*Article*

# Novel Fluorinated Nitrogen-Rich Porous Organic Polymer for Efficient Removal of Perfluorooctanoic Acid from Water

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**Abstract:** The mobility, durability, and widespread use of perfluorinated and polyfluoroalkyl substances (PFAS), notably perfluorooctanoic acid (PFOA), bring about serious contamination of many ground and surface waters. In this study, fluorine and amine-functionalized porous organic polymer (POP-4F) was designed and successfully synthesized as an adsorbent for PFOA removal in water. The characterization results showed that the synthesized material had an amorphous microporous structure, and the BET surface area was up to 479 $m^2$ $g^{-1}$. Its versatile adsorption property was evaluated by batch adsorption experiments using PFOA as a probe. The experiments show that the polymer was able to remove 98% of the PFOA in 5 min from water and then desorb within 3 min in methanol ($[PFOA]_0$ = 1 mg $L^{-1}$; [POP-4F] = 200 mg $L^{-1}$). Specifically, the adsorption capacity of POP-4F is up to 107 mg $g^{-1}$, according to the Langmuir fit. The rapid adsorption and desorption of PFOA by POP-4F offers the possibility of economical, environmentally friendly, and efficient treatment of real wastewater.

**Keywords:** perfluoro octanoic acid; porous organic polymer; adsorption removal

## 1. Introduction

PFAS are a class of artificial organofluorine compounds consisting of perfluorinated or partially fluorinated alkyl chains and polar acid groups [1]. The polar groups of PFAS give them a certain capability of water solubility, while the fluorine groups provide a low surface tension giving them unique hydrophobic and oleophobic properties [2]. The physical properties of PFAS make these chemicals ideal surfactants. Therefore, they are widely used as surfactants in the production of polytetrafluoroethylene (Teflon), fire-fighting foams, electroplating, and water/stain-resistant coatings in consumer products [3,4]. The stable C-F bond provides PFAS with great thermal and chemical stability, supporting their use as additives in the manufacture of flame retardants in the fields of semi-electronics, packaging, anti-adhesion, and metal surface treatment [5,6]. They are also thermally, chemically, and biologically stable and resistant to microbial degradation. Hence, they are called "forever chemicals" [7]. Although all PFAS have surfactant properties, the octa-carbon chemicals are most effective [2], thereby causing the massive worldwide use of Perfluorooctanoic acid (PFOA, a typical PFAS). Although the fluorocarbon chain of PFOA is typically hydrophobic, the carboxyl functional group of PFOA allows it to be highly water-soluble and mobile in an aqueous system [8]. The fluidity, durability, and widespread use of PFOA has resulted in its wide distribution across the global environment. It has been found in surface water [9–11], air [12], sludge [13], soil [14], sediment [15] and ice caps [16–18]. Recent studies show that PFOA has a negative impact on human health, including liver damage [19], thyroid

disease [20,21], kidney cancer [22], testicular cancer [23], and more. PFOA was detected in up to 99% of serum samples collected in a representative U.S. population during 1999–2012. People are exposed to PFOA through the use of consumer products, occupational contact, and consumption of contaminated food or drinking water [24]. PFOA in drinking water is a growing concern around the world, with different levels of regulations or guidelines being created around the world. For individual and combined PFOA and PFOS in drinking water, the EPA announced a non-regulatory lifetime Health Advisory (HA) of 70 ng $L^{-1}$ in 2016 [25,26]. Based on the data from studies in Ohio and West Virginia communities, Kate Hoffman et al. [27] noted an increase in serum PFOA concentrations of 141.5 µg $L^{-1}$ for every 1 µg $L^{-1}$ increase in PFOA in drinking water. The concentrations of PFOA in groundwater and surface water around fluorinated chemical plants, civilian airports, and military firefighting training areas were also found that were 3–4 orders of magnitude higher than U.S. EPA drinking water health advisory levels [27–29].

To efficiently eliminate the contamination of PFOA in water, various removal methods have been developed, such as photocatalytic degradation [30–33], electrocoagulation [34,35], UV irradiation [36,37], oxidation [38,39], biodegradation [40], reverse osmosis and nanofiltration [41,42]. These techniques are often inefficient, energy-intensive, or costly, rendering them unsuitable for large-scale applications. Among the different approaches for PFOA removal, adsorption has received much attention for its low cost and high efficiency. A variety of adsorbents have been explored to remove PFOA from water effectively, including activated carbon [43,44], anion exchange resins [45], molecularly imprinted polymers [46], and covalent organic framework [47]. Among them, covalent organic frameworks and granular activated carbon (GAC) have become the most used PFOA adsorbents because of their high capacity. However, the synthesis of COF is prohibitively expensive and need harsh condition, while GAC performs poorly in the presence of other organic contaminants [48]. Different from COFs, porous organic polymers with high specific surface area and abundant reactive sites were raised as a new candidate for PFOA removal because they can be synthesized under mild conditions with low cost. Moreover, the present observations found that aminated adsorbents exhibit superior adsorption capacity, tunability of synthesis, and recoverability [49]. For example, Woojung Ji et al. [50] found that the amine content in COFs plays an important role in the removal of 12 PFAS by adjusting the reduction ratio of the azide group in COF to an amine group.

