



Development of laboratory-cooked, water-resistant, and high-performance Cu-MOF: an economic analysis of Cu-MOF for PFOS pollution management and remediation

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Abstract

Water pollution is a pressing global concern, with per- and polyfluoroalkyl substances (PFAS) being considered as “forever contaminants.” Among them, perfluorooctanesulfonic acid (PFOS) has received significant attention for its adverse effects on human health and aquatic ecosystems. This study aimed to design an innovative adsorbent for effective PFOS removal with exceptional water stability, improving its cost-performance trade-off. The current work simultaneously improved the stability of water of Cu-based metal–organic framework (CMOF) and increased its PFOS removal capacity by modifying it with amine-functionalized SiO₂ nanoparticles (AF-CMOF). AF-CMOF presented a lower specific surface area of 999 m² g⁻¹ compared to CMOF with a surface area of 1098 m² g⁻¹. AF-CMOF showed remarkable PFOS uptake performance of 670 mg/g compared to the performance of the Cu-based MOF which exhibited a PFOS uptake capacity of only 22 mg/g. The most suitable pH for PFOS removal using both adsorbents was determined to be 3. In addition, AF-CMOF demonstrated excellent water stability, retaining its structural integrity even after seven days of water contact, while CMOF structure collapsed rapidly after four days of water exposure. Moreover, the study identified the significant pH influence on the PFOS uptake process, with electrostatic interactions between protonated amine functionalities and PFOS molecules identified as the dominant mechanism. The study’s findings present the potential of synthesized adsorbent as a superior candidate for PFOS uptake and contribute to the development of effective water treatment technologies.

Keywords Adsorption · PFOS pollution management · Metal–organic framework (MOF) · Water treatment

Introduction

Over the last few years, concern has grown over time among scientists regarding the issue of environmental pollution (Ly and El-Sayegh 2023, Mousazadeh et al. 2024, Yu et al. 2024a, b). However, the ongoing process of industrialization

has continued, resulting in the pollution of the environment, especially water sources (Liu et al. 2023; Xu et al. 2023; Wang et al. 2024a, b). The imperative to control environmental pollution is paramount due to its profound implications for ecological integrity, public health, and sustainable development initiatives (Bozorgnezhad et al. 2015c, a, b;

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Jiang et al. 2022; Liu et al. 2022; Kong et al. 2023; Xue et al. 2023a, b). Leveraging renewable energy sources holds significant potential for mitigating environmental pollution (Ashrafi et al. 2016; Liu and Yang 2022; Yan et al. 2023). Hence, numerous studies are conducted on renewable energy as a substitute for conventional fuels (Bozorgnezhad et al. 2014; Hussaini and Wang 2022; Kennedy et al. 2023). For renewable energy, various technologies play a pivotal role. Battery storage systems are crucial for storing and managing energy from intermittent sources, ensuring a stable and reliable supply (Bozorgnezhad et al. 2015c, a, b; Bozorgnezhad et al. 2016). Solar energy technologies, including photovoltaic panels and solar thermal systems, harness sunlight to generate electricity and heat (Verma et al. 2024). These advancements in renewable energy not only reduce dependence on fossil fuels but also contribute significantly to sustainable development and the mitigation of climate change (Fatemi et al. 2023; Li et al. 2023a, b).

Furthermore, effective water management practices can yield favorable outcomes for environmental cleanliness (Bozorgnezhad et al. 2015c, a, b). Water resources play diverse roles in various industrial processes, underscoring the critical importance of water management in contemporary times (Hasheminasab et al. 2014; Kanani et al. 2015; Song et al. 2023; Zhao et al. 2024). Water sources encounter a notable obstacle as a result of widespread presence of harmful contaminations particularly per- and polyfluoroalkyl substances (PFAS) (Brusseau et al. 2020; Xu et al. 2023; Xue et al. 2023a, b). Among the various PFAS pollutants, perfluorooctanesulfonic acid (PFOS) has gained great attention because of its utilization in a broad range of industries (Gole et al. 2018). The widespread use of PFOS in industries such as textiles and equipment manufacturing has resulted in its presence in drinking water, municipal sewage, and surface water (Gole et al. 2018). PFOS is highly resistant to natural processes, conventional water treatment techniques, and biodegradation, making it a persistent contaminant in the aquatic system (Erkoç and Erkoç 2001). Moreover, water pollution especially PFOS exposure has been linked to adverse effects on fertility, liver, and the immune system (Espartero et al. 2022; Fatima et al. 2023, Gupta et al. 2023). As such, there is an immediate need to create innovative methodologies for combating PFOS contamination in water sources.

Numerous strategies have been recently looked at ways to lessen the negative impacts of pollutants. Numerous strategies encompass a diverse array of methodologies, including adsorption, electrochemistry, membrane, and sonochemistry (Liu et al. 2008; Lyu et al. 2020; Shen et al. 2023). However, complete eradication of PFAS presents a significant challenge due to its intricate physicochemical properties, which encompass varying chain lengths and substitutions of hydrogen with fluorine atoms (Rayne and Forest 2009).

Owing to the robust carbon–fluorine (C–F) bonds and extensive fluorination, PFAS exhibits remarkable resistance to degradation, along with oleophobic and hydrophobic characteristics, as well as exceptional thermal stability (Gao and Chorover 2012). Biological techniques exhibit the capacity to break carbon–carbon bonds but are limited in their ability to break carbon–fluorine bonds (Zhang et al. 2022). In contrast, oxidation methods like electrochemical oxidation can be employed for PFAS degradation. However, the generation of toxic by-products that are more resistant hinders its widespread application (Ahmed et al. 2020). Hence, the effective elimination of these newly formed smaller PFAS compounds from the water environment poses a new challenge when employing oxidative methods for treating long-chain PFAS compounds (Mirabediny et al. 2023). On the other hand, sorption methods offer the advantage of removing contaminants from water without requiring their degradation (Leung et al. 2022; Yu et al. 2024a, b).

