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Efficient Removal of PFCs from Fluoropolymer Production Wastewater Using Functionalized MCM-41 Adsorbents

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Abstract

Perfluorinated compounds (PFCs), especially perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), are persistent organic pollutants of increasing concern because of their extensive use in fluoropolymer production and their environmental persistence. In this work, mesoporous MCM-41 was synthesized and further functionalized by post-grafting to obtain amino-modified MCM-41 (MCM-41-NH_2) and fluorinated MCM-41 (MCM-41-3F-Cl). Their adsorption performances toward representative PFCs were systematically evaluated through structural characterization, adsorption isotherm analysis, regeneration tests, and treatment of real fluoropolymer emulsions. The results showed that surface functionalization significantly improved the adsorption performance of MCM-41. Structural characterization confirmed that the mesoporous framework was retained after modification, while the introduced functional groups effectively altered the surface properties of the adsorbents. Both functionalized materials exhibited high adsorption capacities toward PFOA, with maximum values of approximately 380-390 mg/g. In addition, high removal efficiencies were obtained for PFOS and PFBA. Among the tested materials, MCM-41-3F-Cl showed the most balanced overall performance, including good regeneration stability over five adsorption–desorption cycles and effective treatment of real fluoropolymer emulsions. The removal efficiency of PFOA remained above 90%, and the residual concentration was reduced to below 25 μg/L. These results indicate that functionalized MCM-41, especially MCM-41-3F-Cl, is a promising adsorbent for the treatment of PFC-containing fluoropolymer wastewater.

Keywords

Perfluorinated Compounds; MCM-41; Surface Functionalization; Adsorption; Fluoropolymer Wastewater.

1. Introduction

PFAS, including legacy compounds such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been widely used in fluoropolymer production because of their excellent surface activity, thermal stability, and chemical resistance [1]. Although fluoropolymers are often discussed separately from other PFAS, increasing evidence indicates that fluoropolymer manufacture, use, and associated processing aids can still contribute substantially to environmental PFAS releases and related health concerns [1].

Because of the exceptionally strong carbon–fluorine bond, PFAS are highly persistent, mobile, and resistant to conventional degradation processes. They have been widely detected in surface water, groundwater, drinking water, wastewater, and sludge, which has led to increasing concern regarding long-term environmental accumulation and human exposure [2,3]. Recent reviews have emphasized that wastewater treatment plants and industrial discharges can act not only as sinks but also as secondary sources of PFAS, especially for short-chain and emerging analogs that are not effectively removed by conventional treatment processes [3,4].

Industrial wastewater is particularly important in this context. A recent review of PFAS in industrial wastewater summarized contamination across multiple industrial sectors and highlighted the need for source-oriented treatment strategies in high-strength industrial streams [5]. In addition, field investigations in chemical industrial parks in eastern China have shown that PFAS concentrations in wastewaters and receiving waters can remain elevated around industrial sources, further confirming that industrial activities are major contributors to local PFAS burdens [2].

In response to the persistence and widespread occurrence of PFAS, treatment technologies such as advanced oxidation, plasma processes, membrane-based separation, ion exchange, and adsorption have been extensively explored [6,7]. However, many destructive technologies still face practical limitations, including high energy consumption, incomplete mineralization, and the potential formation of secondary byproducts, while non-destructive separation technologies require efficient adsorbents and appropriate management of PFAS-laden residuals [6]. Among currently available treatment options, adsorption remains one of the most practical approaches because of its operational simplicity, relatively low cost, and compatibility with complex water matrices [8].

Nevertheless, conventional adsorbents such as activated carbon and ion-exchange resins do not always provide satisfactory performance for all PFAS species, especially short-chain compounds, and their efficiency can be strongly influenced by water chemistry and competing solutes [9]. Recent reviews have therefore highlighted the importance of developing novel adsorbents with tailored pore structures, surface charge, and specific interfacial interactions to improve PFAS capture under realistic treatment conditions.

Silica-based porous materials are promising candidates in this regard. Mesoporous silica materials such as MCM-41 possess ordered pore channels, large specific surface area, and abundant surface silanol groups, which allow convenient post-synthetic functionalization [10]. Recent studies on tailored silica adsorbents have demonstrated that surface functionalization can substantially improve the removal of long- and short-chain PFAS by introducing specific interaction sites, including electrostatic, hydrophobic, and fluorophilic domains [10]. These findings suggest that functionalized mesoporous silica may offer a useful route for improving PFAS removal from fluoropolymer-related wastewater.

