Synergistic Adsorption for Parabens by an Amphiphilic Functionalized Polypropylene Fiber with Tunable Surface Microenvironment

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ABSTRACT: A series of novel amphiphilic functionalized fibers with polarity tunable surface microenvironment were constructed by introducing hydrophilic polyamines and hydrophobic linear alkyl chain groups, aiming to selectively remove parabens from water. In addition, Fourier-transform infrared spectroscopy, X-ray powder diffraction, scanning electron microscopy, etc. were employed to determine the successful preparation of amphiphilic functionalized fibers. The adsorption experimental data indicated that the amphiphilic fibers showed excellent selectivity for parabens. In the amphiphilic fibers, hydrogen bonding and hydrophobic interaction existing in one molecular unit can effectively act together to enhance the interaction between substrate and fibers. Kinetic studies illustrated that the adsorption process was a physical adsorption with chemical characteristics. The overall initial adsorption rate together with the stepwise adsorption rate was quantified, and it is inferred that the hydrophobic interaction plays a leading role in the first step of the adsorption process. Moreover, the Freundlich model well described the sorption process with a maximum adsorption of 138.4 mg/g. What’s more, the fiber still keeps excellent adsorption capacity (>90%) even after 10 adsorption/desorption cycles, which certifies it is an excellent adsorbent and can be utilized to remove paraben in practice.

1. INTRODUCTION
Parabens are esters derived from p-hydroxybenzoic acid, containing methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), butylparaben (BuP), and octylparaben (OcP); they are quite stable in acidic solutions, and their hydrolysis rate in alkaline solutions decreases with the increase of alkyl chain length.1 Parabens as preservatives have been widely applied in food, medicine, cosmetics, and other fields.2,3 Relevant reports show that these substances have estrogen activity and are detected in human breast tumor tissues, which may be the cause of male infertility and breast cancer.4–6 Nowadays, parabens are considered as endocrine-disrupting compounds and are acknowledged as environmental pollutants.7 Around the world, many countries have introduced legislations to regulate the use and release of parabens into the environment. Regarding this, the maximum allowable concentration of individual parabens in cosmetics is set at 0.4% in China and 1.0% in Japan.8 In recent years, these substance has been detected in sludge,9 soil, environmental water,10 and even humans,11,12 which is attributed to the excessive use of paraben compounds. Therefore, it is necessary and meaningful to remove parabens from aqueous solution.

Currently, among all of the parabens treatment methods, such as heterogeneous photocatalysis, advance oxidation, and photo-Fenton,13–16 adsorption has attracted much attention. In this method, pollutants in waste water can be efficiently captured through a variety of forces, such as electrostatic interactions,17,18 complexation,19 π−π interactions,20 and other interaction forces.21–24 However, some adsorbent carriers have complex surface properties,25 which makes the interaction mechanism with pollutants relatively ambiguous. In addition, since the forces rarely act alone, this greatly interferes with the study of the mechanical interactions of certain forces.26 Hence, it is also a great challenge to systematically explore the interaction mechanism of specific forces between adsorbents and pollutants.

In recent years, organic textile fibers, such as polypropylene fiber (PPF), polyacrylonitrile fiber (PANF), etc., have proved to be good carrier materials due to their stable nature and environmentally friendly properties.27–34 The support material with simple and clear surface can be applied to control the number of interaction mechanisms to simplify the adsorption process. Polypropylene fiber (PPF) provides a way for this challenge with low cost, simple surface chemical structure, and simple production technology. These attractive advantages make PPF an excellent carrier for adsorbent. Furthermore, the
surface of polypropylene fiber can be modified through different chemical methods to construct active sites. For example, in our previous works, ionic liquid-functionalized polypropylene fibers were prepared and used for the first time to catalyze some organic reactions.27 Parabens are amphiphilic organic substances with hydrophobic hydroxyl group and hydrophobic alkyl group coexisting in their molecules. This will encourage us to construct a specific surface on the fiber according to the structure of target pollutants.

In this work, the amphiphilic structure functionalized fibers (PPA<sub>n</sub>F-C<sub>6</sub>) with adjustable surface microenvironment were constructed through a three-step reaction originated from polypropylene fiber (PPF) (Scheme 2) and used to selectively remove parabens from water. In the amphiphilic fibers, the type of adsorption driving force is limited, so it is convenient to study the adsorption mechanism of different interactions. The effect of the degree of hydrophobicity of the amphiphilic structural fibers on the adsorption process was also discussed. Thereafter, the adsorption behaviors of functionalized fibers for parabens were studied in detail and the overall initial adsorption rate was calculated. In addition, cycle performance was also explored to further verify the superiority and application potential of amphiphilic functionalized fibers.