Numerous studies have been carried out on various adsorbents, including activated carbon, clay, and carbon-dot hydrogels, to address the challenge of PFOS removal from water environments (Das et al. 2013; Ross et al. 2018; Wang et al. 2024a, b). However, these adsorbents have inherent limitations in terms of selectivity, efficiency, and kinetics, prompting the need for innovative and sophisticated approaches (Liu et al. 2018; He et al. 2021; Chang et al. 2022). Among the promising alternatives, MOFs have been introduced as a highly encouraging solution for PFOS elimination (Chang et al. 2022). The coordination interactions between organic ligands and metal clusters enable the creation of customizable structures with efficient active sites, superior porosity, and exceptional surface areas (Mohammadi et al. 2021; Li et al. 2023a, 2023b; Li et al. 2024). Consequently, MOFs have gained significant attention for their numerous, exciting uses among a wide range of fields (Han et al. 2022; Hamoule et al. 2023). Despite their exceptional potential, many MOFs have certain drawbacks that limit their practical applications, such as inadequate thermal and water durability (Burtch et al. 2014, Guo et al. 2023). The insufficient water durability of MOFs is a major drawback for their use in actual water refining practices, since extended exposure to water can cause structural deterioration (Ding et al. 2019; Yu et al. 2024a, b). The primary influences on MOFs' water resistance are steric and electrical hindrance effects on the metal cluster, which can weaken the metal–ligand coordination (Ding et al. 2019). In order to make MOFs water tolerant, the metal cluster's inertness is an essential structural feature that inhibits the deterioration process (Wang et al. 2016). To address the issue of weak water stability, one promising approach is to propose modification methods that can enhance the water tolerance of MOFs (Yang et al. 2019). Furthermore, enhancing the structural stability of MOFs has cost efficiency implications.

A techno-economic analysis of MOFs demonstrated that the production cost at an industrial scale ranges from 35 to 71 dollars (DeSantis et al. 2017). This high cost currently limits the widespread application of MOFs in real-world scenarios. However, if MOFs can exhibit prolonged stability in water for water treatment applications, it can significantly improve their cost-performance trade-off efficacy.

In recent years, surface modification techniques have gained attention as a viable approach for enhancing the water stability of MOFs (Weiss et al. 2015). This method involves modifying the MOF's surface by introducing steric hindrance on metal centers, which obstructs water molecules from accessing the metal centers and ultimately leading to their degradation (Liu et al. 2014). By applying a PDMS layer by vapor deposition, researchers have successfully enhanced the water stability of MOFs such as HKUST-1, MOF-5, and ZnBT. This has led to noticeably enhanced resilience for a maximum of one day of water exposure (Zhang et al. 2014). Additionally, studies by Lin et al. have showed that modifying the metal nodes of acetonitrile functionalization Cu-BTC can significantly enhance water resistance, extending its performance for as long as 20 days (Lin et al. 2018). These findings have opened up new avenues for further research into surface modification techniques in order to improve MOF's water stability. Moreover, surface modification is a critical aspect of improving the performance of MOFs for various uses, including pollutant removal (Lv et al. 2019). Through surface modification, MOFs can be tailored to have enhanced surface functionalities, leading to higher adsorption capacity (Pauletto et al. 2023). The electrostatic driving force among the electrophobic head of PFOS and cationic functional groups of the sorbent has been found as a promising mechanism for PFOS removal. Studies have revealed that aminated polyacrylonitrile fibers with protonated amine functionalities at pH 3 for PFOS exhibit remarkable adsorption capacities of up to 15.0 mmol/g owing to the strong electrostatic forces among the positively charged amine groups and the anionic PFOS headgroup (Meng et al. 2017). Similarly, triazine- and heptazine-based porous organic polymer networks have shown excellent adsorption of PFOA by utilizing the electrostatic interactions among nitrogen groups within the polymer framework and PFOA particles (Abdullatif et al. 2022).

As the Cu-based MOF has become commercially available, a method is sought to enhance its stability in water and make it appropriate for practical uses in water treatment. Cu-based MOF, unlike certain other MOFs, has metal nodes facing the inner pore space, which render them susceptible to water attacks. To overcome this challenge, this study aims to immobilize $\text{NH}_2\text{-SiO}_2$ nanoparticles onto CMOF, which serves a dual purpose of increasing steric hindrance on the metal sites and introducing NH_2 functionalization onto the adsorbent to improve PFOS adsorption capacity.

By doing so, the accessibility of water to the metal centers within CMOF is notably impeded, making it more stable in aqueous environments and more effective at removing PFOS. The morphological attributes and water resistance of the synthesized adsorbent were examined using nitrogen adsorption–desorption pattern, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM) methods. The experimental conditions, which play a crucial role in PFOS adsorption, were evaluated such as pH level of the water, PFOS content, process time, and reusability of the adsorbent, as well as isothermal and kinetic studies.

Experiments and methodology

Chemicals

The reagents used in this research were obtained from sources such as Sigma-Aldrich and Merck companies, and were used without any additional purification. The chemical substances included 3-aminopropyl triethoxysilane (APTS), silicon dioxide nanopowder, benzene-1,3,5-tricarboxylic acid, hydrochloric acid, cupric nitrate trihydrate, sodium hydroxide, and ammonia aqueous solution.

Synthesis of adsorbents

To synthesize CMOF, two distinct solutions denoted as (A) and (B) were prepared. Solution (A) was composed of 3.15 g of trimesic acid (H_3BTC) dissolved in 90 mL of ethanol, while solution (B) comprised 6.522 g of copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) dissolved in 90 mL of distilled water. These solutions were subsequently combined under continuous agitation for a duration of 45 min. The resulting mixture was transferred into a stainless-steel autoclave, securely sealed, and subjected to a heating process lasting 12 h at 120 °C. Following the completion of the reaction, the resulting product underwent a washing procedure utilizing distilled ethanol and water, followed by dehumidification at 150 °C for a period of one day. The synthesized material was designated as CMOF. For the synthesis of $\text{NH}_2\text{-SiO}_2$ nanoparticles, a solution comprising 280 mL ethanol and distilled water was prepared, and 2.2 mL of concentrated ammonia solution and 1 g of SiO_2 NPs were added. Simultaneously, 2.25 g of APTS was introduced gradually into the stirring mixture over a 6-h period. Following centrifugation, the resulting mixture underwent purification through successive washes with deionized water and ethanol, followed by dehydration at 60 °C for 10 h. To synthesize the modified CMOF, a blend of 45 mL of DMF and ethanol (1:1 by volume) with 1.575 g of trimesic acid (H_3BTC) was prepared. Following this, 0.11 g of amine-functionalized silica

nanoparticles (NH₂-SiO₂ NPs) and 10 mL of ethanol were added to the mixture, which was then heated to 70 °C. Subsequently, 45 mL of deionized water containing 3.261 g of copper nitrate trihydrate (Cu (NO₃)₂·3H₂O) was introduced, and the entire solution was agitated for a duration of four hours. The resulting mixture was transferred to a stainless-steel autoclave and subjected to 12 h of heating at 120 °C in an oven. Following centrifugation and subsequent ethanol washing, a white powder termed AF-CMOF was obtained. This powder was then preserved for future applications.