In this work, MCM-41 was synthesized and modified by post-grafting to obtain amino-functionalized MCM-41 (MCM-41-NH2) and fluorinated MCM-41 (MCM-41-3F-Cl). Their structural characteristics and adsorption performances toward representative PFCs were systematically investigated, with emphasis on pH effects, adsorption kinetics, adsorption isotherms, regeneration behavior, and treatment performance in real fluoropolymer emulsions. The aim of this study was to evaluate the potential of functionalized mesoporous silica adsorbents for the efficient removal of fluorinated contaminants from fluoropolymer wastewater.

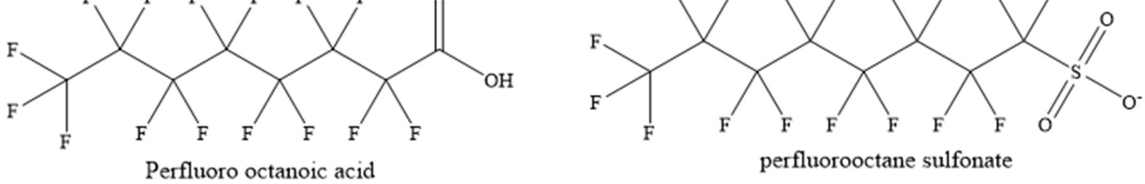


Figure 1. PFOA and PFOS chemical structures.

2. Materials and Methods

2.1 Chemicals and Materials

Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), ammonia solution, toluene, and ethanol were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. 3-Aminopropyltriethoxysilane (APTES) and (3,3,3-trifluoropropyl) methyldichlorosilane (TFDCMS) were obtained from Adamas Reagent Co., Ltd. Standard compounds of PFOA, PFOS, and PFBA were purchased from AccuStandard (China). Real fluoropolymer emulsions, including PFA and FEP latex samples, were provided by Sinochem Chenguang Chemical Research Institute. The overall experimental workflow for material preparation and adsorption evaluation is illustrated in Figure 2.

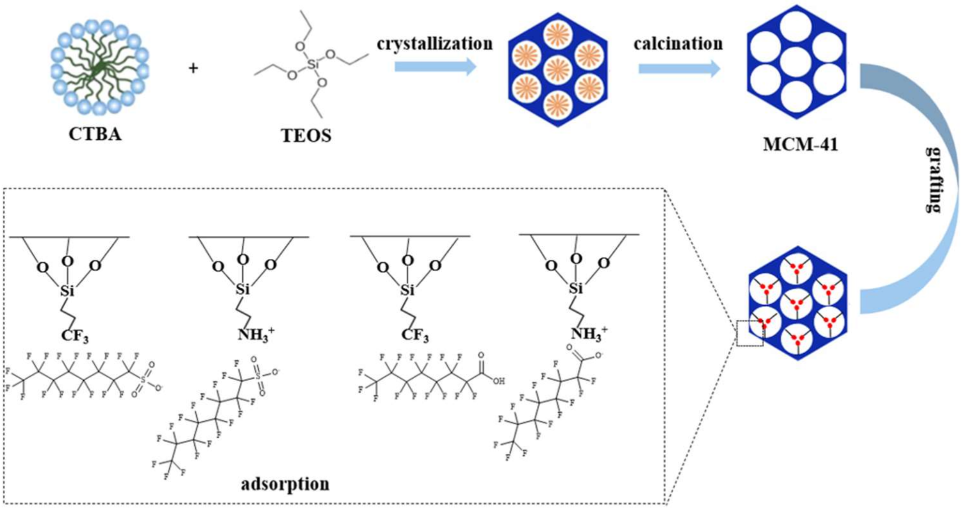


Figure 2. Schematic diagram of material preparation and adsorption.

2.2 Preparation of Adsorbents

MCM-41 was synthesized using a hydrothermal route. CTAB was dissolved in deionized water, and the pH of the solution was adjusted to approximately 12 using ammonia solution. TEOS was then slowly added as the silica source, and the mixture was stirred until a white gel formed. The resulting gel was aged at room temperature for 3 days. The product was filtered, washed, dried, and calcined at 550 °C for 12 h to remove the template and obtain MCM-41.

To prepare MCM-41-NH_2, 1.0 g of activated MCM-41 was dispersed in anhydrous toluene. APTES was added under nitrogen protection, and the mixture was refluxed for 24 h. The product was then washed with toluene and ethanol and dried to obtain amino-functionalized MCM-41. Fluorinated MCM-41 (MCM-41-3F-Cl) was prepared using a similar post-grafting route, except that TFDCMS was used as the modification reagent. The fluorination reaction was conducted at 40 °C for 24 h, followed by washing and drying.

