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A new MIL-101-type chromium-based metal–organic framework with densely packed sulfonic groups: an ultra-high uptake of toxic Pb²⁺ and Cu²⁺ ions from an aqueous medium†

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Metal–organic frameworks have been demonstrated to be effective adsorbents of heavy metal ions in recent decades. Nevertheless, their practical applications remain limited because of their slow uptake rates and a lack of functionalization techniques. To overcome these drawbacks, a new sulfonic-functionalized chromium-based metal–organic framework with a MIL-101-type structure was successfully fabricated, termed MIL-101-SO₃H(N), via a solvothermal procedure, and it demonstrated a unique uptake ability for highly toxic Pb²⁺ and Cu²⁺ cations from solution. Accordingly, MIL-101-SO₃H(N) demonstrated the highest adsorption capacity of 1449.7 mg g^{−1} and 1328.4 mg g^{−1} for Pb²⁺ and Cu²⁺ ions, respectively, which are much higher than those of previously reported adsorbents. It is noteworthy that the obtained data of heavy metal ion adsorption over MIL-101-SO₃H(N) best fit with the pseudo-second-order kinetic and Langmuir isothermal models, indicating that chemisorption occurred during the uptake process. In particular, the effective uptake of Pb²⁺ and Cu²⁺ ions is depicted by the strong electrostatic interaction between the positively charged metal ions and negatively charged sulfonate groups inside the MOF backbone as well as the large and suitable pore sizes of the material, leading to a considerable enhancement of metal ion uptake from an aqueous medium. These findings illustrate that the new SO₃H-modified Cr-based MOF is a potential candidate for use as an efficient adsorbent in eliminating highly toxic heavy metal ions under practical conditions.

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1 Introduction

With the rapid development of industrialization and modernization, highly toxic heavy metal ions are released into the environment without proper treatment, resulting in potential risks to human health and aquatic life underwater. Heavy metal ions, especially Pb²⁺ and Cu²⁺, are widely utilized in industrial fields, including construction and light industry, painting, pigments, and battery technology.^{1–3} Accordingly, wastewater containing even low concentrations of Pb²⁺ and Cu²⁺ ions can cause serious health threats, such as cancer, kidney damage, immune system imbalance, and functional disorders of the heart and brain.^{4–8} Therefore, it is urgent to seek efficient removal solutions for poisonous heavy metal ions before releasing them into the water medium. Different techniques to eliminate heavy metal ions involve ion exchange,^{9,10}

electrochemical treatment,¹¹ chemical precipitation,^{12,13} and adsorption.^{13,14} Among these, adsorption is admitted as one of the most effective procedures to remove heavy metal ions from the aqueous medium due to its uncomplicated design, facile manipulation, high uptake, and versatility.^{15–18} Various adsorptive materials have been employed to eliminate toxic metal ions from water, including composite/inorganic materials,^{19–21} activated carbon,^{22,23} clay,²⁴ and zeolite.^{25,26} Nevertheless, many obstacles were observed in using these materials to treat heavy metal ions from wastewater in the aspects of complicated functionalization, low efficiency, and slow uptake rate because there is no strong and effective interaction between the adsorbent and guest-heavy metal ions. Thus, scientists have focused on designing and constructing novel alternative adsorptive materials, possessing extraordinary performances to overcome the mentioned limitations and efficiently apply them in practical situations. In recent decades, metal–organic frameworks (MOFs) have received much attention in capturing heavy metal ions from wastewater^{27–29} due to their unique properties, such as large porous volume, high specific surface area, low density, and high chemical and thermal robustness.^{30,31} Herein, MOFs are constructed from

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organic ligands and inorganic metal clusters to produce a three-dimensional architecture with various topologies. In particular, the flexible backbone of MOFs facilitates effortless functionalization of organic linkers, driving various applications in fields, such as catalysis,^{32,33} adsorption,^{34,35} sensing,^{36,37} and energy storage.^{38,39} In addition, Cr-based MOFs are well-known for their large pore volume and high water stability, properties that have been widely investigated to enhance the removal of heavy metal ions. In detail, MIL-101(Cr) with a large specific surface area exhibited efficient adsorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} in solution.⁴⁰ Moreover, modifying the organic backbone of the MOF material with rich-electron moieties, such as thiol, amino, hydroxyl, and carboxyl groups, can enhance its uptake capacity for Pb^{2+} and Cu^{2+} ions *via* electron donor–acceptor interactions, forming stable complexes. For example, Zhao *et al.* fabricated a Zr-based MOF with carboxyl groups, displaying a maximum adsorption capacity of 420.2 mg g^{-1} for Pb^{2+} .⁴¹ Subramaniam *et al.* successfully prepared an amino-modified MOF, exhibiting a Cu^{2+} uptake capacity of 125.0 mg g^{-1} .⁴² Furthermore, mixed-ligand-based MOFs and MOF composites exhibited unexpectedly high uptake capacities for heavy metal ions.^{43–47} Specifically, in our previous report, VNU-23 has a densely packed distribution of sulfonate moieties (SO_3^-) within the architecture, which can strongly interact with Pb^{2+} ions through electrostatic attraction, leading to a high uptake ability for Pb^{2+} (*ca.* 617.3 mg g^{-1}).⁴⁸ Consequently, the large pore diameter combined with functional groups incorporated into the MOF material significantly boosts the removal efficiency and rate of Pb^{2+} and Cu^{2+} ions from the aqueous medium. With this in mind, if a new Cr-MOF material is successfully synthesized with large cavities and negatively charged sulfonic groups within the structure, it could considerably improve the adsorption capacity and rate of heavy metal ions. This is a new approach to overcome the drawbacks of traditional adsorbents and serve the demands of real-life conditions in terms of economic efficiency and high treatment performance.

With all of this taken into account, a research plan is proposed focusing on constructing a MOF platform that affords effective adsorption of heavy metal ions with the following combined factors: (i) design of a Cr-based MOF possessing a suitable pore size and high chemical and thermal stability to operate under practical conditions effectively; (ii) introducing a large number of sulfonic moieties onto the MOF structure to efficiently interact with positively charged metal ions *via* electrostatic attraction; and (iii) evaluation of adsorption possibility of heavy metal ions and interpretation of uptake mechanisms over the fabricated MOF. Hence, in this contribution, a new Cr-MOF containing sulfonic groups, namely MIL-101- $\text{SO}_3\text{H}(\text{N})$, was successfully prepared to efficiently remove the highly toxic heavy metal ions of Pb^{2+} and Cu^{2+} *via* strong electrostatic attraction and appropriate pore structure. Accordingly, MIL-101- $\text{SO}_3\text{H}(\text{N})$ exhibited an excellent adsorption capacity of 1449.7 mg g^{-1} for Pb^{2+} and 1328.4 mg g^{-1} for Cu^{2+} , with the uptake efficiency maintained even after eight consecutive cycles. Particularly, the structural features of the material and the adsorption mechanism of Pb^{2+} and Cu^{2+} over MIL-101- $\text{SO}_3\text{H}(\text{N})$ were interpreted through combined modern analytical

methods. These observations show that the sulfonic-functionalized Cr-based MOF is a promising adsorbent that effectively captures poisonous heavy metal ions from wastewater with great uptake capacity and rapid adsorption rate.

2 Experimental section

2.1 Starting chemicals and procedures

All the utilized chemicals, including chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98%), 1,4-naphthalenedicarboxylic acid (1,4- H_2NDC , 98%), sulfuric acid fuming (25%), hydrochloric acid (HCl, 37%), hydrofluoric acid (HF, 98%), lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$, 99%), copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 98%), acetone (99%), and ethanol (EtOH, 99%) were obtained from local vendors and used without further purification. Water employed in this study was double distilled and filtered through a Millipore membrane.

Raman spectra were recorded using a spectrometer (XploRA ONE 532 nm, Horiba). Fourier transform infrared (FT-IR) spectra were recorded using a spectrophotometer (FT/IR-6600, Jasco) with the Attenuated Total Reflectance (ATR) sampling procedure. Powder X-ray diffraction (PXRD) measurements were carried out using a Bruker D8 Advance diffractometer using Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.54718 \text{ \AA}$). The 2θ range was $3\text{--}50^\circ$ with a step size of 0.02° and a fixed counting time of 0.35 s per step. Thermal gravimetric (TG) analysis combined with differential scanning calorimetry (DSC) was performed using a thermal analyzer at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ under dry air (Labsys Evo 1600 TGA, SETARAM), over a temperature range of $25\text{--}800 \text{ }^\circ\text{C}$ at a constant rate of $10 \text{ }^\circ\text{C min}^{-1}$. Scanning electron microscopy (SEM) images were collected using a microscope (FESEM S-4800, Hitachi) at an accelerating voltage of 10 kV, coupled with energy-dispersive X-ray (EDX) mapping conducted on an instrument (EDX H-7593, Horiba). Transmission electron microscopy (TEM) images were obtained using a microscope (Jeon 1010, Hitachi) at a high voltage of 80 kV. $^1\text{H-NMR}$ spectroscopy was carried out using an NMR spectrometer (Advance Neo-600 MHz, Bruker). X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer (PHI 5000, Chigasaki) equipped with a monochromatic $\text{Al K}\alpha$ source operating at 50 W and 15 kV. Atomic absorption spectrophotometry (AAS) was performed using a spectrometer (ICE 300 Series, Thermo Scientific) with an absorption wavelength of 217 nm for Pb^{2+} and 324.7 nm for Cu^{2+} .