### 2. RESULTS AND DISCUSSION

#### 2.1. Synthesis and Characterization of Functionalized Fibers

The degree of modification and the water uptake of functionalized fibers are presented in Table 1. Considering the grafting amount and mechanical strength of the fiber, PPF<sub>F</sub> and PPA<sub>n</sub>F with weight gains of 88.0 and 32.5%, respectively, were selected for the next grafting reaction (Table 1, entries 2 and 3). Different amphiphilic structure fibers (PPA<sub>n</sub>F-C<sub>6</sub>, n = 4, 8, and 12) were constructed and their functional degree was kept at about 0.90 mmol/g so that the measurement standard was the same in subsequent experiments (Table 1, entries 4–6).

The water uptake content is one of the key factors in determining the hydrophilic/hydrophobic properties of the fibers.38 In this work, amino and alkyl groups are used to tune the hydrophilic and hydrophobic surface microenvironment of the fiber adsorbents and the water uptake of different fibers was measured to reveal the hydrophilic/hydrophobic properties of the fibers and the result is listed in Table 1. The original polypropylene fiber shows a very low water uptake of 0.6% because of its strong hydrophobic surface (Table 1, entry 1), and amino groups exhibit strong hydrophilicity; hence, after free radical polymerization and the immobilization of HPEI, the water uptake rate of the modified fibers was remarkably enhanced up to 82.6 and 95.2%, respectively, indicating the successful construction of hydrophilic structures on fiber surface (Table 1, entries 2 and 3). As expected, the water uptake rate of all amphiphilic fibers (Table 1, entries 4–6) obviously decreased with the introduction of hydrophobic alkyl chain and the fiber PPA<sub>4</sub>F-C<sub>12</sub> with the longest carbon chain shows the lowest water uptake (Table 1, entry 6). The experiment results illustrate that the hydrophilic and hydrophobic surfaces were successfully constructed on the amphiphilic structure fiber.

The Fourier-transform infrared (FTIR) spectra of PPF, PPF<sub>F</sub>, PPA<sub>n</sub>F, PPA<sub>n</sub>F-C<sub>6</sub>, PPA<sub>n</sub>F-C<sub>12</sub>, and PPA<sub>n</sub>F-C<sub>12</sub> are shown in Figure 1. Compared with the original PPF (Figure 1a), the PPF<sub>F</sub> (Figure 1b) shows two broad peaks at 3100–3500 cm<sup>−1</sup>, corresponding to the stretching vibration peaks of N–H bond in primary amine and the two peaks at 1660 and 1609 cm<sup>−1</sup> are ascribed to the stretching vibrations of C≡O, -NH, and -C-N-.36,37 These absorption peaks prove the successful introduction of amide group onto the fiber. After amination modification (Figure 1c), the appearance of a peak at 1570 cm<sup>−1</sup> is attributed to the asymmetric bending vibration of the primary amine;38 the N-H deformation vibration and C-N stretching vibration were observed at 810 and 1255 cm<sup>−1</sup>, respectively, which indicates that HPEI was successfully grafted onto the fibers.39,41 It is observed that the IR spectra of the amphiphilic fibers (Figure 1d–f) are similar to that of parent PPA<sub>n</sub>F probably due to the lack of apparent characteristic absorption of alkyl chain moiety.

The elemental analysis was used to demonstrate the successful preparation of PPA<sub>n</sub>F-C<sub>12</sub> and stability during the application process. As listed in Table 2, compared with PPF, the nitrogen content of PPF<sub>F</sub> obviously increased to 8.12% (Table 2, entries 1 and 2). This confirms the successful grafting of acrylamide. After HPEI modification, the carbon and