2.3 Characterization

The prepared materials were characterized to confirm the retention of the mesoporous framework after surface functionalization and to verify the successful introduction of amino and fluorinated groups. Fourier transform infrared spectroscopy (FT-IR) was used to identify characteristic functional groups. X-ray diffraction (XRD) was employed to examine the ordered mesostructure of the adsorbents. The morphology and microstructure were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Nitrogen adsorption–desorption measurements were performed to determine the specific surface area, pore volume, and pore size distribution of the materials. These techniques were employed to correlate structural evolution with adsorption behavior after surface functionalization.

2.4 Batch Adsorption Experiments

Batch adsorption experiments were carried out using PFOA as the model pollutant. The effects of pH, contact time, initial concentration, temperature, and adsorbent dosage on adsorption performance were investigated systematically. Considering both adsorption performance and practical applicability, the optimized conditions were room temperature (25 °C), an adsorbent dosage of 50 mg/L, and a contact time of 2 h. Under these conditions, the adsorption performances of the functionalized adsorbents toward PFOA, PFOS, and PFBA were further evaluated. Adsorption kinetics and isotherm models were used to analyze the adsorption process.

For batch adsorption experiments, a known amount of adsorbent was added to PFOA solution and shaken in a thermostatic shaker. The pH of the solution was adjusted using dilute HCl or NaOH as required. After adsorption, the suspension was separated and the residual concentration of PFOA in the supernatant was determined. The adsorption capacity and removal efficiency were calculated from the initial and final concentrations.

2.5 Regeneration and Application in Real Samples

The reusability of the adsorbents was evaluated through five consecutive adsorption–desorption cycles. After each adsorption cycle, the adsorbent was separated and regenerated, then reused in the next cycle to assess the retention of adsorption performance. In addition, MCM-41-3F-Cl was applied to the treatment of real fluoropolymer emulsions, including PFA and FEP latex samples, to assess its practical applicability in complex wastewater matrices.

For the treatment of real fluoropolymer emulsions, 10 mg of MCM-41-3F-Cl was added to 250 mL of latex sample and shaken for 1 h at room temperature. After adsorption, the supernatant was filtered and analyzed for residual PFOA concentration. Before instrumental analysis, the fluoropolymer emulsions were pretreated to break the emulsion and extract PFOA into a suitable solvent phase. Methanol containing 0.4% formic acid was selected as the extraction solvent because it provided satisfactory recovery without gel formation during pretreatment.

3. Results and Discussion

3.1 Structural Characterization of Functionalized MCM-41

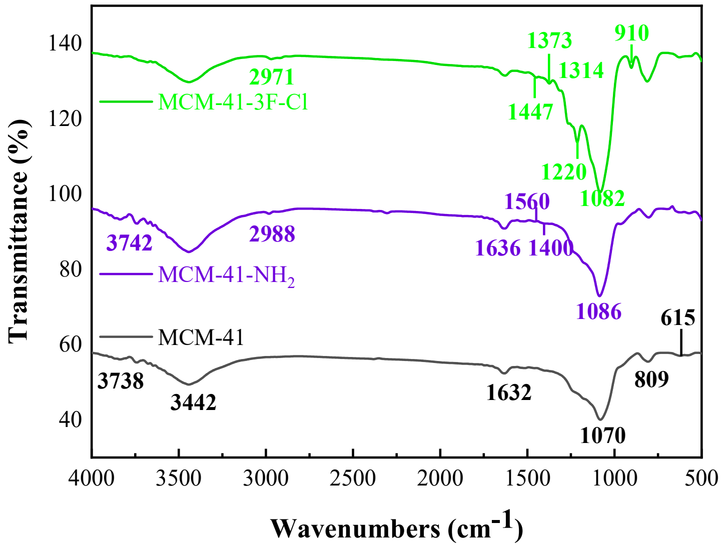


Figure 3. FT-IR spectra of MCM-41 and functionalized MCM-41 adsorbents.

The characterization results confirmed that the mesoporous framework of MCM-41 was largely retained after surface functionalization. FT-IR analysis revealed the appearance of characteristic bands associated with grafted organic groups, indicating the successful modification of the MCM-41 surface. In particular, the fluorinated adsorbent showed a characteristic C–F stretching vibration band, supporting the successful introduction of fluorinated chains onto the mesoporous silica framework.