PFOS adsorption test

In the current work, batch-scale experiments were carried out to examine the ability of CMOF and AF-CMOF to adsorb PFOS from aqueous solutions. Specifically, 140 mg/L dosage of the synthesized adsorbents was introduced into 50 mL of PFOS solution, with concentrations varying from 10 to 100 mg/L. Subsequently, the blend was agitated for a duration of three hours, and then, the adsorbent particles were removed through centrifugation. The remaining PFOS content was measured using LS-MS analysis. The capacity of CMOF and AF-CMOF for PFOS removal was evaluated using the following equations:

$$\text{PFOS adsorption capacity} = q_e = (C_i - C_e) \times \frac{V}{m}$$

$$\text{PFOS adsorption percentage} = (C_i - C_f) \times \frac{100}{C_i}$$

Here, the initial PFOS content in the aqueous solution was represented by C_i (mg/L), while the concentration after the adsorption process was designated as C_f (mg/L). The total volume of the samples was denoted as V (in L), and

the amount of adsorbent used for treatment was represented by m (in g).

Water stability analysis

To determine the water resistance of CMOF and AF-CMOF, samples with a volume of 50 mL containing 100 mg of each adsorbent were prepared. The pH of the samples was fixed to 7, and they were maintained in water for four and seven days, respectively. After each time interval, the samples were characterized to evaluate any changes in their structure. Additionally, the PFOS adsorption capacity of the samples was assessed both before and after a seven-day exposure to water.

Results and discussion

Characterization

XRD spectra were obtained for both AF-CMOF and CMOF, and the findings are presented in Fig. 1. The XRD results of CMOF showed distinctive peaks at 2θ angles of 4.6°, 6.4°, 9.8°, 10.5°, 12.6°, 14.1°, 16.2°, 17.9°, 18.6°, 19.5°, 21.8°, 24.5°, and 25.9°, suggesting that the crystalline structure of the MOF was successfully formed. The alteration had no impact on the crystalline structure of CMOF, as substantiated by the reduction in intensity of certain peaks and the observation of minor shifts (Ke et al. 2011). Specifically, the peak at $2\theta=9.8^\circ$ shifted to 9.9° , and the peak at $2\theta=10.5^\circ$ shifted to 10.4° . Following immersion in water for four and seven days, the intensity of the characteristic peaks for CMOF notably diminished, while new peaks emerged at approximately 10° , signifying the degradation of the crystalline structure upon water contact. The intensity of peaks was only slightly reduced for AF-CMOF, and the peak positions were mostly preserved, suggesting that the sample's

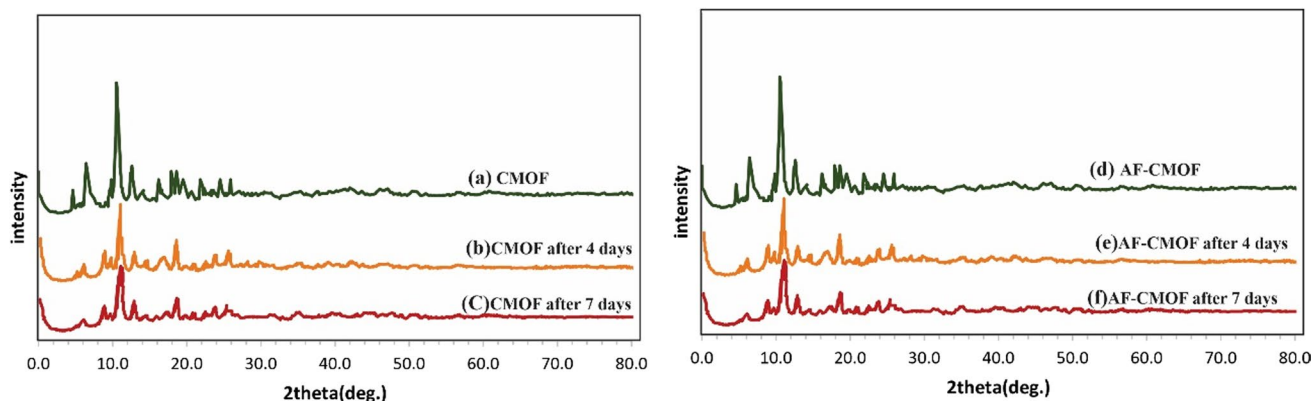


Fig. 1 XRD pattern of **a** CMOF, **b** CMOF following four days of water exposure, **c** CMOF following seven days of water exposure, **d** AF-CMOF, **e** AF-CMOF following four days of water exposure, **f** AF-CMOF following seven days of water exposure

crystallinity remained intact even after being in contact with water molecules for seven days.

The morphological characteristics of both CMOF and AF-CMOF were examined using the FE-SEM technique. As conveyed in Fig. 2, the CMOF showcases an octahedral configuration, featuring the typical particle size of 13.90 μm . After modification with $\text{NH}_2\text{-SiO}_2$ nanoparticles, the MOF morphology shifted from a regular octahedral framework

to an irregular one. It also presents a comparison of SEM images of both samples prior and post water contact (Fig. 2). It was evident that prolonged contact with the aqueous environment led to the loss of CMOF's crystalline structure. In contrast, AF-CMOF exhibited only a minor reduction in crystallinity following exposure to water. These SEM images align with the observations made from the XRD patterns. In Fig. 2, an EDS map of AF-CMOF reveals the presence of