2.2 Synthesis of the 6-sulfonaphthalene-1,4-dicarboxylic acid linker (H_3SNAA)

According to a previously reported study,⁴⁹ a mixture of 1,4-naphthalene dicarboxylic acid (1 g, 4.63 mmol) and 5 mL of sulfuric acid fuming (10 wt%) was introduced into a 100 mL glass flask and then stirred, refluxed, and heated at $130 \text{ }^\circ\text{C}$ for 24 h. After cooling to room temperature, the solid was dissolved in 50 mL of distilled water, filtered, and precipitated with 10 mL of concentrated HCl. Then, the product was filtered, washed with 50 mL of concentrated HCl, and dried at $100 \text{ }^\circ\text{C}$ under vacuum for 24 h to obtain the pure linker, denoted as H_3SNAA .



$^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 600 Hz): $\delta = 9.01$ (s, 1H); 8.75 (s, 1H); 8.11 (d, 2H); and 7.91 ppm (s, 1H) (Fig. S1†).

2.3 Synthesis of MIL-101-SO₃H(N)

A mixture of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.2664 g, 0.666 mmol) and H_3SNAA (0.3944 g, 1.332 mmol) was added to a 20 mL vial containing H_2O (4 mL) and HF (85.1 μL), and ultrasonicated for 15 min. The mixture was then transferred to a 25 mL Teflon stainless steel vessel and heated at 190 °C for 24 h. Next, the mixture was cooled to room temperature, centrifugated, and sequentially washed with H_2O (50 mL in 48 h), EtOH (50 mL in 48 h), and acetone (50 mL in 48 h). Finally, the solid was dried and activated under vacuum at 120 °C for 24 h to obtain a dark green powder (88% yield, based on Cr^{3+}), termed MIL-101-SO₃H(N).

2.4 Adsorption investigations

The pH values of the Pb^{2+} and Cu^{2+} solutions were controlled with 0.1 M NaOH and 0.1 M HCl solutions with the pH ranges of 1–5.5 (for Pb^{2+}) and 1–5.0 (for Cu^{2+}) to prevent the formation of precipitation species of Pb^{2+} and Cu^{2+} .^{50–52} Pb^{2+} and Cu^{2+} uptake studies were performed with a constant stirring rate (400 rpm) at room temperature. To explore the pH_{pzc} parameter of the material, the MIL-101-SO₃H(N) sample (150 mg) was introduced into 100 mL flasks containing 50 mL of NaCl solutions (0.01 M) with different initial pH values from 2 to 12. Subsequently, the systems were stirred at room temperature for 48 h and centrifugated to separate the solid. The final pH value of the solutions after centrifugation was measured. The intersection point between the original and final pH values revealed the pH_{pzc} parameter. The concentration of Pb^{2+} and Cu^{2+} after adsorption

over MIL-101-SO₃H(N) was measured using an atomic absorption spectrophotometer with an absorption wavelength of 217 nm and 324.7 nm, respectively. The adsorption capacity (mg g^{-1}) and removal efficiency (%) at intervals (q_t) and equilibrium (q_e) of the heavy metal ions were determined using the following equations:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

$$q_t = \frac{C_0 - C_t}{m} \times V \quad (3)$$

where C_0 , C_e , and C_t (mg L^{-1}) are the heavy metal ion concentrations at original, equilibrium, and t time. m (mg) is the MOF content, and V (mL) symbolizes the volume of the solution.

Varying amounts of MOF (5–30 mg) were added to the highly toxic heavy metal ion solutions with a specific concentration (50 mg L^{-1}) to determine the optimal dosage. Adsorption isothermal experiments were conducted using the optimal dosage, which was introduced into 100 mL of various initial concentrations of the heavy metal ions ($100\text{--}1000 \text{ mg L}^{-1}$) at the optimal pH value and stirred for 24 h. Pb^{2+} and Cu^{2+} uptake kinetic investigations over MIL-101-SO₃H(N) were performed. In detail, 5 mg of MIL-101-SO₃H(N) was added to 50 mL of Pb^{2+} and Cu^{2+} solutions (40 mg L^{-1}) at $\text{pH} = 5$, and the mixtures were stirred at intervals from 1 to 20 min. Herein, the content of 5 mg and $\text{pH} = 5$ are selected to study the kinetics because the uptake rate of the material is rapid with the MOF content and pH over

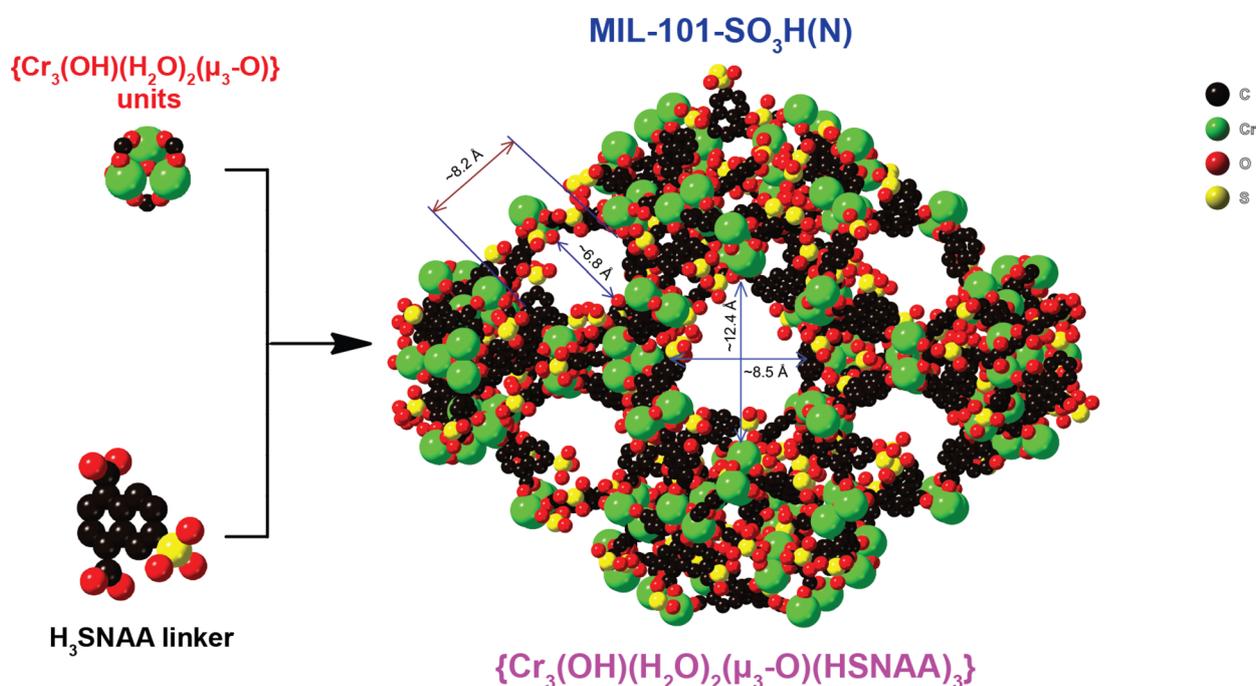


Fig. 1 The backbone of MIL-101-SO₃H(N) is generated from the $\{\text{Cr}_3(\text{OH})(\text{H}_2\text{O})_2(\mu_3\text{-O})\}$ SBU with H_3SNAA . Atom colors: Cr polyhedra, green; C, black; O, red; S, yellow. All H atoms are omitted for clarity.



5 mg and 5, resulting in inaccurate measurement in a short interval.

The reusability of MIL-101-SO₃H(N) was studied by using 1% HNO₃ solution as an effective desorption medium. Accordingly, after removing the heavy metal ions, the sample was isolated by centrifugation, soaked in 1% HNO₃ solution, and stirred for

24 h. To further evaluate the removal efficiency of Pb²⁺ and Cu²⁺ ions from the MOF material, the filtrate was analyzed by AAS, which showed no traces of heavy metal ions. Next, MIL-101-SO₃H(N) was centrifugated, washed with excess distilled water until pH = 7, and exchanged in EtOH and acetone solvents for 24 h, respectively. The sample was then separated by

