Improvement of Ultrafiltration for Treatment of Phosphorus-Containing Water by a Lanthanum-Modified Aminated Polyacrylonitrile Membrane

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ABSTRACT: Phosphorus contamination in fresh water has posed a great risk to aquatic ecosystems and human health due to extensive eutrophication. In this paper, we are reporting a lanthanum (La)-modified aminated polyacrylonitrile (PAN) adsorptive membrane for effective decontamination of phosphorus from the simulated water. The PAN membrane was first aminated to introduce the amine group as an active site for La and then followed by the in situ precipitation of La particles. The kinetics study showed that the rapid adsorption occurred within the initial 4 h with the equilibrium established at 8 h. The membrane worked well in the acidic pH region, with optimal pH 4 and 5 without and with the pH control, respectively. The maximum adsorption capacities were 50 and 44.64 mg/g at pH 5 and 7, respectively. The adsorption of phosphorus was not affected by the existence of commonly existing anions except fluorides in water. In the filtration study, it was observed that the removal of phosphorus remained the optimum, although the operating pressure was increased from 1 to 3 bar. The modified membrane was able to treat 0.32 L of a 10 mg/L phosphate solution to meet the maximum allowable limit of 0.15 mg/L for the trade effluent. The mechanism study revealed that the removal was primarily associated with the ion exchange between a phosphorus ion and a hydroxyl group from the La particles.

1. INTRODUCTION

Water eutrophication, an environmental response to the changes of chemical properties of water, is triggered by the excessive release of nutrients into water bodies.1 The massive growth of the phytoplankton, such as cyanobacteria, can cause severe damage to the ecosystem and eventually affect the water quality for human use and impose health hazards to humans and living organisms. Two major nutrients, nitrogen (N) and phosphorus (P), are key contributors to the rapid growth of the phytoplankton in the eutrophic area. The removal of nitrogen can be achieved through technologies such as denitrification and ion exchange. However, the removal of phosphorus is rather challenging.5 To prevent or minimize the algal growth, the removal of phosphorus from the anthropogenically generated wastewater is of great importance as the end-of-pipe solution. According to the United States Environmental Protection Agency (USEPA) regulations, the maximum allowable limit of phosphorus in the trade effluent is 0.05 mg P/L (namely 0.15 mg-PO$_4^{3-}$/L) before being discharged to the surface water.4

The main technologies for phosphorus removal are biological treatments, precipitation, coagulation, electrocoagulation, ion exchange, adsorption, and membrane filtration.5–11 Among them, adsorption is the most favorable and promising way, owing to its high effectiveness in achieving the treatment expectation at low operating cost. For example, lanthanum (La) species shows excellent performances in phosphate removal in terms of capacity and kinetics in the treatment of simulated and industrial wastewater.12 However, disadvantages such as poor regeneration/reuse and separation of fine spent adsorbents from the treated effluent have retarded the applications of adsorbents in P-contaminated wastewater treatment.

Alternative technologies that show great phosphorus removal are membrane filtration, nanofiltration, and reverse osmosis. Nanofiltration is membrane-based filtration that separates uncharged and charged species (multivalent ions) from water through sieve and Donnan effects.13 Reverse osmosis is a similar process as nanofiltration and can have great monovalent ion removal with lower permeance. Nanofiltration has demonstrated great ability in removing phosphorus mainly due to the repulsion between the negatively charged surface of a membrane and phosphorus in a typical pH range of water.11

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However, drawbacks like high energy and cost and the lack of selective recovery of useful species such as phosphates make nanofiltration a difficult choice to be widely implemented.

To overcome the disadvantages of adsorption and nanofiltration, a combination of both adsorption and membrane filtration technologies, namely, adsorptive ultrafiltration, is proposed, which can not only reduce the energy consumption but also remove and recover certain pollutants with higher selectivity. A membrane can be introduced with adsorptive properties through the addition of adsorptive additives for the formation of mixed matrix membranes such as modified polyacrylonitrile (PAN) membranes for heavy metal removal, mixed matrix membranes for copper adsorption, polysulfone mixed matrix membranes for lead removal.\textsuperscript{14–21} Several research papers demonstrate that the modified membranes possess great adsorptive properties for the P removal.\textsuperscript{22–25}