### Table 1. Weight Gain of Functionalized Fibers and Their Functional Degree and Water Uptake

| entry | fiber         | weight gain (%) | functional degree (mmol/g) | water uptake (%) |
|-------|---------------|-----------------|-----------------------------|------------------|
| 1     | PPF           | 84.79           | 13.61                       | 0.015            |
| 2     | PPF<sub>F</sub> | 80.80           | 7.05<sup>+</sup>              | 82.6             |
| 3     | PPA<sub>4</sub>F | 32.55           | 2.80<sup>+</sup>              | 85.2             |
| 4     | PPA<sub>4</sub>F-C<sub>4</sub> | 5.3             | 0.09<sup>+</sup>              | 71.9             |
| 5     | PPA<sub>4</sub>F-C<sub>8</sub> | 11.2            | 0.09<sup>+</sup>              | 35.8             |
| 6     | PPA<sub>4</sub>F-C<sub>12</sub> | 17.4            | 0.89<sup>+</sup>              | 30.6             |

*The functional degree is obtained by fiber weight gain. The functional degree of PPA<sub>n</sub>F is obtained by acid–base titration.

### Table 2. Elemental Analysis Data

| entry | sample   | C (%)  | H (%)  | N (%)  |
|-------|----------|--------|--------|--------|
| 1     | PPF      | 84.79  | 13.61  | 0.015  |
| 2     | PPF<sub>F</sub> | 65.34  | 9.25   | 8.12   |
| 3     | PPA<sub>4</sub>F | 58.62  | 9.05   | 9.29   |
| 4     | PPA<sub>4</sub>F-C<sub>12</sub> | 59.87  | 9.50   | 9.19   |
| 5     | PPA<sub>4</sub>F-C<sub>12</sub>-1 | 61.54  | 9.86   | 9.12   |
| 6     | PPA<sub>4</sub>F-C<sub>12</sub>-10 | 61.49  | 9.79   | 9.10   |

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hydrogen contents of PPA-PF (Table 2, entry 3) decreased, while the nitrogen content increased due to the high nitrogen content in HPEI. In addition, the carbon and hydrogen contents of PPA-PF-C12 significantly increased (Table 2, entry 4), due to the carbon (85.12%) and hydrogen (14.88%) contents of dodecyl being higher than that of PPA-PF. It is worth mentioning that PPA-PF-C12-1 (the fiber recovered after the first adsorption and desorption cycle) and PPA-PF-C12-10 (the fiber recovered after the tenth adsorption and desorption cycle) possess similar elemental contents compared with fresh PPA-PF-C12, which confirms the excellent recycling performance of PPA-PF-C12.

To further prove the successful construction of the amphiphilic structure into fiber, XPS was applied to analyze the chemical composition of PPF and the functional fibers. As shown in Figure 2a, the XPS full-scan spectra of PPA-PF and PPA-PF-C12 exhibit three peaks at 284.00, 398.60, and 530.61 eV, corresponding to C 1s, N 1s, and O 1s, respectively. The C 1s core spectrum of PPF (Figure 2b) is only curve-fitted into a peak component and the BE is about 283.8 eV, belonging to C-C/C-H species. After modification, the N 1s core spectrum of PPA-PF (Figure 2c) can be deconvoluted into three peak components with BEs of about 398.51, 399.25, and 400.25 eV, which can be assigned to the -NH-, -NH2, and -NR2 species, respectively. This result suggests the successful grafting of HPEI. Furthermore, the C 1s core spectrum of PPA-PF-C12 (Figure 2d) could be deconvoluted into three peaks at 283.8,
respectively. After the modification of PPF by polyethyleneimine (Figure S1b), the diffraction peaks of PPA are broadened, which suggests that part of the crystalline phase has slightly changed. Moreover, after being used to absorb parabens once and ten times (Figure S1c,d), the spectra of recovered fibers are nearly the same as fresh PPF (Figure S1c), which shows that the amphiphilic fiber can be recycled at least 10 times without obvious change.

The surface morphological structure of fibers was characterized by scanning electron microscopy (SEM). The SEM images of PPF, PPAPF-C12, PPAPF-C12-BuP, and PPAPF-C12-OcP at different magnifications are presented in Figure 3. As shown in Figure 3a, the surface of PPF is smooth. After modification and one-time application, the fiber surfaces become a little bit rougher than that of the original PPF (Figure 3b,c). This result suggests that the structure of the fibers is well maintained and can be used in further study. After being used ten times, the mechanical strength is damaged to a certain extent and the fiber surfaces become coarser (Figure 3d). However, the overall integrity of the fiber is not affected, which proves the excellent cycling capacity of PPAPF-C12.

