Electronic Supplementary Information

Hg^{2+} ion-imprinted polymers sorbents based on dithizone-Hg^{2+} chelation for mercury speciation analysis in environmental and biological samples

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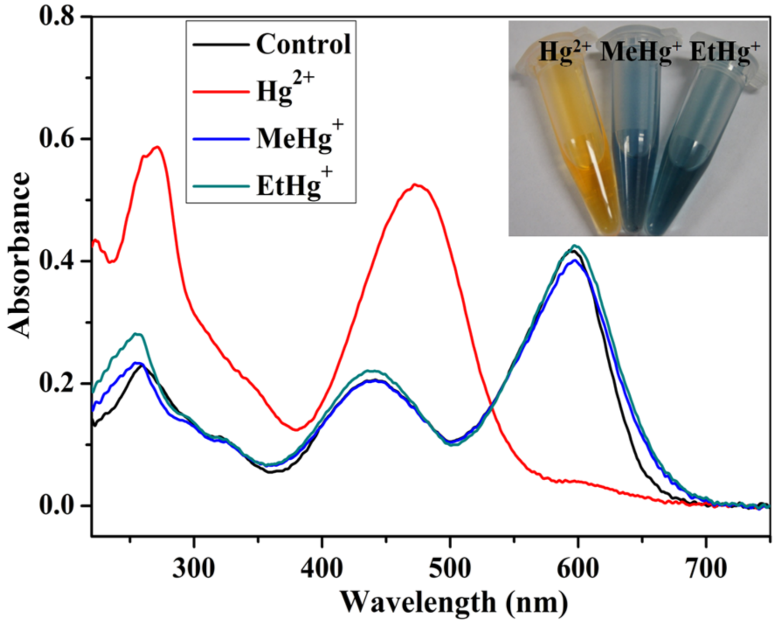
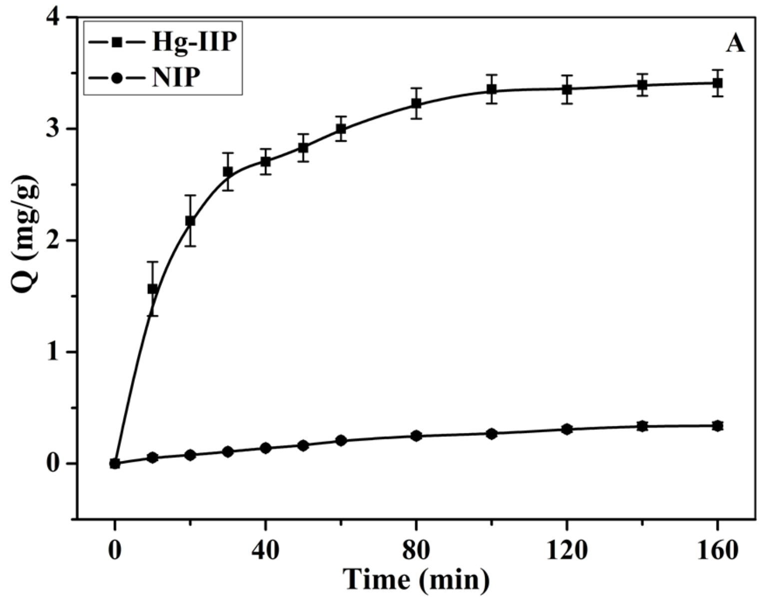


Figure S1. UV-vis spectra of dithizone alone (Control), and the dithizone with Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$, respectively. The inset image shows dithizone with Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ from left to right.



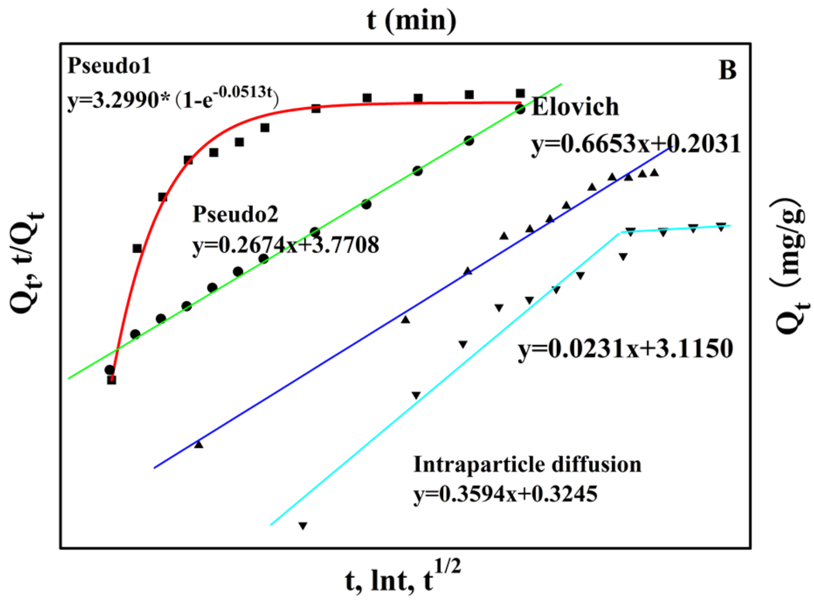


Figure S2. (A) Adsorption kinetics curves of IIPs and NIPs for Hg^{2+} in aqueous solution, and (B) Pseudo-first-order, Pseudo-second-order, Elovich and intraparticle diffusion kinetic models for Hg^{2+} towards IIPs. Experimental conditions: Hg^{2+} concentration, 10 mg/L, V = 10 mL, polymer, 20 mg, room temperature.