Herein, we report F and N-rich porous organic polymers synthesized through the polycondensation of 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene and 2,3,5,6-tetrafluorotelephtal aldehyde. The developed POP-4F is cost-effective and can be synthesized by a simple Schiff base condensation reaction without the use of any expensive or laborious laboratory techniques. The high affinity between POP-4F and PFOA was demonstrated by a beach of experimental results. A regeneration test showed that POP-4F (loaded with PFOA) could be desorbed by sonication for 3 min (in methanol) without a significant loss of adsorption efficiency after five cycles. The rapid adsorption and desorption of PFOA by POP-4F offers the possibility of economical, environmentally friendly, and efficient treatment of real wastewater.

## 2. Materials and Methods

### 2.1. Chemicals

The 1,4-Dicyanobenzene (98%), dicyandiamide (99%), KOH (95%), and 2,3,5,6-tetrafluorotelephtal aldehyde (4F-TPA, 97%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Analytical grade N, N-Dimethylformamide (DMF), methanol, and other reagents were provided by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Perfluoro octanoic acid (PFOA, 98%) was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China).

## 2.2. Instruments

Scanning Electron Microscope (SEM) images were collected on a Helios G4 CX configured with an energy dispersive spectrometer system (Fisher Scientific International, Inc., Brno, Czech Republic). An IRTracer-100 spectrometer (Shimadzu Corporation, Kyoto, Japan) was used to record the Fourier-transform infrared (FT-IR). Sonication was performed with an SK2510LHC ultrasonic (Shanghai Kudos Ultrasonic Instruments Co., Ltd., Shanghai, China) cleaner with a power output of 250 W and a frequency of 35 kHz. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded at 25 °C on Bruker DPX-400 (Bruker Corporation, Zurich, Switzerland). Solid-state NMR spectra (SSNMR) were recorded on AVANCE (3) 400WB (Bruker Corporation, Zurich, Switzerland). $N_2$ adsorption/desorption isotherms were measured on a BELSORP-max II gas adsorption instrument (MicrotracBEL Japan, Inc., Osaka, Japan). Powder X-ray diffraction (PXRD) patterns were collected from an Empyrean diffraction-meter using Cu K$\alpha$ radiation (PANalytical B.V., Almelo, Netherlands). Ultrapure water use in this work was taken from a Milli-Q gradient ultrapure water system (Millipore, Burlington, MA, USA). The determination of PFOA concentration was performed by a high-performance liquid chromatography tandem mass spectrometer (LC-MS/MS). The HPLC separations were performed on Nexera X2 (Shimadzu Corporation, Kyoto, Japan) with an Atlantis T3 column (2.1 × 100 mm,3 μM, Waters, Massachusetts American) and an MS detector (AB SCIEX QTRAP 6500, Danaher Corporation, Washington, DC, USA).

