ABSTRACT: The design of a reusable film adsorbent with easy solid–liquid separation for the removal of phosphate is necessary and significant but remains hugely challenging. Herein, the hyperbranched polyethylenimine-functionalized ethyl cellulose (HPEI-EC) film was successfully synthesized by a one-step solution-casting method. The structure and elemental composition of the HPEI-EC film were characterized by Fourier transform-infrared spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy. The phosphate adsorption capacity of the HPEI-EC film was 15.53 mg g⁻¹, which is 12 times higher than that of EC. Significantly, the elongation at break of the HPEI-EC film was 13.43%, which is higher than that of the EC film (8.9%), and the HPEI-EC film had a considerable tensile strength of 13.21 MPa. Such good mechanical properties of the HPEI-EC film bring about the advantage of the saturated HPEI-EC film, allowing it to be easily taken out using a pair of tweezers, which significantly reduces the operation time and saves the cost in the application process. Furthermore, the HPEI-EC film possessed good reusability, and 71.6% of the original adsorption capacity of phosphate was retained even after five cycles. Moreover, the electrostatic interaction between protonated the amine group (–NH₃⁺) and the phosphate ion (PO₄³⁻) is mainly responsible for the adsorption process. This study presents a low-cost and reusable film adsorbent for the effective removal of phosphate from water and provides an easy solid–liquid separation method for use in the adsorption field.

1. INTRODUCTION
Phosphorus is well recognized as an essential nutrient for sustaining the lives of all living organisms on the Earth. Nevertheless, about 30–50% of global water resources are facing eutrophication because of the superfusively dissolved phosphorus in rivers and lakes.¹,² Most of the phosphorus in water bodies is discharged from many kinds of industrial and agricultural activities. Notably, phosphate is the main form of phosphorus found in these effluents.³ As a result, to control eutrophication, it is essential to remove phosphate from waste effluents before being discharged into the environment.

Various methods have been developed to effectively remove phosphate from water, such as chemical precipitation, biological decomposition, membrane separation, ion exchange, and physical adsorption. Among these methods, adsorption has been recommended because of its operational simplicity, low cost, high removal efficiency, and ability to remove phosphate at a low concentration.⁴–¹⁰ To date, many adsorption materials have been reported, which include metal organic frameworks, mesoporous silica, activated carbon nanofibers, graphene, graphite oxide, layered double hydroxides, and their composites.¹¹–³⁰ Although great achievements on phosphate capture have been made, most of the reported adsorption materials may have some drawbacks that restrict their application in wastewater treatment, such as relatively high cost, nonrecoverability, and nonbiodegradability.³¹ Thus, it is extremely urgent to develop a cost-effective, sustainable adsorbent for phosphate removal using an abundant, sustainable, and environmentally benign material.

As the most abundant natural polymeric raw material, cellulose is highly attractive because of its excellent mechanical property, chemical stability, biodegradability, and biocompatibility.³²–³⁴ Since cellulose is insoluble in many common organic solvents, ethyl cellulose (EC), which is soluble in many solvents, was used to prepare films through solution-casting. Recently, there has been an increasing interest for developing cellulose and its derivatives into sustainable adsorbents for eliminating pollutants owing to its abundant availability, low cost, environmental benignancy, and high reactivity.³⁵–³⁷ Although many studies on the utilization of cellulose and its
derivatives as sustainable adsorbents for removing dyes and metal ions from water have been widely reported, only a few of these studies focused on the exploration of their phosphate adsorbability. However, because of the lack of adsorption sites, the phosphate adsorption capacity of cellulose is relatively lower. For example, cellulose nanofiber has a very low adsorption capacity of 0.1 mg g\(^{-1}\) in phosphate removal. Therefore, in order to improve their adsorption capacity, cellulose and its derivatives should be modified with some chemical agents.