Small-angle XRD patterns further confirmed that both MCM-41-NH_2 and MCM-41-3F-Cl retained the characteristic ordered mesoporous structure after grafting. The presence of a strong diffraction peak assigned to the (100) plane indicates that the hexagonal pore arrangement of MCM-41 was preserved after modification. Although the higher-order reflections became weaker after grafting, suggesting a partial decrease in structural ordering, the overall mesostructural framework remained intact.

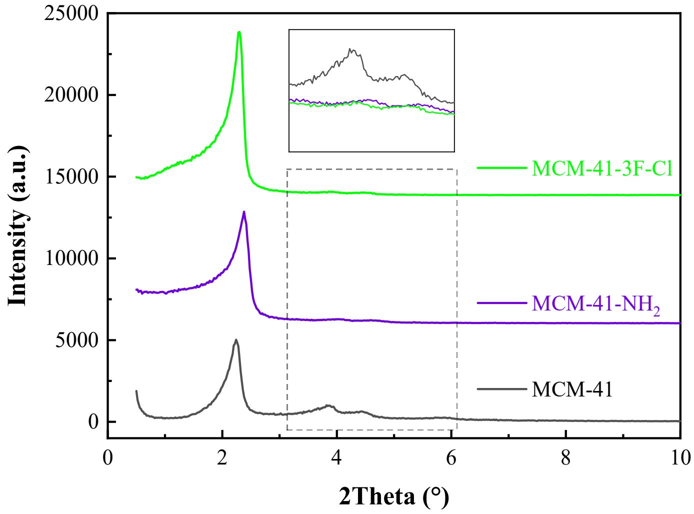


Figure 4. XRD patterns of MCM-41 and functionalized MCM-41 adsorbents.

Nitrogen adsorption–desorption analysis showed that the functionalized materials still exhibited typical mesoporous characteristics. Compared with pristine MCM-41, both MCM-41-NH_2 and MCM-41-3F-Cl showed reduced specific surface area, pore volume, and pore diameter after grafting, indicating that the introduced organic groups occupied part of the accessible pore space. This result further supports the successful anchoring of functional groups on the internal and/or external surface of the mesoporous framework.

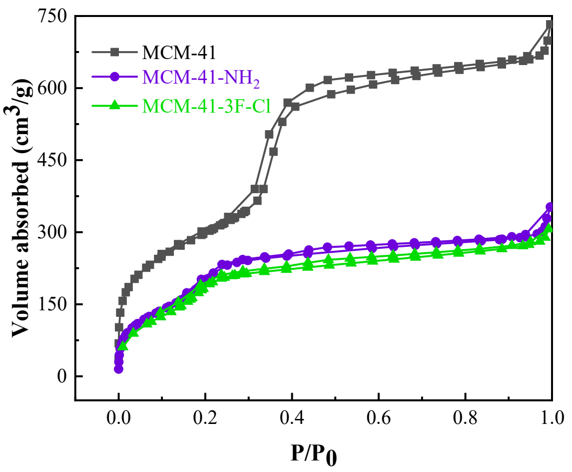


Figure 5. N2 adsorption-desorption isotherms of mesoporous materials.

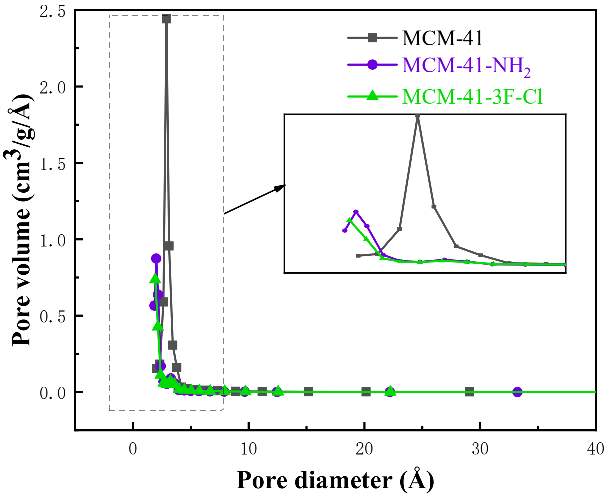
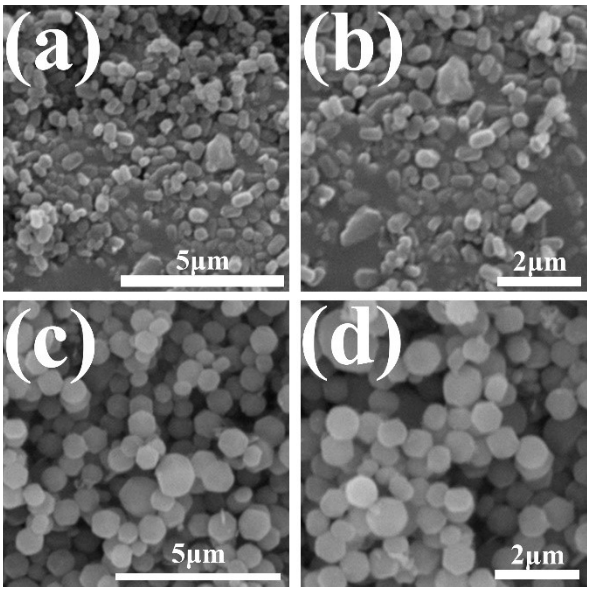


