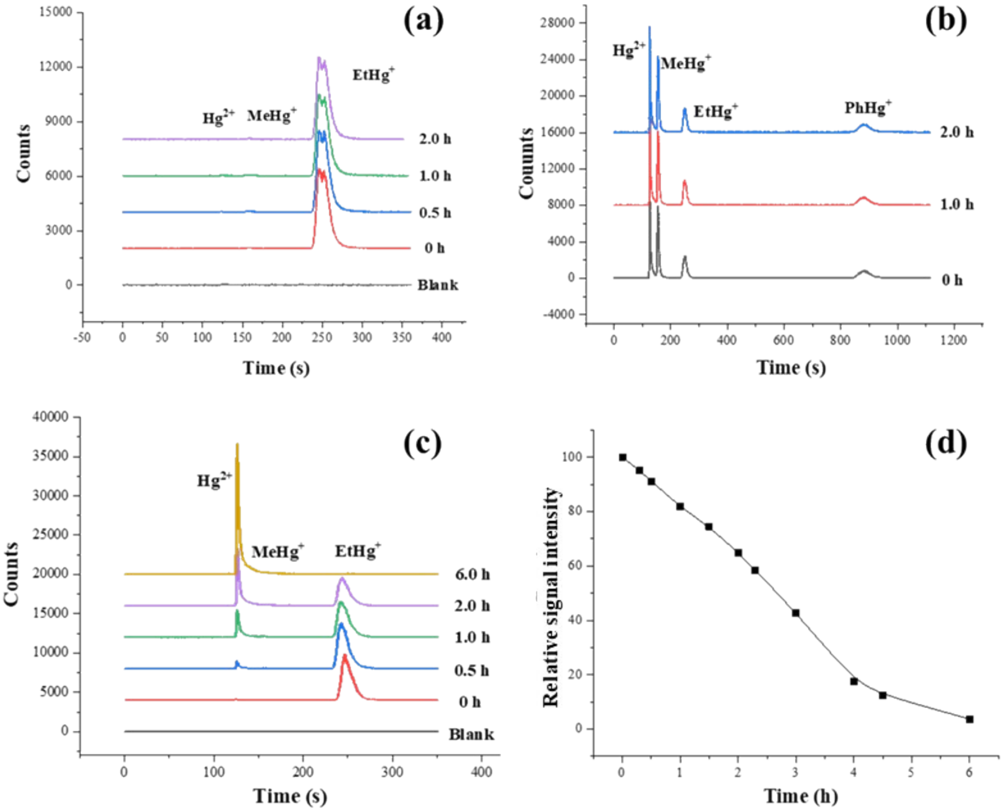

Figure S6 Stability of EtHg$^+$. (a) HPLC-ICP-MS chromatograms of 400 µg L^{-1} EtHg$^+$ in 0.5 M HNO$_3$ for different times, (b) HPLC-ICP-MS chromatograms four mercury species (200 µg L^{-1}) retained on the MOPs with different times prior to elution, HPLC-ICP-MS chromatograms (c) and the conversion rate (d) of 400 µg L^{-1} EtHg$^+$ in 0.5 M HNO$_3$ and 4% (m/v) thiourea solution for different times.