Polyethylenimine (PEI) is a polymeric amine with lots of \(-\text{NH}_2\) and \(-\text{NH}\) groups on its linear macromolecular chains. Notably, hydrogen bonds formed between amino nitrogen of PEI and hydroxyl hydrogen of cellulose are conducive to the construction of a PEI–cellulose composite. Moreover, PEI has a high zero potential point at pH values of up to 10; this makes PEI to be positively charged in neutral and alkaline solutions, which is advantageous for the removal of anionic pollutants like phosphate. At present, PEI-modified composites exhibit several advantages in the removal of phosphate, including excellent adsorption capacity, wide pH range, and fast removal rate. For example, Anirudhan et al.\(^{31}\) synthesized a cellulose-grafted epichlorohydrin-functionalized PEI-grafted copolymer (Cell-g-E/PEI) using azobisisobutyronitrile as the initiator and \(N,N'\)-methylenbisacrylamide as the cross-linking agent. The Cell-g-E/PEI could highly effectively adsorb phosphate ions. Our group has prepared a nanostructured bioadsorbent, PEI-graft-alkali lignin loaded with nanoscale lanthanum hydroxide (AL-PEI-La). The designed AL-PEI-La was found to exhibit high adsorption capacity and have fast phosphate ion removal rate. Unfortunately, the previous PEI-modified composites are powder adsorbents, which are difficult to be separated from water, as they often require energy-consuming processes such as centrifugation or filtration. Therefore, increasing attention has been paid to film adsorbents with large sizes to ensure easy separation of the adsorbents from water. For example, Gore et al.\(^{33}\) have reported a novel versatile LDH/PAN nanocomposite film. The prepared film exhibited high adsorption of Cr(VI) and could be easily separated from aqueous solution after adsorption. Chen et al.\(^{34}\) synthesized an easily separable chitosan–boehmite film that had excellent acid resistance and adsorption affinity toward Pb(II). Thus, the development of a PEI–functionalized cellulose film adsorbent not only can improve the adsorption capacity of phosphate, but also enables the adsorbent to be easily separated from water. However, a HPEI–EC film for phosphate capture has not been reported.

In this work, a low-cost and reusable HPEI-EC film for effective phosphate removal was prepared through a one-step solution-casting method. First, the HPEI-EC film was characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) techniques. The mechanical property and easy separation strategy of the HPEI-EC film were then evaluated. Second, phosphate adsorption experiments were carried out, including the adsorption isotherms and kinetics, the effect of pH and coexisting anions on the phosphate adsorption, and the regeneration property of the HPEI-EC film. Finally, the probable adsorption mechanism was proposed based on the
results from FT-IR and XPS analyses. To the best of our knowledge, this is the first report on the preparation of a HPEI-functionalized EC film adsorbent for the removal of phosphate with such an easy solid–liquid separation mode. This work presents a low-cost and reusable film adsorbent for the effective removal of phosphate from water with easy separation.

2. RESULTS AND DISCUSSION

2.1. Fabrication and Characterization of the HPEI-EC Film. The HPEI-EC film was prepared by hydrogen-bonding interaction between hydroxyl groups on EC and amino groups on HPEI. A branched PEI molecule with many amino ends can interact with several EC molecules, resulting in the formation of HPEI-EC networks (see Figure 1a). Figure 1b shows the FT-IR spectra for the EC and HPEI-EC film. In the FT-IR spectrum of EC, the characteristic peaks at around 3479 and 2980 cm\(^{-1}\) can be assigned to the stretching vibrations of O–H and C–H bonds, respectively. The adsorption peak at 1160 cm\(^{-1}\) can be ascribed to the stretching vibration of the C–O group. After being functionalized with PEI, EC exhibited a considerable decrease in wavenumber at about 31 cm\(^{-1}\) for the O–H peak, confirming that the O–H vibration is affected by the hydrogen-bonding interaction of –NH\(_2\). This indicates that the -OH groups took part in the reaction between PEI and EC. Moreover, three intense peaks at 1645, 1563, and 1465 cm\(^{-1}\) were observed after HPEI functionalization, which can be ascribed to amide bond and amino groups. Moreover, the physical parameters of EC and the HPEI-EC film, including the Brunauer–Emmett–Teller (BET) surface area, pore volume, and average pore diameter, are presented in Figure S1. The HPEI-EC film exhibited a lower BET surface area (2.65 m\(^2\) g\(^{-1}\)) and pore volume (0.0015 cm\(^3\) g\(^{-1}\)) than that of EC, indicative of the formation of a cross-linked HPEI-EC film. Furthermore, XPS was employed to analyze the chemical composition of EC and the HPEI-EC film. For EC, two remarkable peaks centered at 285 and 532 eV can be ascribed to C 1s (70.45 at %) and O 1s (29.55 at %); and signals in the N 1s region were not observed. It should be noted that the peak of N 1s at 400 eV could be observed in the HPEI-EC spectrum, and the N content was estimated as 7.61 at %, which further demonstrates that PEI had been introduced into EC. In summary, the HPEI-EC film adsorbent was successfully prepared.