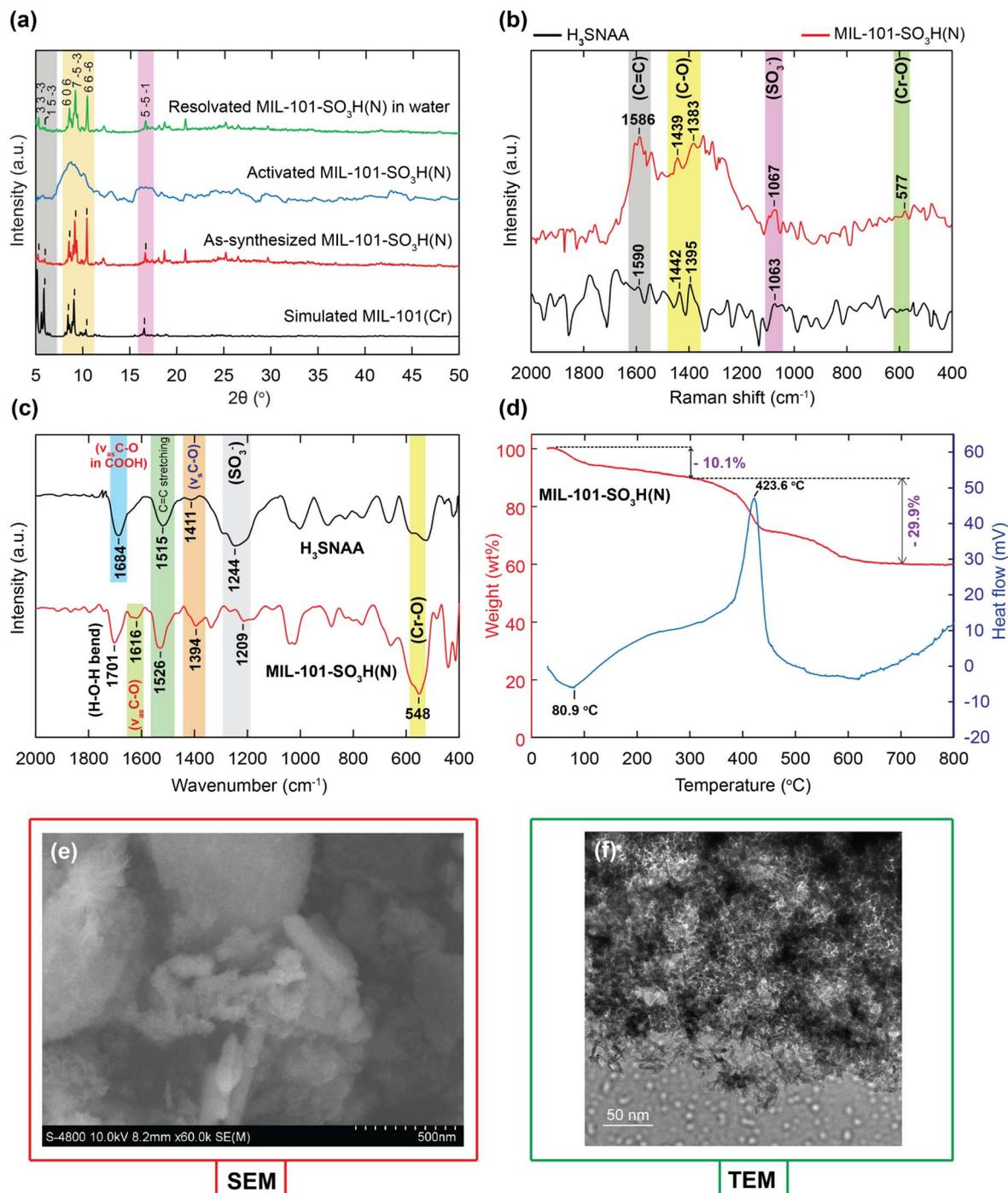


Fig. 2 Powder X-ray diffraction patterns of as-synthesized MIL-101-SO₃H(N) (red), activated MIL-101-SO₃H(N) (blue), and resolvated MIL-101-SO₃H(N) immersed in H₂O (green) in comparison with the simulated MIL-101(Cr) (black) (a); Raman spectra of MIL-101-SO₃H(N) (red) in comparison with the H₃SNAA linker (black) (b); Fourier transform infrared spectra of the H₃SNAA linker (black) and activated MIL-101-SO₃H(N) (red) (c); TGA curve (red) and DSC diagram (blue) of activated MIL-101-SO₃H(N) (d); SEM image of MIL-101-SO₃H(N) at a scale bar of 500 nm (e); TEM image of activated MIL-101-SO₃H(N) at a scale bar of 50 nm (f).



centrifugation, dried at 120 °C under a dynamic vacuum for 24 h, and employed for subsequent uptake investigations.

3 Results and discussion

3.1 Full characterization of MIL-101-SO₃H(N)

To confirm the extraordinary adsorption properties of Pb²⁺ and Cu²⁺ over the MOF backbone, a MOF design strategy is

proposed based on the following incorporated factors: (a) MOFs with large cavities will support the rapid and efficient mobility of the heavy metal ions into internal pore walls, significantly enhancing the removal capacity and rate; (b) the dense distribution of sulfonic groups within the MOF architecture to generate negatively charge moieties *via* deprotonation, resulting in strong attraction with the Pb²⁺ and Cu²⁺ ions through electrostatic interactions; (c) high chemical and thermal

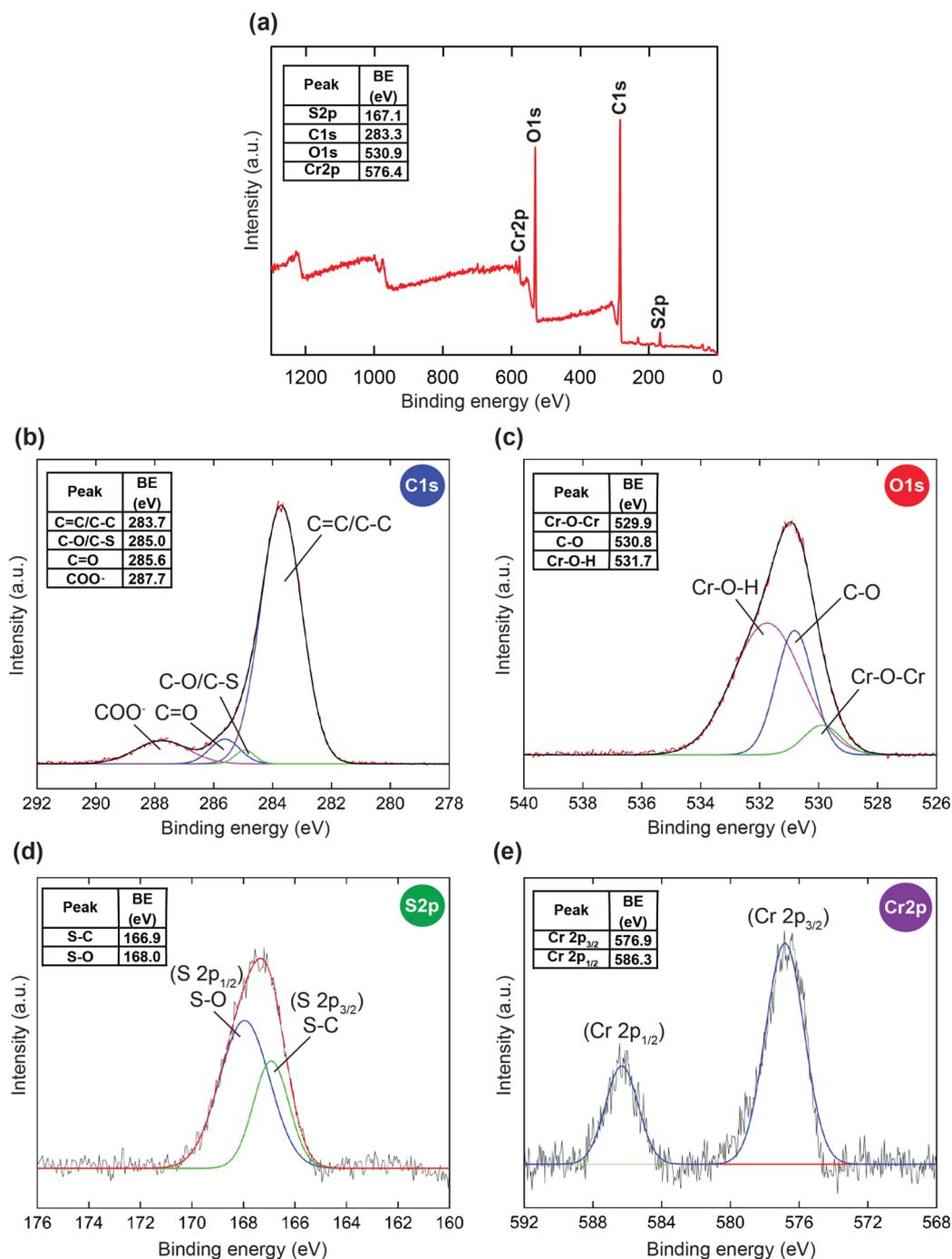


Fig. 3 The XPS analysis of MIL-101-SO₃H(N): the XPS survey of MIL-101-SO₃H(N) (red) (a); high-resolution spectrum of C 1s in MIL-101-SO₃H(N) (b); high-resolution spectrum of O 1s in MIL-101-SO₃H(N) (c); high-resolution spectrum of S 2p in MIL-101-SO₃H(N) (d); high-resolution spectrum of Cr 2p in MIL-101-SO₃H(N) (e).



stability to ensure performance under harsh practical conditions. With all this in mind, a mixture of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt and the H_3SNAAL linker was dissolved in water as a mild solvent in the presence of hydrofluoric acid and heated at $190\text{ }^\circ\text{C}$ for 24 h to obtain a dark green powder, termed MIL-101- $\text{SO}_3\text{H}(\text{N})$ (Fig. 1). Next, the solid was sequentially washed with water, ethanol, and acetone, to remove any residual precursors. The sample was then dried under dynamic vacuum at $120\text{ }^\circ\text{C}$ for 24 h to remove the solvents from the MOF structure. It is noteworthy that MIL-101- $\text{SO}_3\text{H}(\text{N})$ is constructed from trinuclear $\{\text{Cr}_3(\text{OH})(\text{H}_2\text{O})_2(\mu_3\text{-O})\}$ building units and bridging 6-sulfonaphthalene-1,4-dicarboxylate ligands to generate pentagonal and hexagonal windows measuring $6.8 \times 8.2\text{ \AA}$ and $8.5 \times 12.4\text{ \AA}$ in diameter, which are combined into mesoporous cages (Fig. 1). The window diameters of the structure were measured using CrystalMarker version 10.8 software, considering the van der Waals radii of the atoms. These pore window values agree with the pore distribution analysis of MIL-101- $\text{SO}_3\text{H}(\text{N})$ (Fig. S2†). Interestingly, MIL-101- $\text{SO}_3\text{H}(\text{N})$ possesses densely packed SO_3H groups and appropriate pore diameters, driving efficient capture of the heavy metal ions onto the MOF

backbone *via* electrostatic attraction between the negatively charged sulfonate moieties and the heavy metal cations, the selectivity of which is governed by the window pore size. Additionally, to evaluate the influence of the sulfonic groups on the adsorption capacity of the Pb^{2+} and Cu^{2+} ions, we prepared a Cr-based MOF with a structure similar to that of MIL-101- $\text{SO}_3\text{H}(\text{N})$, denoted as MIL(Cr)-Z1. MIL(Cr)-Z1 was synthesized by blending Cr^{3+} salt and the non- SO_3H -modified 1,4- H_2NDC linker in H_2O solvent in the presence of a mixture of acetic acid and HF as the modulators to support the crystal growth process, and the mixture was heated at $210\text{ }^\circ\text{C}$ for 10 h.⁵³