## 2.3. Preparation of the POP-4F

### 2.3.1. Synthesis of 1,4-Bis-(2,4-diamino-1,3,5-triazine)-benzene

The synthesis of 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene (BDTB, as shown in Figure 1) referred to the reported method by Dr. Roman Fasel [51]. Briefly, KOH (1.02 g), dicyandiamide (7.4 g), and 200 mL of DMF were sequentially added in a 500 mL two-necked round-bottom flask. The solution was mixed well, and the temperature was raised to 100 °C. Then a solution of 1,4-Dicyanobenzene (2.88 g) in 100 mL of DMF was slowly added, and the temperature was raised to reflux temperature under nitrogen atmosphere. The reaction was carried out for 8 h. After stopping the heating and cooling naturally, the precipitate was filtered and washed several times with methanol. The solid product was dried in a vacuum oven at 110 °C for 12 h to give 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene as a white powder. The characterization of the POP-4F was conducted using $^1$H-NMR (400 MHz, DMSO-d$^6$: δ = 8.32 (s, 4H, Ar-H); 6.80 (s, 18H, -NH$_2$).
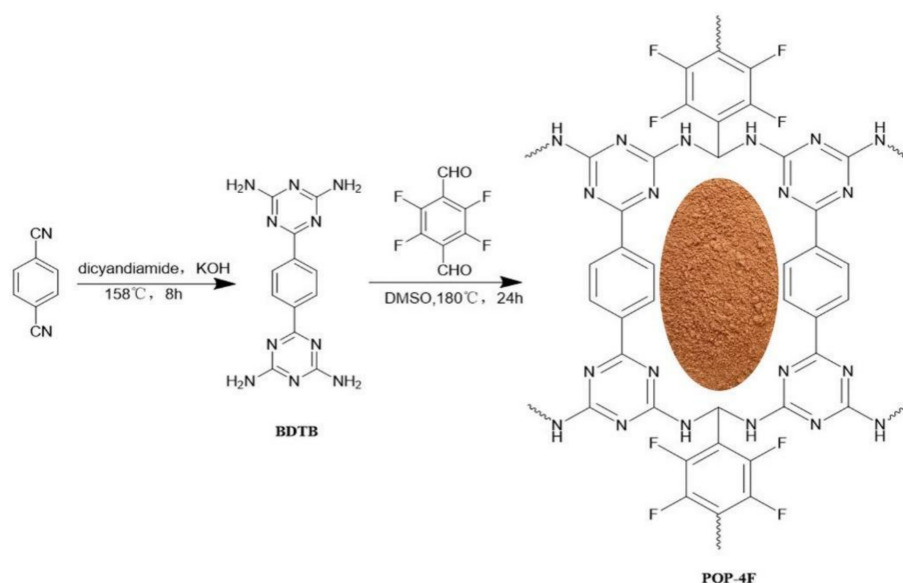


**Figure 1.** Synthesis Routes of POP-4F.

### 2.3.2. Synthesis of the POP-4F

The synthesis of POP-4F was carried out based on previous literature [52] with slight modifications (Figure 1). 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene (1185.2 mg, 4 mmol), 2,3,5,6-tetrafluorotelephtal aldehyde (824.4 mg, 4 mmol) and DMSO (50 mL) were added sequentially in a 100 mL two-necked round-bottom flask and mixed well. The reaction was then heated to 180 °C under a nitrogen atmosphere for 24 h. The reaction flask was then cooled naturally to room temperature. The solid obtained was filtered and washed with DMSO and methanol. Soxhlet extraction with methanol was carried out for 24 h and then dried under vacuum at 120 °C to afford POP-4F as an orange powder in 79% yield.

### 2.4. Adsorption Experiments

During sample preparation and storage, all utensils (sample bottles, caps, measuring cups, measuring cylinders, droppers, etc.) were made of polypropylene (pp), and contact with glass/fluorinated plastics was avoided Because fluorinated plastics such as PTFE may contain target compounds and cause interference [53,54], PFOA can adsorb on the glass thereby inducing inaccurate experimental results [29,55]. Despite contrary views [56,57], PP has been used as the first choice material in most previous studies [58–61]. In addition to the choice of vessel, filtration is another important factor in sample handling and preparation. In this work, all samples were filtered using polyethersulfone filters (0.22 μM × 13 mm). All the following experiments were performed in triplicate, and the results are provided as mean ± standard deviation.

### 2.4.1. The Impact of pH

Experiments were carried out at pH 2, 3, 4, 5, 6, 7, 8, and 9 to assess the influence of pH on the effectiveness of POP-4F for PFOA removal, with a specified amount of 0.1 mol L1 HCl or NaOH solution added. Under these conditions, no pH adjustment was performed during the adsorption process as there was no significant change in pH [62]. To achieve equilibrium, the bottles were shaken at 200 rpm for 24 h on an orbital shaker at 25 °C. Filtration of all samples was performed using 0.22-micron inorganic syringe filters (polyethersulfone membrane), and the filtrate was transferred to LC vials for further analysis using LC-MS [47]. Blank studies were carried out, and no difference in PFOA content was noticed as a result of the use of polypropylene bottles [10].

### 2.4.2. Kinetics of Adsorption

Individual batch tests in pp bottles at a pH of $3 \pm 0.2$ were used to obtain each data point for the kinetic investigations. (Unless otherwise noted, all subsequent adsorption tests were conducted at a pH of $3 \pm 0.2$). Tests were carried out under the following conditions: an initial concentration of 1 mg $L^{-1}$ PFOA, and 200 mg $L^{-1}$ adsorbent. The mixture was shaken at 200 rpm on an orbital shaker at 25 °C. After a certain time interval, samples were collected and filtered through 0.22 μm inorganic syringe filters (polyethersulfone membranes). The filtrate was refrigerated until further measurements.

