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High and rapid perfluorooctanoic acid capture by MOF-818 via synergistic adsorption

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The persistent environmental contamination and toxicity of perfluorooctanoic acid (PFOA) necessitate adsorbents that combine high capacity, fast kinetics, and robust recyclability. Metal–organic frameworks (MOFs) offer tunable porosity and functionality, yet integrating these attributes into a single material remains challenging. Here, we demonstrate that MOF-818, a mesoporous MOF featuring two distinct secondary building units (Zr₆ and Cu₃ clusters) with abundant open metal sites (OMSs), achieves exceptionally efficient PFOA removal via a synergistic adsorption mechanism. The OMSs enable strong chemisorption of PFOA carboxylate groups, while the hierarchical mesopores (3.8 nm) facilitate rapid diffusion and subsequent physisorption of PFOA chains. This synergy yields an adsorption equilibrium within 5 minutes and a high capacity of 1.51 g g^{−1} (3.65 mmol g^{−1}), with effective removal even at trace concentrations (from 250 μg L^{−1} to ~15 μg L^{−1}). MOF-818 also exhibits excellent selectivity against common coexisting ions and retains 97% of its capacity after eight regeneration cycles. Combined experimental and computational analyses confirm that chemisorption at OMSs initiates the process and enables subsequent physisorption. This work highlights the power of engineering dual adsorption modes within a single MOF platform as a superior strategy for rapid and high-capacity remediation of per- and polyfluoroalkyl substances (PFAS).

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals characterized by fully fluorinated carbon chains, imparting exceptional thermal and chemical stability.^{1–3} This very stability, however, renders them persist-

ent “forever chemicals” in the environment, leading to widespread contamination of water resources and bioaccumulation in living organisms.^{4–7} Among PFAS, perfluorooctanoic acid (PFOA) has been extensively studied due to its historical prevalence and documented links to adverse health effects, including cancer,^{8–10} thyroid disease,^{11,12} and developmental issues.¹³ Consequently, regulatory bodies worldwide are enforcing increasingly stringent limits on PFOA in drinking water, highlighting the urgent need for effective removal technologies.^{2,14,15}

Current methods for PFAS removal include adsorption,^{16–18} ion exchange,^{19,20} advanced oxidation,^{21–23} and membrane filtration.^{24–27} Among these, adsorption is often preferred for its operational simplicity, cost-effectiveness, and potential for regenerability. Activated carbon and ion-exchange resins are the most widely used adsorbents but often suffer from slow kinetics, moderate capacities, and poor selectivity in complex water matrices.^{28–31} The porous organic polymer functionalized with synergistic electrostatic/hydrophobic sites exhibits an exceptionally high PFOA adsorption capacity of over 2000 mg g^{−1} and rapid removal kinetics, although its practical application may be constrained by complex synthesis and imperfect structural control.^{1,32} Hence, the pursuit of next-generation adsorbents demands a focus on three key attributes: high performance, synthetic simplicity, and structural definability, which together form a vital research objective.

Metal–organic frameworks (MOFs), defined crystalline porous materials constructed from metal ions/clusters and organic linkers in easy one-pot strategy, have emerged as promising candidates for environmental remediation.^{33–35} These features—high surface area, tunable pore geometry, and customizable chemical functionality—collectively enable the precise design of host–guest interactions, thus holding great promise for PFAS removal.^{36–39} In particular, zirconium-based MOFs (Zr-MOFs) are renowned for their exceptional chemical and thermal stability, a prerequisite for practical water treatment applications.^{40–42} The incorporation of open metal sites (OMSs), or coordinatively unsaturated sites (CUS), within MOF structures provides specific, high-affinity binding points for

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target molecules containing Lewis basic groups, such as the carboxylate group in PFOA.^{43,44}

While recent studies have begun exploring MOFs for PFAS capture, achieving a combination of high capacity, ultrafast kinetics, and a clear mechanistic understanding remains a significant challenge.^{43–45} For instance, the novel Zr-MOF, PCN-999, featuring unique biformate-bridged (Zr₆)₂ clusters with OMSSs, demonstrated a high PFOA capacity of 1089 mg g^{−1}, attributed to synergistic chemical and physical adsorption. However, its adsorption equilibrium was reached in 12 hours.⁴⁶

In this work, we turn our attention to MOF-818, a chemically robust MOF comprising both [Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₆(μ-PyC)₆(H₂O)₆] (Zr₆) and Cu₃(μ₃-O)(μ-PyC)₃(H₂O)₃ (Cu₃) clusters connected by a simple pyrazole-carboxylate linker.^{47–49} This structure creates a mesoporous cage (the ‘wuh’ cage) with diameter of 3.8 nm and a microporous supertetrahedra with size of 1.8 nm, more importantly, a high density of OMSSs on both types of metal clusters. We hypothesized that these OMSSs could serve as primary anchors for PFOA molecules *via* coordination of the carboxylate group, while the spacious mesopores would facilitate rapid diffusion and accommodate subsequent multilayer physical adsorption through hydrophobic interactions between fluorinated chains (Fig. 1).

Herein, we detail the synthesis of MOF-818 and systematically evaluate its PFOA adsorption performance, including capacity, kinetics, selectivity, and reusability. The results confirm that MOF-818 exhibits a high PFOA uptake capacity of 1.51 g g^{−1} (3.65 mmol g^{−1}) along with fast kinetics, achieving adsorption equilibrium within 5 minutes. Through diverse post-adsorption characterization, we provide compelling evidence for a synergistic adsorption mechanism, wherein coordination to OMSSs, initiates a chemisorption process that is complemented by efficient physisorption within the mesopores.^{50–53} This study not only introduces MOF-818 as a good performing adsorbent for PFOA but also offers valuable

insights into the molecular-level design principles for advanced PFAS capture materials.