However, most of the adsorptive membranes were prepared through direct blending of a polymer and an additive, which could lead to the potential leakage of adsorbents during filtration. In addition, the reported membranes have demonstrated their ability in treating only low-P-concentration water (0.216–6.131 mg/L), which limits their applications. Due to a great increase in the production and applications of phosphate-containing fertilizers and food products, the development of advanced ultrafiltration membranes for the treatment of relatively high-P-content municipal wastewater (9.2–45.98 mg/L) with low leakage and energy consumption indeed becomes crucial.\textsuperscript{26}

Since several La species demonstrate fast adsorption kinetics and strong affinity toward phosphates (the \(K_{sp}\) of lanthanum phosphate is 26.16), they are great candidates as an additive in the modification of ultrafiltration membranes.\textsuperscript{24,27} As the capsule of La species, a polymer, PAN, not only can serve as a growth and agglomeration controller but also can be chemically modified to have specific functional groups (e.g., amine and carboxylate groups).\textsuperscript{28} He et al. reported a La/PAN nanofibrinous membrane for a high phosphate removal with great kinetics.\textsuperscript{24} However, the lack of modification on PAN can result in the loss of La during filtration since there is no interaction between these two materials. It is of great importance to develop a fabrication method for the La-modified PAN flat sheet membrane that can perform well in the uptake of phosphates while keeping the La element stable in the membrane.

In this research article, we are reporting a La-modified aminated PAN flat sheet membrane for phosphate capture. The PAN membrane was first modified by introducing the amine group, followed by the in situ precipitation of La particles. The adsorptive membrane was characterized in detail. The membrane properties such as morphology, point of zero charge (PZC), total porosity, mean pore size, and pure water flux (PWF) were examined. Batch and filtration studies were conducted to evaluate the adsorption performance of the membrane. The mechanism study was conducted via the X-ray photoelectron spectroscopic (XPS) analysis.

### 2. MATERIALS AND METHODS

#### 2.1. Materials

All chemicals were of analytical grade unless specifically stated and were used without further purification. PAN powder, lanthanum(III) nitrate hexahydrate (\(\text{La(NO}_3\text{)}_3 \times 6\text{H}_2\text{O}\)), 1-methyl-2-pyrrolidinone (NMP), ammonia solution (\(\text{NH}_4\text{OH} \times 25\%\)), ethanol (\(\text{C}_2\text{H}_5\text{OH}\)), diethylenetriamine (DETA), potassium dihydrogen phosphate (\(\text{KH}_2\text{PO}_4\)), sodium sulfate (\(\text{Na}_2\text{SO}_4\)), sodium chloride (\(\text{NaCl}\)), sodium nitrate (\(\text{NaNO}_3\)), sodium bicarbonate (\(\text{NaHCO}_3\)), and sodium hydroxide (\(\text{NaOH}\)) were purchased from Sigma-Aldrich (Singapore). Nitric acid (\(\text{HNO}_3\), 69%), sodium fluoride (\(\text{NaF}\)), and anhydrous sodium carbonate (\(\text{Na}_2\text{CO}_3\)) were procured from Fisher Scientific.

The phosphate stock solution (1000 mg/L) was prepared by dissolving a desired amount of \(\text{KH}_2\text{PO}_4\) in 1 L of deionized (DI) water. The working solutions were obtained by diluting the stock solution to the required concentrations for various experimental studies. DI water was used throughout the entire experiment. Diluted \(\text{HNO}_3\) and \(\text{NaOH}\) were used for the pH adjustment. In addition, water from the local reservoir was taken and used in the study of membrane filtration.

#### 2.2. Membrane Preparation

The PAN flat sheet membrane was prepared through the phase inversion method. First, 18 wt% PAN was dissolved in 82 wt% NMP under stirring at 60 °C. After the complete dissolution, the polymer solution was placed in an oven to degas for 24 h. The PAN solution was then uniformly cast on a nonwoven fabric and immersed in the DI water for the solvent exchange. The formed membrane was washed by the DI water to completely remove the residual solvent and kept in the DI water for further modification.

The amination of the PAN membrane was conducted according to Neghlani et al. with additional modified conditions (temperature and time) for the suitability of the flat sheet membrane.\textsuperscript{29} In brief, 2 pieces of a 5 cm × 5 cm PAN membrane were immersed in a mixture of DETA (31.515 g), \(\text{Na}_2\text{CO}_3\) (1 g), and DI water (100 mL). The reaction was carried out at 40 °C for 4 h. Afterward, the modified membrane was washed by the DI water until the pH of 7 was reached. The aminated PAN (PAN-NH2) membrane was kept in the DI water for the further process.