Figure 2a,b shows the optical photograph of EC and HPEI-EC, respectively. Figure 2b presents the photograph of the HPEI-EC film prepared using white commercial powder EC (see Figure 2a) by the solution-casting method. It can be observed that a light yellow-colored adsorbent film material with a controllable size and in a large scale was obtained by the facile preparation process. Moreover, Figure 2c,d shows the corresponding micrographs of EC and the HPEI-EC film, respectively. EC had an irregular pore structure and a rough surface. With regard to the HPEI-EC film, a very flat and smooth surface could be observed. These results indicate that PEI had been distributed in EC to form the HPEI-EC film.

2.2. Mechanical Properties and Easy Separation Strategy. Tensile testing was performed to evaluate mechanical properties of the fabricated HPEI-EC film. Mechanical properties, especial for the tensile strength and the elongation at break, are highly important parameters of recycling materials used in water treatment. As displayed in Figure 3a, the elongation at break of the HPFEC film was 13.43%, which is higher than that of the EC film (8.9%). This indicates that EC was successfully functionalized with PEI through hydrogen-bonding interaction. Moreover, the HPFEC shows a considerable tensile strength of 13.21 MPa. This result indicates that the HPEI-EC film had good mechanical properties (see Figure 3b), and thus is strongly desirable as a reusable adsorbent. Significantly, the good mechanical property and large size of the HPFEC film ensure the easy separation of the adsorbent from water, although after a long soaking time. As shown in Figure 3c, the saturated HPEI-EC film could be easily taken out using a pair of tweezers after being used in the adsorption of phosphate for 48 h. This easy solid–liquid separation strategy is advantageous to the practical applications in phosphate removal, since it can significantly reduce the operation time and save the cost of the application process.

2.3. Phosphate Adsorption Isotherm. In order to obtain the phosphate adsorption capacity of the HPEI-EC film and EC, adsorption isotherm experiments were conducted at 25 °C. The results are presented in Figure 4a. For EC, the highest adsorption amount of phosphate was 1.13 mg g\(^{-1}\) at the equilibrium phosphate concentration of 24.55 mg L\(^{-1}\), indicating that EC had poor phosphate adsorption affinity. For functionalized HPEI, the adsorption amount of phosphate was 15.53 mg g\(^{-1}\) at the equilibrium phosphate concentration of 23.63 mg L\(^{-1}\), and the values of \(q_e\) increased with the
increase of phosphate concentration. These results confirm that functionalized HPEI had improved phosphate adsorption capacity on the HPEI-EC film. To further clarify the adsorption behaviors between the adsorbate and the adsorbent, the adsorption isotherm data were fitted with the Langmuir, Freundlich, and Temkin equations of which the linear forms are as follows:

**Langmuir model:**

\[\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_mbC_e}\]  

**Freundlich model:**

\[\ln q_e = \ln K_f + \frac{1}{n} \ln C_e\]  

**Temkin model:**

\[q_e = A + BC_e\]

where \(C_e\) (mg L\(^{-1}\)) is the equilibrium phosphate concentration, \(q_e\) (mg g\(^{-1}\)) is the adsorption amount at equilibrium, \(q_m\) (mg g\(^{-1}\)) is the maximum phosphate adsorption capacity according to the Langmuir equation, \(b\) is the Langmuir constant, \(K_f\) and \(n\) are the constants for the Freundlich equation, and \(A\) and \(B\) are the constants for the Temkin equation.

The fitting curves of the Langmuir, Freundlich, and Temkin equations at 25 °C are displayed in Figure 4b,c, and the corresponding parameters are summarized in Table 1. According to the values of the correlation coefficient \(R^2\), the Freundlich model better fitted with the adsorption data of the HPEI-EC film. The slightly higher \(R^2\) (0.92) value of the Freundlich model indicates that the adsorption on the HPEI-EC film is maybe multilayer.\(^{46}\) Besides, when the equilibrium phosphate concentration was 23.63 mg L\(^{-1}\), the phosphate adsorption capacity of the HPEI-EC film was 15.53 mg g\(^{-1}\), which is 12 times larger than that of EC. Additionally, the Freundlich constant \(n\) for the HPEI-EC film was 1.62, which is between 1 and 10, suggesting that the film had favorable phosphate adsorption.\(^{42,47}\) Moreover, the HPEI-EC film had similar phosphate adsorption capacity with some ammonium-functionalized adsorbents, such as ammonium-functionalized MCM-41 (14.97 mg g\(^{-1}\))\(^{48}\) and ammonium-functionalized lignin (14.90 mg g\(^{-1}\)).\(^{49}\) These results indicate that the HPEI-EC film can promisingly be used as an adsorbent for the removal of phosphate.