Experimental

Materials

All chemicals and solvents are commercially available and can be used as received without further purification. Zirconyl chloride octahydrate (ZrOCl₂·8H₂O), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), trifluoroacetic acid, *N,N*-dimethylformamide (DMF), perfluorooctanoic acid (PFOA), 2,2,2-trifluoroethanol, ferric chloride, aluminum trichloride, potassium chloride, sodium sulfate, acetic acid, magnesium nitrate, zinc chloride, manganese(II) chloride, calcium sulfate, and sodium chloride were purchased from Shanghai Titan Scientific Co., Ltd (China). 1*H*-Pyrazole-4-carboxylic acid (H₂PyC) was purchased from Bide Pharmatech Co., Ltd (China). Acetone was purchased from Sinopharm Chemical Reagent Co., Ltd (China).

Instruments

The powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Da Vinci powder diffractometer with a Cu microfocus tube ($\lambda = 1.54178 \text{ \AA}$) at 40 kV and 25 mA. Transmission electron microscope (TEM) images were recorded on Thermo Fisher Talos L120C G2 at an accelerating voltage of 120 kV. The morphology and elemental distribution analysis were recorded on an Apreo 2S field emission scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) at 15 kV acceleration voltage. X-ray photoelectron spectroscopy (XPS) was analyzed using an ESCALAB Xi+ instrument from Thermo Scientific and the C 1s peak at 284.8 eV. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet iS50 using an attenuated total reflection (ATR) attachment. ¹⁹F NMR spectra were obtained on a Bruker 500

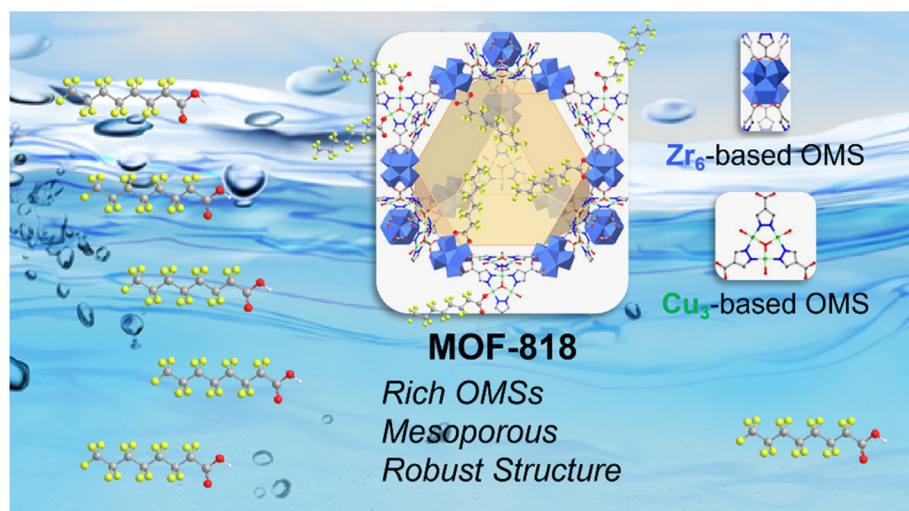


Fig. 1 Structure of MOF-818 and the accessible OMSSs within two clusters.

spectrometer. Thermogravimetric analysis (TGA) measurement was conducted on a TGA550 under nitrogen (N_2) atmosphere with a ramp rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature and $800\text{ }^\circ\text{C}$. N_2 adsorption–desorption measurement was performed on an ASAP 2460 system and measured at 77 K . The low concentration of PFOA was detected through ultra-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC-MS/MS). Inductively coupled plasma mass spectrometry (ICP-MS) (i CAP Q, Thermo) was used to detect the selective adsorption of PFOA over various salts.

Preparation of MOF-818

MOF-818 was synthesized according to previous reports.⁴⁷ Briefly, $ZrOCl_2 \cdot 8H_2O$ (212.5 mg), $Cu(NO_3)_2 \cdot 3H_2O$ (620.0 mg), H_2PyC (162.5 mg), and DMF (50 mL) were successively added to a 100 mL reaction vessel. Ultrasonication was applied to achieve a homogeneous mixture. Subsequently, trifluoroacetic acid (TFA, 0.6 mL) was introduced, and the mixture was heated at $100\text{ }^\circ\text{C}$ for 10 hours. After cooling to room temperature, the product was isolated by centrifugation (10 000 rpm, 10 min). The collected solid was then soaked in DMF for three days, with solvent exchange performed five times per day, followed by soaking in acetone for four days under the same exchange regimen. Finally, the sample was dried under vacuum at room temperature to yield MOF-818 as a solid powder. The structural and morphological properties of MOF-818 were investigated by PXRD, TEM, and SEM-EDS. Additionally, its porosity and specific surface area were evaluated through nitrogen adsorption–desorption measurements, with the data being analyzed using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models.

Evaluation of MOF-818's adsorption performance for PFOA

PFOA, as a representative PFAS, is widely used as a model compound in studies investigating the adsorption and degradation behaviors of PFAS in various materials.^{54–56} In this work, PFOA is employed to evaluate key processes such as concentration-gradient adsorption, adsorption kinetics, selective adsorption, and cyclic adsorption performance.