2.2. Relationship between Fiber Structure and Adsorption Ability. The superiority of the amphiphilic fiber structure was evaluated by comparing the adsorption properties of different fibers to ethylparaben (EtP), butylparaben (BuP), and octylparaben (OcP). As displayed in Figure 4a, the original PPF shows the weakest adsorption ability to the three compounds due to lack of adsorption site on the fiber surface. The adsorption amount of PPAPF obviously increases owing to the hydrogen bond interaction between fiber and parabens. After the introduction of polyethyleneimine to PPAPF, the adsorption capacity of PPAPF is slightly better than that of parent PPAPF. The result probably is due to the stronger hydrogen bonding formed between -NH2 group and parabens. After hydrophobic modification, the resulting amphiphilic fiber PPAPF-C12 shows excellent adsorption ability to parabens, as shown in Figure 4a. That may be because the objective compound parabens have hydrophilic hydroxyl group and lipophilic aliphatic group and therefore can be effectively adsorbed by these amphiphilic fibers through hydrophobic interaction and hydrogen bonding interaction. In addition, the adsorption amount of fiber increases with different degrees of hydrophobic modification. Especially, the PPAPF-C12 has almost no adsorption for the paraben. However, PPAPF-C12 shows excellent selectivity for parabens, as shown in Figure 4b, obviously, PPAPF-C12 has almost no adsorption for phenol and it can adsorb PHBA in a small adsorption amount with 17.3 mg/g because of the existence of -NH2 on fiber. However, PPAPF-C12 shows excellent selectivity for paraben compounds and the selectivity of amphiphilic fiber increases with the hydrophobicity increase of the paraben. BuP was selected as the model compound in a subsequent research due to its medium carbon chain length. The competitive
adsorption experiments were performed by adsorbing a mixed solution of tetracycline (TC) and butylparaben (BuP) at the same concentration. The results are shown in Figure S2. As displayed in Figure S2, PP_A,F-C_{12} exhibits excellent selectivity, with 7 times the adsorption capacity for BuP than TC, which further proves the outstanding selectivity of PP_A,F-C_{12}.

After adsorption of BuP compounds, PP_A,F-C_{12}-BuP was characterized by FTIR and solid UV−vis spectra. As presented in Figure 4c, PP_A,F-C_{12}-BuP contains some characteristic peaks of BuP after adsorption; for example, the peaks at 1283 and 1162 cm$^{-1}$ belong to the stretching vibration of C−O−C and the absorption peak at 1681 cm$^{-1}$ is due to stretching vibrations of C$\equiv$O in BuP. In addition, the solid UV−vis spectra of the fiber verify the successful adsorption of BuP (Figure 4d). After adsorption, PP_A,F-C_{12}-BuP displays a strong absorption band at 256 nm, which is fully consistent with the maximum absorption wavelength of BuP measured by a UV−vis spectrometer.

2.3. Synergistic Adsorption Mechanism. A possible adsorption mechanism of amphiphilic fiber for parabens was proposed in Scheme 1 with BuP as the model compound. There are two kinds of interaction force (hydrophobic interaction and hydrogen bonding interaction) between the amphiphilic fiber and parabens. The -NH$_2$ group of polyamine in the amphiphilic fibers is the main hydrogen bond absorption site, which can form hydrogen bond with the hydroxyl group in the BuP molecules to remove BuP from waste water. At the same time, the amphiphilic fibers can also utilize their hydrophobic carbon chain to enrich and absorb BuP molecules that also have hydrophobic alkyl groups. In the amphiphilic fibers, two kinds of functional groups are located in one molecular unit, so the synergistic adsorption of the two interaction forces increases the adsorption efficiency, and the hydrophobic interaction plays a major role in the adsorption process (Scheme 1).

2.4. Effect of Dodecyl Density. The different functional degrees of PP_A,F-C_{12} were investigated to explore the effect of dodecyl density on adsorption capacity. As shown in Figure S3a, to some extent, the adsorption capacity of PP_A,F-C_{12} for BuP enhances with the increase of the modified density and the maximum can reach 98.3 mg/g (the functional degree is 0.89 mmol/g). After that, the adsorption of BuP becomes unfavorable due to excessive hydrophobicity of the fiber.

