

Supplementary Material for

## **Development of a Novel MOFs-Based Nanofiber for Highly Selective Removal of Cobalt from Aqueous Solutions**

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## **Section 1 Experimental instruments**

The crystalline phase structure was observed using X-ray diffraction (XRD, Shimadzu, Japan, 7000), and the surface morphology of pristine (pure PAN), material was recorded using a field-emission scanning electron microscope (FESEM, Nihon Electronics, JSM-7800F). FT-IR spectra of the materials were obtained with a Fourier transform infrared spectrometer (FT-IR, Thermo Fisher Scientific, NICOLET iS10, USA) in the spectral range of 4000-500  $\text{cm}^{-1}$  at room temperature. The hydrophilic changes of Co(II)-PIIMs-*x* were investigated using a surface analysis system (SINDIN SDC-200S, China) by dropping drops of deionized water on all membrane surfaces and measuring the contact angle. To study the elemental type and binding energy of the adsorbent before and after adsorption, X-ray photoelectron spectroscopy (XPS, Thermo Fisher, USA) was used. Atomic Absorption Spectroscopy (AAS) was used to measure the metal concentrations for the selectivity experiments. Nanofibers were prepared using an electrostatic spinner (YFSP-T, China). Adsorption experiments were carried out using an air-bath thermostatic shaker (China, HZQ-F160), and after adsorption, the cobalt ion concentration in the supernatant was quantitatively measured by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher, USA, EXPEC 7000).

## Section 2 Adsorption experiment

The adsorption amount of adsorbent  $q_t$  (mg g<sup>-1</sup>) was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad \text{S1}$$

where  $C_0$  and  $C_t$  are the concentrations of cobalt ions at the initial and time  $t$ ,  $m$  is the mass of the MOFs nanofibers, and  $V$  is the volume of the solution in which the adsorption experiments were performed.

### Adsorption experimental conditions

Table S1 The setting of experimental conditions

pH	pH=5\6\7\8\8.3\9, m=10 mg, Time=12 h, T=298.15 K, C <sub>0</sub> =10 ppm, V=100 mL
Adsorbent dosage	m=5\10\15\20\25\30\35\40 mg, pH=8.3, T=298.15 K, C <sub>0</sub> =10 ppm, V=50 mL
Time	Time=10\20\30\60\120\180\240\300\420\480\720 min, m=10 mg, pH=8.3, T=298.15 K, C <sub>0</sub> =10 ppm, V=50 mL
C <sub>0</sub>	C <sub>0</sub> =5\10\20\30\40\50\60 ppm, m=10 mg, pH=8.3, Time=12 h, T=298.15 K, V=100 mL
T	T=288.15\298.15\308.15\318.15 K, m=10 mg, pH=8.3, Time=12 h, C <sub>0</sub> =10 ppm, V=100 mL
Reusability	Cycle time=1\2\3\4\5, m=10 mg, pH=8.3, Time=12 h, T=298.15 K, C <sub>0</sub> =10 ppm, V=100 mL
Selective	Metal ion=K\Co, Ca\Co, Mg\Co, Ni\Co, m=10 mg, pH=8.3, Time=12 h, T=298.15 K, V=100 mL, C <sub>0</sub> =10 ppm

### Selective adsorption experiments

To investigate the selectivity of Co(II)-PIIMs- $x$  and PNIMs- $x$  for coexisting metal ions, experiments were carried out by exploring the effect of other metal ions (K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>) that may be present in the actual cobalt-containing wastewater on cobalt. Ion concentrations were determined using an atomic absorption spectrometer. The

partition coefficient ( $K_d$ ) and selectivity coefficient ( $k$ ) were obtained from the following Eq.

$$K_d = \frac{(c_0 - c_e)V}{mc_e} \quad \text{S2}$$

$$k = \frac{k_{d1}}{k_{d2}} \quad \text{S3}$$

where  $C_0$  (mg/L) and  $C_e$  (mg/L) are the corresponding metal ion concentrations after initial and adsorption equilibrium, respectively.  $k_{d1}$  and  $k_{d2}$  are the partition coefficients of the template ion cobalt and other competing metal ions, respectively.  $k$  is the selectivity coefficient for other competing adsorbed ions.