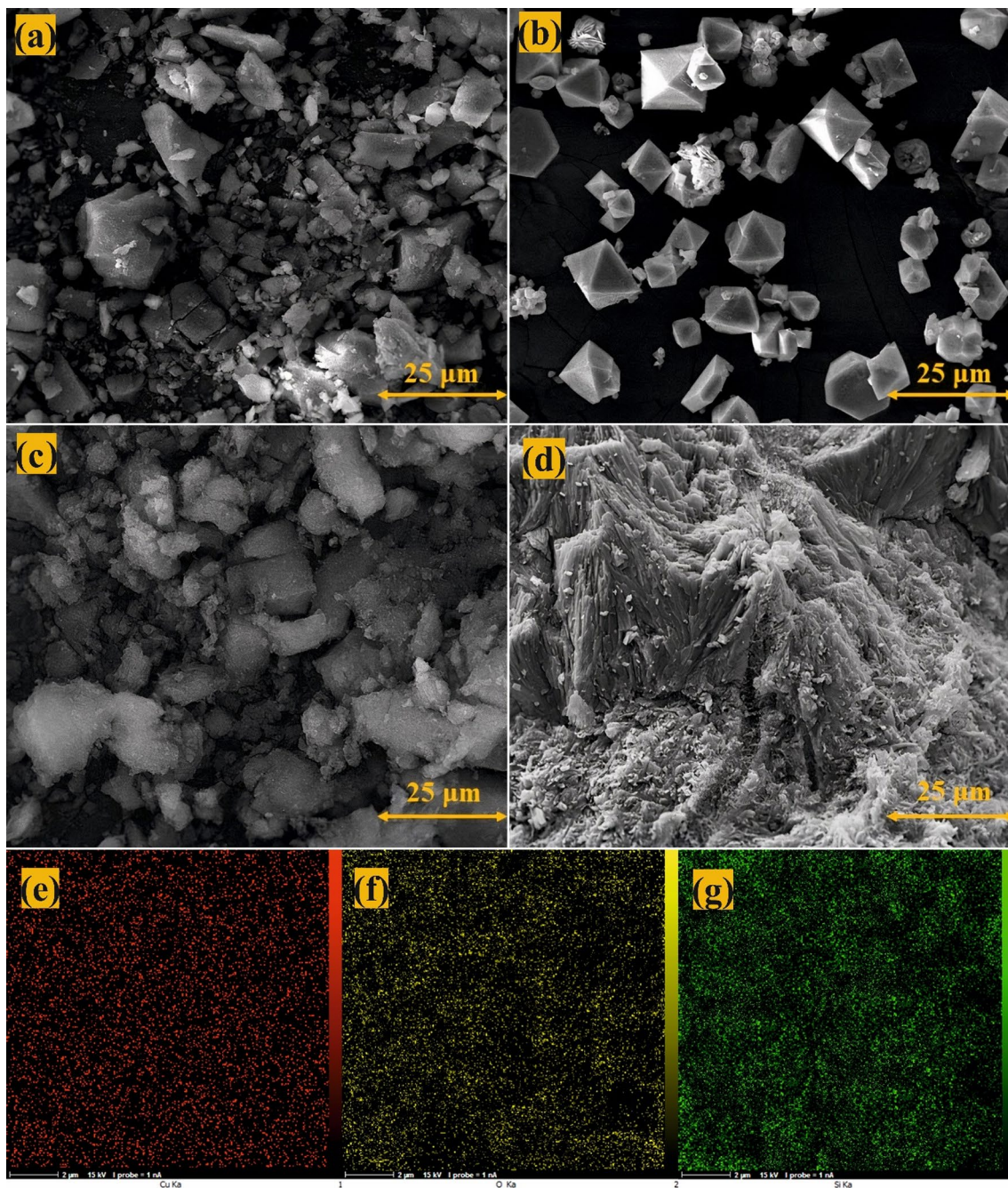


Fig. 2 A SEM image of CMOF (10 μm), B SEM image of CMOF (200 nm), C SEM image of AF-CMOF (10 μm), D SEM image of AF-CMOF(200 nm)

Table 1 Textural features of AF-CMOF and CMOF

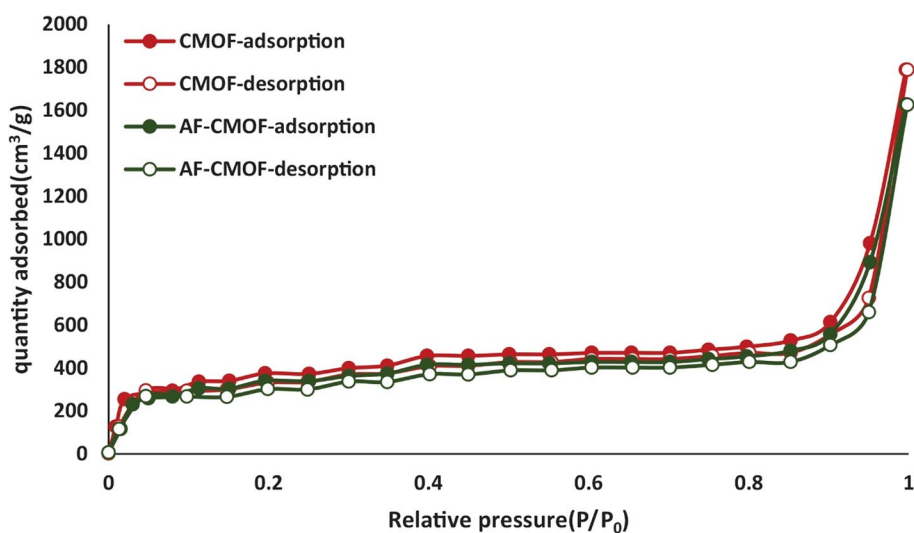
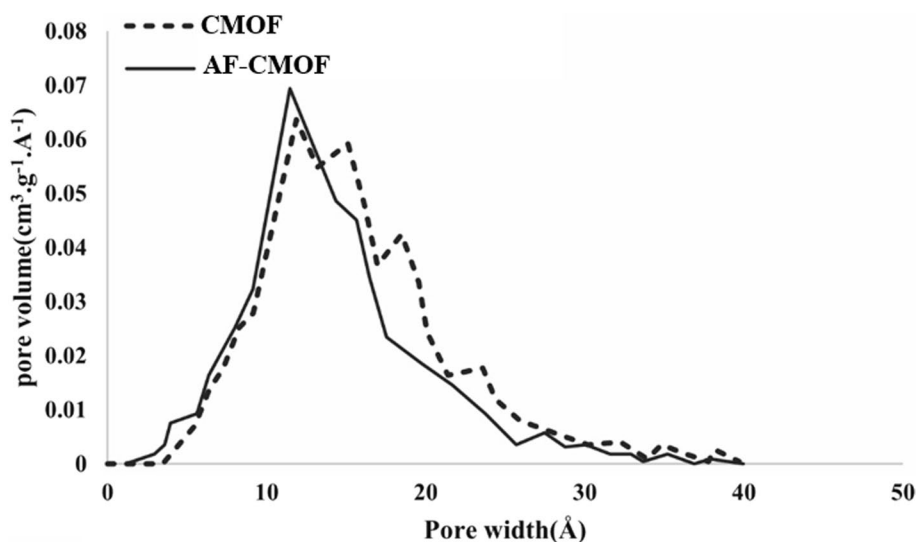
Adsorbent	S_{BET} (m^2/g)	Total pore volume (cm^3/g)
CMOF	1098	0.67
AF-CMOF	999	0.52

