Supplementary Information

Green Synthesis of Water-Stable Thiol-Decorated Zr-MOF for Selective Heavy Metal Removal

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Materials. All reagents were of analytical grade and used as received without further purification. The chemicals including $ZrCl_4$, mercaptoacetic acid (MA), and $Cu(NO_3)_2$•$2.5(H_2O)$ were purchased from Sigma-Aldrich. Mercaptosuccinic acid (MSA), formic acid (FA), and ethanol were purchased from Merk. $Cd(NO_3)_2$•$4(H_2O)$ from Acros Organics, $Pb(NO_3)_2$, $Fe(NO_3)_3$•$9(H_2O)$, $Zn(NO_3)_2$•$6(H_2O)$ $Co(NO_3)_2$•$6H_2O$, $Ni(NO_3)_2$•$6(H_2O)$ from Fisher Scientific, UK. Deionized water (DI) was used to prepare the solutions (MilliQ).

Characterization. Fourier transform Infrared (FTIR) spectroscopy was conducted on ThermoScientific iS-10. Scanning, electron microscopy (SEM) was conducted on Thermofisher (USA) Quattro S Field Emission Gun, Environmental SEM (FEGSEM). X-ray diffraction (XRD) patterns were acquired on a Bruker powder diffractometer equipped with Cu Kα radiation (35kV, 15mA) at a scan rate of 10° min^{-1} with step width 0.015°and Scan range 5 ~ 80°. Inductively coupled plasma mass spectrometer (ICP-MS) was employed to determine the content of various elements in aqueous solutions.

Synthesis of Zr-MSA. In a clean, dry scintillation vial, $ZrCl_4$ (150 mg, 0.64 mmol), MSA (100 mg, 0.66 mmol), and 100 µL of formic acid, used as the modulator in this reaction, (FA, 4eq. relative to $ZrCl_4$) were combined in 2 mL of DI water and sonicated for 10 minutes. Then, the mixture was kept in thermal block at 80°C. After 2 hours, the reaction mixture was cooled down to room temperature, and the white precipitate was collected by centrifugation, followed by washing with 10mL of DI water (twice) then 10mL of ethanol (three times). Finally, the solid was dried under vacuum at 60°C overnight. (**Yield=160mg**).

Synthesis of Zr-MSA-MA.
In a clean, dry scintillation vial, $ZrCl_4$ (125 mg, 0.53 mmol), MSA (80 mg, 0.53 mmol), 50 µL of MA, and 50 µL of FA, used as the modulator in this reaction, were combined in 2mL of DI water and sonicated for 10 minutes. Then, the mixture was kept in thermal block at 80°C. After 2 hours, the reaction mixture was cooled down to room temperature, and the white precipitate was collected by centrifugation, followed by washing with 10 mL of DI water (twice) then 10 mL of ethanol (three times). Finally, the solid was dried under vacuum at 60°C overnight. **(Yield=130 mg).**

Kinetics Studies.

Cadmium. In eight sealed glass vials,10.5mg of Zr-MSA-MA was left to stir at room temperature with 20 mL of 200 ppm Cd(II) for specific time intervals (0.5, 1, 1.5, 2, 3, 4, 5, and 6 hours). After each time interval, the supernatant was collected from each vial separately by centrifugation at 6000 rpm for 10minutes, followed by microfiltration membrane (pore size, 0.22 µm). The Cd(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Lead . In eight sealed glass vials,10.5mg of Zr-MSA-MA was left to stir at room temperature with 20mL of 200 ppm Pb(II) for different time intervals (0.5, 1, 1.5, 2, 3, 4, 5, and 6 hours). After each time interval, the supernatant was collected from each vial separately by centrifugation at 6000rpm for 10minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Pb(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Dose-dependency Studies.

Cadmium. In five sealed glass vials, different weights of Zr-MSA-MA (5, 10, 20, 30 and 40 mg) was left to stir at room temperature with 20 mL of 200 ppm Cd(II) for 4h. After which, the supernatant was collected from each vial separately by centrifugation at 6000 rpm for 10 minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Cd(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Lead. In five sealed glass vials, different weights of Zr-MSA-MA (5, 10, 20, 30 and 40 mg) was left to stir at room temperature with 20mL of 200 ppm Pb(II) for 4h. After which, the supernatant was collected from each vial separately by centrifugation at 6000rpm for 10minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Pb(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

pH-dependency Studies.