Figure 6. BJH pore size distribution plot of mesoporous materials.

SEM and TEM observations revealed that the functionalized materials maintained relatively uniform particle morphology and ordered mesoporous channels. MCM-41-NH_2 exhibited a slightly rougher surface after grafting, while MCM-41-3F-Cl showed a relatively smoother and more regular particle morphology. The TEM images further confirmed that the one-dimensional mesoporous channels remained visible after functionalization, demonstrating that the post-grafting process did not destroy the ordered mesoporous architecture.



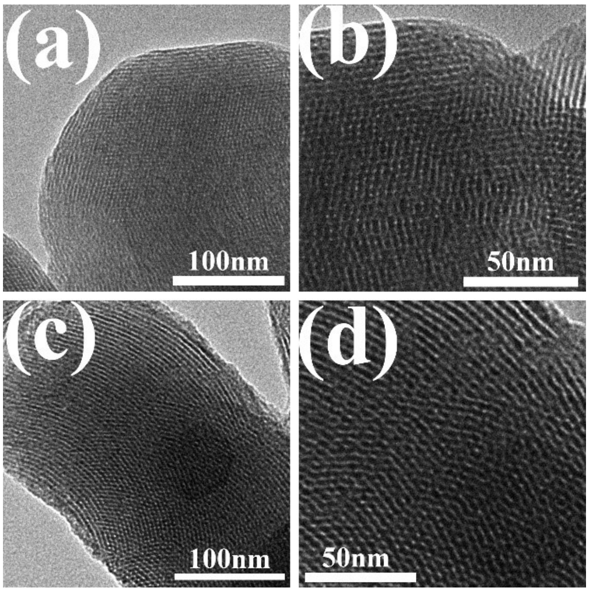


Figure 7. SEM images of mesoporous materials. **Figure 8.** TEM images of mesoporous materials.

3.2 Adsorption Isotherms

To further evaluate the adsorption behavior of functionalized MCM-41 toward PFOA, adsorption isotherms were analyzed at different temperatures. The adsorption capacity increased with increasing equilibrium concentration, indicating progressive occupation of available adsorption sites on the adsorbent surface. The results also showed that surface functionalization significantly enhanced the affinity of MCM-41 toward PFOA.

For MCM-41-NH_2, the adsorption data were better described by the Langmuir model, suggesting relatively homogeneous adsorption sites and monolayer adsorption characteristics under the tested conditions. The calculated maximum adsorption capacities were 379.28, 391.93, and 385.67 mg/g at 308.15, 318.15, and 328.15 K, respectively. The corresponding Langmuir fitting correlation coefficients increased from 0.86 to 0.96 with increasing temperature, indicating improved model applicability at higher temperatures.

For MCM-41-3F-Cl, the adsorption behavior showed a more complex fitting trend. At lower temperatures, the Freundlich model gave better fitting results, implying a relatively heterogeneous adsorption surface and the possible coexistence of multiple interaction modes. The Freundlich constants also indicated strong adsorption affinity. At 328.15 K, the Langmuir model exhibited a higher correlation coefficient, suggesting that monolayer adsorption characteristics became more pronounced at elevated temperature. The maximum adsorption capacity calculated by the Langmuir model reached 371.51 mg/g at 328.15 K. Overall, both functionalized adsorbents exhibited adsorption capacities in the range of approximately 380–390 mg/g, confirming the effectiveness of the surface modification strategy.