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c04955)

**Table 1. Parameters for the Langmuir, Freundlich, and Temkin Models**

| isotherm model | parameter      | value  |
|---------------|---------------|--------|
| Langmuir      | \(q_m\) (mg g\(^{-1}\)) | 14.8   |
|               | \(b\) (L mg\(^{-1}\)) | 0.18   |
|               | \(R^2\)       | 0.89   |
| Freundlich    | \(n\)         | 1.62   |
|               | \(K_f\) (L mg\(^{-1}\)) | 2.13   |
|               | \(R^2\)       | 0.92   |
| Temkin        | \(A\)         | −2.81  |
|               | \(B\)         | 5.80   |
|               | \(R^2\)       | 0.69   |
2.4. Adsorption Kinetics. Kinetic parameters are important for designing a large-scale adsorption process and are indicators of adsorption material performance. Thus, the effects of contact time on phosphate adsorption by the HPEI-EC film were studied, and the result is shown in Figure 5a. It can be seen that a rapid increase occurred in the first 1 min, during which almost 53.5% of phosphate was adsorbed, and the adsorption equilibrium was reached within around 240 min at which 90.1% removal efficiency was achieved. This indicates that the HPEI-EC film has high phosphate adsorption efficiency in water, which should remarkably shorten the operation time. Such fast and high phosphate removal efficiency of the HPEI-EC film is mainly attributed to a large number of −NH₂/−NH− groups on HPEI-EC, which allow it to adsorb phosphate more efficiently. Furthermore, in order to understand the adsorption process, the kinetic data were fitted with three kinetic models, namely, the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, and the intraparticle diffusion model; their linear equations are as follows:

The pseudo-first-order kinetic model:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  

The pseudo-second-order kinetic model:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

The intraparticle diffusion model:

\[ q_t = k_{id} t^{1/2} + C \]  

where \( q_e \) and \( q_t \) represent the adsorption capacities (mg g\(^{-1}\)) of the HPEI-EC film at equilibrium and at time \( t \) (min), respectively; \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the adsorption rate constants for the pseudo-second-order model; \( k_{id} \) (mg g\(^{-1}\) min\(^{-1/2}\)) and \( C \) (mg g\(^{-1}\)) are the rate constant and the thickness of the boundary layer, respectively.

As shown in Figure 5c and Table 2, the pseudo-second-order model resulted in a better correlation coefficient (\( R^2 = 0.999 \)).

Table 2. Parameters for the Pseudo-First-Order, Pseudo-Second-Order, and Intraparticle Diffusion Models

| kinetic model                | parameter | value |
|------------------------------|-----------|-------|
| pseudo-first-order           | \( k_1 \) (min\(^{-1}\)) | 0.010 |
|                              | \( R^2 \) | 0.9976 |
| pseudo-second-order          | \( q_e \) (mg g\(^{-1}\)) | 7.07 |
|                              | \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | 0.014 |
|                              | \( R^2 \) | 0.999 |
| intraparticle diffusion      | \( k_{id} \) (mg g\(^{-1}\) min\(^{-1/2}\)) | 0.1871 |
|                              | \( R^2 \) | 0.6873 |
|                              | \( C \) (mg g\(^{-1}\)) | 3.2493 |

It can be seen that the \( q_e \) value (7.07 mg g\(^{-1}\)) calculated from this model is consistent with the experimental value (6.97 mg g\(^{-1}\)). This indicates that the adsorption of phosphate on the HPEI-EC film can be described by the pseudo-second-order model. Meanwhile, as shown in Figure 5d, a plot of \( q_t \) versus \( t^{1/2} \) exhibited three linear correlations, which are indicative of the three steps of the whole adsorption process. The first
step is the external film diffusion, where a fast movement of phosphate ions from water to the HPEI-EC film surface occurs. The second step is the gradual adsorption process in which the intraparticle diffusion is the rate-limiting step. The third step represents the equilibrium adsorption, where the intraparticle diffusion begins to slow down because of very low phosphate concentration in water. It should be noted that the obtained \( k_{d1} \) value (3.99 mg g\(^{-1}\) min\(^{-1/2}\)) was higher than the \( k_{d2} \) value (0.2023 mg g\(^{-1}\) min\(^{-1/2}\)) and the \( k_{d3} \) value (0.0261 mg g\(^{-1}\) min\(^{-1/2}\)), indicating that the external film diffusion controls this adsorption process.\(^{41}\)