Table S1. Specific surface area and other related data of Hg-IIPs and NIPs obtained by BET analysis.

IIPs	Specific surface area (m^2/g)	Cumulative pore volume (mL/g)	Average pore diameter (nm)	Cumulative pore area (m^2/g)
Hg-IIPs	43.27	0.1758	9.42	90.23
NIPs	22.92	0.0994	5.62	63.13

Table S2. Isotherm model parameters for Hg-IIPs and NIPs.

Isotherm Model	Parameter	Hg-IIPs	NIPs
Langmuir	$R^{2(a)}$	0.998	0.998
($\frac{C_e}{Q_e}=\frac{1}{Q_{\max}}C_e+\frac{1}{K_l Q_{\max}}$)	$Q_{\max}^{(b)}$	4.451	0.633
	$K_l^{(c)}$	1.306	0.121
Freundlich	R^2	0.980	0.989
($\lg Q_e=\frac{1}{n}\lg C_e+\lg K_f$)	$K_f^{(d)}$	6.315	0.003
	$1/n^{(e)}$	0.353	0.621
Langmuir-Freundlich	R^2	0.979	0.992
($B=\frac{N_t\alpha F^m}{1+\alpha F^m}$)	$N_t^{(f)}$	4.730	0.688
	$\alpha^{(g)}$	1.115	0.112
	$m^{(h)}$	0.721	0.956

(a) Correlation coefficient.

(b) Maximum binding capacity, mg/g.

(c) Langmuir constant.

(d) Indicative constant for adsorption capacity of the adsorbent.

(e) Reflect the adsorption intensity or surface heterogeneity, ranging from 0 to 1.

(f) Total number of binding sites, mg /g.

(g) Equal to the median binding affinity constant, g/mg.

(h) Heterogeneity index, which will be equal to 1 for a homogeneous material, or will take values within 0 and 1 if the material is heterogeneous.

Table S3. Parameters obtained of Hg^{2+} adsorption towards Hg-IIP from four kinetic models.

Kinetic Models	Parameters		
Pseudo-first-order	k_1 (min^{-1}) (a)	Q_e(μmol/g) (b)	R^2
$ln(Q_e - Q_t) = lnQ_e - k_1 t$	0.051	3.298	0.983
Pseudo-second-order	k_2(g/(μmol·min)) (c)	Q_e(μmol/g)	R^2
$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$	0.019	3.740	0.999
Elovich	α (μmol/g) (d)	β (min·g/μmol)	R^2
$Q_t = \frac{1}{\beta} ln(a\beta) + \frac{1}{\beta} ln(t)$	0.902	1.503	0.982
Intraparticle diffusion	k_p(μmol/(g min$^{0.5}$)) (e)	C (μmol/g) (f)	R^2
$Q_t = k_p t^{1/2} + C$	0.359	0.3245	0.974
	0.023	3.115	0.989

(a) k_1 is the rate constant of adsorption in pseudo-first-order model.

(b) Q_e is the final adsorption amount at equilibrium, Q_t is the instantaneous adsorption amount in the adsorbent at time t.

(c) k_2 is the rate constant of adsorption in pseudo-second-order model.

(d) α and β represent the initial adsorption rate and desorption constant in Elovich model.

(e) k_p indicates the intraparticle diffusion rate constant and relates to the particle size R with the equation $k_p = \frac{6Q_e}{R}\sqrt{\frac{D}{\pi}}$,

(f) C provides information about the thickness of the boundary layer.

Table S4. Method performance comparisons for mercury species by IIPs based SPE.

Template	Functional monomer	Polymerization method	Preparation feature	Detection technology	pH	LOD (μg/L)	Real sample	Ref.
The chelate of dithizone and Hg^{2+}	APTES[(a)]	Sol–gel process	Using chelate as template	AFS	7.0-8.0	0.015 (Hg^{2+}) 0.02 ($MeHg^{+}$, $EtHg^{+}$)	Seawater, lake water, human hair, fish meat	This work
Hg^{2+}	T-IPTS[(b)]	Sol–gel process	Synthesizing new monomer	AFS	8.0	0.03 (Hg^{2+})	River water, tap water	1
The chelate of PDC and Hg^{2+}	MAA[(c)]	Grafting and copolymerization	Forming P(PDC-Hg)/SiG[(d)]	CV-AAS[(e)]	6.0-7.0	0.02 (Hg^{2+}, $MeHg^{+}$)	Wine	2
Hg^{2+}	VP[(f)]	Copolymerization	Copolymerizing of Hg^{2+}, DAAB[(g)] and VP	CV-AAS	8.0	0.05 (Hg^{2+})	Tap water, river water, seawater	3

(a) 3-Aminopropyltriethoxysilane (APTES).
(b) 3-Isocyanatopropyltriethoxysilane (IPTS) bearing thymine (T) base.
(c) Methacrylic acid.
(d) Using silica gel chemically modified with 3-(trimethoxysilyl)propyl methacrylate (TSPM) as supporting material, and the Hg(II) IIP layer was grafted by copolymerization of MAA and trimethylolpropane trimethacrylate in the presence of Hg(II) complexes with the chelating agent 1-pyrrolidinedithiocarboxylic acid (PDC).
(e) Cold vapor atomic absorption spectrometry.
(f) Vinylpyridine.
(g) Diazoaminobenzene.

References

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