The single-phase level of MIL-101- $\text{SO}_3\text{H}(\text{N})$ was determined by powder X-ray diffraction (PXRD) measurement, which is in high accordance with the simulated structure based on lattice planes such as (3 3 -3), (1 5 -3), (6 0 6), (7 -5 -3), (6 6 -6), (5 -5 -1) (Fig. 2a). In particular, the crystallinity of MIL-101- $\text{SO}_3\text{H}(\text{N})$ is decreased during the activation process. This can be attributed to the strong interaction between the solvent molecules and the sulfonic groups *via* hydrogen bond networks, resulting in a structural order decline upon activation due to the release of guest molecules from the framework. This

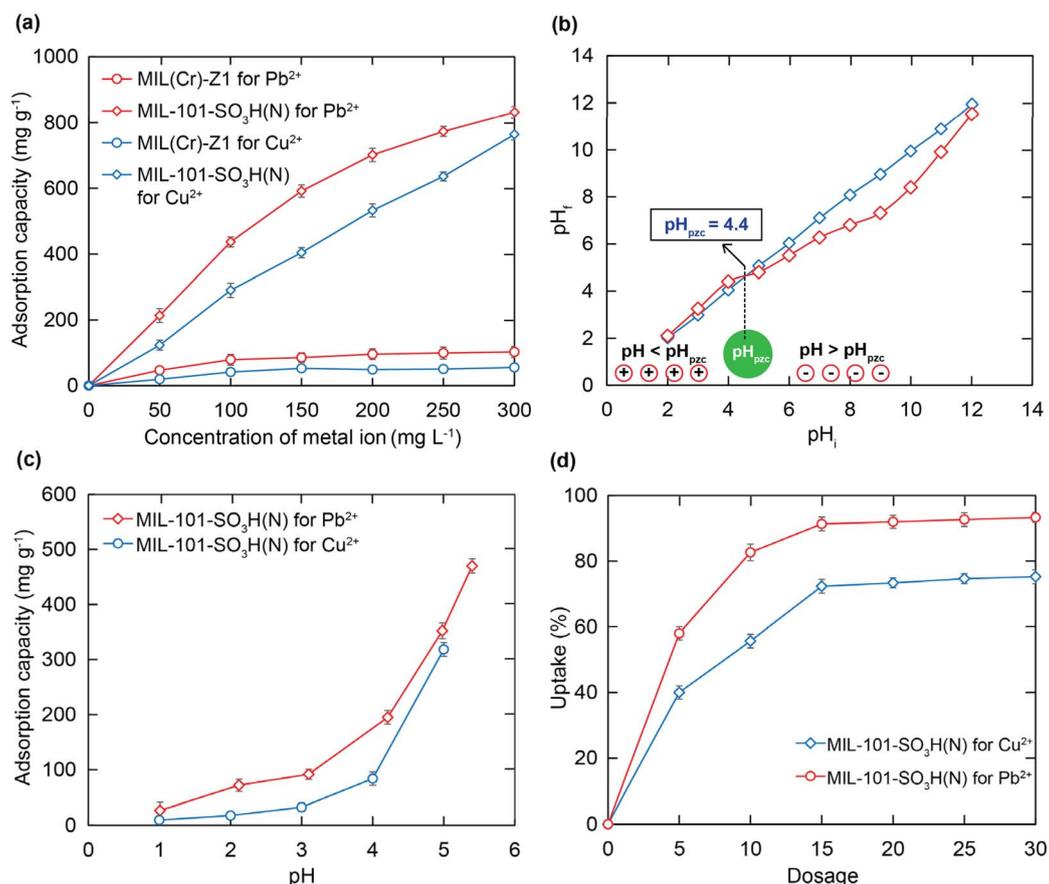


Fig. 4 Effect of the amount of SO_3H groups within the structures of MIL(Cr)-Z1 and MIL-101- $\text{SO}_3\text{H}(\text{N})$ on the Pb^{2+} and Cu^{2+} uptake capacity (a) [$m = 10\text{ mg}$, $V = 100\text{ mL}$, $C_0 = 50\text{--}300\text{ mg L}^{-1}$, $t = 24\text{ h}$, $\text{pH} = 5$]; the dependence of the original pH on the final pH for calculating pH_{pzc} (b); influence of solution pH on the adsorption capacity of Pb^{2+} and Cu^{2+} over MIL-101- $\text{SO}_3\text{H}(\text{N})$ at different concentrations of Pb^{2+} and Cu^{2+} (c) [$m = 10\text{ mg}$, $V = 100\text{ mL}$, $C_0 = 250\text{ mg L}^{-1}$, $t = 24\text{ h}$, $\text{pH} = 1\text{--}5.5$ for the Pb^{2+} uptake and $\text{pH} = 1\text{--}5$ for the Cu^{2+} uptake]; influence of MIL-101- $\text{SO}_3\text{H}(\text{N})$ content on the Pb^{2+} and Cu^{2+} uptake (d) [$m = 5\text{--}30\text{ mg}$, $V = 100\text{ mL}$, $C_0 = 50\text{ mg L}^{-1}$, $t = 24\text{ h}$, $\text{pH} = 5.5$ for the Pb^{2+} uptake and $\text{pH} = 5$ for the Cu^{2+} uptake].



phenomenon is also observed in the N_2 adsorption measurement at 77 K for the activated MIL-101-SO₃H(N) (Fig. S2†). Accordingly, the Langmuir and BET surface areas are 337.5 and 263.8 m² g⁻¹, respectively, which are much smaller than the specific surface values of non-SO₃H-functionalized MIL(Cr)-Zl.⁵³ The phenomenon is similar to that reported in previously published studies.^{32–34} Interestingly, the architectural order is restored after MIL-101-SO₃H(N) is immersed in water (Fig. 2a).

Furthermore, Raman spectra of activated MIL-101-SO₃H(N) and the H₃SNAA linker are clearly shown in Fig. 2b. In detail, the vibrational bands observed at 1067, 1383, 1439, and 1586 cm⁻¹ in the MIL-101-SO₃H(N) spectrum correspond to the SO₃⁻, C–O

and C=C bonds, respectively, but appear at different wavenumbers in the H₃SNAA linker spectrum. Particularly, the characteristic signal at 577 cm⁻¹ is assigned to the Cr–O absorption band in MIL-101-SO₃H(N), which is absent in the linker spectrum. Besides, the FT-IR spectra of H₃SNAA and MIL-101-SO₃H(N) are recorded and illustrated in Fig. 2c. Accordingly, vibrational modes corresponding to asymmetric C–O stretching, C=C stretching, symmetric C–O stretching, and SO₃⁻ groups located at 1616, 1526, 1394, and 1209 cm⁻¹, respectively, are observed in the MOF spectrum, while these bands appear at various positions in the linker spectrum. This can be explained by the formation of the coordination bonds