Concentration gradient adsorption experiment. Aqueous PFOA solutions were prepared at concentrations of 100, 300, 500, 700, 900, 1200, 2000, and 3000 mg L^{-1} (2 mL each). MOF-818 powder (2 mg) was added to each vial. The mixtures were thoroughly agitated and then shaken on a rotary mixer for 2 hours. Subsequently, the samples were centrifuged, and the supernatant was collected. After adding trifluoroethanol as an internal standard, the residual PFOA concentration in the supernatant was quantified using ^{19}F NMR spectroscopy. This procedure allowed for the determination of the concentration-dependent adsorption capacity of MOF-818 for PFOA.

Low condition adsorption. 1 mg of MOF-818 powder was added to 2 mL of an aqueous PFOA solution ($250\text{ }\mu\text{g L}^{-1}$). The mixture was agitated on a rotary mixer for 2 h, followed by centrifugation. The PFOA concentration in the supernatant was then analyzed by UHPLC-MS/MS.

Adsorption kinetics. A 2000 mg L^{-1} aqueous solution of PFOA was prepared. Then, 2 mL of this solution was transferred into each of five sample vials, followed by the addition of 2 mg of MOF-818 powder to each vial. The mixtures were agitated on a rotary mixer for 2, 5, 10, 20, 40, and 60 minutes, respectively. After centrifugation, the supernatants were collected. Trifluoroethanol was added as an internal standard, and the residual PFOA concentration in each supernatant was quantified using ^{19}F NMR spectroscopy.

Adsorption selectivity. A 2000 mg L^{-1} aqueous solution of PFOA was prepared, and 2 mL aliquots were transferred into each of sample vials. To each vial, one of the following common aquatic components was added (2 mg each): ferric chloride, aluminum chloride, potassium chloride, sodium sulfate, acetic acid, magnesium nitrate, zinc chloride, manganese(II) chloride, calcium sulfate, sodium chloride; one vial served as a control without additional interfering ions. Subsequently, 2 mg of MOF-818 powder was added to each vial, and the samples were shaken on a rotary mixer for 2 hours. After centrifugation, the supernatant was collected and trifluoroethanol was introduced as an internal standard. The residual PFOA concentration was quantified using ^{19}F NMR spectroscopy and the residual metal contents was quantified using ICP-MS, to evaluate the selective adsorption.

Cyclic adsorption performance. The PFOA-loaded MOF-818 (PFOA@MOF-818) was treated with a hydrochloric acid solution ($\text{pH} = 4$) and shaken on a rotary mixer for 24 hours.⁵⁷ After centrifugation and removal of the supernatant, the solid was dried, yielding regenerated MOF-818. Desorption efficiency was confirmed using ^{19}F NMR spectroscopy. The regenerated MOF-818 was immersed in a 2000 mg L^{-1} PFOA aqueous solution (2 mL) and rotated for 2 hours. After centrifugation, the supernatant was collected and analyzed *via* ^{19}F NMR spectroscopy to determine the cyclic adsorption capacity. The desorption–adsorption cycles were repeated to evaluate the reusability and stability of MOF-818 for PFOA removal.

The PFOA@MOF-818 was comprehensively characterized using SEM-EDS, XPS, N_2 adsorption–desorption analysis, TGA, and FT-IR to corroborate the adsorption performance and assess the structural stability of the material.

Calculation method

We used the DFT as implemented in the MS in all calculations. The exchange–correlation potential is described by using the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is employed to treat interactions between ion cores and valence electrons. μ models were relaxed until the Hellmann–Feynman forces smaller than $-0.01\text{ eV }\text{\AA}^{-1}$ and the change in energy smaller than 10^{-6} eV was attained. During the relaxation, the Brillouin zone was represented by a Γ centered k -point grid of $5 \times 5 \times 1$. Grimme's DFT-D3 methodology was used to describe the dispersion interactions among all the atoms in adsorption models.

Results and discussion

Structural characterizations of MOF-818

To confirm the structure of MOF-818 synthesized *via* solvothermal method, we characterized its crystallinity and morphology using PXRD, TEM, SEM-EDS, with the results presented in Fig. 2. The PXRD pattern of MOF-818 shows a flat baseline and sharp diffraction peaks at $2\theta = 4.9^\circ, 6.0^\circ, 6.8^\circ, 7.5^\circ, 9.7^\circ, 10.1^\circ, 11.3^\circ, 12.0^\circ, 17.2^\circ, 22.6^\circ, 23.2^\circ$, and 26.3° (Fig. 2a). These narrow and intense peaks closely match the simulated pattern derived from the single-crystal structure of MOF-818 reported in previous work,⁴⁷ confirming the successful synthesis of highly crystalline MOF-818 with the intended structure. Fig. S1 presents the full XPS survey spectrum of pristine MOF-818. Characteristic peaks corresponding to Zr 3d, Cu 2p, C 1s, N 1s, O 1s and F 1s are clearly observed, which is consistent with the theoretical elemental composition of MOF-818 constructed from Zr/Cu clusters and pyrazole-4-carboxylate ligands with the aid of TFA. The Zr 3d region exhibited two characteristic peaks at binding energies of 182.5 eV ($3d_{5/2}$) and 184.9 eV ($3d_{3/2}$), confirming the presence of zirconium in the +4 oxidation state (Zr^{4+}) (Fig. 2b). Structural analysis indicates that these Zr^{4+} ions are incorporated in the $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_6(H_2O)_6]$ secondary building units (SBU). In these clusters, each Zr^{4+} center adopts an eight-coordinate geometry,