### Section 3 Preparation of materials

SIM-1 was prepared according to the reported method. as follows: 9.5 g of zinc acetate was dissolved in 36 mL of methanol. 9.5 g of 4-methyl-5-imidazolecarboxaldehyde was dissolved in 72 mL of tetrahydrofuran. The methanol solution was added to the tetrahydrofuran solution and stirred vigorously at room temperature for 24 h ( $N_2$  atmosphere). The sample was centrifuged and washed clean with methanol. The sample obtained was dried in air at room temperature for 48 h.

Cobalt ion selective fillers were prepared on the basis of reported literature. The non-selective packing (SIM-NIP) was prepared in the same way as the cobalt ion selective packing except that cobalt nitrate hexahydrate was not added.

0.5 g of polyvinylpyrrolidone (PVP K30, Aladdin) was taken and co-dissolved with an amount of Co(II)-SIM-IIP or SIM-NIP (8%, 10% and 12%, respectively) in 5 mL of DMF. Subsequently dried, the dried mixture was then mixed with a solution of 0.5 g of polyacrylonitrile (PAN, molecular weight 150,000 g/mol)/5 mL of DMF, which was prepared to obtain the electrostatic spinning precursor solution by stirring for 2 h at room temperature. The voltage of electrostatic spinning was 18 KV, and the flow rate of the suspension was 0.0020 mm/s. After the electrostatic spinning, to remove the residual solvent, the nanofibers were dried in a vacuum drying oven at 60 °C for 6 h. Finally, they were transferred to deionized water, and the PVP K30 was eluted and removed to obtain nanofiber materials (Co(II)-PIIMs- $x$ ,  $x=8\%$ , 10%, 12% and PNIMs-10%).

## Section 4 Characterization

Surface SEM micrographs and pore size distribution of SIM-NIP, Co(II)-PIIMs-8%, and Co(II)-PIIMs-12% are shown below. Co(II)-PIIMs with 10% doping level had moderate specific surface area ( $28 \text{ m}^2/\text{g}$ ) and pore volume ( $0.070 \text{ cm}^3/\text{g}$ ), as well as large average pore size ( $13.18 \text{ nm}$ ). This pore structure may provide optimal porosity and pore size distribution for the adsorption process, which facilitates the diffusion of adsorbent molecules and the accessibility of adsorption sites. The 10% doping level of the materials may have resulted in a more homogeneous distribution of the particles during the preparation process, which reduces the particle agglomeration, thus improving the adsorption performance of the materials. This can be seen by scanning electron microscopy (SEM). The larger average pore size ( $13.18 \text{ nm}$ ) implies that the material with 10% doping level has better accessibility to the adsorption sites, which contributes to the adsorption efficiency.