2.5. Effect of pH. The pH of solution is critical for adsorption because it may affect the state of the adsorbent and adsorbate.$^{16}$ Therefore, the effect of a series of different pH (3−10) on the adsorption capacity of PP_A,F-C_{12} was investigated and the results are shown in Figure S3b. At lower pH values (3−5), the adsorption capacity enhances with the increase of pH values. Under acidic condition, all interactions between PP_A,F-C_{12} and BuP were reduced due to hydrolyzation of BuP and protonation of PP_A,F-C_{12}. In alkaline condition (pH = 8−10), the reduction of hydrophobic interaction plays a major role so the adsorption capacity decreased rapidly. In summary, the optimum pH range for the adsorption of BuP is 5.0−8.0.

2.6. Adsorption Kinetics. The adsorption kinetics of PPF, PP_A,F, and PP_A,F-C_{12} for BuP were investigated to reveal the adsorption mechanism (Figure 5). It can be seen that PP_A,F-C_{12} displays the best adsorption for BuP with the maximum adsorption amount of 98.5 mg/g, which is more than 4 times that of PPF (26.2 mg/g) and the original PPF (9.2 mg/g), respectively. Moreover, as shown in Figure 5, the fiber PP_A,F-C_{12} can achieve half-saturation adsorption within 5 min and reach adsorption equilibrium at 120 min.

To better understand the adsorption kinetic process, two kinetic models, including pseudo first-order and pseudo second-order model, were used to interpret the kinetic characteristics of BuP adsorption process. The pseudo first-order eq 1 and pseudo second-order eq 2 can be given in the following form$^{17,18}$

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (1)

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$  \hspace{1cm} (2)

where $Q_e$ (mg/g) is the amount of BuP adsorbed on the adsorbent at a given time $t$ (min) and $Q_t$ (mg/g) is the
equilibrium adsorption of the adsorbent, while \( k_1 \) (min\(^{-1}\)) and \( k_3 \) (g/(mg min)) are pseudo first-order and pseudo second-order rate constants, respectively.

The kinetic experimental data were fitted by the pseudo first-order eq 1 and pseudo second-order eq 2, and the fitting plots are presented in Figure S4. The values of \( k_1 \), \( k_2 \), \( Q_{exp} \) (experimental value), \( Q_{cal} \) (calculated value based on model), and the corresponding correlation value (\( R^2 \)) are shown in Table 3. Compared with \( Q_{cal} \), Values of pseudo first order, the \( Q_{exp} \) values are closer to \( Q_{cal} \) values of pseudo second-order and the values of \( R^2 \) for the pseudo second-order are greater than the pseudo first-order model, which indicates that the pseudo second-order model is more suitable for fitting experimental data.

Whether the adsorption process is driven by hydrophobic interaction or hydrogen bonding interaction, it belongs to physical interaction. However, the kinetic data conforming to the second-order model means that this adsorption process is chemisorption. Therefore, we define the adsorption of the functionalized fibers for molecule BuP as physical adsorption with chemical characteristics based on modification active sites.

Moreover, the Weber–Morris intraparticle diffusion model was used to identify the limiting step in the adsorption process and it can be described by the following formula\(^{53,55}\):

\[
Q_t = k_{int} t^{1/2} + C
\]

where \( k_{int} \) is the intraparticle diffusion rate constant (mg/(g min\(^{1/2}\))) and the intercept \( C \) is a constant relevant to the thickness of the boundary layer.

The fitting plots are depicted in Figure 6. The plot exhibits three linear regions, which means the intraparticle diffusion is not the sole rate-limiting step during the fiber adsorption process according to Mittal.\(^{51}\) The first stage is external mass transfer, including the diffusion of the boundary layer of the solute molecules and the diffusion of the solute molecules to the outer surface of the adsorbent. The second stage is the diffusion in the fiber modified layer, which is the rate-determining step. The intercept \( C \) increases at this stage (\( C = 65.93 \), Table S2), indicating an increase in the thickness of the boundary layer and the mass transfer resistance of the external liquid. Therefore, the opportunity of external mass transfer is reduced and the possibility of internal mass transfer is increased. The third stage is the adsorption dynamic balance phase.