The La solutions with concentrations ranging from 0.05 to 0.4 M were obtained by dissolving the desired amounts of \(\text{La(NO}_3\text{)}_3 \times 6\text{H}_2\text{O}\) in 100 mL of ethanol. A PAN-NH2 membrane was immersed in the La solution for 3 h and then exposed to ammonia vapor overnight for the in situ precipitation process at room temperature.\textsuperscript{31} The membrane was washed by the DI water and subjected to ultrasound to remove loosely attached La particles. The synthesis process of La-modified aminated PAN (PAN-NH2-La0.3) membrane is illustrated in Figure 1.

#### 2.3. Membrane Characterization

The surface morphology of membranes was investigated by field emission scanning electron microscopy (FESEM, JSM-6700F, JOEL). The membranes without nonwoven fabric were cut in liquid nitrogen for the cross-sectional examination. The membrane samples were coated with platinum before the procedure of operation (e.g., imaging) was started. The thickness of membranes was measured from the cross-sectional view and used for the total porosity calculation.

The crystalline structure of membranes was determined by X-ray diffraction (XRD, D/Max-3A, Rigaku) operated with Cu Kα radiation at a voltage of 40 kV and a current of 30 mA. The functional groups of membranes were identified by a Fourier transform infrared (FTIR) spectrometer (Vertex 70, Bruker), which was equipped with the attenuated total reflection (ATR) accessory. The ATR-FTIR spectrometer was operated in the transmission mode at the wavelength range of 400–4000 cm\(^{-1}\).

The elemental analysis of membranes and the change in the material chemistry of both the membrane and phosphorus
were conducted by XPS (Kratos AXIS Ultra, Kratos Analytical Ltd.). The XPS instrument was operated at a voltage of 15 kV and a current of 5 mA with monochromatic Al Kα radiation. Calibration was made with the binding energy at 284.5 eV as the reference for carbon 1s signal. A nonlinear least-square curve fitting software (XPSPEAK41) was used for the fitting of XPS raw data. The water contact angle of membranes was measured by contact angle goniometry (Rame Hart) with DI water at room temperature.

The point of zero charge (PZC) of membranes was identified by the modified method described by Yu et al.31 In short, the membrane was suspended in a 0.01 M NaNO₃ solution for 24 h. Then, the pH of the solution was adjusted to the range of 3–10. After 60 min equilibration, the initial pH was measured and the concentration of NaNO₃ was increased to 0.45 M. After 3 h of equilibrium time, the concentration of phosphates at time t (mg/L), respectively; and V is the volume of the phosphate working solution (L), while w is membrane dosage (g).

The effect of La concentration during fabrication of membranes was evaluated according to the adsorption capacity of membranes. The La content in each membrane was identified by dissolving the embedded La particles membranes in 1 M HNO₃. Each membrane was tested with a 100 mg/L phosphate solution at neutral pH for one day.

The pH effect on adsorption was studied by suspending a 1 g/L membrane in a 100 mg/L phosphate solution in the pH range of 2–10. Two sets of the pH effect experiment were conducted: one with the pH control, while another without the pH control throughout the 24 h of contact time at 200 rpm. The leaching of La was determined at different pH values by measuring its concentration in the solution after the adsorption.

In the adsorption kinetics experiment, the procedure was similar to that of the pH effect study. A 1 g/L membrane was added into a 200 mL phosphate solution (C₀ = 100 mg/L) at pH 5. The pH of the solution was constantly maintained throughout the experiment. The samples were taken at predetermined time intervals, and the concentrations of phosphates were measured by the ICP-OES.

In the adsorption isotherm experiment, a 1 g/L membrane was suspended in a phosphate solution with the initial concentration ranging from 5 to 120 mg/L. The pH of the solution was maintained at pH 5 and 7 for 24 h. Other experimental conditions were the same as the pH effect study.

In the experiment on the impact of co-existing anions on the uptake of phosphorus, NaF, Na₂SO₄, Na₂CO₃, NaCl, and NaNO₃ were used as the anions because they are common in natural water and/or industrial wastewater. Each co-existing anion was added separately at three different concentrations (0.1, 1, and 10 mM) into a 50 mg/L phosphate solution at pH 5. The membrane dosage and other experimental conditions were similar to those of the pH effect study.