Cadmium. In five sealed glass vials, 10.5 mg of Zr-MSA-MA was left to stir at 450 rpm at room temperature with 20mL of 200 ppm Cd(II) of different pH (2, 4, 5, 6, and 8). After 4h, the supernatant was collected from each vial separately by centrifugation at 6000 rpm for 10 minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Cd(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Lead. In five sealed glass vials, 10.5mg of Zr-MSA-MA was left to stir at 450 rpm at room temperature with 20 mL of 200 ppm Pb(II) of different pH (2, 4, 5, 6, and 8). After 4h, the supernatant was collected from each vial separately by centrifugation at 6000 rpm for 10 minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Pb(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

The desired pH of each stock solution was adjusted through the addition of either 0.1M HCl or NaOH.

Adsorption Isotherm Studies.

Cadmium. In sealed glass vials, eight separate samples of 10.5 mg Zr-MSA-MA was added into 20 mL of Cd(II) solutions of different concentrations (25, 50, 100, 200, 400, 600, 800, 1000 ppm) and stirred at 450 rpm (pH=6). After 4h, the supernatant from each vial was separately collected by centrifugation at 6000 rpm for 10 minutes, followed by microfiltration membrane (pore size,

0.22 μm). The Cd(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Lead. In sealed glass vials, eight separate samples of 10.5 mg Zr-MSA-MA was added into 20 mL of Pb(II) solutions of different concentrations (25, 50, 100, 200, 400, 600, 800, 1000 ppm) and stirred at 450 rpm (pH=6). After 4h, the supernatant was collected from each vial separately by centrifugation at 6000 rpm for 10 minutes, followed by microfiltration membrane (pore size, 0.22 μm). The Pb(II) concentration in the supernatant was then measured using an inductively coupled plasma mass spectrometer (ICP-MS).

Regeneration Studies.

Cadmium. To probe the regeneration ability of Zr-MSA-MA MOF, a 0.45 μm nylon syringe filter was loaded with 30 mg of Zr-MSA-MA after being suspended in 10 mL of DI water. Then, 20 mL of 15 ppm of Cd(II) solution was passed through the loaded syringe filter, and the filtrate was collected for ICP analysis. The syringe filter was then washed with 1M HCl (20mL) followed by 20 mL of DI water. The Cd^{2+} uptake and washing were repeated for 10 cycles.

Lead. To probe the regeneration ability of Zr-MSA-MA MOF, a 0.45 μm nylon syringe filter was loaded with 30 mg of Zr-MSA-MA after being suspended in 10 mL of DI water. Then, 20 mL of 15 ppm of Pb(II) solution was passed through the loaded syringe filter, and the filtrate was collected for ICP analysis. The syringe filter was then washed with 1M HCl (20 mL) followed by 20 mL of DI water. The Pb(II) uptake and washing were repeated for 10 cycles.

Selectivity Studies.

The effect of competing ions on the uptake efficiency was investigated using a batch-ion exchange protocol in which 40 mg of Zr-MSA-MA was immersed in mixture made by mixing 5 mL of 25 ppm from each of the following metal ions: Pb(II), Cd(II), Cu(II), Zn(II), Mn(II), Fe(III), Co(II), and Ni(II) with stirring. After 4h, the supernatants were collected by centrifugation followed by microfiltration for determining the concentration of each ion using an inductively coupled plasma mass spectrometer (ICP-MS). The same procedure was repeated but utilizing 100 ppm of each metal ion to test the selectivity in more demanding environment.