Si, Cu, and O atoms. The uniform distribution of N and Si atoms within the AF-CMOF structure, positioned near the Cu atoms, underscores the role of $\text{NH}_2\text{-SiO}_2$ nanoparticles in creating a barrier against water penetration.

Table 1 displays the structural features of both AF-CMOF and CMOF. Nitrogen adsorption isotherms were employed to evaluate the pore size distribution and surface area. All samples showcased a Type I isotherm, indicating the

existence of micropores and mesopores. Both materials had a high surface area, with the CMOF having a surface area of $1098 \text{ m}^2/\text{g}$ according to Fig. 3. However, after the modification of the CMOF with $\text{NH}_2\text{-SiO}_2$, the surface area of AF-CMOF was slightly decreased to $999 \text{ m}^2/\text{g}$ according to Fig. 3. Based on Fig. 4, the pore volume of AF-CMOF was also found to be lower than that of CMOF, indicating that the surface coverage using $\text{NH}_2\text{-SiO}_2$ particles has occurred.

Figure 5 presents a comparison of the FTIR results of AF-CMOF and CMOF. Both samples showed similar profiles, indicating that the modification with $\text{NH}_2\text{-SiO}_2$ nanoparticles did not alter the structure of the CMOF. This observation aligns with the outcome derived from the XRD results. The identification of C=O and C-H was observed at 1645 cm^{-1} and 2936 cm^{-1} , respectively; also, O-H , C-O- , and -O- groups were identified at peaks around 3500 , 1431 , and 1583 cm^{-1} , respectively

Fig. 3 Nitrogen sorption–desorption isotherms for both AF-CMOF and CMOF**Fig. 4** Pore size distribution of AF-CMOF and CMOF

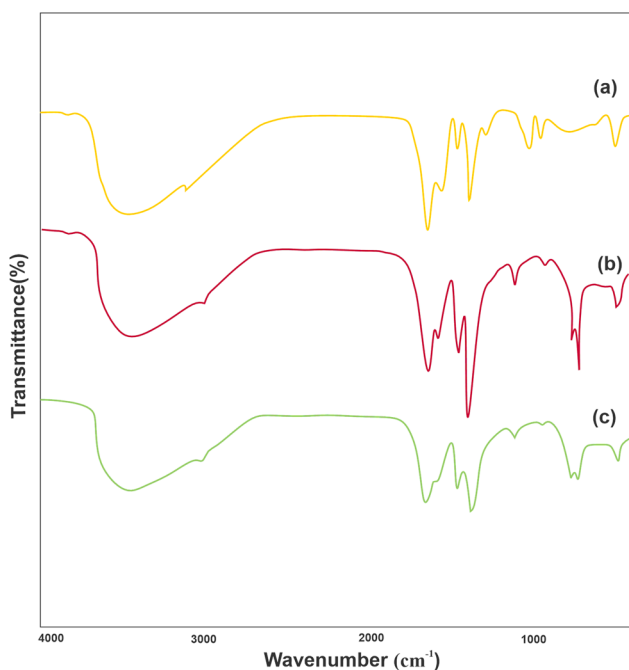


Fig. 5 FTIR results of **a** CMOF, **b** AF-CMOF, and **c** AF-CMOF after adsorption

(Madden et al. 2022). Additionally, the FTIR spectrum of AF-CMOF demonstrated some characteristic peaks of NH₂-SiO₂, including Si-O-Si at approximately 1036 cm⁻¹ and Si-O at around 808 cm⁻¹. Also, C-N stretches were observed at 1257 and 1340 cm⁻¹ and N-H bending was identified at 764 cm⁻¹ (Bhoria et al. 2020).

Assessment of PFOS adsorption onto CMOF and AF-CMOF

The effectiveness of CMOF and AF-CMOF in PFOS removal after exposure to water for four and seven days was examined in this study. As mentioned in Fig. 6, CMOF showed a significant reduction in its PFOS adsorption performance after only four days of contact with water, with the adsorption capacity dropping to a mere 2 mg/g. After seven days, CMOF exhibited almost no adsorption capacity. In contrast, AF-CMOF demonstrated remarkable water stability, retaining 89% of its initial PFOS adsorption capacity even after seven days of water exposure. These results indicate that AF-CMOF has exceptional water resistance compared to CMOF. Moreover, the aim of this section was to evaluate the PFOS elimination using CMOF and AF-CMOF via analyzing Freundlich and Langmuir isotherm equations in addition to pseudo-first- and second-order models to investigate the kinetic data. The corresponding equations are given below:

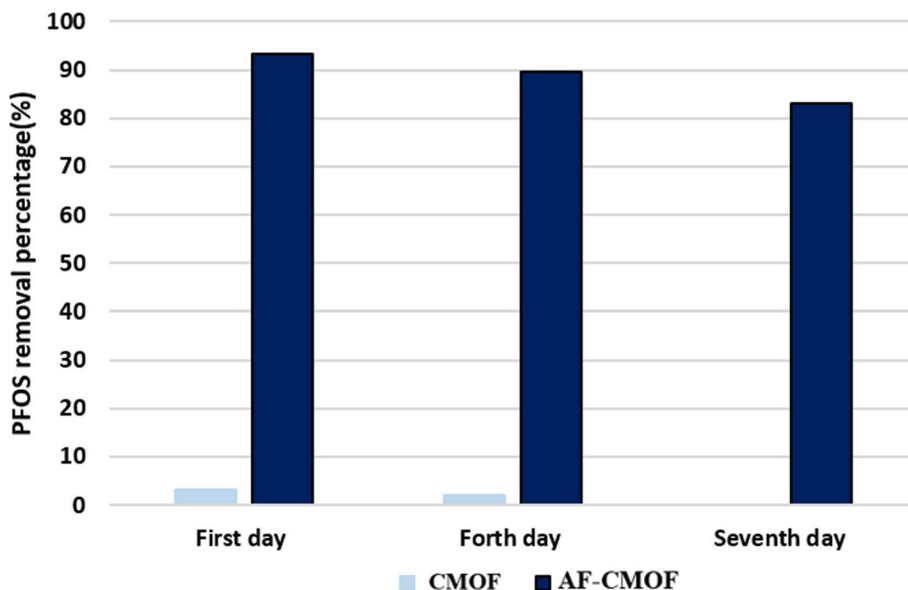
$$1/q_e = 1/(C_e \times q_m \times K_l) + 1/q_m \quad (\text{Langmuir isotherm equation})$$