bonded to oxygen atoms from μ_3-O , μ_3-OH , hydroxyl groups, and water molecules. Importantly, the six terminal water molecules coordinated to each Zr_6 cluster can be removed upon activation, generating open zirconium sites that function as strong Lewis acid centers. The copper species in MOF-818 were identified as Cu^+ and Cu^{2+} oxidation states, as evidenced by the Cu 2p XPS spectra (Fig. 2c). The higher BE peak at 935.2 eV was assigned to Cu^{2+} , along with the characteristic Cu^{2+} shake-up satellite peaks at 943.6 eV. In contrast, the lower BE peak at 933.6 eV suggested the presence of Cu^+ species.⁵⁸ The copper atoms are integrated into triangular $[Cu_3(\mu_3-O)(\mu-PyC)_3(H_2O)_3]$ SBUs. Within these units, each Cu center adopts a four-coordinate, square-planar geometry, ligated by one μ_3-O bridging oxygen, two pyrazole nitrogen atoms from different pyrazole-4-carboxylate linkers, and one coordinated water molecule. The three water molecules bound to each Cu_3 cluster can be readily removed upon activation, generating accessible unsaturated copper sites with high affinity for Lewis basic adsorbates. In summary, the unique dual-cluster SBU architecture of MOF-818, comprising both Zr_6 and Cu_3 units, gives rise to a synergistic adsorption system featuring accessible OMSs. The Zr_6 clusters serve as stable coordination anchors, while the Cu_3 clusters provide geometrically tailored binding pockets. This complementary dual-metal environment underpins the efficient and selective capture of

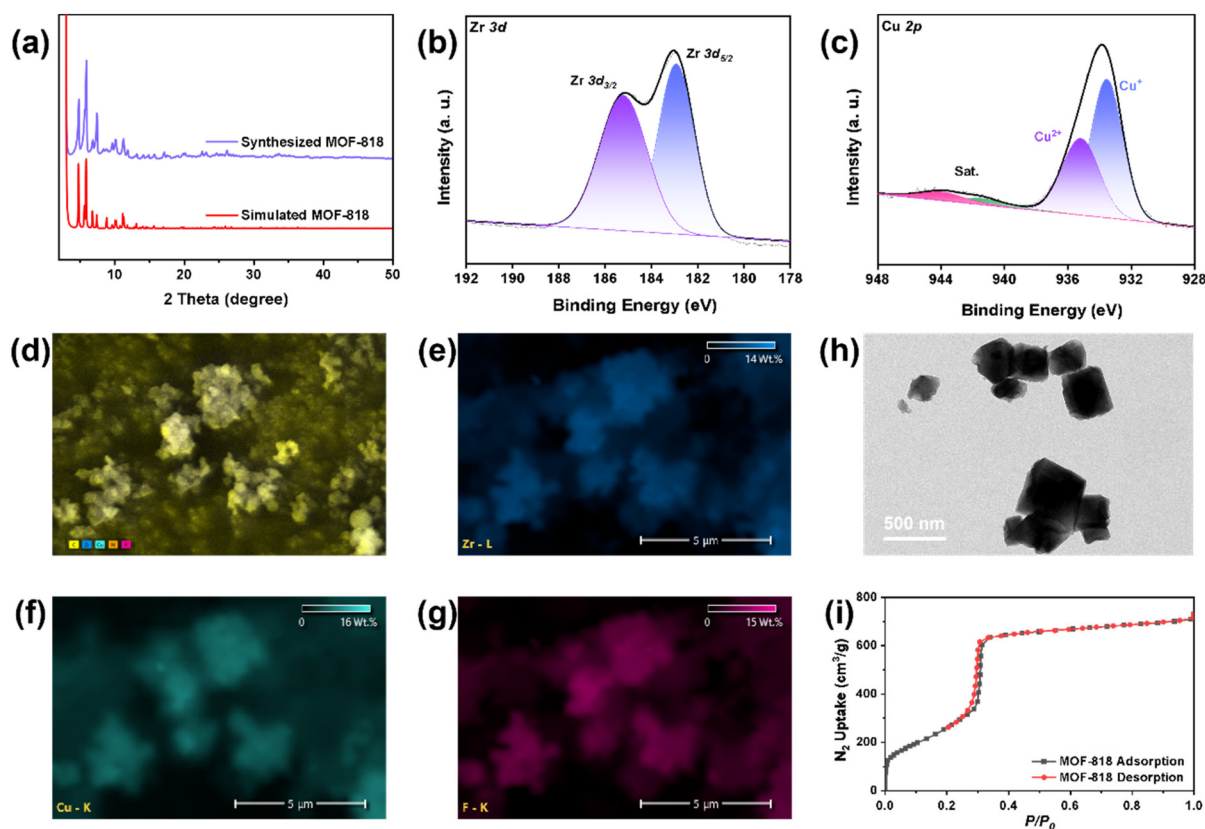


Fig. 2 Structural characterizations of MOF-818. (a) PXRD and simulated XRD patterns. (b, c) Zr and Cu high resolution XPS curves. (d–g) SEM image and elemental distribution. (h) TEM image. (i) N_2 adsorption–desorption isotherm plot.

PFOA, establishing a robust structural basis for its good adsorption performance.