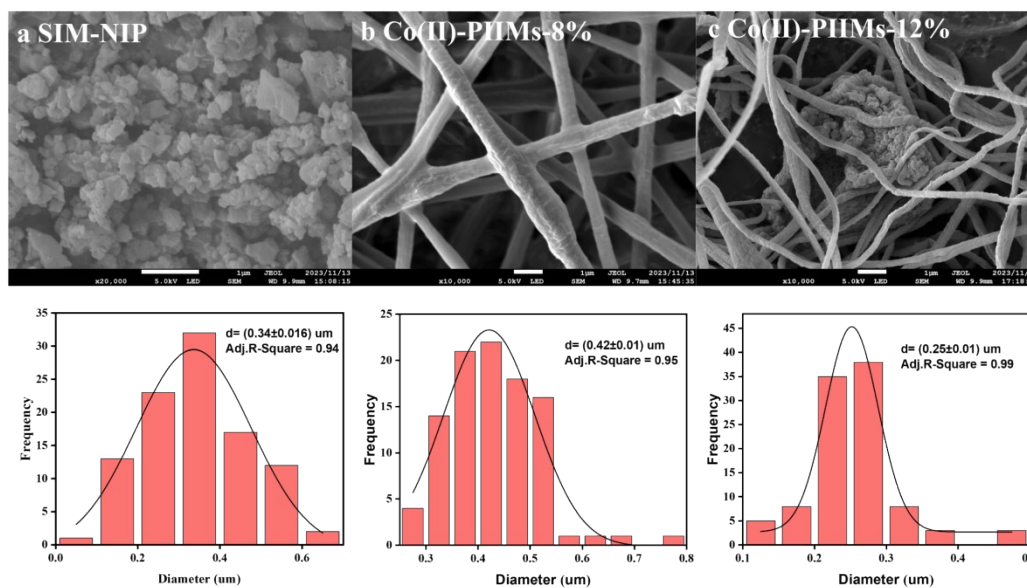


Fig. S1 SEM micrographs and pore size distribution of SIM-NIP (a), Co(II)-PIIMs-8% (b), and Co(II)-PIIMs-12% (c).

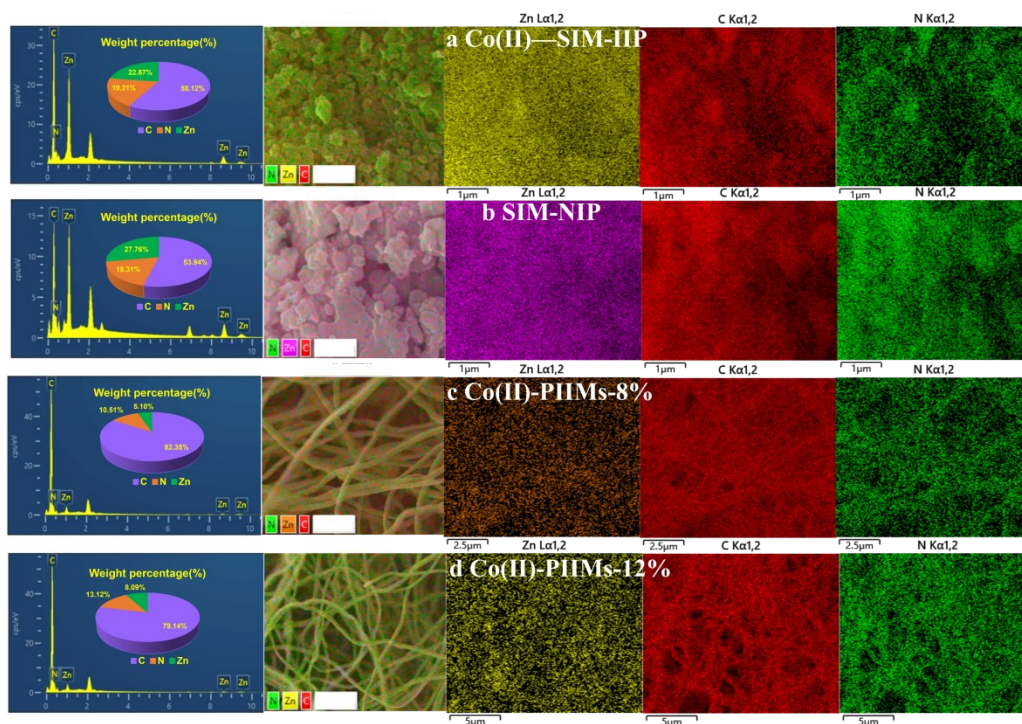


Fig. S2 EDS mapping images of Co(II)-SIM-IIP (a), SIM-NIP (b), Co(II)-PIIMs-8% (c), and Co(II)-PIIMs-12% (d).

The Brunauer-Emmett-Teller (BET) isothermal adsorption/desorption curves of the adsorbent materials are presented below.