$$\text{Log } q_e = \text{Log } K_f + 1/n \times \text{Log } C_e \quad (\text{Freundlich isotherm equation})$$

$$= \text{Ln } q_m - K_1 \times t \quad (\text{pseudo - first order kinetic equation})$$

$$t/q_t = 1/K_2 \times q_m^2 + t/q_m \quad (\text{pseudo - second order kinetic equation})$$

Fig. 6 PFOS removal by CMOF and AF-CMOF after four- and seven-day exposure to water



The Langmuir model showed the highest theoretical PFOS uptake performance for CMOF ($R^2=0.9975$) and AF-CMOF ($R^2=0.999$) according to Fig. 7 and Table 2 to be 24 and 689 mg/g, respectively. Though, the actual highest PFOS adsorption was recorded as 23 mg/g for CMOF and 650 mg/g for AF-CMOF, signifying a lower real PFOS sorption performance for both materials than the theoretical capacity. The PFOS uptake onto adsorbents rapidly achieved the maximum capacity within a time of 25 and 20 min according to Fig. 8 and Table 3 for AF-CMOF and CMOF, respectively. The slight time difference in the equilibrium time might be due to the existence of $\text{NH}_2\text{-SiO}_2$ nanoparticles that confined the pore network of the MOF. PFOS adsorption adhered to the pseudo-second-order model, indicating that the sorption rate is dictated by the chemisorption phase. The Langmuir model demonstrated good agreement with the adsorption isotherms on both CMOF and AF-CMOF, suggesting that the PFOS adsorption took

place on a uniform surface with a limited number of equivalent sorption sites. The results highlighted the potential of these MOFs as effective adsorbents for removing PFOS from water environments. It should be mentioned that the AF-CMOF showed a better performance in PFOS removal than most of the similar adsorbents, including magnetic carbon nitride and porous silica adsorbents. For instance, magnetic carbon nitride adsorbent exhibited a PFOS uptake performance of 454.55 mg/g, while porous silica adsorbents exhibited PFOS elimination performance in the range of 70–490 mg/g (Punyapalakul et al. 2013; Yan et al. 2014).

Assessment of the PFOS removal mechanism and the effect of pH value

The present study extensively examined the pH influence on the PFOS adsorption onto AF-CMOF. The findings proposed that the most effective adsorption of AF-CMOF was

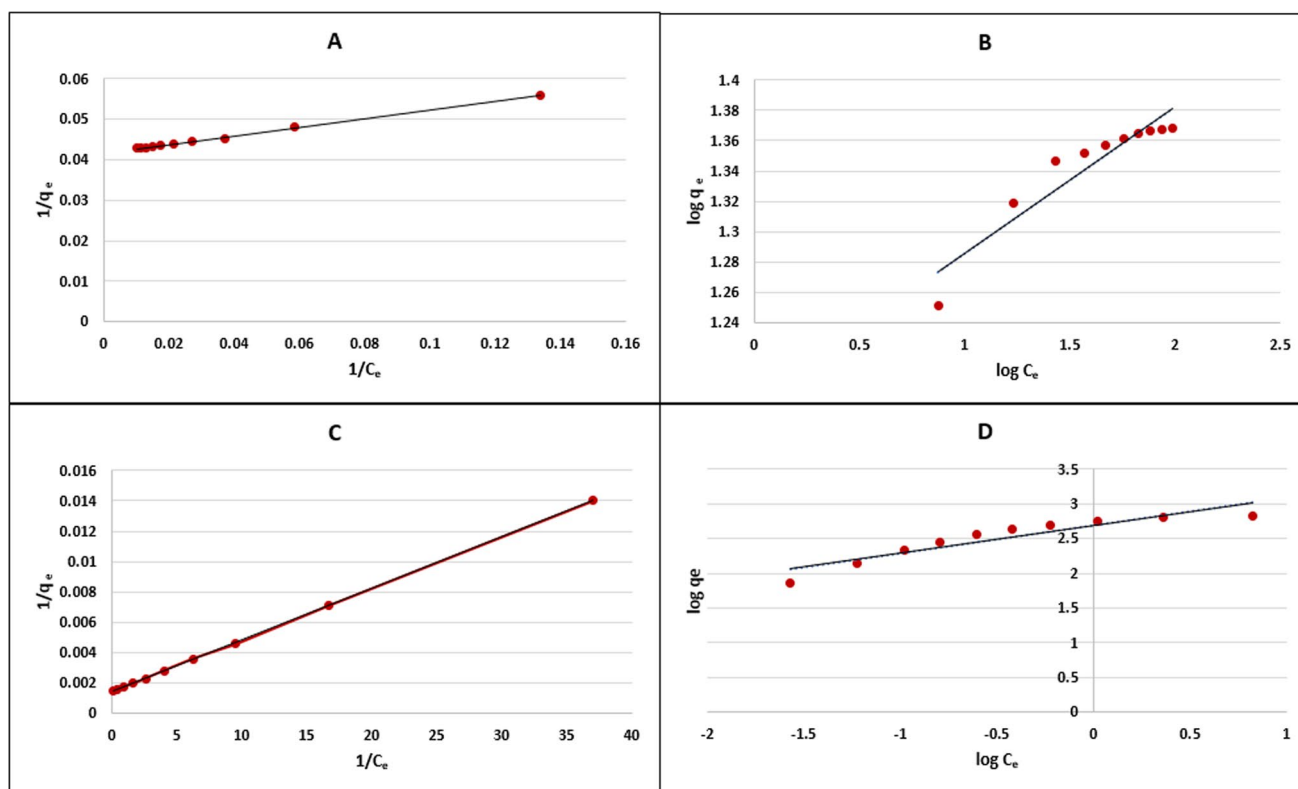


Fig. 7 A Langmuir isotherm of CMOF, B Freundlich isotherm of CMOF, C Langmuir isotherm of AF-CMOF, D Freundlich isotherm of AF-CMOF