### 2.4.3. Adsorption Isotherm

A PFOA adsorption isotherm was built in a 50 mL PP bottle using [POP-4F] = 200 mg $L^{-1}$ and [PFOA]$_0$ ranging from 1 to 20 mg $L^{-1}$. The bottles were shaken at 200 rpm on an orbital shaker at 25 °C for 24 h to reach equilibrium. After treatment, the samples were extracted under the same experimental conditions as described 2.4.1.

### 2.4.4. Matrix Effect and Reusability

The PFOA removal efficiency of POP-4F was tested by batch equilibrium adsorption experiments in simulated natural water, which was prepared by adding 200 mg $L^{-1}$ NaCl and 20 mg $L^{-1}$ humic acid to Milli-Q water [63]. The studies were conducted and in 50 mL PP bottles with a polymer concentration of 200 mg $L^{-1}$ and a PFOA concentration

of 1 mg L$^{-1}$ (prepared in simulated natural water). After treatment, the samples were extracted under the same experimental conditions as described Section 2.4.1.

To investigate the specificity of POP-4F for the removal of PFOA, a competitive adsorption preparation was performed. The experiment was conducted in a mixture of 9 PFCAs (perfluorobutanoic acid, perfluoropentanoic acid, perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid) all at a concentration of 1 mg L$^{-1}$. The experimental adsorption procedure and sample treatment were performed as described Section 2.4.1.

Adsorption-desorption studies were carried out in Milli-Q water for a total of five regeneration cycles. Adsorption experiments: 10 mg of POP-4F was added to a PP vial containing 50 mL of PFOA (1 mg L$^{-1}$) solution. The vial was shaken on an orbital shaker at 25 °C for 6 h at 200 rpm. The suspension obtained was filtered through a 0.22 µM inorganic syringe filter (polyethersulfone membrane), and the filtrate was transferred to LC-MS/MS analysis. During the desorption studies, the used POP-4F (which had been loaded with PFOA) was cleaned by soaking and sonicating it for 3 min in 50 mL of methanol and then recovered by syringe filtering. The filtrate was then sent to LC vials, where it was analyzed by LC-MS/MS. The POP-4F particles were used for the next adsorption step. The used adsorbent is separated by filtration through a nylon membrane (50 mm × 0.2 µm).

### 2.5. Instrumental Analysis

The PFOA concentrations were analyzed using an LC-MS/MS equipped with an Atlantis T3 column. The aqueous or organic phase (methanol) samples for the experiments were collected by filtration in a syringe equipped with a 0.22 µM inorganic membrane filter. The collected samples were transferred into LC vials stored in a refrigerator (4 °C) away from light and analyzed within 24 h. LC-MS/MS was operated in negative ionization mode by electrospray ionization using methanol and water as mobile phases.

## 3. Results and Discussion

### 3.1. Characteristics of POP-4F

The external morphology of POP-4F was first characterized and analyzed using a scanning electron microscope. As shown in Figure 2a, the synthesized POP-4F presents as an irregularly bulky structure composed of small particles. The physicochemical structure of POP-4F was characterized by FTIR, solid-state $^{13}$C NMR, N$_2$ adsorption analysis, and XPS. As shown in Figure 2b, the formation of POP-4F was confirmed by FT-IR. In BDTB monomer and POP-4F, the presence of a sharp IR band at 1542 cm$^{-1}$ (characteristic band of the triazine ring) indicates that the polycondensation reaction has proceeded successfully. The imine (-C=N-) stretching band at around 1620 cm$^{-1}$ is absent, while a very broad band at 3422 cm$^{-1}$ indicates that the polymer network is formed by C-NH-C bonding, as well as the negligible -CO-H stretching band at 2913 cm$^{-1}$ and the C=O stretching band at 1702 cm$^{-1}$, indicating an almost complete conversion of the amine and aldehyde groups to secondary amines. In Figure 2c, the peaks in the $^{13}$C NMR spectra can be assigned to the corresponding carbon atom in the chemical structure of POP-4F. The resonance signals appearing at 166.8 and 128.2 ppm were assigned to the triazine carbon atom and the benzene ring carbon atom, respectively. The characteristic peaks at 48.9–56.6 ppm are associated with alkyl carbon atoms, further demonstrating that the polymer network is linked by C-NH-C rather than C=N bonds. The peak at 207.7 ppm belongs to the terminal aldehyde group in the material. The peak at 13.7 ppm may be related to the adsorption of some impurities to the material (e.g., compounds produced by DMSO at high temperatures). The powder X-ray diffraction (PXRD, Figure 2d) patterns of the polymer display only a broad peak at 2θ = 21.6°, indicating an amorphous structure. As illustrated in Figure 2e, the nitrogen adsorption-desorption isotherm of POP-4F was determined at 77 K. A very obvious hysteresis loop can be seen in the figure, which is a typical type IV adsorption isotherm feature, indicating the presence of mesopores in POP-4F. The desorption curve in