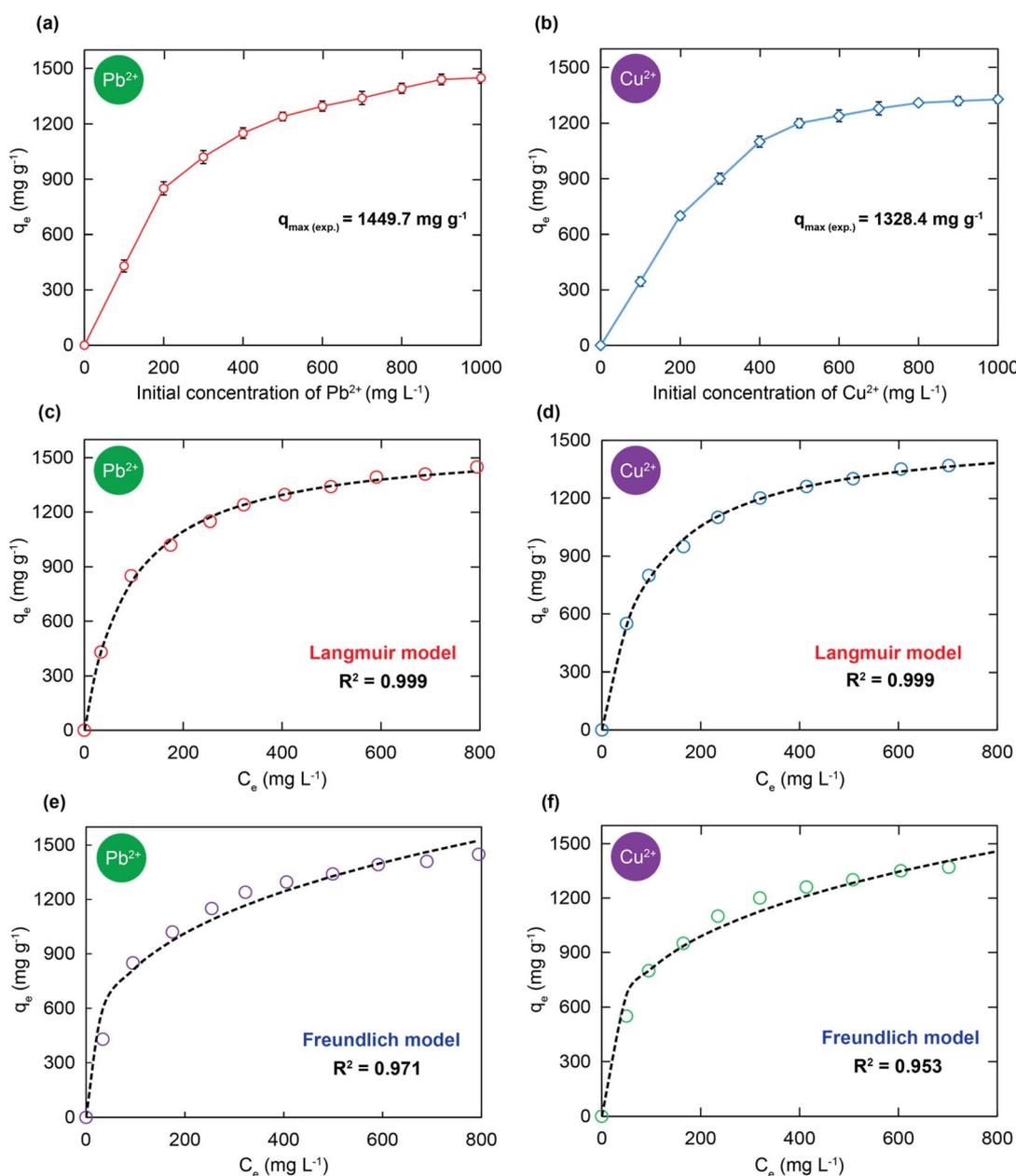


Fig. 5 Effect of initial concentration on the Pb²⁺ adsorption capacity (a), and the Cu²⁺ uptake capacity (b) over MIL-101-SO₃H(N) [$m = 15$ mg, $V = 100$ mL, $C_0 = 100$ – 1000 mg L⁻¹, $t = 24$ h, pH = 5.5 for the Pb²⁺ uptake, and pH = 5 for the Cu²⁺ uptake]. Data fitting with the adsorption isotherm models: Langmuir for Pb²⁺ (c), Langmuir for Cu²⁺ (d), Freundlich for Pb²⁺ (e), and Freundlich for Cu²⁺ (f).



within the MOF backbone. Notably, the Cr–O vibration is also found at 548 cm^{-1} , similar to the mentioned Raman spectrum.

To further gain insight into the features of MIL-101-SO₃H(N), TGA-DSC, SEM-EDX-mapping, TEM, and XPS analyses were carried out on the MOF sample. Accordingly, the TGA-DSC curve was recorded under dry air conditions (80% N₂ and 20% O₂) and is clearly illustrated in Fig. 2d. As a result, a weight loss of 10.1% from room temperature to 300 °C is assigned to the evaporation of surface absorbed and coordinated water molecules within the clusters of the material, owing to a maximum endothermic signal at 80.9 °C. Next, the weight loss of 29.9% with a strong exothermic signal at 423.6 °C is ascribed to the complete decomposition of the framework in the range of 300 to 700 °C. Hence, the architectural robustness of MIL-101-SO₃H(N) is indicated at about 300 °C. This shows that MIL-101-SO₃H(N) is a potential candidate for applications in practical situations. It is noteworthy that SEM and TEM measurements reveal that MIL-101-SO₃H(N) particles exhibit needle-like rod shapes with a highly uniform distribution with an average size of about 25–30 nm (Fig. 2e and f). In addition, the EDX-mapping spectrum exhibits a uniform presence of C, O, S, and Cr elements on the surface of the material (Fig. S3†). Particularly, XPS analyses display the coexistence of C, O, S, and Zr elements in MIL-101-SO₃H(N) (Fig. 3a). High-resolution spectra were utilized to assess the valence states of each element present on the surface of the material. In the high-resolution C 1s spectrum of MIL-101-SO₃H(N), different signals at 283.7, 285.0, 285.6, and 287.7 eV can be attributed to the existence of C=C/C–C, C–O/C–S, C=O, and COO[−] bonds inside MIL-101-SO₃H(N) (Fig. 3b).^{54–56} The O 1s curve is divided into three distinctive peaks at 529.9 eV for the Cr–O–Cr bond, 530.8 eV for the C–O bond, and 531.7 eV for the Cr–O–H bond (Fig. 3c).^{57,58} Subsequently, the high-resolution S 2p spectrum indicates the characteristic signals at 166.9 and 168.0 eV, corresponding to S 2p_{3/2} (S–C) and S 2p_{1/2} (S–O), respectively (Fig. 3d).⁵⁴ Notably, the Zr core level spectra in the MOF sample show two peaks at 576.9 and 586.3 eV, corresponding to Cr 2p_{3/2} and Cr 2p_{1/2}, respectively (Fig. 3e).^{57,59} These findings demonstrate the efficient functionalization of sulfonic moieties onto the MOF framework and the high phase purity of the material.

3.2 Effect of sulfonic groups

A series of survey experiments were conducted to interpret the influence of the amount of sulfonic moieties inside the MOF architecture on the metal ion uptake capacity. Consequently, 10 mg of MIL-101-SO₃H(N) and non-SO₃H-functionalized MIL(Cr)-Z1 were each added to 100 mL of heavy metal ion solutions with initial concentrations ranging from 50 to 300 mg L^{−1}. In detail, the MIL(Cr)-Z1 material possesses a low adsorption capacity for Pb²⁺ (102.7 mg g^{−1}) and Cu²⁺ (55.3 mg g^{−1}) with an original metal ion concentration of 300 mg L^{−1} at pH = 5 (Fig. 4a). This poor uptake can be attributed to the lack of negatively charged SO₃[−] moieties inside MIL(Cr)-Z1, causing weak interaction between the capturing sites and the metal cations. In contrast, the Pb²⁺ and Cu²⁺ uptake capacity of MIL-101-SO₃H(N) is 831.7 and 764.1 mg g^{−1} at pH = 5, respectively

(Fig. 4a). It is noted that the excellent adsorption capacity of metal ions over MIL-101-SO₃H(N) is attributed to the generation of the effective electrostatic attraction between the negatively charged carriers and the Pb²⁺ and Cu²⁺ ions. Thus, we choose MIL-101-SO₃H(N) to investigate the subsequent uptake studies in this work.

3.3 Effect of pH

Solution pH is well known as a key parameter, as it considerably influences the electrostatic interactions between the MOF surface and charged moieties.^{60,61} Investigations were performed to explore the pH_{pzc} of MIL-101-SO₃H(N). As indicated in Fig. 4b, the pH_{pzc} of the material is 4.4, indicating that the surface carries a positive charge below this point of zero charge and a negative charge above it. Continuously, experiments were performed to prove the effect of solution pH in a range from 1 to 5.5 for Pb²⁺ and from 1 to 5 for Cu²⁺. It is worth noting that the precipitation of Pb²⁺ and Cu²⁺ occurs at pH values ≥6 and ≥5.5,^{52,62} respectively, and they will separate from the mixture, driving difficulties in quantifying whether they appear due to precipitation or adsorption into the material. Fig. 4c shows the significant dependence of the solution pH on the adsorption capacity. In detail, in the pH region from 1 to 4 (<pH_{pzc}), relatively low adsorption levels of metal ions are observed. This can be explained by the protonation of sulfonic species within the MOF to form the SO₃H₂⁺ states, resulting in a great repulsion of positively charged types such as metal cations, H⁺ ions, and inner/external walls of MIL-101-SO₃H(N). Meanwhile, the uptake capacity of Pb²⁺ and Cu²⁺ promptly increases in a pH

Table 1 The fitting result confirmed from the adsorption isothermal models of Pb²⁺ and Cu²⁺ over MIL-101-SO₃H(N)

| Isothermal models | Parameters | Value | |
|----------------------------------|---|---|---------------------------|
| Uptake of Pb²⁺ | | | |
| | Langmuir | q_m (mg g ^{−1}) K_L (L mg ^{−1}) R^2 | 1586.7 0.0111 0.999 |
| | Freundlich | $1/n$ K_F (mg g ^{−1} (L g ^{−1}) ^{1/n}) R^2 | 0.297 210.61 0.971 |
| DR | K_{DR} (mg g ^{−1}) R^2 | 0.173 0.993 | |
| Temkin | K_T (L mg ^{−1}) β R^2 | 0.134 7.813 0.989 | |
| Uptake of Cu²⁺ | | | |
| | Langmuir | q_m (mg g ^{−1}) K_L (L mg ^{−1}) R^2 | 1545.1 0.0107 0.999 |
| | Freundlich | $1/n$ K_F (mg g ^{−1} (L g ^{−1}) ^{1/n}) R^2 | 0.281 222.84 0.953 |
| DR | K_{DR} (mg g ^{−1}) R^2 | 0.176 0.992 | |
| Temkin | K_T (L mg ^{−1}) β R^2 | 0.142 8.239 0.987 | |



range over pH_{pzc} , which can be assigned to the deprotonation process of sulfonic groups to create a high negative charge density at the surface and inside the MOF backbone, leading to effective electrostatic interaction between the $\text{Pb}^{2+}/\text{Cu}^{2+}$ ions and MIL-101- $\text{SO}_3\text{H}(\text{N})$.^{35,48,63} Hence, the optimal pH values, such as 5.5 for Pb^{2+} and 5 for Cu^{2+} , are selected for the subsequent studies.