The SEM image (Fig. 2d–g) shows that Zr, Cu, and F are uniformly distributed throughout the structure of the synthesized MOF-818 powder, and Fig. S2 shows the SEM-EDS results of MOF-818, illustrating the coexistence of major elements and their contents. Additionally, a small amount of fluorine is uniformly detected, originating from the TFA used during synthesis. As shown in Fig. 2h and S3, TEM images reveal that MOF-818 exhibits a regular octahedral morphology with uniform particle size (approximately 300 nm) and excellent crystallinity. The porosity of MOF-818 was evaluated by N_2 adsorption–desorption isotherm (Fig. 2i), MOF-818 exhibits a type-IV curve, confirming its mesoporous nature. The material exhibits a specific surface area of $1108 \text{ m}^2 \text{ g}^{-1}$, as determined by the BET method. By measuring the distances between the centers of corresponding atoms in the structure, the diameter and pore size of MOF-818 were determined to be 3.8 nm and 3.1 nm, respectively. When the van der Waals radii of the relevant atoms are taken into account, these values adjust to 3.7 nm and 3.0 nm, respectively. As shown in Fig. S4, the pore size distribution of MOF-818 calculated by the BJH method indicates that the main pore structure is centered at approximately 2.8 nm closely matching the theoretical pore size, showing typical mesoporous characteristics. Combined with the nanoscale size, high BET specific surface area, this hierarchical mesoporous structure provides sufficient space and rapid diffusion pathways for PFOA molecules, favoring high-capacity and fast adsorption.

Adsorption behaviour of MOF-818 toward PFOA

The adsorption performance of MOF-818 toward PFOA was quantitatively evaluated through ^{19}F NMR spectroscopy, with emphasis on concentration-dependent adsorption, kinetics, selectivity, and reusability. The ^{19}F NMR signal of trifluoroethanol is observed at -77.08 ppm , while that of PFOA occurs between -127 to -81 ppm . Given the significant difference in these signals, trifluoroethanol can therefore serve as an internal standard, enabling the quantitative evaluation of PFOA adsorption.

Aqueous PFOA solutions at various concentrations were prepared. A fixed amount of MOF-818 powder was introduced into each solution, followed by shaking for 2 hours. After centrifugation, the supernatant was collected for ^{19}F NMR analysis. Fig. S5 displays the ^{19}F NMR spectra of PFOA solutions after adsorption by MOF-818. The intensity of characteristic PFOA signals in the supernatant gradually increases with the increase of initial PFOA concentration. Quantitative integration of these signals enabled the construction of a concentration-dependent adsorption profile, as presented in Fig. 3a. It reveals that no detectable PFOA residues remain in the supernatant at low concentrations ($\leq 900 \text{ mg L}^{-1}$), indicating nearly complete adsorption (Fig. 3d). At higher concentrations, residual PFOA is observed, with spectral signals corresponding to fluorine atoms in PFOA. The results demonstrate a saturated adsorption capacity of 1.51 g g^{-1} for PFOA on MOF-818, follow-

ing the Langmuir adsorption model with a correlation coefficient (R^2) of 0.99. To further quantify the adsorption performance of MOF-818, a comparative analysis of PFOA adsorption capacities among representative MOFs from current literature was conducted, as summarized in Fig. 3c. The results indicate that MOF-818 exhibits a high adsorption capacity compared to previously reported adsorbents. To evaluate the adsorption performance toward trace PFOA under near-ambient conditions, an adsorption test was conducted. After treatment, the PFOA concentration dropped from an initial $250 \mu\text{g L}^{-1}$ to approximately $15 \mu\text{g L}^{-1}$ in the supernatant. These results demonstrate that the material possesses good removal performance for PFOA at low concentrations.

Similarly, we investigated its adsorption kinetics by adding an equal amount of MOF-818 powder to PFOA solutions of identical concentration and volume. After shaking for varying time intervals, the mixtures were centrifuged and the supernatant was collected. Following the addition of an internal standard, ^{19}F NMR spectroscopy was used to quantify residual PFOA, producing the adsorption kinetic curves shown in Fig. 3b. The results indicate that adsorption equilibrium was shorter than 5 minutes, demonstrating rapid uptake of PFOA by MOF-818. This kinetic behaviour supports a coordination adsorption mechanism and represents a substantial improvement over the slow adsorption processes typically exhibited by conventional porous materials. In addition, the mesoporous structure and nanoscale sizes of MOF-818 enable rapid diffusion of PFOA molecules into the adsorbent.

The adsorbed PFOA could be effectively desorbed from MOF-818 using a mixture of dilute hydrochloric acid, and the regenerated material retained its original saturation adsorption capacity upon reuse. Owing to the predominantly chemisorption-based interaction and strong binding affinity between MOF-818 and PFOA, conventional desorption using methanol consequently requires a prolonged duration. The adsorbent exhibited excellent recyclability, maintaining a high capacity retention of 97% over eight cycles, which underscores its robust stability for practical applications (Fig. 3e). A gradual decrease in adsorption capacity occurs due to a combination of factors: the destruction and removal of inherently labile sites in MOF-818 during acidic desorption/centrifugation, coupled with minor material loss throughout the cyclic process. To evaluate the selective adsorption of PFOA by MOF-818 in complex aqueous environments, the saturation adsorption capacity was measured in the presence of ten common water constituents. The capacity remained consistently high at 1.51 g g^{-1} , indicating strong resistance to interference, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Zn^{2+} , Cl^- , NO_3^- , SO_4^{2-} and CH_3COO^- (Fig. 3f). ICP-MS results indicate that the residual metal ions in supernatant are more than 99.2% (Table S1). These results confirm that MOF-818 possesses excellent reusability and selectivity for PFOA adsorption.