2.5. Effect of Solution pH. The pH of solution is important for the whole adsorption process, as it can influence the charge of the HPEI-EC film surface, as well as the anionic forms of phosphate.\(^{54}\) Therefore, the effect of pH on phosphate adsorption on the HPEI-EC film was studied, and the related result is presented in Figure 6. We found that phosphate adsorption on the HPEI-EC film was highly pH-dependent.\(^{47}\) The adsorption capacity decreased with increasing pH value, and the maximum adsorption amount of phosphate was 16.23 mg g\(^{-1}\) at a pH of around 3. This high phosphate adsorption performance is attributed to the fact that under acidic conditions, amino groups on the HPEI-EC film surface can be protonated to produce positively charged active adsorption sites like \(-\text{NH}_3^+\), which can form electrostatic interactions with negatively charged PO\(_4^{3-}\) ions,\(^{23}\) leading to an increase in the adsorption amount of phosphate. On the other hand, at a pH above 6, increasing the solution pH value not only reduces the protonation of the amino groups on the surface of the HPEI-EC film, but also improves the concentration of hydroxyl groups in solution. This can enhance the competition between anionic phosphate and hydroxyl groups while reducing the adsorption amount of phosphate. This phenomenon inspires the regeneration method in which the used HPEI-EC film is treated with NaOH solution.

2.6. Effect of Coexisting Anions. In general, natural water or wastewater contains many coexisting anions, including chloride (Cl\(^-\)), nitrate (NO\(_3^-\)), sulfate (SO\(_4^{2-}\)), and bicarbonate (HCO\(_3^-\)).\(^{35}\) Based on this, the effect of coexisting anions on phosphate was examined in the presence of 200 mg L\(^{-1}\) each of Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), and HCO\(_3^-\), and the results are displayed in Figure 7. As can be seen, the adsorption amount of phosphate on the HPEI-EC film without coexisting anions was 10.8 mg g\(^{-1}\). After adding Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), and HCO\(_3^-\) into the phosphate solution, the adsorption amount of phosphate on the HPEI-EC film was reduced to 10.75, 9.8, 6.04, and 5.59 mg g\(^{-1}\), respectively. This phenomenon is possibly attributed to the competition between the coexisting anions and the phosphate anions. It should be noted that the presence of HCO\(_3^-\) had the highest effect on the adsorption amount of phosphate ions. This is because the pH value of HCO\(_3^-\) solution is the highest among all the four types of anions; it is also because the largest hydrolysis constant resulted in the lowest adsorption amount of phosphate under a high pH value.\(^{10}\) Moreover, we also found that the presence of SO\(_4^{2-}\) had a great influence on phosphate adsorption. This is probably because SO\(_4^{2-}\) has a higher suppressive effect on phosphate adsorption than monovalent anions (e.g., Cl\(^-\) and NO\(_3^-\)).\(^{37}\)

2.7. Regeneration Study. The ability of the saturated HPEI-EC film to be regenerated can significantly affect its suitability for practical applications.\(^{15}\) According to the pH study, a low adsorption amount of phosphate occurred at a high pH value; thus, the used HPEI-EC film can be desorbed using NaOH solution.\(^{56}\) The adsorption–desorption experimental data (at the initial phosphate solution was 50 mg L\(^{-1}\)) for the HPEI-EC film after five cycles are presented in Figure 8. It can be seen that 84.8% of the adsorption amount of phosphate was retained in the regenerated HPEI-EC film after the first regeneration cycle; specifically, the value was 20.6 mg g\(^{-1}\) compared to the original value of 24.3 mg g\(^{-1}\). Although after the fifth adsorption–desorption cycle, the adsorption amount of phosphate remained at about 71.6% of the original value, indicating that the HPEI-EC film possesses good recyclability. Moreover, the SEM images of the HPEI-EC film after five adsorption–desorption cycles are presented in Figure 8b; as compared with the original HPEI-EC film (see Figure 2d), the morphology of the HPEI-EC film after five regeneration cycles showed no significant change, and their element compositions were also very similar (see Figure 8c,f). These results indicated that the HPEI-EC film is stable for NaOH solution treatment, and thus can be regenerated by the treatment with NaOH solution. Furthermore, the desorption performance of the HPEI-EC film using NaOH as the desorbent was investigated. After first phosphate adsorption, the EDX of the HPEI-EC film exhibited a new element P, and the P content on the HPEI-EC surface was calculated to be
2.99%, which indicated that the phosphate was attached on the surface of the HPEI-EC film (see Figure 8d). After first desorption with NaOH, element P disappeared on the surface of the HPEI-EC film (see Figure 8e). Similarly, no element P was detected on the HPEI-EC film after the fifth desorption (see Figure 8f). Therefore, NaOH solution was an effective phosphate desorbent for the HPEI-EC film. Based on the above results and analysis, the as-prepared HPEI-EC film exhibits good regeneration and reuse performance for phosphate adsorption.