3.4 Influence of the MOF dosage

To evaluate the best dosage of the material during the uptake of the metal ions, various contents of MIL-101- $\text{SO}_3\text{H}(\text{N})$ from 5 to 30 mg were introduced into the metal ion solutions and stirred for 24 h at the previously optimised pH. As shown in Fig. 4d, the adsorption efficiency increased from 58 to 91% for Pb^{2+} and from 40 to 72% owing to raising the dosage from 5 to 15 mg. It can be described that the number of capturing sites and adsorption spaces will rise with the increase of the MOF content, driving the efficient removal of the heavy metal ions

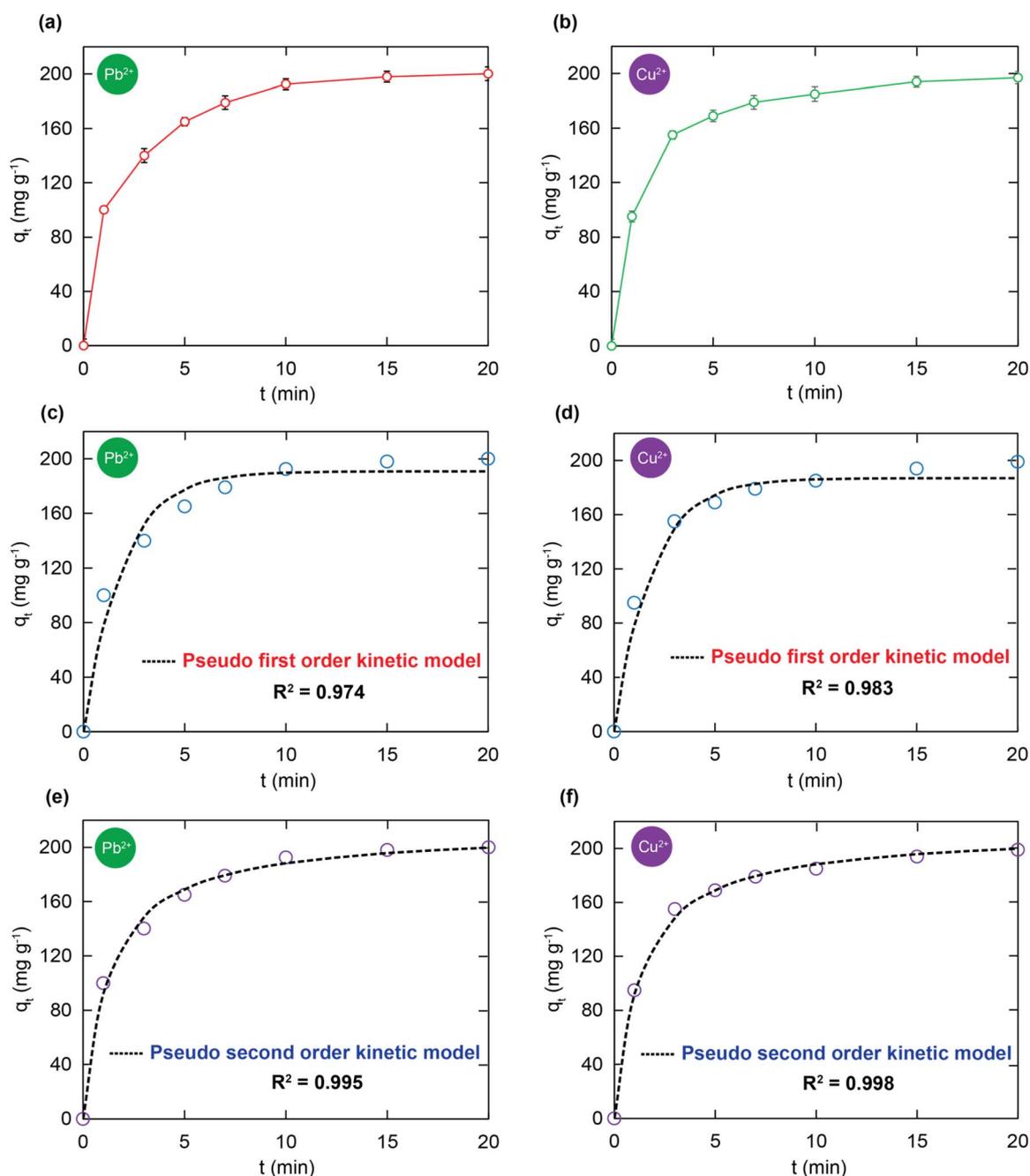


Fig. 6 The kinetic results for the Pb^{2+} (a) and Cu^{2+} (b) uptake by MIL-101- $\text{SO}_3\text{H}(\text{N})$ [$m = 5$ mg, $V = 50$ mL, $C_0 = 40$ mg L^{-1} , $t = 1$ –20 min, $\text{pH} = 5$]; fitting results with the adsorption kinetic models: pseudo-first-order for Pb^{2+} (c) and for Cu^{2+} (d), pseudo-second-order for Pb^{2+} (e) and for Cu^{2+} (f).



from an aqueous medium. However, there is no significant change in the uptake of Pb^{2+} and Cu^{2+} as the MIL-101- $\text{SO}_3\text{H}(\text{N})$ content increases from 15 to 30 mg, indicating that the adsorption equilibrium has been reached. Therefore, the optimal dosage of 15 mg is employed for the subsequent studies.

3.5 Uptake isotherms

To explore the nature of the Pb^{2+} and Cu^{2+} uptake by MIL-101- $\text{SO}_3\text{H}(\text{N})$, adsorption isotherm studies were carried out. Interestingly, the dominant rise in the capturing capacity of the heavy metal ions was confirmed by the increase of the Pb^{2+} and Cu^{2+} original concentration from 100 to 1000 mg L^{-1} (Fig. 5a and b). Accordingly, the highest adsorption capacity of MIL-101- $\text{SO}_3\text{H}(\text{N})$ is 1449.7 mg g^{-1} for Pb^{2+} and 1328.4 mg g^{-1} for Cu^{2+} . Furthermore, to elucidate the adsorption mechanism of Pb^{2+} and Cu^{2+} onto the MOF material, isothermal models such as Langmuir, Freundlich, Dubinin-Radushkevich (DR), and Temkin were used with non-linear fittings revealed in eqn (S1)–(S4) (see Section S7†).

As illustrated in Fig. 5c–f and S4,† non-linear fitting curves and data of the uptake models for the heavy metal ion adsorption over MIL-101- $\text{SO}_3\text{H}(\text{N})$ are described and clearly indicated in Table 1. Consequently, the value of the non-linear fitting coefficient for the Langmuir type ($R^2 = 0.999$ for both Pb^{2+} and Cu^{2+}) is greater than those of the Freundlich ($R^2 = 0.971$ for Pb^{2+} and 0.953 for Cu^{2+}), DR ($R^2 = 0.993$ for Pb^{2+} and 0.992 for Cu^{2+}), and Temkin ($R^2 = 0.989$ for Pb^{2+} and 0.987 for Cu^{2+}) models. In particular, the theoretical adsorption capacity of the heavy metal ions determined from the intercept of the Langmuir model is 1586.7 mg g^{-1} for Pb^{2+} and 1545.1 mg g^{-1} , which are very close to the experimental data (1449.7 mg g^{-1} for Pb^{2+} and 1328.4 mg g^{-1} for Cu^{2+}). The obtained results indicate that a monolayer of Pb^{2+} and Cu^{2+} is formed at the interface between the MOF material and heavy metal ions. Additionally, it is supposed that capturing metal ions over MIL-101- $\text{SO}_3\text{H}(\text{N})$ is a chemisorption process based on the strong electrostatic attraction between the positively charged heavy metal ions and negatively charged SO_3^- moieties within the MOF architecture.

3.6 Adsorption kinetics

The effect of contact time on the adsorption capacity of the metal ions onto MIL-101- $\text{SO}_3\text{H}(\text{N})$ was investigated. Consequently, 5 mg of MIL-101- $\text{SO}_3\text{H}(\text{N})$ was added to 50 mL of the $\text{Pb}^{2+}/\text{Cu}^{2+}$ solution with an initial concentration of 40 mg L^{-1} at $\text{pH} = 5$. To prevent incorrect measurements in the short reaction time, the pH of 5 and the content of 5 mg are selected to explore the uptake kinetics because the $\text{Pb}^{2+}/\text{Cu}^{2+}$ adsorption rate is rapid at a higher material content and pH over 5. As illustrated in Fig. 6a and b, the removal rate of Pb^{2+} and Cu^{2+} over the MIL-101- $\text{SO}_3\text{H}(\text{N})$ material rises promptly in the original 5 min and reaches equilibrium after 10 min. Herein, the rapid adsorption rate is a key factor for practical applications of the material, overcoming the obstacles of the previously reported traditional materials. Besides, the uptake property is influenced by several factors, including diffusion time and

chemical reaction. Kinetic models including pseudo-first-order, pseudo-second-order, and intra-particle diffusion (see the eqn (S5)–(S7) in Section S7†) were applied to obtain a deeper insight into the removal mechanism of the heavy metal ions on the MOF.

As a result, the non-linear fitting curves and data are revealed in Fig. 6c–f and Table 2. Accordingly, the non-linear fitting coefficient values of the pseudo-second-order model ($R^2 = 0.995$ for Pb^{2+} and 0.998 for Cu^{2+}) are higher than those of the pseudo-first-order model ($R^2 = 0.974$ for Pb^{2+} and 0.983 for Cu^{2+}). Thus, the adsorption of Pb^{2+} and Cu^{2+} over MIL-101- $\text{SO}_3\text{H}(\text{N})$ is characterized as chemisorption, indicating electron transport by the interaction between the sulfonate moieties inside the framework and the heavy metal cations.^{48,64,65} It is noteworthy that, as shown in Fig. S9,† the uptake of $\text{Pb}^{2+}/\text{Cu}^{2+}$ can be divided into three steps. In the first step, the metal ions will rapidly move to the external surface of the material from the solution. Next, the $\text{Pb}^{2+}/\text{Cu}^{2+}$ ions diffuse into the internal channels of MIL-101- $\text{SO}_3\text{H}(\text{N})$, facing increased diffusion resistance. Finally, these metal ions slowly penetrate the pores of the MOF material and interact with the sulfonic groups of the backbone until the equilibrium state is established.