In summary, the mesoporous architecture and abundant accessible OMSs in MOF-818 facilitate highly efficient and rapid adsorption of PFOA with excellent selectivity, recyclability, and structural stability (Table S2).

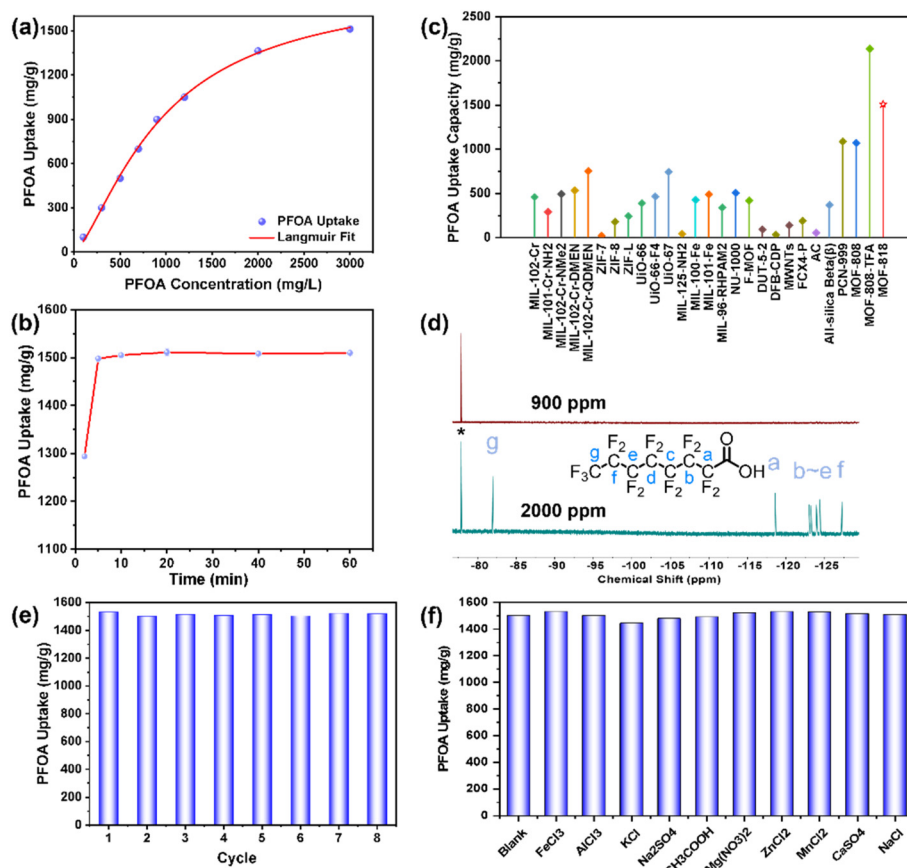


Fig. 3 PFOA adsorption behaviour of MOF-818. (a) Langmuir-fitting of the equilibrium adsorption isotherm. (b) Adsorption kinetics of PFOA with an initial concentration of 2000 mg L⁻¹. (c) Comparison of maximum PFOA uptake with other MOFs and active carbon. (d) ¹⁹F NMR spectra of supernatants after adsorption at varying concentrations (*: trifluoroethanol internal standard). (e) Cyclic adsorption performance. (f) Selectivity test in the presence of interfering ions.

Adsorption mechanism investigation

To further corroborate the superior adsorption performance of MOF-818 toward PFOA, further characterizations were conducted on PFOA@MOF-818. Fig. 4a–d demonstrate that the distributions of Zr, Cu, and F remain uniform after adsorption with a more intense fluorine signal. The uniformly distributed fluorine within MOF-818 particles rather than merely enriched on the surface, demonstrating that PFOA molecules have fully diffused into the internal pores and channels of MOF-818 instead of only surface adsorption. The uniform distribution of Zr, Cu, and F also verifies the structural integrity of MOF-818 and the homogeneous interactions between PFOA and adsorption sites. Fig. S6 shows the SEM-EDS elemental contents after adsorption. The fluorine content increases significantly (from 3.9 at% to 7.9 at%), which directly confirms the successful loading of PFOA. The N₂ adsorption-desorption isotherms (Fig. 4e) and pore size distribution of PFOA@MOF-818 (Fig. S7) demonstrate that the mesoporous peak is significantly weakened and nearly disappears, accompanied by a sharp decrease in pore volume and specific surface area. This result indicates that PFOA molecules have

entered and filled the mesoporous channels of MOF-818. TGA results (Fig. 4f) show that pristine MOF-818 possesses high thermal stability below 280 °C and undergoes approximately 50% weight loss near 350 °C. In contrast, PFOA@MOF-818 exhibits over 80% weight loss near the same temperature, consistent with a saturated PFOA adsorption capacity of about 1.50 g g⁻¹, close to the ¹⁹F-NMR results.