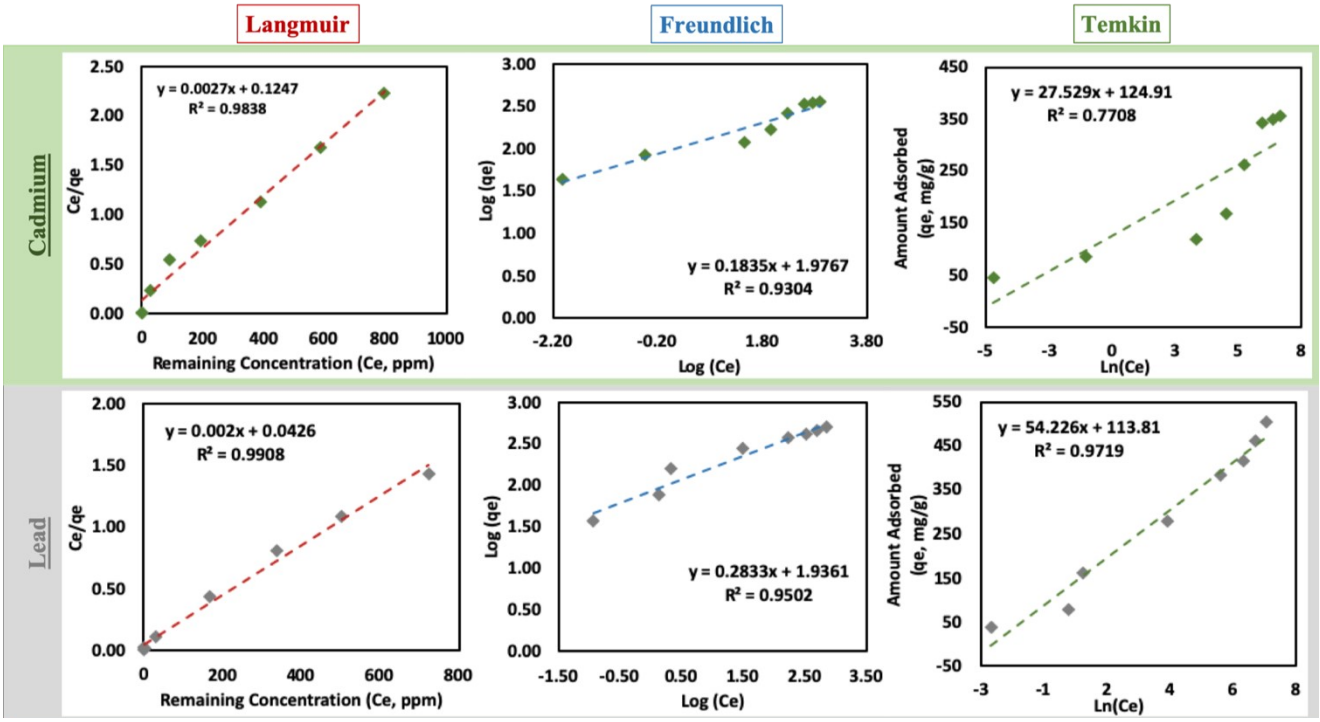

Figure S1. Investigation of Zr-MSA-MA MOF uptake behavior toward different contaminants Cd(II), Pb(II). Linear adsorption isotherms plots fitted by the (a) Langmuir, (b) Frendluich, and (c) Temkin models.