the adsorption-desorption isotherm is relatively flat, indicating that the isotherm belongs to the H2 (b) type in the type IV adsorption isotherm, which reflects the more uniform pore size distribution of POP-4F. The Brunauer–Emmett–Teller (BET) surface area of POP-4F is up to 479 $m^2\ g^{-1}$. Additionally, the POP-4F pore sizes were mostly 1.07 and 2.05 nm (Figure 2f).
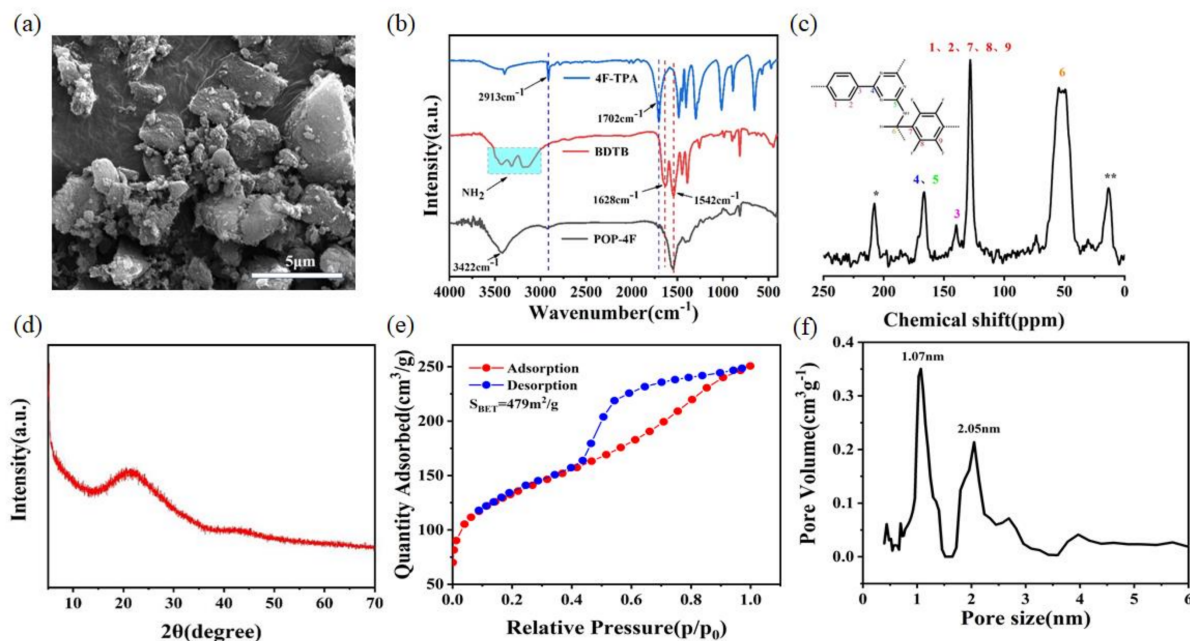


**Figure 2.** Characterization of POP-4F. (**a**) SEM; (**b**)FT-IR; (**c**) solid-state 13C NMR; (**d**) XRD; (**e**) $N_2$ adsorption-desorption isotherms; (**f**) Pore size distribution.

To gain insight into the local chemical environment, X-ray photoelectron spectroscopy (XPS) was conducted (Figure 3). The low-resolution XPS spectra demonstrated the existence of C 1s, O 1s, F 1s, and N1s (Figure 3a). The high-resolution XPS spectra of the C 1s spectrum (Figure 3b) could be deconvoluted into two peaks at 284.6 and 286.8 eV, which were assigned to C–C/C–H and triazinic C–N species, respectively. The high-resolution XPS spectra of the N 1s spectrum (Figure 3c) could be deconvoluted into two different peaks at 398.0 and 399.2 eV, which were assigned to nitrogen-atoms of triazinic and secondary amines, respectively. There is only one peak in the F 1s spectrum (Figure 3d), relative to the material containing only one type of fluorine. Whatmore, the presence of large amounts of F and N again indicates that the reaction was successfully carried out.