2.8. Adsorption Mechanism Analysis. According to the study on the effect of pH, the electrostatic interaction between the protonated amine group (−NH₃⁺) and phosphate ion (PO₄³⁻) is considered to be the main factor initiating the adsorption process. To better illustrate the adsorption mechanism, SEM, FT-IR, and XPS spectra of the HPEI-EC film and HPEI-EC-P (after phosphate adsorption) were examined, and the results are displayed in Figure 9. Compared with the HPEI-EC film (see Figure 2), some white particles can be seen in the SEM image of HPEI-EC-P (see Figure 9a). Meanwhile, the SEM–EDX spectrum of HPEI-EC-P (see Figure 8d) had a novel element P, confirming the successful adsorption of phosphate on the HPEI-EC film. Moreover, the FT-IR spectrum of HPEI-EC-P (see Figure S2) showed that the adsorption peaks at around 3448, 1645, and 1563 cm⁻¹ were weakened compared with those in the spectrum of the HPEI-EC film. This indicates that the amino groups on the HPEI-EC film surface play a primary part in phosphate adsorption. Furthermore, the XPS spectrum of HPEI-EC-P (see Figure 9b) exhibited a new peak at 132.9 eV, which can be ascribed to P 2p, confirming that phosphate was adsorbed by the HPEI-EC film. The above results are in agreement with the FT-IR and EDX results. As shown in Figure 9c, the fitted peaks at 398.7 and 399.3 eV can be assigned to −N= and −NH₂, respectively. As presented in Figure 9d, a novel peak appearing at 400.6 eV can be ascribed to −NH₃⁺, and both −N= and −NH₂ peaks were shifted to higher binding energies after phosphate adsorption, suggesting that amino groups from PEI play a part in the phosphate adsorption process. Combined with the analyses and the related results mentioned above, a possible adsorption mechanism between phosphate and amino groups on the HPEI-EC film surface was proposed, as presented in Figure 9e. At a lower solution pH value, the amino groups on the HPEI-EC film could be effectively protonated to −NH₃⁺, and the phosphate anions could be attached to the HPEI-EC film through electrostatic attraction.

3. CONCLUSIONS

In this work, a low-cost and reusable HPEI-EC film was successfully fabricated. FT-IR, XPS, and SEM analyses demonstrated the successful functionalization of HPEI with EC. The isotherm of the phosphate adsorption could be fitted.
with the Freundlich model, and the adsorption capacity was 15.53 mg g\(^{-1}\) at the equilibrium phosphate concentration of 23.63 mg L\(^{-1}\), which is 12 times higher than that of EC. The kinetics of the phosphate adsorption is well in agreement with the pseudo-second-order model. The adsorption of phosphate was highly pH-dependent, and the adsorption capacity decreased as the pH increased. Moreover, both HCO\(_3\)\(^-\) and SO\(_4\)\(^{2-}\) had great influences on the phosphate adsorption. Furthermore, the HPEI-EC film possessed good reusability, and 71.6% of the original adsorption capacity of phosphate was retained after five cycles. Importantly, the good mechanical properties of the HPEI-EC film bring about the advantage of the saturated HPEI-EC film, allowing it to be easily taken out with a pair of tweezers, which remarkably simplifies the separation procedure and shortens the process time. The electrostatic interaction was found to be mainly responsible for the adsorption process. This work demonstrates a low-cost and reusable film adsorbent that can effectively remove phosphate from water and presents an easy separation method for use in the adsorption field.