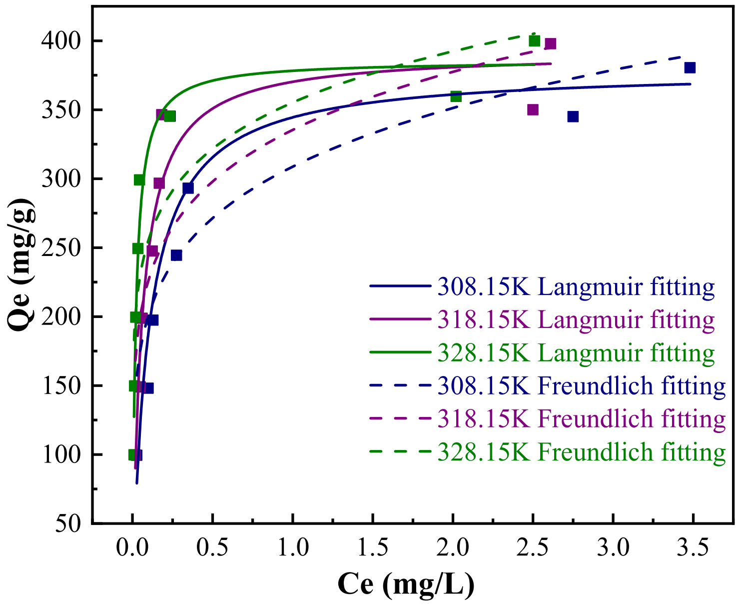


Figure 9. Isotherms of adsorption of PFOA on MCM-41-NH2 at different temperatures.

Table 1. Parameters of adsorption isotherm of PFOA onto MCM-41-NH2 at different temperatures.

temperatures (K)	Langmuir			Freundlich		
	Q_m(mg/g)	K_L(L/mg)	R^2	K_F	1/n	R^2
308.15	379.28	9.89	0.86	308.76	0.186	0.72
318.15	391.93	17.07	0.93	335.38	0.171	0.73
328.15	385.67	50.86	0.96	335.26	0.143	0.76

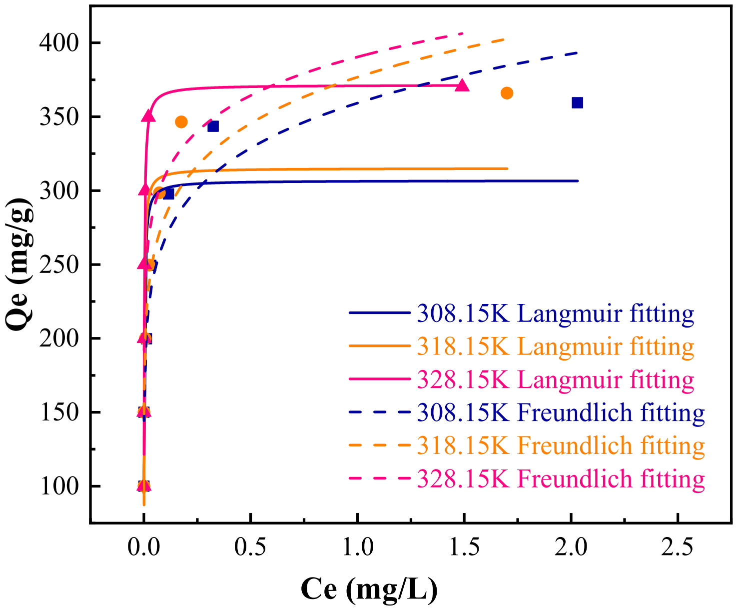


Figure 10. Isotherms of adsorption of PFOA on MCM-41-3F-Cl at different temperatures.

Table 2. parameters of adsorption isotherm of PFOA onto MCM-41-3F-Cl at different temperatures.

temperatures (K)	Langmuir			Freundlich		
	Q_m(mg/g)	K_L(L/mg)	R^2	K_F	1/n	R^2
308.15	306.81	561.63	0.76	359.26	0.13	0.90
318.15	315.12	638.58	0.78	376.81	0.13	0.88
328.15	371.51	607.05	0.97	390.46	0.1	0.62

3.3 Adsorption Selectivity toward Different PFCs

To evaluate the adsorption selectivity of the functionalized materials toward representative PFCs with different chain lengths and functional groups, adsorption experiments were further conducted using PFOA, PFOS, and PFBA. Both MCM-41-NH_2 and MCM-41-3F-Cl exhibited high removal efficiencies for PFOA and PFOS, while the removal of short-chain PFBA was relatively lower but still remained above 79%. These results indicate that the functionalized MCM-41 materials possess broad applicability toward different classes of PFCs, although adsorption affinity is still influenced by molecular structure and chain length.

Table 3. Removal efficiencies of PFOA, PFBA, and PFOS by functionalized MCM-41 adsorbents.