3.7 Regeneration investigation

The reusability of the adsorption material is considered a valuable factor in reducing product costs. Hence, the regeneration of MIL-101- $\text{SO}_3\text{H}(\text{N})$ in Pb^{2+} and Cu^{2+} adsorption was performed for eight consecutive cycles. As shown in Fig. 7a and b, the uptake yield was 93% for Pb^{2+} and 92% for Cu^{2+} after eight recycles without any considerable decrease in adsorption efficiency. Notably, the complete reusability of the material was confirmed by PXRD and FT-IR measurements. In detail, the PXRD patterns of MIL-101- $\text{SO}_3\text{H}(\text{N})$ after desorption of Pb^{2+} and Cu^{2+} ions show good agreement with those of the material before adsorption (Fig. 7c). Subsequently, the vibrational modes of MIL-101- $\text{SO}_3\text{H}(\text{N})$ after heavy metal ion desorption show no

Table 2 Pseudo first order and second order model parameters for the Pb^{2+} and Cu^{2+} uptake by MIL-101- $\text{SO}_3\text{H}(\text{N})$

| Kinetic models | Parameters | Value |
|--|--|-------|
| Uptake of Pb^{2+} | | |
| Pseudo first order | $q_{e,\text{exp}}$ (mg g^{-1}) | 199.8 |
| | $q_{e,\text{cal}}$ (mg g^{-1}) | 180.8 |
| | k_1 (min^{-1}) | 0.529 |
| | R^2 | 0.974 |
| Pseudo second order | $q_{e,\text{cal}}$ (mg g^{-1}) | 212.8 |
| | k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) | 2385 |
| | R^2 | 0.995 |
| Uptake of Cu^{2+} | | |
| Pseudo first order | $q_{e,\text{exp}}$ (mg g^{-1}) | 199.1 |
| | $q_{e,\text{cal}}$ (mg g^{-1}) | 177.0 |
| | k_1 (min^{-1}) | 0.538 |
| | R^2 | 0.983 |
| Pseudo second order | $q_{e,\text{cal}}$ (mg g^{-1}) | 211.1 |
| | k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) | 2347 |
| | R^2 | 0.998 |



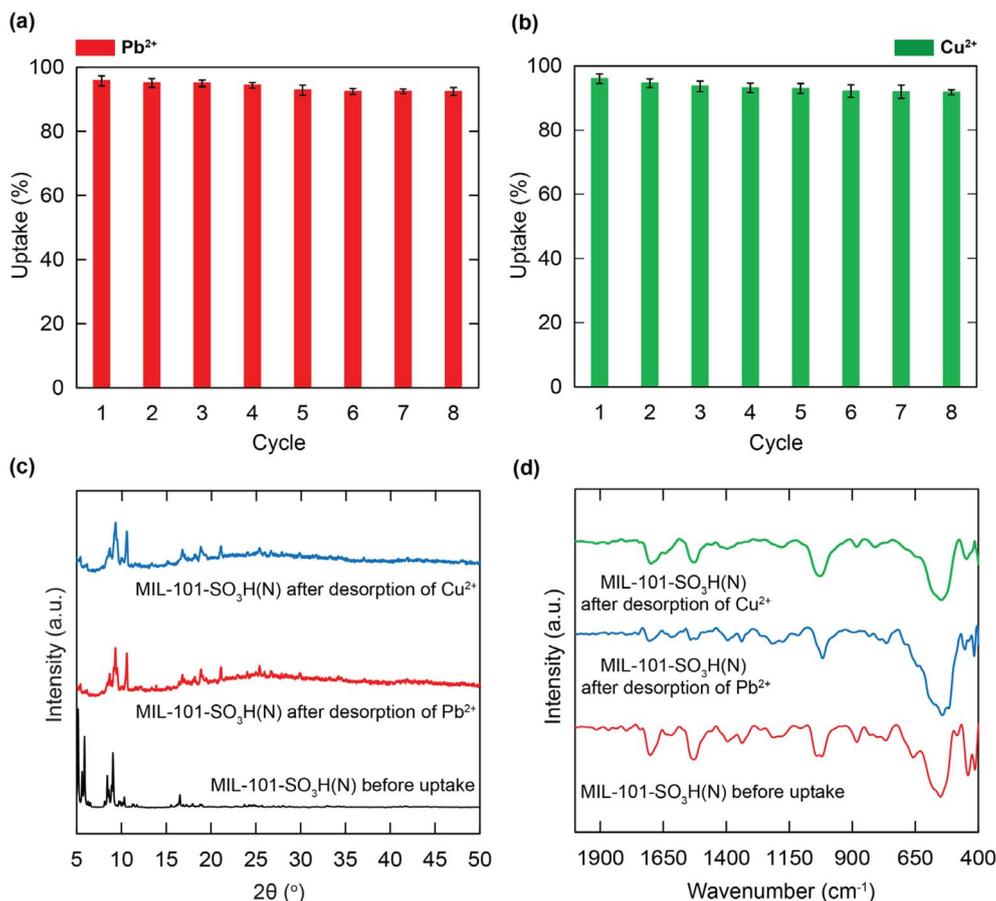


Fig. 7 The reusability of MIL-101-SO₃H(N) in Pb²⁺ uptake (a), and in Cu²⁺ uptake (b); the PXRD analysis of MIL-101-SO₃H(N) before uptake (black) in comparison with the PXRD pattern of MIL-101-SO₃H(N) after desorption of Pb²⁺ (red), and Cu²⁺ (blue) (c); the FT-IR spectra of MIL-101-SO₃H(N) before uptake (red) and after desorption of Pb²⁺ (blue) and Cu²⁺ (green) (d).

Table 3 The maximum adsorption capacity of Pb²⁺ onto MIL-101-SO₃H(N) in comparison with other materials

| Adsorption of Pb ²⁺ | | | |
|---|----------------------------------|------------|-------------------|
| Materials | q_{\max} (mg g ⁻¹) | pH | Ref. |
| VNU-23 | 617.3 | 5.5 | 48 |
| MIL-101(Cr)-NH ₂ | 88.0 | 6.0 | 56 |
| Tb-MOFs | 547.0 | 5.5 | 62 |
| Active carbon | 43.9 | 5.7 | 66 |
| MoS ₂ biochar | 189 | 5.0 | 67 |
| UiO-66-(COOH) ₂ | 420.2 | 4.8 | 68 |
| HCMUE-2 | 1115.9 | 5.5 | 69 |
| Fe-MIL-88NH ₂ | 106.0 | 7.0 | 70 |
| COF-NHOH | 368.7 | 5.0 | 71 |
| COF-SH | 239.0 | 5.0 | 72 |
| Mn-Goethite 4 | 90.1 | 5.0 | 73 |
| Fe ₃ O ₄ -SO ₃ H | 108.9 | 7.0 | 74 |
| MIL(Cr)-Z1 | 102.7 | 5.0 | This study |
| MIL-101-SO₃H(N) | 1449.7 | 5.5 | |

significant change as compared to the material before Pb²⁺/Cu²⁺ uptake (Fig. 7d). These data proved that MIL-101-SO₃H(N) could be used as an efficiently reusable adsorbent in removing highly toxic heavy metal ions from wastewater.

To further confirm the features of the MIL-101-SO₃H(N) material, the maximum Pb²⁺/Cu²⁺ adsorption capacity of the material was compared with those of other adsorbents in Tables 3 and 4. MIL-101-SO₃H(N) has a much higher adsorption

Table 4 The maximum adsorption capacity of Cu²⁺ onto MIL-101-SO₃H(N) in comparison with other materials

| Adsorption of Cu ²⁺ | | | |
|---|----------------------------------|------------|-------------------|
| Materials | q_{\max} (mg g ⁻¹) | pH | Ref. |
| HAP/HA | 58.4 | 5.0 | 75 |
| MOF-5 | 290.0 | 5.2 | 76 |
| MIL-68(Ga) | 130.0 | 3.0 | 77 |
| TEPA-MIL-101(Cr) | 217.7 | 6.5 | 78 |
| [[Zn ₃ L ₃ (H ₂ O) ₆]][(Na)(NO ₃)] | 379.1 | 6.0 | 79 |
| ZIF-8/PAN | 275.7 | 4.0 | 80 |
| Biochar acrylic-based hydrogel | 678.0 | 6.0 | 81 |
| ZIF-8 | 454.7 | 5.1 | 82 |
| ZIF-67 | 617.5 | 5.2 | 82 |
| Chitosan-grafted-poly (acrylic acid) | 333.3 | 5.5 | 83 |
| Natural clays | 56.6 | 5.5 | 84 |
| MIL(Cr)-Z1 | 53.3 | 5.0 | This study |
| MIL-101-SO₃H(N) | 1328.4 | 5.0 | |



capacity than the other adsorption materials. This can be demonstrated by the sulfonate moieties incorporated and the large pore diameter of the MOF structure, which play an important role in heavy metal ion uptake.

3.8 Plausible uptake mechanism

The ultra-high adsorption performance boosted further investigation into the attraction between the SO_3^- groups inside MIL-101- $\text{SO}_3\text{H}(\text{N})$ and the $\text{Pb}^{2+}/\text{Cu}^{2+}$ cations by measurements, including FT-IR and XPS analyses.