To elucidate the adsorption mechanism of PFOA on MOF-818, XPS and FT-IR were conducted on both pre- and post-adsorption samples. Fig. S8 shows the full XPS survey spectrum of PFOA@MOF-818 with a strong F 1s signal originating from the adsorbed PFOA. Meanwhile, the characteristic peaks of Zr 3d and Cu 2p remain clearly identifiable, confirming that the structure of MOF-818 remain stable after adsorption. The appearance of the F signal and the retention of metal element signals jointly validate the successful adsorption of PFOA. As shown in Fig. 4g and h, the Zr 3d spectrum of PFOA@MOF-818 displays a pronounced shift relative to pristine MOF-818: the Zr 3d_{5/2} peak moves from 183.0 eV to 183.5 eV, and the Zr 3d_{3/2} peak moves from 185.1 eV to 185.5 eV, both toward higher binding energy. Concurrently, the Cu 2p XPS spectrum of PFOA@MOF-818 exhibits a distinct change

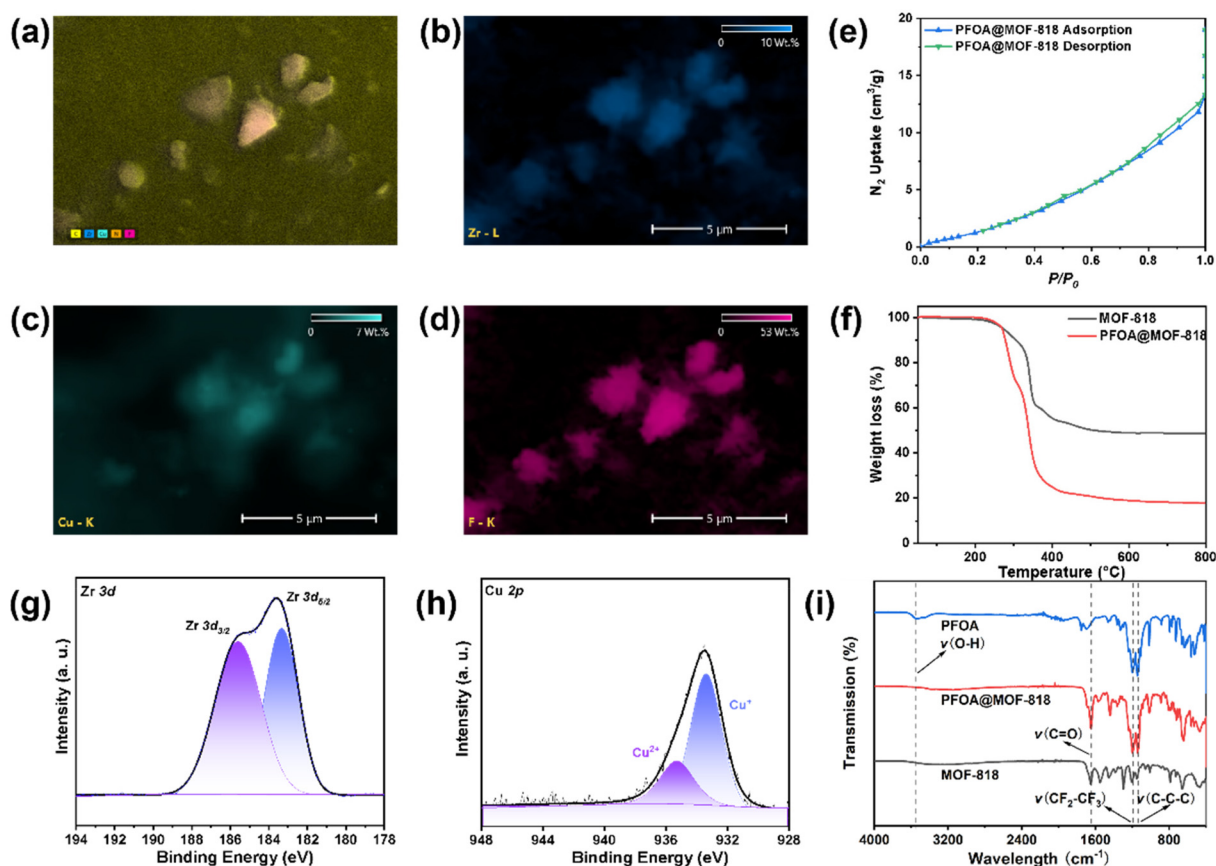


Fig. 4 Structural characterizations of PFOA@MOF-818. (a–d) SEM image and elemental distributions. (e) N_2 adsorption–desorption isotherms. (f) TGA plots of MOF-818 before and after PFOA adsorption. (g and h) Zr and Cu high resolution XPS curves. (i) FT-IR spectrum of MOF-818 before and after PFOA adsorption.

after adsorption: the Cu $2p_{3/2}$ main peak shifts from 933.9 eV to 933.5 eV, corresponding to a decrease in binding energy, accompanied by a noticeable alteration in the signal-to-noise ratio. These findings demonstrate unequivocally that chemical adsorption has taken place between PFOA and the OMSs within MOF-818.

Compared to pristine MOF-818, the FT-IR spectrum of PFOA@MOF-818 (Fig. 4i) exhibits two new characteristic bands at ~ 1200 and ~ 1140 cm^{-1} , which are assigned to the C–F stretching vibration and C–C–C bending vibration of the PFOA molecule, respectively, confirming the successful loading of PFOA onto MOF-818. More importantly, the characteristic C=O stretching vibration of the PFOA carboxylate group, originally appearing at ~ 1700 cm^{-1} in PFOA, undergoes a distinct red-shift to ~ 1691 cm^{-1} after adsorption. This significant shift directly indicates the formation of strong coordination interactions between the carboxylate oxygen atoms of PFOA and the OMSs within MOF-818, which weakens the C=O bond order and thus reduces its stretching frequency. Furthermore, the disappearance of the free O–H stretching band at 3546 cm^{-1} (originating from the carboxylic acid group in PFOA) in PFOA@MOF-818 provides additional evidence for the deprotonation and coordination of the carboxylate moiety with the

OMSs, unambiguously confirming the occurrence of chemical adsorption *via* coordination bonds.