Name	MCM-41-NH_2			MCM-41-3F-Cl		
	PFOA	PFBA	PFOS	PFOA	PFBA	PFOS
C_0 (μg/L)	2500	2500	2500	2500	2500	2500
Ct (μg/L)	90.1	207	59.3	16.2	202	9.31
η (%)	90.99	79.3	94.07	98.38	79.8	99.07

Among the tested materials, MCM-41-3F-Cl showed the best overall adsorption performance, especially for PFOS and PFOA. The superior performance of this material may be attributed to the

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synergistic effect of the mesoporous framework and fluorinated surface groups, which enhanced the affinity of the adsorbent toward fluorinated organic molecules. The high PFOS removal efficiency also suggests that fluorinated surface modification is beneficial for strengthening interactions with strongly fluorinated contaminants.

3.4 Regeneration Performance

The regeneration performance of the functionalized adsorbents was evaluated by five consecutive adsorption–desorption cycles using PFOA as the model pollutant. After each adsorption cycle, the adsorbent was separated, regenerated, washed to near neutral conditions, and reused. The results showed that the adsorption capacity decreased only slightly after repeated cycling, and more than 85% of the initial adsorption performance was retained after five cycles. This result demonstrates that the functionalized mesoporous materials possess good reusability and structural stability during repeated operation.

The favorable regeneration behavior is important for practical application because it can reduce material consumption and improve process feasibility. In addition, the hydrophobicity of MCM-41-3F-Cl promoted aggregation and facilitated solid–liquid separation after adsorption, which is a favorable feature for industrial wastewater treatment.

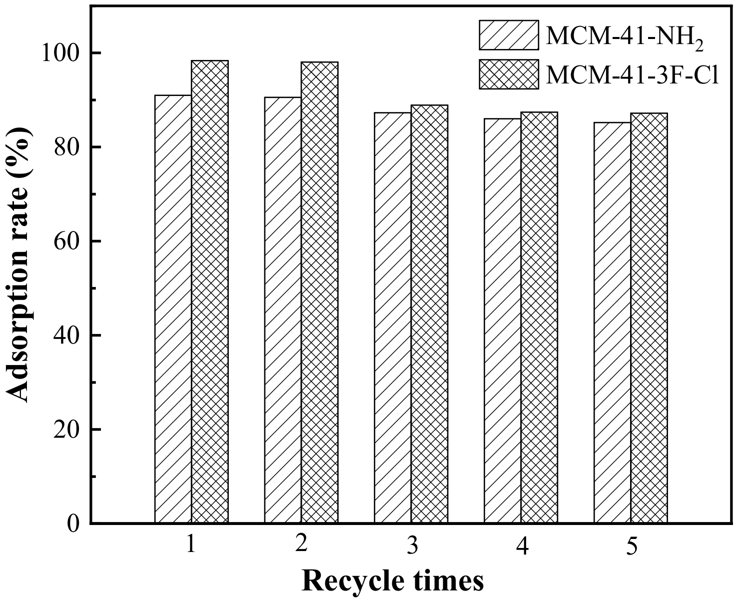

Figure 11. Regeneration performance of the functionalized adsorbents over five adsorption–desorption cycles.

3.5 Treatment of Real Fluoropolymer Emulsions

To examine the practical applicability of the adsorbent, MCM-41-3F-Cl was applied to the treatment of real fluoropolymer emulsions, including PFA and FEP latex samples obtained from industrial production. Compared with model solutions, these real matrices are more complex and may contain coexisting organic components, surfactants, and colloidal substances, which often interfere with adsorption processes. Therefore, the treatment of real emulsions provides a more rigorous evaluation of adsorbent performance.

Before instrumental analysis, the fluoropolymer emulsions were pretreated to break the emulsion and extract PFOA into a suitable solvent phase. Optimization of the pretreatment conditions showed that methanol containing 0.4% formic acid provided satisfactory PFOA recovery and avoided gel formation during sample preparation. This pretreatment step improved the reliability of the subsequent quantitative analysis.