### 3.2. Adsorption Experiments

#### 3.2.1. The Impact of pH

The pH value has a tendency to alter the adsorbent's surface charge, which may further impair the adsorbent's effectiveness. As shown in Figure 4, the polymer maintained a high removal rate of PFOA, more than 95% within a wide pH range (pH $\leq$ 6). Interestingly, the removal rate of PFOA was up to 99.9% at pH 3, while slightly decreased when pH < 3, but significantly decreased to 77.3% when the pH of the solution was increased to 9. This is because when the pH is equal to 3, the secondary amines of POP-4F are fully protonated, while PFOA is in a deprotonated state, and the electrostatic force between the host and guest molecules is the strongest. When the pH is less than 3, the deprotonation state of PFOA is slightly weakened, so the removal rate slightly fluctuates. However, the protonation of POP-4F was significantly weakened when the pH was greater than 6, which in turn significantly reduced the electrostatic interaction between host and guest molecules, resulting in a significant reduction in the removal rate. Thus, we infer that those electrostatic interactions between the positive charges formed by protonation of the

nitrogen atoms in the polymer and the negatively charged groups of the PFOA dominate the adsorption process [8,64]. This is consistent with literature reports [65–67]. These observations suggest that the polymer has great potential for the efficient removal of PFOA from acidic industrial wastewater.
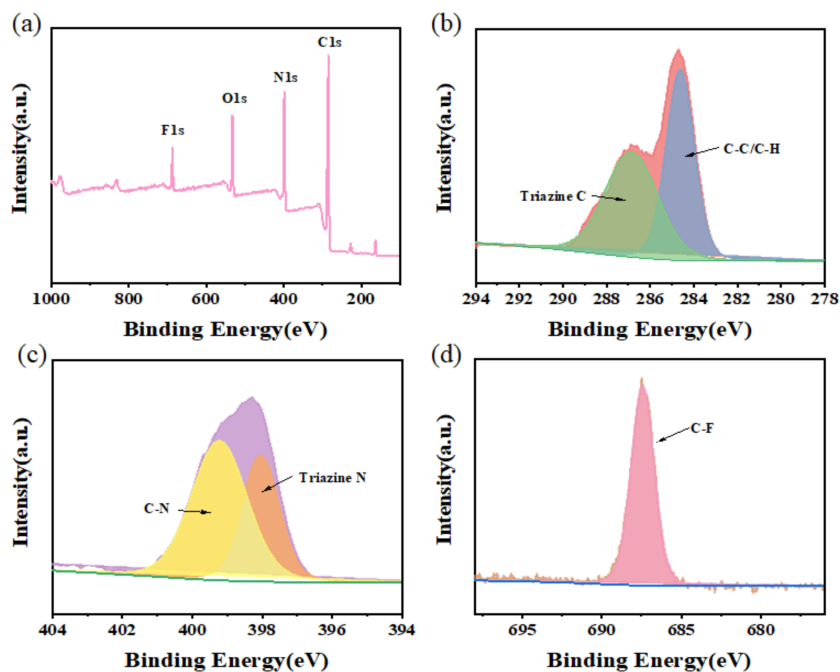


**Figure 3.** XPS spectra of POP-4F: (**a**) wide-scan survey spectra; high-resolution of (**b**) C 1s; (**c**) N 1s; (**d**) F 1s.



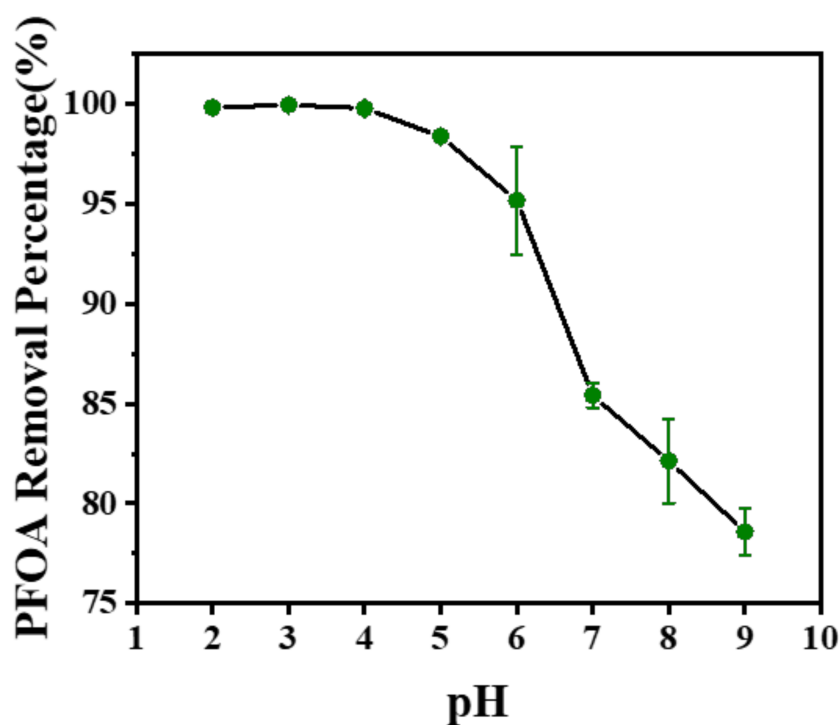**Figure 4.** The effect of pH on the removal of PFOA at initial concentrations of 1 mg $L^{-1}$, an adsorbent dose of 200 mg $L^{-1}$, and contact time of 24 h. Vertical error bars represent standard deviation from triplicated experiments.