The double-exponential model can be used to describe the diffusion-controlled mechanism. And according to this model, the adsorption process is divided into two steps. The first step involves external film diffusion and internal diffusion; then, a slow step follows, which is controlled by intraparticle diffusion.\(^{52-54}\) The formula is presented as\(^{55}\):

\[
Q_t = Q_e = \frac{D_1}{m_{ads}} \exp(-K_{D1}t) - \frac{D_2}{m_{ads}} \exp(-K_{D2}t)
\]  

The overall initial rate of different fibers can be determined by the derivative eq \(^5^{56}\):

\[
v = \frac{dQ_t}{dt} = \frac{D_1}{m_{ads}} K_{D1} \exp(-K_{D1}t) + \frac{D_2}{m_{ads}} K_{D2} \exp(-K_{D2}t)
\]

For initial conditions

\[
t = 0, \quad v = v_0 = \frac{D_1}{m_{ads}} K_{D1} + \frac{D_2}{m_{ads}} K_{D2}
\]

where \( D_1 \) and \( D_2 \) are sorption rate parameters (mg/L) of the rapid and the slow step, respectively, and \( K_{D1} \) and \( K_{D2} \) are diffusion parameters (min\(^{-1}\)).

Obviously, the adsorption amounts \( Q_{cal} \) (calculated by the double-exponential equation) as shown in Table 4 are quite close to the experimental result \( Q_{exp} \) as shown in Table 3. Therefore, the model also responds well to this adsorption process, although there are differences between polypropylene fibers and porous materials.

The overall initial adsorption rate \( v_0 \) of the amphiphilic fiber PP\(_{A,P,F,C12}\) is significantly higher than that of PPF and PP\(_{A,F}\), which is consistent with its excellent adsorption ability. The overall initial rate can be further decomposed into \( v_{01} \) and \( v_{02} \) belonging to the rapid and the slow step rates, respectively, as shown in Table 4. The PPF fiber displays an extremely low order of magnitude of rate in both steps according to its poor adsorption ability. The initial rates of the fiber PP\(_{A,P,F,C12}\) and PP\(_{A,F}\) for the slow step are comparable (1.776 and 1.310, respectively), while the fiber PP\(_{A,P,F,C12}\) exhibits quite higher initial rates (3.304) in the rapid step. It’s stated that the main differences between the two fibers exist in the rapid step. These results demonstrate that in the rapid step, the fiber PP\(_{A,P,F,C12}\) can enrich the organic molecule quickly taking advantage of the hydrophobic interaction corresponding to its long carbon chain structure and accelerate the adsorption process. It can be inferred that the hydrophobic effect plays the most important role in the whole adsorption process.

![Figure 6. Intraparticle diffusion model plot.](https://dx.doi.org/10.1021/acsomega.9b03765)
2.7. Adsorption Isotherm. The effect of the initial concentration of BuP on adsorption by PP\textsubscript{A,F}-C\textsubscript{12} was examined. Two isotherm models containing the Langmuir model and the Freundlich model were used to fit the experimental data, and the fitting plots are presented in Figure S5. All of the equations are expressed as:\cite{15, 57-59}

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e
\]

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}
\]

where \(n\) is the heterogeneity and \(K_F\) and \(K_L\) are the Freundlich adsorption constant (mg/g) and Langmuir adsorption constant (L/mg), respectively. The isotherm parameters are displayed in Table 5.

Table 5. Parameters for Freundlich and Langmuir Models

| adsorbents       | \(Q_{\text{max}}\) (mg/g) | \(K_F\) (L/mg) | \(R^2\) | \(K_L\) (mg/g) | \(n\) | \(R^2\) |
|------------------|-----------------------------|----------------|--------|----------------|------|--------|
| PP\textsubscript{A,F} | 99.1                        | 0.596          | 0.1386 | 3.304          |      |        |
| PP\textsubscript{A,F}-C\textsubscript{12} | 26.9                        | 0.094          | 0.3747 | 1.412          |      |        |
| PP              | 9.5                         | 0.004          | 0.1680 | 0.029          |      |        |

The Freundlich isotherm depicts nonideal adsorption, which can be used in the multilayer adsorption with diverse adsorption heat and affinities on the heterogeneous surface. The Langmuir model assumes ideal monolayer adsorption with identical adsorption energy. According to the correlation coefficient \(R^2\), the experimental data are more consistent with the Freundlich isotherm model \((R^2 = 0.9934, \text{Table 5})\) than with the Langmuir isotherm model \((R^2 = 0.9717, \text{Table 5})\), clarifying that the adsorption process is multilayer heterogeneous adsorption. It is noted that the maximum adsorption amount \(Q_{\text{max}}\) of PP\textsubscript{A,F}-C\textsubscript{12} for BuP at equilibrium concentrations from the adsorption isotherm curve is 138.4 mg/g (Figure S6). So the amphiphilic structure adsorbent has a good advantage and application prospect.