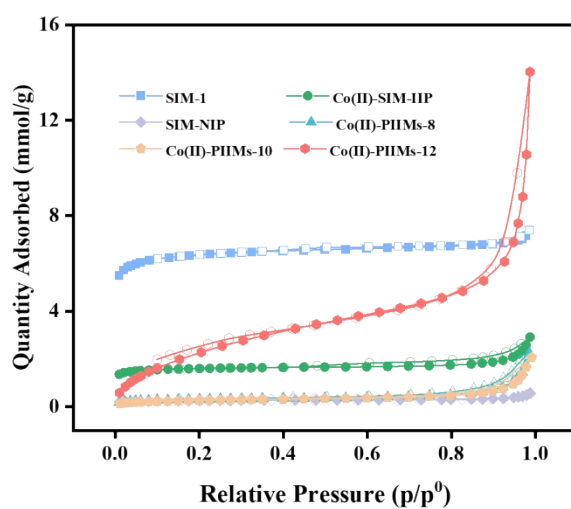


Fig. S3 N<sub>2</sub> adsorption-desorption curves of materials.

## Section 5 Adsorption performance

pH is a very important factor that affects the adsorption of heavy metal ions, according to Visual MINTEQ software to simulate the existence of metal ions in solution at different pH form and zeta potential of Co(II)-PIIMs-10%, as follows.

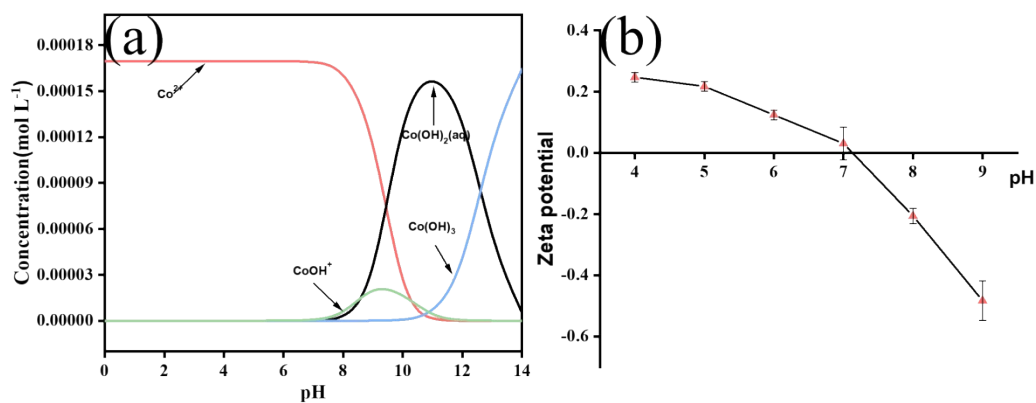


Fig. S4 Several major forms of cobalt ions at different pH (a) and zeta potential of Co(II)-PIIMs-10% (b).



## Section 6 Adsorption kinetics

Adsorption kinetics is a subdiscipline that focuses on the study of adsorption and desorption rates and various influencing factors. Four adsorption kinetic models were used in this study to describe the removal process and fit the experimental data. The Pseudo-first-order model suggests that the adsorption process is controlled by physical adsorption, the Pseudo-second-order model suggests that the adsorption process is chemisorptive. The Pseudo-first-order (Eq. S4), Pseudo-second-order (Eq. S5) can be described as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{S4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{S5}$$

Where  $q_t$  and  $q_e$  are the adsorption amounts (mg/g) at time  $t$  and at equilibrium, respectively, and  $k_1$ , and  $k_2$  are the adsorption rate constants in the Pseudo-first-order kinetic model, and Pseudo-second-order kinetic model.

