Supporting Information

Highly Efficient and Facile Removal of Pb²⁺ from Water by Using a Negatively Charged Azoxy-functionalized Metal-organic Framework

Cai-Xia Yu,[†] Ke-Zhong Wang,[†] Xue-Jing Li,[†] Dong Liu,^{*,‡} Lu-Fang Ma[§] and Lei-Lei Liu^{*,†}

[†] School of Environment and Material Engineering, Yantai University, Yantai 264005, P. R. China
[‡] Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian 223300, Jiangsu, P. R. China
§ College of Chemistry and Chemical Engineering, Henan Province Function-oriented Porous Materials Key Laboratory, Luoyang Normal University, Luoyang 471934, P. R. China

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Section 1. Materials and physical measurements

The H₂ADB and L ligands were prepared according to the literature method.¹ All other chemicals were commercially available reagents of analytical grade unless otherwise specified, and were used without further purification. Fourier transform infrared (FT-IR) spectrum was conducted on a Thermo Nicolet iS50 spectrometer. Powder X-ray diffraction (PXRD) data was collected on PANalytical X'Pert PRO MPD system (PW3040/60). The energy-dispersive X-ray (EDX) data was obtained using a Bruker XFlash 6130 at 15 KV. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA-449F3 thermogravimetric analyzer in the nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The metal ion concentrations in solution before and after adsorption were measured using ICP-OES (PerkinElmer Optima 8000) and AAS (Shimadzu AA-6300, for lower concentrations).

Section 2. X-Ray data collection and structure determination

Single crystal of **1** was obtained directly from the above preparation. All measurement was made on a Bruker Smart Apex-II CCD area detector by using graphite monochromated Mo K_{α} ($\lambda = 0.071073$ nm). Its crystal was mounted on glass fibers at 296 K. Cell parameter was refined by using the program Bruker *SAINT*. The collected data was reduced by using the program Bruker *SAINT* A, and the absorption correction (multi-scan) was applied. The reflection data was also corrected for Lorentz and polarization effect. The crystal structure of **1** was solved by direct method refined on F^2 by full-matrix least-squares technique with the SHELXTL-97 program.² All H atoms in **1** were placed in geometrically idealized positions and constrained to ride on their parent atoms. Moreover, the diffused electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.³ The formula of {[(Zn(ADB)L_{0.5}]·1.5DMF}_n was derived from thermogravimetric characterization. The crystal data for **1** was summarized as follows: C₄₀H₃₀N₄O₇Zn, Mr = 744.07, orthorhombic, space group *Pnna*, *a* = 13.829(3) Å, *b* = 24.535(5) Å, *c* = 23.988(5) Å, *a* = 90°, $\beta = 90^\circ$, $\gamma = 90^\circ$, V = 8139(3) Å³, *Z* = 8, $D_c = 1.214$ g cm⁻³, *F*(000) = 3072 and $\mu = 0.653$ mm⁻¹, 67859 reflections collected, 7167 unique ($R_{int} = 0.0569$), $R_1 = 0.0697$, $wR_2 = 0.2134$ and S = 1.066. Crystallographic data have been submitted to the Cambridge Structural Database with deposition number CCDC 1972144.

Section 3. Adsorption experiments

The adsorption kinetics data were fitted with different kinetic models, pseudo first-order model, pseudo-second-order, expressed as follows:

$$\ln(q_{e} - q_{t}) = \ln q_{e} - k_{1}t$$
(1)
$$\frac{t}{q_{t}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{t}{q_{e}}$$
(2)

where q_t (mg g⁻¹) and q_e (mg g⁻¹) are the adsorption capacity at any time t (min) and at equilibrium; k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are kinetic rate constants for the pseudo-first-order and pseudo-second-order models, respectively.

The Langmuir and Freundlich isotherm model were employed to simulate the adsorption isotherm data and can be described as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}$$
(4)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

Where $q_e \pmod{g^{-1}}$ is the adsorption amounts at equilibrium and $C_e \pmod{L^{-1}}$ is the equilibrium concentration of Pb(II). $q_m \pmod{g^{-1}}$ is the maximum amount or the saturated adsorption amount. $K_L \pmod{g^{-1}}$ is the Langmuir constant, quantitatively reflecting the affinity of binding sites to energy of adsorption. $K_F \pmod{g^{-1}}{(\text{Lmg}^{-1})^{1/n}}$ is the Freundlich constant which indicates the adsorption capacity and n is an empirical parameter related to the intensity of adsorption. The Langmuir model assumes that the solid surface active sites can be occupied only by one layer of adsorbates and there is no interaction between the adsorbate molecules. On the contrary, the Freundlich model is based on a heterogeneous adsorption.