Table 2 Fitting parameters for Langmuir and Freundlich isotherms

	Langmuir			Freundlich		
	$q_m(\text{mg/g})$	$K_f(\text{L/mg})$	R^2	n	$K_f(\text{mg/g})$	R^2
CMOF	24	0.4	0.9975	10.37	15.47	0.8816
AF-CMOF	689	4.24	0.999	2.52	485.96	0.8538

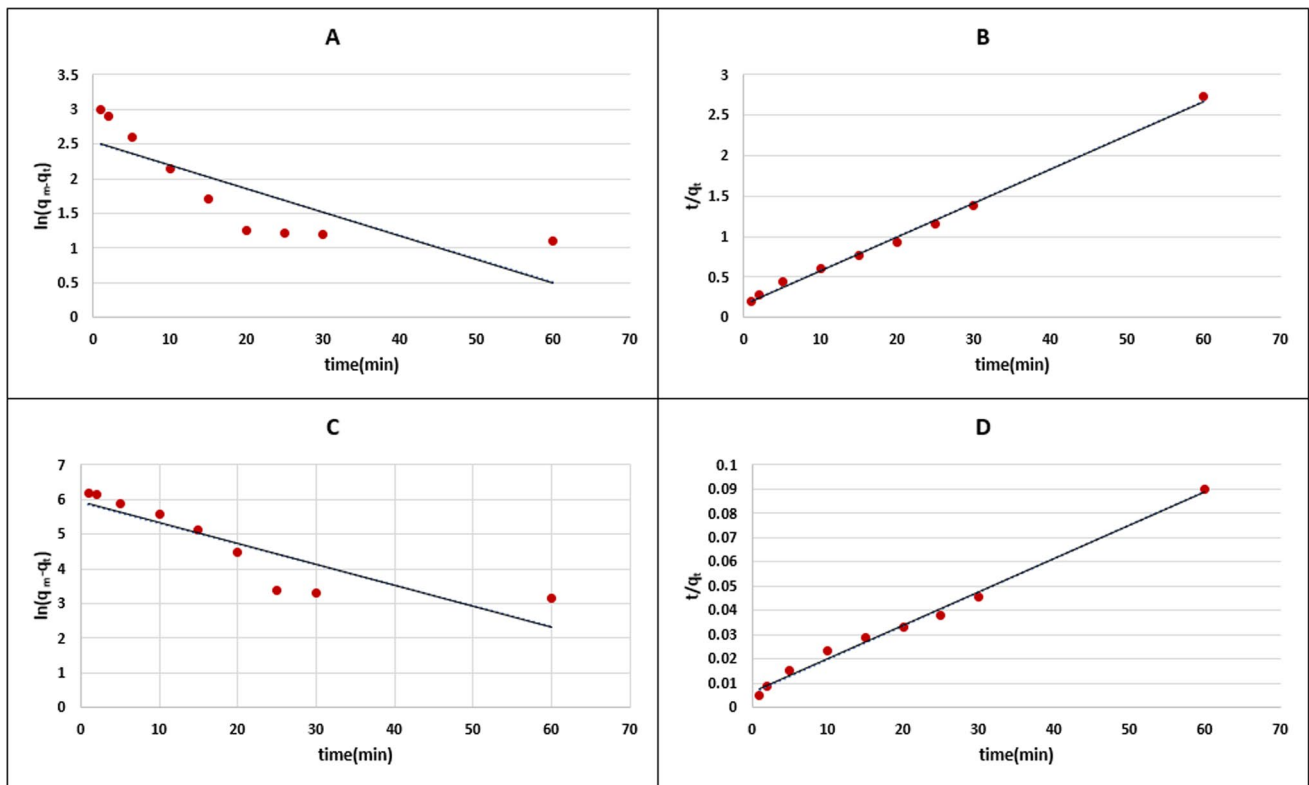


Fig. 8 A Pseudo-first-order model of CMOF, B Pseudo-second-order model of CMOF, C Pseudo-first-order model of AF-CMOF, D Pseudo-second-order model of AF-CMOF

Table 3 Calculated parameters from pseudo-first and second-order kinetic equations

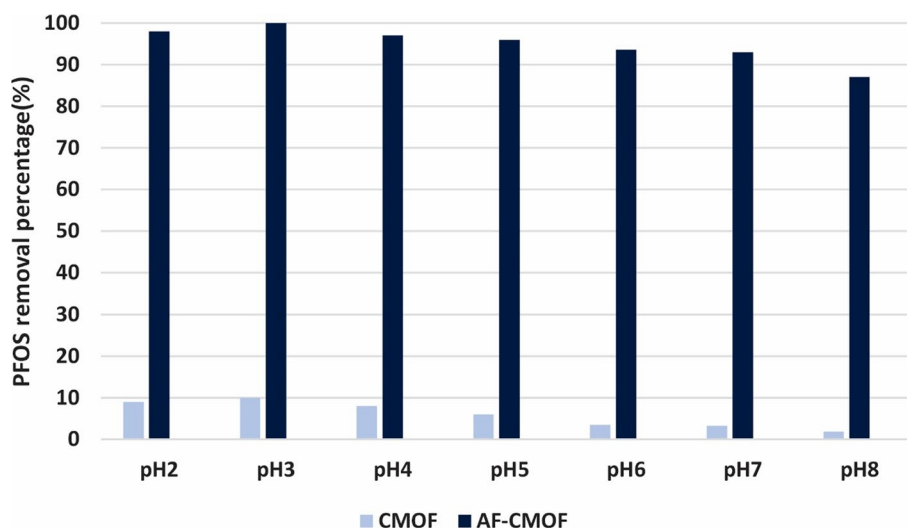
Materials	Pseudo-first-order			Pseudo-second-order		
	q_m (mg/g)	K_1 (1/min)	R^2	q_m (mg/g)	K_2 (g/mg.min)	R^2
CMOF	12.6	0.0339	0.6598	23.92	0.0107	0.9962
AF-CMOF	371.59	0.06	0.7754	714.29	0.0003	0.9919

attained at a pH level of 3, as illustrated in Fig. 9. It could be attributed to the protonation of amine functionalities at acidic pH levels. As a result, the positively charged amine groups create active sites for the sulfonate headgroup of PFOS molecules, facilitating the adsorption process. However, at pH levels exceeding 7, the presence of OH^- ions compete with PFOS during the adsorption process, consequently exerting a detrimental influence on the conditions for PFOS removal. These findings align with previous studies investigating PFOS adsorption through aminated adsorbents, which emphasized the importance of the initial pH value in determining the adsorption efficiency (Zhang et al. 2011a, b; Aly et al. 2019).