2.8. Adsorption Thermodynamics. The adsorption thermodynamics of PP\textsubscript{A,F}-C\textsubscript{12} and PP\textsubscript{A,F} for the model compound BuP were tested, and the thermodynamics curve is presented in Figure 7. The results show that high temperature promotes the adsorption of PP\textsubscript{A,F}-C\textsubscript{12} (Figure 7a) while low temperature benefits the adsorption of PP\textsubscript{A,F} (Figure 7b) because only hydrogen bonding interaction exists in PP\textsubscript{A,F} and the extent of hydrogen bonding decreases with an increase of temperature.\cite{60}

Reaction rate constants \(k\) at different temperatures were acquired by pseudo second-order fitting of above data, and Table 6 displays all parameters. The experimental results illustrate that the adsorption activation energy (activation energy was calculated by the Arrhenius equation) of the amphiphilic fiber is much smaller than that of the PP\textsubscript{A,F} fiber.\cite{15} This is due to the synergistic effect of hydrogen bonding and hydrophobic interaction existing in the PP\textsubscript{A,F}-C\textsubscript{12} fiber, which can obviously decrease the energy barrier.

2.9. Desorption and Reusability. The recyclability is an important indicator of the potential applicability of the fiber. The desorption kinetics of the amphiphilic fiber PP\textsubscript{A,F}-C\textsubscript{12} was investigated using ethanol as eluent, as shown in Figure 8a. As shown Figure 8a, BuP could be almost completely desorbed from the fiber in 30 min. After 10 times of the adsorption−desorption cycle (Figure 8b), the adsorption amount slightly decreased and the removal efficiency still remained above 90%. Moreover, the FTIR spectra (Figure S7) verify that the fibers show no significant change after 10 times of the recycling experiment. This means that the amphiphilic structured fiber has excellent reusability and stability.

Figure 7. Effect of temperature on the adsorption for BuP by (a) PP\textsubscript{A,F}-C\textsubscript{12} and (b) PP\textsubscript{A,F}.
3. CONCLUSIONS

In this paper, a series of functionalized polypropylene fibers was prepared and applied to remove parabens from water. Among the modified fibers, PP\text sub{A-F-C_{12}} with amphiphilic structure exhibited the most powerfully selective adsorption ability for parabens due to the synergistic effect of hydrophobic interaction and hydrogen bonding interaction and a possible adsorption mechanism of amphiphilic fiber for parabens was proposed. In addition, it is found that the adsorption of BuP by PP\text sub{A-F-C_{12}} is multilayer heterogeneous physical adsorption with chemical characteristics based on active sites and the adsorption process can be described better by the pseudo second-order kinetic model. According to the Weber–Morris intraparticle diffusion model, the intraparticle diffusion is not the sole rate-limiting step during the fiber adsorption process. The overall initial adsorption rate as well as the stepwise adsorption rate calculated by the double-exponential model indicate that the hydrophobic effect plays a leading role in the adsorption system. Moreover, the Freundlich model well describes the sorption process with a maximum adsorption of 138.4 mg/g. The activation energy of PP\text sub{A-F-C_{12}} (25.08 kJ/mol) is much lower than that of PP\text sub{A-F} (43.96 kJ/mol) due to the constructed synergistic adsorption. Importantly, PP\text sub{A-F-C_{12}} can be reused more than 10 times and the removal rate is still above 90%, which means that the fiber has high stability and superior reusability. Therefore, the amphiphilic structure PP\text sub{A-F-C_{12}} fiber has great potential application in water treatment.

4. EXPERIMENTAL SECTION

4.1. Materials. Commercially available PPF with a length of 1.5 cm and diameter of 30 ± 0.5 μm (purchased from the Sheyang Enyu Chemical Fiber Co. Ltd of China) was used. Acrylamide, benzoyl peroxide (BPO), (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, FeSO\textsubscript{4}·6H\textsubscript{2}O, hyperbranched polyethyleneimine (HPEI) ((M\textsubscript{w} = 1800), 1-butylobromide, 1-bromocetane, 1-bromododecane, phenol, p-hydroxybenzoic acid (PHBA), ethylparaben (EtP), butylparaben (BuP), octylparaben (OcP), and the other reagents are all analytical grade and used without further purification. All water used was deionized and double-distilled unless otherwise specified.