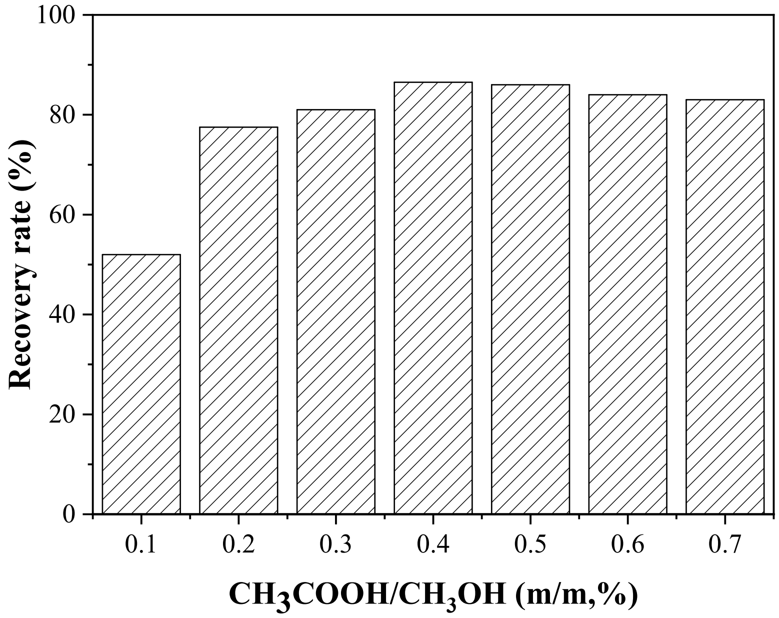

Figure 12. Effect of formic acid content on PFOA recovery from fluoropolymer emulsions.

The results showed that MCM-41-3F-Cl maintained high PFOA removal efficiency in both PFA and FEP emulsions, with removal rates above 90%. For PFA and FEP emulsions with initial PFOA concentrations of approximately 55–60 μg /L, the residual PFOA concentration after treatment decreased to below 4.6 μg /L. More importantly, all treated samples were reduced to below 25 μg /L, indicating that the adsorbent was effective in meeting the control threshold referenced in this study. This result demonstrates that the fluorinated MCM-41 adsorbent was not only effective in simplified laboratory systems but also applicable to actual fluoropolymer wastewater matrices.

The satisfactory performance in real emulsions can be attributed to two factors. First, the mesoporous structure of MCM-41 provides abundant accessible surface area and adsorption sites. Second, the fluorinated surface groups improve the affinity of the adsorbent toward perfluorinated molecules and reduce the dependence of adsorption on pH. In addition, the hydrophobic surface of MCM-41-3F-Cl facilitates post-treatment separation, which is beneficial for engineering implementation. These features suggest that fluorinated mesoporous adsorbents are promising candidates for the treatment of fluoropolymer production wastewater containing residual PFCs.

Table 4. Removal efficiency of MCM-41-3F-Cl for PFOA in real fluoropolymer emulsions.

Parameter	PFA			FEP		
	PFA-1	PFA-2	PFA-3	FEP-1	FEP-2	FEP-3
C_0 (μg/L)	59.85	56.75	57.1	57.55	55.95	54.7
Ct (μg/L)	3.48	4.36	4.58	3.77	4.44	3.6
η (%)	94.18	92.32	91.98	93.44	92.06	93.42

4. Conclusion

In this work, amino-functionalized and fluorinated mesoporous MCM-41 adsorbents were successfully prepared through hydrothermal synthesis combined with post-grafting surface modification. Structural characterization confirmed that the ordered mesoporous framework of MCM-41 was retained after functionalization, while the introduction of amino and fluorinated groups significantly altered the surface properties of the adsorbents.

The adsorption results demonstrated that surface functionalization markedly enhanced the adsorption performance of MCM-41 toward PFCs. MCM-41-NH_2 showed enhanced adsorption under acidic conditions because of electrostatic attraction between protonated amino groups and PFOA anions. In contrast, MCM-41-3F-Cl exhibited relatively stable adsorption over a wide pH range, indicating the important contribution of hydrophobic and fluorophilic interactions. Both functionalized adsorbents showed rapid adsorption kinetics, and equilibrium was reached within about 120 min. Isotherm analysis further demonstrated high adsorption capacity, with maximum values in the range of approximately 380–390 mg/g.

The functionalized materials also exhibited broad applicability toward different PFCs. High removal efficiencies were obtained for PFOA and PFOS, while acceptable performance was maintained for PFBA. In addition, the adsorbents showed good regeneration stability over five adsorption–desorption cycles. Among the materials tested, MCM-41-3F-Cl exhibited the most balanced overall performance, including high adsorption efficiency, good reusability, and easy phase separation after treatment.

Application to real fluoropolymer emulsions further demonstrated the practical potential of the fluorinated adsorbent. PFOA removal remained above 90%, and the residual concentration was reduced to well below the threshold referenced in this study. Overall, the results indicate that fluorinated functionalized MCM-41 is a promising adsorbent for the treatment of PFC-containing industrial wastewater and may provide a useful material basis for pollution control in fluoropolymer production.

Acknowledgments

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