It is noteworthy that the FT-IR spectra of $\text{Pb} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$ and $\text{Cu} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$ exhibit shifts to new

positions at 533 (517), 1196 (1201), 1384 (1377), and 1611 (1608) cm^{-1} , corresponding to the characteristic modes of Pb-O (Cu-O), SO_3^- , symmetric C-O, and asymmetric C-O, respectively (Fig. S5 and S6[†]). These findings demonstrate the strong interaction, resulting in the generation of robust chemical bonds between the sulfonate groups and the $\text{Pb}^{2+}/\text{Cu}^{2+}$ ions and moving the characteristic frequency bands to lower wave-number regions. This phenomenon has also been observed in previous studies.^{48,69} In addition, the adsorption mechanism was further confirmed with the XPS analysis. As shown in Fig. 8a, the XPS spectra of $\text{Pb} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$ and $\text{Cu} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$ indicate the presence of C, O, S, and Cr elements,

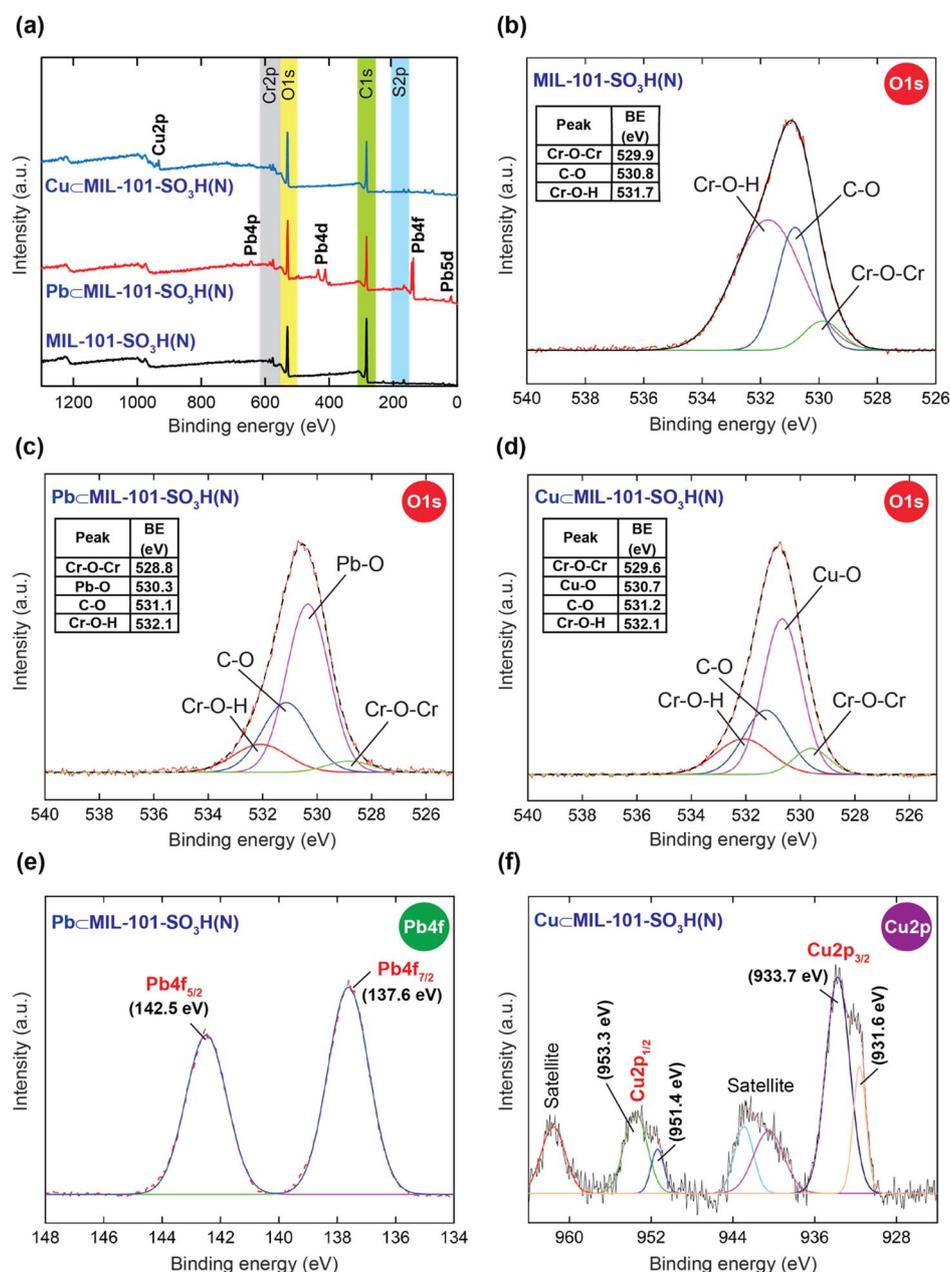


Fig. 8 The XPS measurement of MIL-101- $\text{SO}_3\text{H}(\text{N})$ before and after Pb^{2+} and Cu^{2+} adsorption: (a) the XPS survey; (b) high-resolution curve of O 1s in MIL-101- $\text{SO}_3\text{H}(\text{N})$; (c) high-resolution spectrum of O 1s in $\text{Pb} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$; (d) high-resolution spectrum of O 1s in $\text{Cu} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$; (e) the Pb 4f XPS spectrum in $\text{Pb} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$; (f) the Cu 2p XPS spectrum in $\text{Cu} \subset \text{MIL-101-SO}_3\text{H}(\text{N})$.



consistent with the MIL-101-SO₃H(N) spectrum. In detail, new different peaks appeared at 20.5, 138.5, 433.8, and 642.6 eV, corresponding to Pb 5d, Pb 4f, Pb 4d, and Pb 4p, respectively, in the Pb◊MIL-101-SO₃H(N) spectrum. Meanwhile, in the Cu◊MIL-101-SO₃H(N) spectrum, there is a new peak at 933.3 eV, corresponding to the Cu 2p signal within the material, indicating that MIL-101-SO₃H(N) efficiently captured the Pb²⁺/Cu²⁺ cations over the MOF backbone. Next, the O 1s spectra of Pb◊MIL-101-SO₃H(N) (Cu◊MIL-101-SO₃H(N)) are divided into four characteristic peaks located at 528.8 (529.6), 530.3 (530.7), 531.1 (531.2), and 532.1 (532.1) eV, which are assigned to the Cr–O–Cr, Pb–O (Cu–O), C–O, and Cr–O–H bonds (Fig. 8c and d).^{48,59} It is interesting to note that these peaks move to various binding energy ranges as compared to MIL-101-SO₃H(N), such as 529.9 eV for Cr–O–Cr, 530.8 eV for C–O, and 531.7 eV for Cr–O–H (Fig. 8b).^{48,59} Furthermore, the Pb–O and Cu–O peaks are not present in the O 1s curve of MIL-101-SO₃H(N). This can be explained by the strong interaction between the heavy metal cations and the adsorption sites within the framework. Considerably, the high-resolution band of Pb 4f in the Pb◊MIL-101-SO₃H(N) sample is separated into signals at 137.6 and 142.5 eV, corresponding to Pb 4f_{7/2} and Pb 4f_{5/2}, respectively. Similarly, the Cu 2p high-resolution spectrum is deconvoluted into peaks at 931.6 and 933.7 eV for Cu 2p_{3/2}, and at 951.4 and 953.3 eV for Cu 2p_{1/2}, along with the satellite peaks of Cu◊MIL-101-SO₃H(N). The Pb 4f and Cu 2p peaks have different signals compared with the pure solution of Pb²⁺ and Cu²⁺.^{64,68,85} This further strengthens the explanation that the O species originating from the sulfonic groups, μ-OH-containing clusters, and COO[−] in the linkers within the MOF structure can effectively coordinate with the Pb²⁺ and Cu²⁺ ions to create metal-oxo bonds.

4 Conclusion

In summary, a new MIL-101-type Cr-based MOF incorporating a large number of sulfonic moieties and having a suitable pore diameter was fabricated and investigated for its uptake performance for Pb²⁺ and Cu²⁺ cations. Accordingly, MIL-101-SO₃H(N) exhibited the highest adsorption capacity for the heavy metal ions, reaching 1449.7 mg g^{−1} for Pb²⁺ and 1328.4 mg g^{−1} for Cu²⁺ at an optimal pH value. To the best of our knowledge, these values are much larger than those of other adsorbents reported for capturing highly toxic heavy metal ions. Additionally, the uptake of Pb²⁺ and Cu²⁺ occurs *via* chemisorption, as evidenced by the good agreement with the Langmuir isotherm and pseudo-second-order kinetic models. Furthermore, regeneration experiments reveal that Pb²⁺ and Cu²⁺ adsorption is maintained for at least eight consecutive cycles without any significant loss in efficiency. Notably, the uptake mechanism is elucidated through combined modern techniques. All achieved data exhibit that the adsorption mechanism can be confirmed by the formation of strong chemical attraction through the electrostatic interaction of the sulfonate groups located in the MOF backbone and the metal cations. These observations affirm that the sulfonic-modified Cr-based MOF is a potential adsorbent in removing Pb²⁺ and Cu²⁺ ions from wastewater. In

addition, the structural order of sulfonic-based MOFs is lost upon activation due to the high flexibility of SO₃H groups. Therefore, future research should focus on immobilizing sulfonic moieties through functional group incorporation to form a rigid backbone for applications in the gaseous phase, as well as comprehensively evaluating the competition of other ions during Pb²⁺ and Cu²⁺ uptake.

Data availability

Data available on request from the corresponding author.

Author contributions

M. V. N. formulated this project. M. V. N., H. K. D., T. M. N., L. C. L., and H. N. N. prepared the materials and collected the PXRD, FT-IR and Raman spectra, and TGA/DSC curves. M. V. N. analyzed all experimental data. M. V. N. wrote the paper and all authors contributed to revising it. All authors have approved the final version of the manuscript.

Conflicts of interest

The authors maintain that they have no conflict of interest for this communication.

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