Section 4. Supporting Tables

Adsorbents	$K_{\rm d} ({\rm mL}~{\rm g}^{-1})$	Reference
MOF 1a	8.88× 10 ⁶	this work
Fe-BTC/PDA	1.7×10^{6}	4
Zn ₃ (AZO) ₃ (BPE) _{1.5}	2.3×10^{6}	5
$Fe_3O_4@Cu_3(btc)_2$	$1.23 imes 10^4$	6
ED-MIL-101-Cr	1.18×10^{3}	7
MoS ₄ -LDH	2.6×10^{5}	8
68(W)	3.17×10^5	9
PbIMS	2.97×10^{3}	10
PDA-Ms	2.39×10^{3}	11
K-MPS-1	5.36 ×10 ⁵	12

Table S1. Comparison of distribution coefficient (K_d) with top performing materials for Pb²⁺ removal.

Table S2. Kinetic parameters for adsorption of Pb^{2+} .

		Pseudo-first-order kinetics		Pseudo-second-order kinetics			
<i>T/</i> K	<i>q</i> _{e, <i>exp</i>}	k_1	$q_{ m e, \ cal}$	<i>R</i> ²	<i>k</i> ₂	q _{е, cal}	<i>R</i> ²
298	79.93	0.0261	4.050	0.660	0.0193	80.19	0.999

	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
T/K	$q_{ m m}$	KL	<i>R</i> ²	$K_{ m F}$	п	<i>R</i> ²
298	462.96	3.288	0.999	179.47	3.326	0.701

 Table S3. Adsorption constants for Langmuir and Freundlich isotherm models.

Table S4. Comparison of maximum adsorption capacities of Pb^{2+} with various adsorbents.

Adsorbents	Maximum adsorption capacity (mg g^{-1})	Reference
CeO ₂ -MoS ₂ hybrid magnetic biochar	263.6	13
WS-BC+BM	134.68	14
CDCS-EDTA	114.8	15
LDH@VMT	142.65	16
TA@Zr	99	17
COF-TE	185.7	18
Fe ₃ O ₄ @MIL-88A(Fe)/APTMS	536.22	19
MIL-125-HQ	262.1	20
UiO-66-RSA	189.8	21
1a	463.52	this work

Mixed ions	M ⁿ⁺ removal (%)	$K_{\rm d} ({\rm mL}~{\rm g}^{-1})$	k	
Pb ²⁺	99.05	8.341× 10 ⁵		
Na ⁺	0.11	8.8097	94680.42	
Mg^{2+}	0.38	30.51596	27333.41	
K^+	0.21	16.83535	49544.86	
Ca ²⁺	0.58	46.67069	17872.14	
Mn^{2+}	3.18	262.7556	3174.452	
Co ²⁺	2.85	234.6886	3554.093	
Ni ²⁺	4.03	335.9383	2482.912	
Cd^{2+}	10.62	950.5482	877.4991	

Table S5. Selective adsorption parameters of 1a toward Pb²⁺ and other metal ions in the mixed solution.

Note: k is selective coefficient calculated from K_d (Pb²⁺)/ K_d (competition ion).

Section 5. Supporting Scheme and Figures



Scheme S1. Chemical structures of the L and H₂ADB ligands.



Figure S1. Gas adsorption and desorption isotherms of 1a and 1a-Pb.



Figure S2. TGA curves of the as-synthesized sample 1 and the activated sample 1a.



Figure S3. PXRD patterns of the simulated single crystal data **1**, as-synthesized sample **1**, activated sample **1a** and sample **1** after being immersed in aqueous solution at pH = 3, 4, 5, 7, 9, 11 (24 h).



Figure S4. EDX spectra of the section for 1a-Pb.



Figure S5. The PXRD patterns of 1a and 1a-Pb.



Figure S6. (a) SEM image of 1a. (b) SEM image of 1a-Pb.



Figure S7. The removal ratio of 1a toward Pb²⁺ at different initial concentrations.

Section 6. Supporting References

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