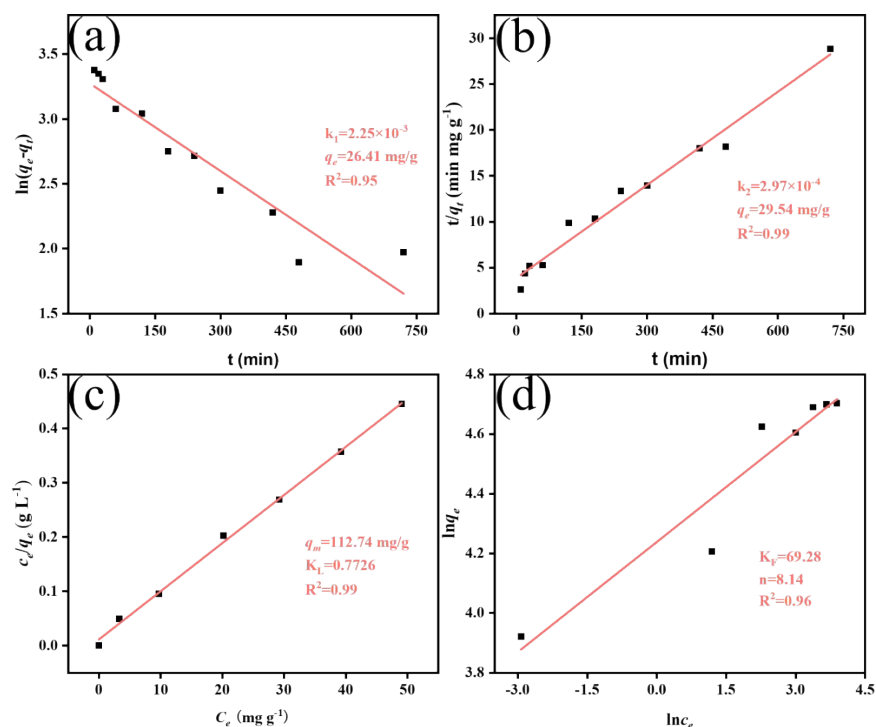


Fig. S5 The fitting curves of Pseudo-first-order model (a), Pseudo-second-order model (b), Langmuir model (c), Freundlich model (d).

## Section 7 Adsorption isotherms

The adsorption isotherm curve is the relationship curve between the solute molecules' concentrations in the two phases when they reach equilibrium during the adsorption process at the interface of the two phases at a certain temperature and can be used to explain the mechanism between the cobalt-containing wastewater and the adsorbent. Four models were used to analyze the adsorption behavior of  $\text{Co}^{2+}$ . The Langmuir model indicates that (i) the adsorption process is a monolayer surface adsorption; (ii) the adsorbent surface is homogeneous, and the amount of adsorption at each adsorbent site is equal; (iii) each adsorbent site is independent, and there is no interaction between the adsorbent and adsorbates; and (iv) the rates of adsorption and desorption are equal. the Freundlich model represents a multilayer adsorption assumption based on a nonhomogeneous surface. The multilayer adsorption assumption, there is a strong correlation between the amount of adsorption and the concentration of adsorbent at the moment of equilibrium. The Langmuir (Eq. S7), and Freundlich (Eq. S8), adsorption isothermal models are as follows.

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m k_L} \quad \text{S6}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad \text{S7}$$

Where  $c_e$  (mg/L) is the equilibrium  $\text{Co}^{2+}$  concentration,  $q_e$  and  $q_m$  ( $\text{mg g}^{-1}$ ) are the equilibrium and maximum theoretical adsorption of  $\text{Co}^{2+}$ , respectively,  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir adsorption equilibrium constant, and  $K_F$  ( $\text{mg g}^{-1}(\text{L mg}^{-1})^{1/n}$ ) and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption strength, respectively.

## Section 8 Thermodynamic study of adsorption

The thermodynamic parameters change. The calculation equation is as follows:

$$\Delta G = \Delta H - T\Delta S \quad \text{S8}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{S9}$$

Where  $K_d$  is the thermodynamic equilibrium constant,  $T$  is the open temperature (K), and  $R$  is the molar gas constant (8.314 J/mol·K).

Table S2 The thermodynamic parameters.

Temperature(K)	$\ln K_d$	$\Delta G^0(\text{kJ/mol})$	$\Delta H^0(\text{kJ/mol})$	$\Delta S^0(\text{J/mol}\cdot\text{K})$
288.15	0.99	-2.63		
298.15	2.01	-4.26		
308.15	2.20	-5.90	44.47	163.45
318.15	2.81	-7.53		