To elucidate the chemical adsorption mechanism of PFOA, the molecular electrostatic potential (MESP) distributions of the two types of clusters were first calculated. As shown in Fig. 5a, oxygen atoms within Zr_6 cluster exhibit negative MESP values, indicating weak Zr–O coordination bonds in the OMS sites, while oxygen atoms within Cu_3 cluster show positive MESP values, suggesting stronger coordination interactions. These findings imply that the Zr_6 cluster are capable of undergoing ligand exchange with PFOA. To further understand the differences between the two clusters, binding energies (E_{binding}) were also computed. Based on symmetry and chemical/spatial environment analysis, two potential binding sites were identified for two clusters. DFT calculation shows the binding energy of PFOA with two sites were -1.66 and -1.41 eV, respectively (Fig. 5b and c). The moderate and comparable binding energies not only facilitate effective adsorption for both clusters but also lay the foundation for their reversible adsorption–desorption behaviour. The binding energy results, along with the MESP distributions, collectively highlight the distinct chemical properties of the OMSs in two clusters. Theoretical counting of PFOA chemisorption on defective

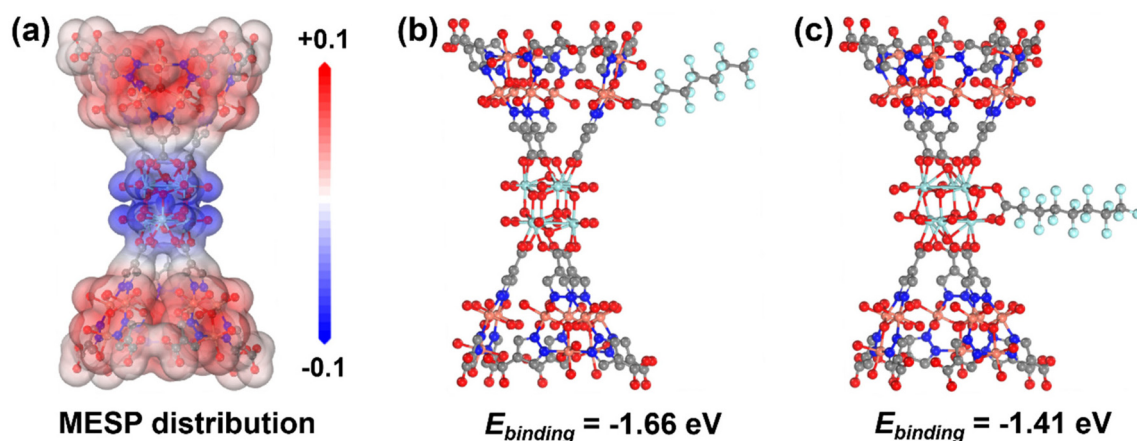


Fig. 5 (a) Molecular electrostatic potential (MESP) distribution of two clusters. Optimized model structures of (b) Cu_3 and (c) Zr_6 clusters after PFOA binding on possible binding positions. C, O, F, Zr, and Cu atoms are represented by gray, red, light cyan, cyan, and orange, respectively. Hydrogen atoms in the structures are omitted for clarity.

MOF-818 indicated a maximum capacity of 1.20 g g^{-1} when all OMSs are occupied, which means the other 0.31 g g^{-1} contributed to physisorption. This integration of computational and experimental evidence leads us to conclude that PFOA adsorption on MOF-818 proceeds primarily *via* chemisorption, with a secondary contribution from physisorption.

Conclusions

In this work, we establish a synergistic adsorption strategy for efficient PFOA removal by deliberately designing a MOF platform that integrates two distinct adsorption modes within a single framework. The innovation lies in the simultaneous utilization of open metal sites (OMSs) on both Zr_6 and Cu_3 clusters for chemisorption, and the mesoporous structure and high surface area for subsequent physisorption. This dual-function architecture overcomes the conventional trade-off between binding affinity and diffusion kinetics: the OMSs provide strong, selective anchoring of PFOA carboxylate groups, while the hierarchical pores ensure rapid mass transport and accommodate high loading. Beyond demonstrating one of the most efficient PFOA adsorbents reported to date, our work offers a broader design principle for tackling persistent per- and polyfluoroalkyl substances (PFAS). By tuning the density and distribution of OMSs alongside pore geometry, similar MOF platforms can be adapted to capture other PFAS variants or emerging anionic micropollutants. Looking forward, integrating such synergistic adsorbents into fixed-bed or membrane-based continuous flow systems could enable practical, scalable water remediation. Moreover, the reversible chemisorption behaviour opens avenues for adsorbent regeneration and PFAS enrichment, supporting a circular treatment process. This study thus not only presents MOF-818 as a high-performance material but also provides a transferable blueprint for engineering next-generation adsorbents *via* synergistic chemical–physical capture mechanisms.

Author contributions

Xingyue Yang: writing – original draft, methodology, investigation, data curation. Xin Fang: methodology, investigation, data curation. Xinyuan Zhu: resource support. Meina Liu, Youfu Wang, Xin Jin: writing – review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this study are available within the article and its supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6nr00915h>.

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