### 3.2.2. Adsorption Kinetics

To evaluate the removal efficiency, the removal kinetics of PFOA were conducted and are shown in Figure 5a. As we can see, the PFOA removal rate is up to 98% in 5 min, and the adsorption can achieve equilibrium in 6 h with a removal rate of 99.8%. All those results demonstrated that POP-4F could be applied to the rapid removal of PFOA from water. Moreover, there is no desorption observed after 24 h, which suggests that the adsorption of PFOA into the POP-4F is irreversible under these conditions.
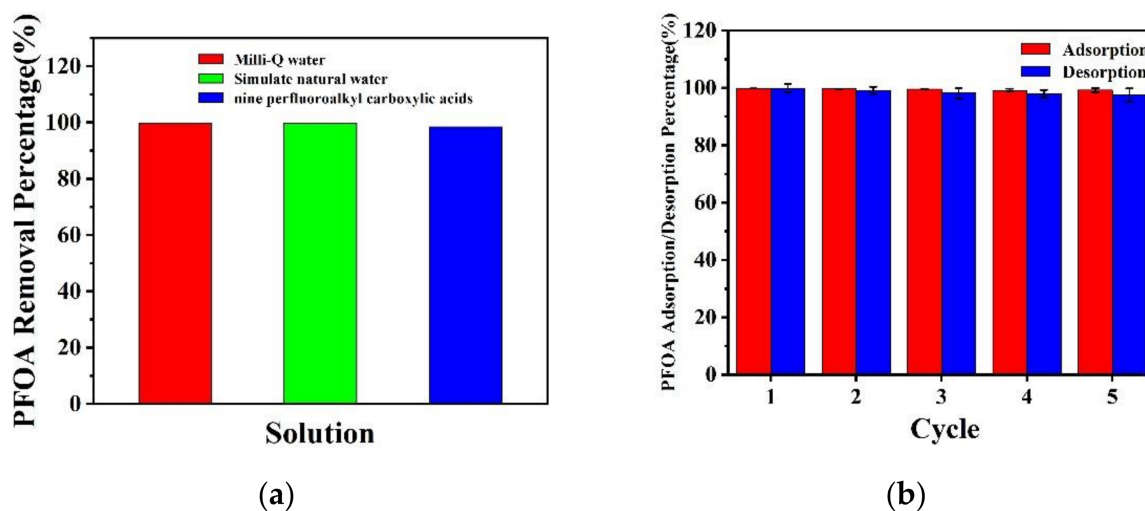


(**a**)