To conduct additional research the adsorption mechanism of PFOS onto the AF-CMOF and to determine the specific functionalities participated in the process, an analysis of the FTIR result of the adsorbent sample was conducted

following the adsorption. The intensity of the peaks related to NH_2 functionalities, including the C–N stretches at 1257 and 1340 cm^{-1} and the N–H bending band at 764 cm^{-1} , reduced after the adsorption of PFOS. This observation demonstrates that the amine functionalities act as a significant role in the PFOS uptake process. The amine functionalities become protonated and obtain a positive charge at low pH values, which allows them to provide electrostatic interactions to capture PFOS. The obtained results are consistent with published literature that have shown the involvement of amine groups in the sorption of anionic PFAS. An instance of this phenomena is the FTIR analysis of cross-linked chitosan adsorbent after PFOS adsorption, which revealed a slight decrease and a shift in the characteristic peaks of N–H groups from 3429 to 3470 cm^{-1} and from 1649 to 1635 cm^{-1} , attributed to the N–H stretches and bending, respectively (Zhang et al. 2011a, b; Ateia et al.

Fig. 9 pH effect on the PFOS adsorption performance at $C = 100\text{mg/L}$



2019). These results suggest that the amine moieties that exist in the adsorbent were in direct interaction with the adsorbed PFOS. In addition, the point of zero charge (PZC) for an adsorbent is the pH at which the solution exhibits constancy despite the introduction of additional acid or base. At this point, the adsorbent carries a neutral charge, and subsequent additions of acid or base have no impact on pH. Accurately determining the PZC is essential for comprehending the adsorbent's behavior and refining its application across diverse scenarios. In the specific instance of AF-CMOF, the point of zero charge was ascertained to be 5.6.

Assessment of adsorbent reusability

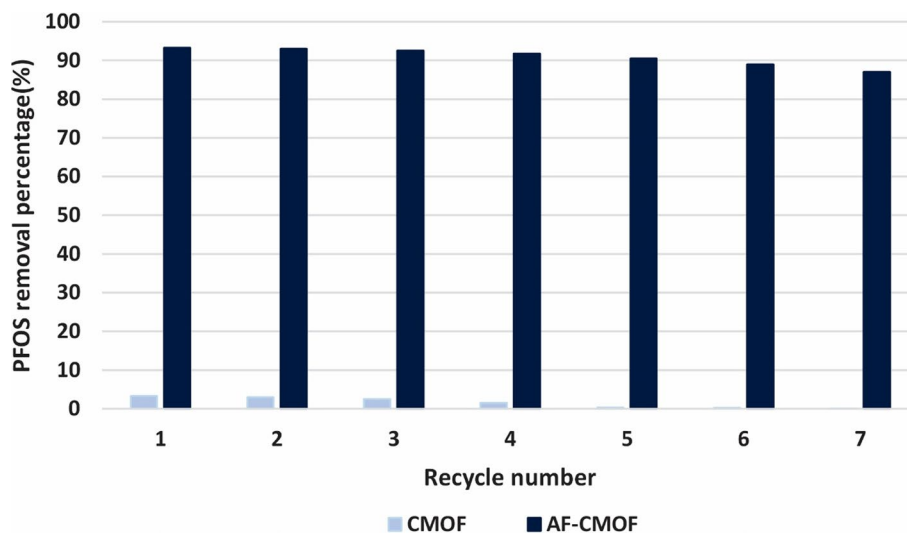
Recovery and reuse of the adsorbent is a critical factor in industrial applications. The potential for reuse of the synthesized MOF was evaluated by performing adsorption/

desorption cycles. The obtained results demonstrated that there was a slight decline in the PFOS removal performance after the recovery of adsorbent, which may be related to either the saturation of active sites or the chemical behavior of the adsorption process. Nevertheless, as depicted in Fig. 10, AF-CMOF demonstrated an acceptable capacity for reuse, maintaining 93% of its initial PFOS removal capacity for up to eight cycles. This suggests that AF-CMOF could be a potential candidate for real-life water treatment situations, especially where repeated use is required.

Conclusion

In conclusion, this study introduces an innovative approach to designing an adsorbent for efficient PFOS removal from water media. Through the modification of a coordination

Fig. 10 Recovery study of CMOF and AF-CMOF for lead ions adsorption process at $\text{pH} = 7$ and $C = 100\text{ mg/L}$



microporous organic framework (CMOF) with amine-functionalized SiO₂ nanoparticles, the synthesized product demonstrated an outstanding PFOS uptake capacity of 670 mg/g, surpassing the capacity of the unmodified CMOF by over 30 times. AF-CMOF, despite having a reduced specific surface area of 999 m² g⁻¹ compared to CMOF's surface area of 1098 m² g⁻¹, displayed superior PFOS adsorption characteristics. The PFOS uptake process adhered to a monolayer chemisorption, as indicated by the pseudo-second-order kinetic model and Langmuir isotherm. Additionally, the modified adsorbent exhibited remarkable water stability, maintaining its structural integrity even after seven days of water exposure, unlike CMOF, which experienced rapid collapse after four days of water exposure. The study highlighted the significant impact of solution pH on the PFOS uptake process, emphasizing the dominance of electrostatic interactions between protonated amine functionalities and PFOS molecules. In summary, the findings of this research hold significant implications for the development of highly effective and durable adsorbents for PFOS removal from contaminated water sources.

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Declarations

Conflict of interest All authors declare no conflict of interest.

Ethical approval The authors did this research in compliance with ethical standards.

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