4.2. Characterization Techniques. An FTIR spectrometer (model Nicolet 460) and elemental analyzers were used to analyze the functional groups and related element contents in the fibers, respectively. Scanning electron microscopy (SEM) (model Nova 450) was used to characterize the surface morphological structure of the fibers. An X-ray diffractometer (BrukerAXS, model Ultima IV) recorded XRD spectra. X-ray photoelectron spectroscopy (XPS) was obtained using a model...
PHI-5000 versaprobe spectrometer. The pH values were measured with a model PHS-25 pH meter.

4.3. Synthesis of the Functionalized Fibers. The amphiphilic functionalized fibers were synthesized by the following three steps: formation of amide-functionalized fiber PPaF, preparation of aminated fiber PPA-F, and alkylation reaction. First, commercially available PPF was refluxed in ethanol for 12 h to remove surface additives. The treated fiber PPF (0.5 g), deionized water (20 g), (NH4)2SO4, FeSO4·6H2O (0.05 g), benzoyl peroxide (BPO) (0.02 g), and toluene (5 mL) were immersed in a 50 mL round bottom flask. The reaction system was protected by nitrogen and kept at 65 °C for 30 min. Then, 10 g of acrylamide (AM) in 20 mL of water was gradually added into the above reaction mixture and kept at 85 °C for 1.5 h. After reaction, the fiber was washed with hot water and dried to get PPaF (Scheme 2).

Second, PPaF was placed in a 15 wt% aqueous solution of HPEI and reacted at 100 °C. The aminated fiber (PPaF) was washed with water and ethanol to neutral and dried.

Third, the obtained PPA-F (0.5 g) was placed in a solution of 15 mL of ethanol containing 0.5 equiv bromoalkane and reacted under reflux. The final fiber was washed repeatedly with water and ethanol until no residue remained and dried overnight at 60 °C. The weight gain (%) of PPA-F-Cn (n = 4, 8, and 12) and the functionality degree of the alkyl group (mmol/g) was obtained by the following formula61

\[ W(\%) = \frac{W_f - W_i}{W_i} \times 100\% \quad (9) \]

\[ f(\text{mmol/g}) = \frac{W_f - W_i}{W_iM_W} \times 1000 \quad (10) \]

where \( W_f \) and \( W_i \) are the weights of PPaF and PPaF-Cn, and \( M_W \) is the molecular weight of the alkyl chain, respectively.

4.4. Adsorption Experiment. Batch adsorption experiments of fibers on target contaminants were carried out. The solute molecules ethylparaben (EtP), butylparaben (BuP), and octylparaben (OpP) were dissolved in a slight amount of ethanol and diluted with water to obtain a range of target contaminant solutions with different concentrations (ranging from 10 to 500 mg/L). Then, the fibers (25 mg) were added to the solution of parabens (35 mL, pH = 7) and stirred for 24 h. Then, the fibers were taken out and the parabens concentration of the residue was detected by a UV–vis spectrometer. The adsorption capacity \( (Q_e) \) can be obtained as stated by the following formula:

\[ Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (11) \]

where \( C_0 \) (mg/L) is the concentration of the solution before adsorption and \( C_e \) (mg/L) is the concentration at equilibrium.

4.5. Adsorption Kinetics, Isotherm, and Thermodynamics Experiments. The kinetic experiments were carried out by placing the modified fiber (25 mg) in each 35 mL solution (200 mg/L, pH = 5), then stirring at room temperature for the required time. The isotherm experiments were performed at different concentration solutions. Similarly, the thermodynamics experiments are kinetic experiments at different temperatures (298, 303, and 308 K). After adsorption, the experimental data were detected by a UV–vis spectrometer.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03765.

Detailed experimental section, the additional XRD and FTIR analyses, diagram of the effects of dodecyl density and pH, adsorption kinetics and isotherms models fitting diagram, comparison of the adsorption capacities of PPaF-C12 with other different adsorbents, comparison of adsorption capacities of PPaF-C12 for TC and BuP, the parameters of intraparticle diffusion models, and adsorption isotherm curve (PDF).

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Notes

The authors declare no competing financial interest.

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