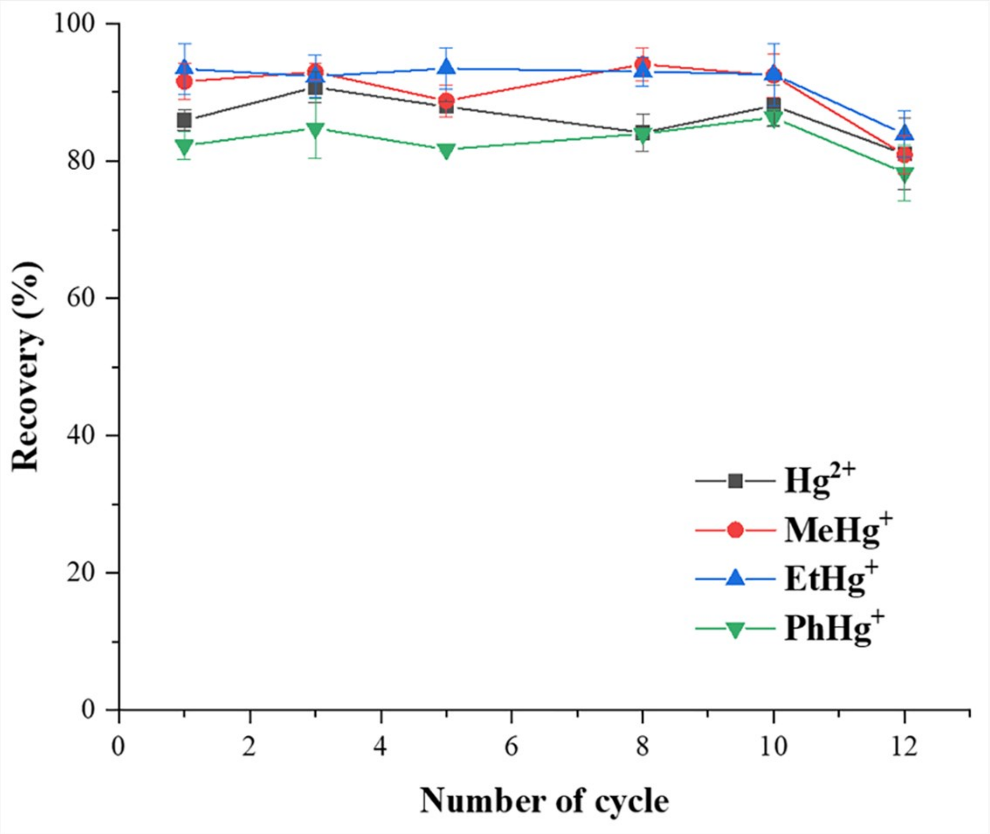

Figure S7 The lifetime of the Fe_3O_4@BD-TpMA-S-SH MOPs.

Table S1 Optimized operating conditions for HPLC-ICP-MS

Instruments	Factor	Condition
HPLC	Column	C18 column (Hypersil ODS2, 250×4.6 mm, 5 μm)
	Mobile phase	8.0 mM L-cysteine, 12.5 mM $(NH_4)_2HPO_4$, 0.05% Triethylamine, pH 7.0, methanol (8:92)
	Temperature	50 ℃
	Flow rate	1.5 mL min^{-1}
	Injection volume	50 μL
ICP-MS	RF power	1150 W
	Plasma gas flow rate	14.0 L min^{-1}
	Carrier gas flow rate	1.0 L min^{-1}
	Auxiliary gas flow rate	0.5 L min^{-1}
	Sampling depth	6.9 mm
	Quantification	Peak area
	Dwell time	100 ms
	Monitored isotope	^{199}Hg, ^{200}Hg, ^{202}Hg

Table S2 The elemental composition and content of Fe_3O_4@BD-TpMA-S-SH

Element	At.%	Wt.%
C	72.4	58.0
O	11.9	12.7
N	3.60	3.70
S	12.1	25.9

Table S3 Comparison of Fe_3O_4@BD-TpMA-S-SH MNPs with other sorbents

Analytes	Sorbents	Application	Samples	Sulfur content (wt.%)	Magnetic intensity (emu g^{-1})	Adsorption capacity (mg g^{-1})	Ref.
Hg^0, Hg^{2+}	COF-S-SH	Metal removal	Water, air	20.9	--	1350 (Hg^{2+})	4
Hg^0, Hg^{2+}	POP-SH	Metal removal	Water, air	16.3	--	1216(Hg^{2+})	5
Hg^{2+}	PAF-1-SH	Metal removal	Water	17.6	--	1014	6
Hg^{2+}	TAPB-BMTTPA -COF	Metal removal	Water	15.5	--	734	7
Hg^{2+}, Pb^{2+}	PTMT	Metal removal	Water	52.7	--	735(Hg^{2+})	8
Hg^{2+}	MOP-SH AzoPOP-SH	Metal removal	Water	12.4	16.0	703 910	9
Hg^{2+}	SH-Fe_3O_4-MNPs	Metal removal	Water	--	6.47	523	10
Hg^{2+}	THS-DES@M-GO	Metal removal	Water	--	19.9	215	11
Hg^+, $MeHg^+$, $EtHg^+$	Fe_3O_4@SiO_2-RSH	DSPE-HPLC-AFS	Ground and river water	0.2	--	12.7($MeHg^+$) 12.9($EtHg^+$)	12
Hg^{2+}	Fe_3O_4@HKUST-1	MSPE-CV-AAS	Fish samples	--	19.0	254	13
Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}	γ-MPTS-SCMNPs	MSPE-ICP-MS	Environmental and biological samples	--	--	83.8 (Hg^{2+})	14
Hg^{2+}, $MeHg^+$, $PhHg^+$	Fe_3O_4@SiO_2@γ-MPTS	MSPE-HPLC-ICP-MS	Water and fish samples	0.61	--	29.8(Hg^{2+})	2
Hg^{2+}, $MeHg^+$, $PhHg^+$	Fe_3O_4@SiO_2@GMA-S-SH	MSPE-HPLC-ICP-MS	Farmland water, soil and rice samples	2.5	6.94	141(Hg^{2+}) 142($MeHg^+$) 32.1($PhHg^+$)	3

Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$, $PhHg^{+}$	BD-TpMA-S-SH	MSPE-HPLC-ICP-MS	East Lake water, fish	25.9	--	940(Hg^{2+})	This work
	MOP-1				39.2	636(Hg^{2+})	
	MOP-2				51.1	520(Hg^{2+})	
	MOP-3				59.5	379(Hg^{2+})	

Table S4 Tolerance limits of coexisting ions

Coexisting ions	Tolerance limit (mg L^{-1})	Tolerance fold [a]
K^+, Na^+	10,000	1,000,000,000
Ca^{2+}, Mg^{2+}	5,000	500,000,000
Al^{3+}	2,000	200,000,000
Zn^{2+}, Fe^{3+}, Mn^{2+}	200	20,000,000
Cu^{2+}, Cd^{2+}, Pb^{2+}	100	10,000,000
NO_3^-	30,000	3,000,000,000
Cl^-	5,000	500,000,000
SO_4^{2-}	5,000	500,000,000
PO_4^{3-}	5,000	500,000,000

a: tolerance fold is the ratio of the tolerance limit to the concentration of target mercury species (10 ng L^{-1})

Table S5 The comparison of analytical performance of methodologies for mercury speciation

Sample	Analytes	Analytical Technique	Sample preparation time (min)	Separation time (min)	EFs	LOD (ng L^{-1})	Linear range (ng L^{-1})	Ref.
Human hair, water	Hg^{2+}, $MeHg^{+}$	MSPE-ICP-MS	15	--	50	1.6-1.9	10-10000	15
Water, fish	Hg^{2+}, $MeHg^{+}$, $PhHg^{+}$	MSPE-HPLC-ICP-MS	17	8	174-179	0.5-0.7	5-5000	2
Natural water	Hg^{2+}, $MeHg^{+}$	MSPE-HPLC-ICP-MS	10	5	200	0.3-1	5-30	16
Farmland water, soil, rice	Hg^{2+}, $MeHg^{+}$, $PhHg^{+}$	MSPE-HPLC-ICP-MS	7	17	329-380	0.4-1.4	5-5000	3
Atmospheric particles, water, fish, plant, sediment	Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$, $PhHg^{+}$	HF-LLLME-HPLC -ICP-MS	30	12	221-236	2.9-5.6	20-5000	17
Sediment, water	Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$, $PhHg^{+}$	SPE-HPLC-ICP-MS	100-250	10	100	500-1000	1000-10000	18
Fish	Hg^{2+}, $MeHg^{+}$	MSPD-HPLC-ICP-MS	35	4	10	8400-9900	--	19
Water	Hg^{2+}, $MeHg^{+}$	SPE-CV-AAS	10	--	25	1.5-2.1	--	20
Water, Caprine Blood	Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$	SPE-CV-AAS	3	--	10	10	30-65	21
Water	Hg^{2+}, $MeHg^{+}$	GC-pyro-AFS	30	6	150	5.4	20-2000	22
Ground and river water	Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$	DSPE-HPLC-AFS	5	6	428-596	0.26-1.7	2-15	23
East Lake water, fish	Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$, $PhHg^{+}$	MSPE-HPLC-ICP-MS	7	17	346-383	0.43-1.1	5-5000	This work

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