(**b**)
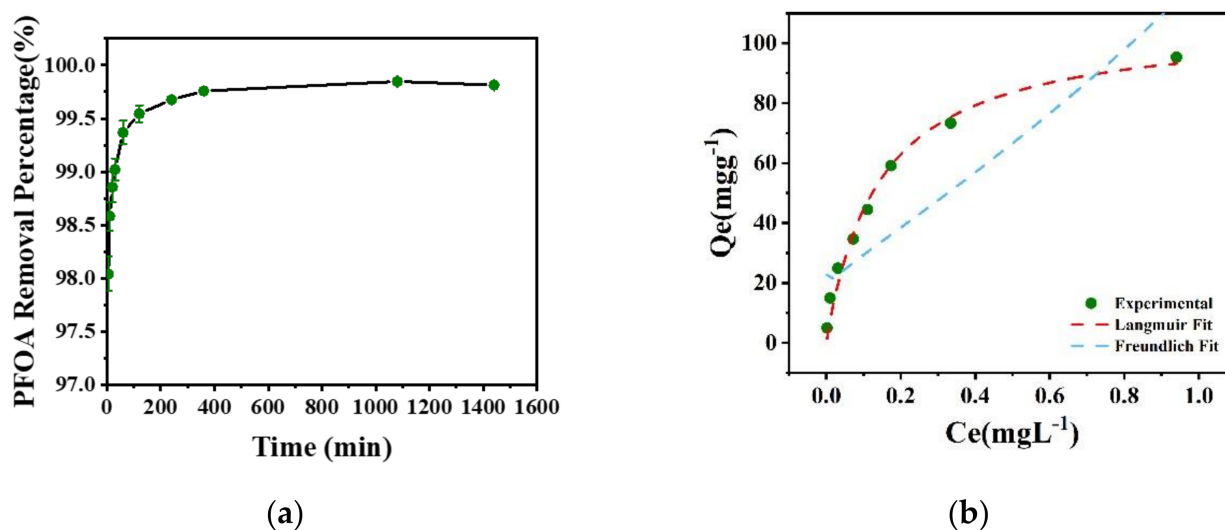
**Figure 5.** (**a**) Kinetics of PFOA adsorption by POP-4F ($[PFOA]_0 = 1$ mg L$^{-1}$; [POP-4F] = 200 mg L$^{-1}$) at 25 °C; (**b**) Isotherm of PFOA adsorption by POP-4F ($[PFOA]_0 = 1-20$ mg L$^{-1}$; [POP-4F] = 200 mg L$^{-1}$) at 25 °C. The lines are Langmuir (red) and Freundlich (blue) fitted curves. Error bars: standard deviation of three experiments.

### 3.2.3. Adsorption Isotherm

Adsorption isotherm experiments at 298 K were performed to better understand the PFOA adsorption process and evaluate the adsorption capacity. The results of these experiments were analyzed using Langmuir isotherm and Freundlich models. As shown in Figure 5b, the Langmuir model fits well with the experimental data ($R^2 = 0.98$), which indicates the dominant role of monolayer adsorption. In addition, the estimated capacity of POP-4F was 107 mg g$^{-1}$ based on the Langmuir fit.

### 3.2.4. Matrix Effect and Reusability

The matrix effect is critical for adsorbents when additional contaminants are present. Therefore, different aqueous mixture solutions, including, Milli-Q water, simulate natural water (200 mg L$^{-1}$ NaCl and 20 mg L$^{-1}$ humic acid), and nine perfluorobutanoic carboxylic acid aqueous solutions (1 mg L$^{-1}$ of each initial concentration) were used to investigate the matrix effect. As shown in Figure 6a, the removal rate of PFOA is almost constant in various aqueous solutions, which indicates that POP-4F has a strong anti-interference ability and an excellent ability to remove PFOA in complex water samples. This indicates that POP-4F has a great potential for treating acidic industrial wastewater and for environmental remediation around the plant.

**Figure 6.** (**a**) Kinetics of PFOA adsorption by POP-4F ($[PFOA]_0$ = 1 mg $L^{-1}$; [POP-4F] = 200 mg $L^{-1}$) at 25 °C; (**b**) Regeneration of POP-4F by MeOH washing. Error bars: standard deviation of three experiments.

When considering the practical applications, regeneration of adsorbents is critical. Hence, the desorption experiment was conducted in methanol solution assisted by ultrasonic. As shown in Figure 6b, the adsorption performance of POP-4F did not decrease significantly and maintained high recovery after five cycles. Compared with the first cycle, the adsorption efficiency decreased by 0.63%, and the desorption efficiency decreased by 2.4% in the fifth cycle. The small decrease in adsorption and desorption efficiency is caused by the loss of POP-4F during the treatment process. In addition, the desorption experiments proved that POP-4F could cause rapid and efficient regeneration in methanol within 3 min. The great selectivity, environmental friendliness, and cost-effectiveness of the POP-4F were shown by these findings.

## 4. Conclusions

In conclusion, we synthesized a new porous organic polymer by a simple Schiff base condensation reaction. The external morphology and the physicochemical structure of the prepared polymer were characterized by a series of methods. The results show that the polyporous material exhibited mixing characteristics of micropore and mesopore with a larger surface area (479 $m^2$ $g^{-1}$). In the meantime, POP-4F exhibited high adsorption capacity toward PFOA from water without the effect of humic acid. The maximum capacity is up to 107 mg $g^{-1}$, and 98% clearance effectiveness can be achieved within 5 min. Additionally, the preparation of POP-4 is very easy and cost-effective. Especially, the large surface area and heteroatomic effects endow POP-4F with versatile adsorption capacity for trace and ultra-trace targets in a complex matrix. Therefore, we believe that POP-4F has great potential application value for sample pretreatment.

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