4. EXPERIMENTAL SECTION

4.1. Materials. EC (with 44—51% ethoxy content), L-ascorbic acid (C\(_6\)H\(_8\)O\(_6\) AR), potassium dihydrogen phosphate (KH\(_2\)PO\(_4\) AR), potassium sulfate (K\(_2\)SO\(_4\) AR), and potassium nitrate (KNO\(_3\) AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Potassium antimonyl tartrate (K(SbO)C\(_4\)H\(_6\)O\(_6\)·0.5H\(_2\)O, AR) was obtained from Shanghai QingXi Chemical Technology Co., Ltd. (Shanghai, China). Ammonium molybdate tetrahydrate ((NH\(_4\))\(_6\)Mo\(_7\)O\(_24\)·4H\(_2\)O, AR) was purchased from Shanghai Reagent Factory, China (Shanghai, China). PEI \([M_\text{w}}: 10,000, 99\%, \text{branched polymer (} -\text{NHCH}_2\text{CH}_2- \text{)}_x [\text{N} - (\text{CH}_2\text{CH}_2\text{NH}_2- \text{)} - \text{CH}_2\text{CH}_2-]_y\] was purchased from Aladdin Chemistry Co., Ltd.. Potassium hydrogen carbonate (KHCO\(_3\), AR), sodium chloride (NaCl, AR), and hydrochloride acid (HCl, AR) were purchased from Zhejiang Zhongxing
The bath adsorption experiments were performed at 25 °C, as shown in Figure 1. In brief, 4.0 g of EC was added into a 1000 mL beaker containing 400 mL of anhydrous ethanol and was stirred until homogeneous. The EC solution was ultrasonicated for 5 min and then mechanically stirred for 1 h. After that, 1.0 g of HPEI was added into 50 mL of anhydrous ethanol and stirred to obtain a PEI solution. Next, the HPEI solution was added dropwise into the EC solution and stirred continuously for 1 h at room temperature. The obtained homogeneous solution was heated in a water bath at 70 °C to evaporate ethanol, and the obtained concentrated solution was poured into a surface dish and dried in a vacuum oven at 50 °C for 12 h. After that, the HPEI-EC film was prepared.

4.3. Characterization. FT-IR spectra of EC and HPEI-EC were collected in transmission configuration at a wavenumber ranging from 400 to 4000 cm⁻¹ using a Nicolet iS50 FT-IR instrument. XPS data of EC and HPEI-EC were acquired with a PHI 5000 Versa Probe equipped with a mono-Al Kα radiation source, and the XPS curves were calibrated with the reference of the C 1s peak (binding energy at 284.8 eV). SEM imaging of EC and HPEI-EC was conducted on a Hitachi S-4800 field emission microscope. Phosphate concentrations in the solution were determined using a T6 UV−vis spectrophotometer. Phosphate concentrations in the solution were determined using a T6 UV−vis spectrophotometer. Phosphate concentrations in the solution were determined using a T6 UV−vis spectrophotometer.

4.4. Adsorption Experiments. A stock standard solution with a concentration of 1000 mg L⁻¹ (computed in P) was prepared by weighing and dissolving 4.3940 g of anhydrous potassium dihydrogen into 1000 mL of de-ionized water, and then the target concentrations of phosphate were obtained by dilution with de-ionized water. Batch adsorption experiments were conducted to evaluate the phosphate adsorption performance of the designed HPEI-EC film. The batch experiments were carried out in Teflon-lined screw capped glass tubes at the solid-to-liquid ratio value of 1.25 mg L⁻¹, which was reached, and this was followed by drying in a vacuum drier at 40 °C for 24 h and utilizing in the next adsorption−desorption cycles. After each test of adsorption experiment, the solution was then filtered with 0.45 μm membrane filters and the residue phosphate concentration was determined using the molybdenum blue method on a T6 UV−vis spectrophotometer at a detection wavelength of 700 nm. The equilibrium uptake capacity for phosphate was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m}$$  (7)

where $q_e$ (mg g⁻¹) represents the adsorption amount of phosphate under equilibrium, $C_o$ refers to the original concentration, $C_e$ (mg L⁻¹) stands for the equilibrium concentration of phosphate, $V$ (mL) represents the volume of the solution, and $m$ (g) refers to the weight of the used adsorbent.

## ASSOCIATED CONTENT

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04955.

**BET isotherms of (a) EC and (b) the HPEI-EC film; FT-IR spectra of the HPEI-EC film before and after phosphate adsorption (PDF)**

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## Notes

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