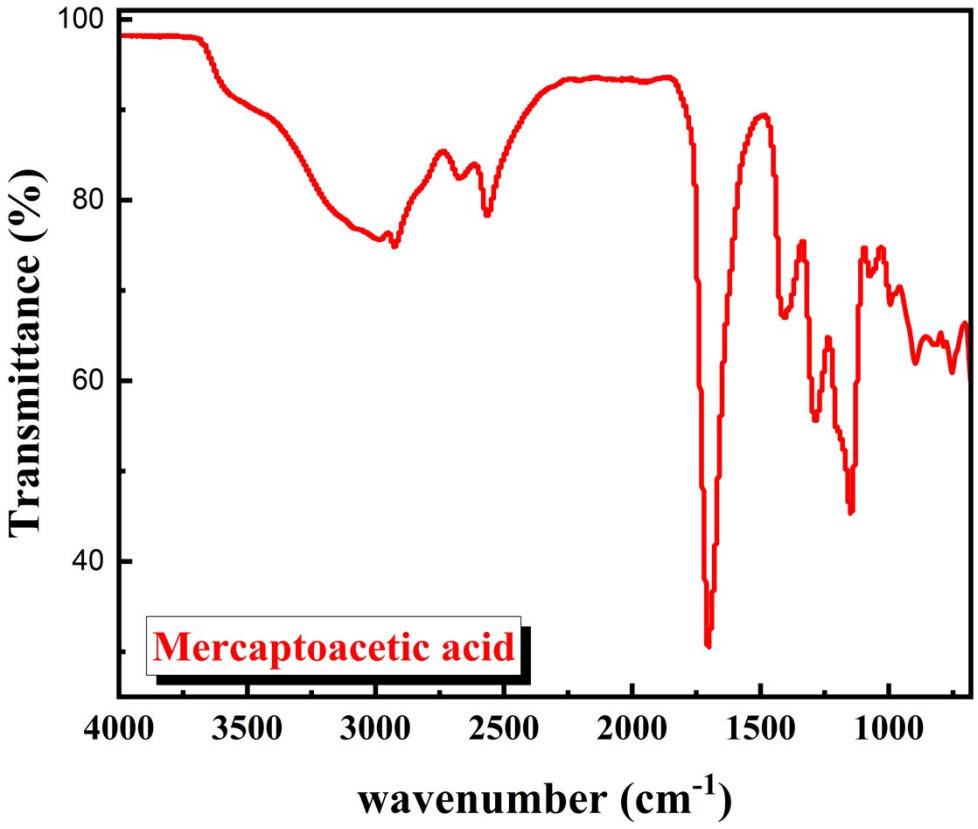

Figure S2. FTIR spectrum of the mercaptoacetic acid.

Table S1. Adsorption Isotherm Fitting Parameters of the Langmuir, Frendluich, and Temkin Models for the Three Contaminants.

Model	Cd(II)	Pb(II)
Langmuir		
slope	0.0027	0.0020
q_m	**370.37**	**500.00**
Uptake mmol/g	**3.29**	**2.41**
intercept	0.1247	0.0426
b	0.0217	0.0469
R^2	**0.9838**	**0.9908**
Frendluich		
slope	0.1835	0.2833
n	5.4496	3.5298
intercept	1.9767	1.9361
K_f	94.776	86.318
R^2	0.9304	0.9502
Temkin		
Slope	27.529	54.226
b	90.04	45.71
Intercept	124.91	113.81
K_T	93.447	8.156
R^2	0.7708	0.9719

Table S2. Maximum Adsorption capacities (mg/g) for Pb(II), Cd(II), and Cr(VI) species by MOF-based sorbents.

	Adsorbent	Capacity (mg/g)	Ref.
	Zr-MSA-MA	**500.00**	**This Work**
Pb(II)	Zn(ADB)L0.5]·1.5DMF	463.52	[1]
	TIF-A1/ chitosan	397.3	[2]
	AMCA-MIL-53(Al)	390	[3]
	UiO-66-ATA	387	[4]
	ED-MIL-100(Fe)	378.8	[5]
	MOF/Gum carrageenan composite (MGC)	374.7	[6]
	UiO-66-EDTA	357.9	[7]
	ZnO/ZnFe2O4/C	344.83	[8]
	MOF-808-EDTA(BS-HMT)	313	[9]
	MIL-125-HQ	262.1	[10]
	Zinc (II) metal−organic framework (TMU-5)	251	[11]
	Fe–Mg MOF	196	[12]
	SS-NH2-UiO-66-5	186.14	[13]
	UiO-66-NH2	177.35	[14]
	MIL-100(Fe)-DE hybrid material	155	[15]
	CS-ZIF-8 composite	131.14	[16]
	DUT-67	98.5	[17]
Cd(II)	MOF-808-EDTA(BS-HMT)	528.00	[1]
	LDH/MOF	415.30	[2]
	Zr-MSA-MA	**370.37**	**This Work**
	FJI-H9	286	[3]
	MOF-808@PAN	225	[4]
	UiO-66-EDA	217.39	[5]
	MOF@CSC composite sponge	193.35	[6]
	Fe–Mg MOF	191	[7]
	UiO-66-NH2	177.35	[8]
	Fe_3O_4@MOF-235(Fe)-OSO_3H	163.9	[9]
	Modified UiO-66 with melamine (MUiO-66)	146.6	[10]
	MIL-125-HQ	103	[11]
	UiO-66-SH	77.42	[12]
	Zr-DMBD	43.8	[13]

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