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The total porosity (ε) of membranes without nonwoven fabric was obtained via the gravimetric method, with the equation shown as follows:32

\[
\varepsilon = \frac{W_w - W_d}{A \times L \times \rho_w}
\]  

(1)

where \(W_w\) and \(W_d\) are the weights of wet and dry membranes, respectively; \(A\) is the membrane top surface area (4 cm²); \(L\) is the membrane thickness (m); and \(\rho_w\) is the density of water (998 kg/m³). The mean pore size \((r_m)\) of membranes was calculated by the Guerout–Elford–Ferry equation as shown below:

\[
r_m = \frac{2}{\sqrt{\varepsilon}} L \times \frac{Q}{\eta \times A \times \Delta P}
\]

(2)

where \(Q\) is the permeation rate of pure water (m³/s), \(\eta\) is the water viscosity (8.9 × 10⁻⁴ Pa·s), and \(\Delta P\) is the transmembrane pressure (1 bar).

A 2 cm × 2 cm dry membrane was weighed as \(W_d\) and then soaked in DI water for 24 h. Afterward, the residual water on the membrane was removed gently and the wet membrane was weighed as \(W_w\).

The pure water flux (PWF, \(J_w\)) of the membranes was determined using a Merck Millipore stirred cell module (8050) at an operating pressure of 1 bar. The permeated water was collected at a specific duration after 30 min pressurization, and the PWF was calculated by the following equation:

\[
J_w = \frac{Q}{A_e \times \Delta P}
\]

(3)

where \(A_e\) is the effective membrane surface area (namely, 12.56 cm² in this study).

2.4. Membrane Performance. 2.4.1. Batch Adsorption.

All experiments were conducted thrice at room temperature, and the average values were presented as the results in this paper. The concentrations of phosphate and La in an aqueous solution were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 3000DV, PerkinElmer) after extraction and filtration.

The adsorption capacity and removal efficiency (RE) of phosphates are calculated as follows:

\[
q_t = \frac{(C_o - C_t) V}{m}
\]

(4)

\[
RE(\%) = \frac{(C_o - C_t)}{C_o} \times 100\%
\]

(5)

where \(q_t\) is the adsorption capacity at a predetermined time (t) (mg·PO₄³⁻/g); \(C_o\) and \(C_t\) are the initial concentration and the concentration of phosphates at time t (mg/L), respectively; and \(V\) is the volume of the phosphate working solution (L), while \(m\) is membrane dosage (g).

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2.4.2. Filtration. The filtration process was conducted in a stirred cell module paired with an 800 mL feed tank (Model 8050, Merck Millipore). Nitrogen gas was used to pressurize the feed solution through the membrane. A membrane with an effective surface area of 12.56 cm² was inserted into the module with an attached elastic O-ring. To study the effect of transmembrane pressure on the removal performance of membranes, the pressure was varied from 1 to 3 bar with 0.5 bar incremental pressure. The influent concentrations of the phosphate solution were 1, 10, and 20 mg/L without pH adjustment. The filtrate with a volume of 5 mL was collected at each operating pressure, and the concentration of phosphates was measured by the ICP-OES. The removal performance and flux of the membrane are calculated by the equations shown as follows:

\[
\text{removal (\%)} = \left( \frac{C_{\text{inf}} - C_{\text{eff}}}{C_{\text{inf}}} \right) \times 100\% 
\]  
\[
\text{flux (LMH)} = \frac{Q}{A_e} 
\]  

where \( C_{\text{inf}} \) and \( C_{\text{eff}} \) are the phosphate concentrations (mg/L) in the influent and the effluent, respectively; \( A_e \) is the effective contact area of membrane in filtration.

To investigate the filtration performance of the membrane over time, it was subjected to the continuous filtration operation with the 10 mg/L synthetic phosphate solution at 1.5 bar. The filtrates were collected at predetermined time intervals until the breakthrough point was achieved. The concentration of phosphates in the filtrate and permeance of the membrane were monitored over the filtration time. The permeance was calculated with eq 3. The leakage of La was measured after mixing the filtrate in a 1 M HNO₃ solution. Bed volume (BV) was calculated as the volume of the treated solution per volume of the membrane.

\[
\text{number of BV} = \frac{\text{volume of treated solution (m}^3\text{)}}{\text{volume of membrane (m}^3\text{)}}
\]  

After the filtration, the spent membrane was regenerated at the condition that provides the best recovery of phosphates and retains the most original adsorption capacity in the second cycle, as shown in Table S3. The regenerated membrane was reused for a similar phosphate filtration study. The experiment was repeated with surface water collected from a reservoir, which contained approximately 11 mg/L phosphates at pH 7.26 with the COD of 6 mg/L.

3. RESULTS AND DISCUSSION

3.1. Characterization of Membranes. 3.1.1. Field Emission Scanning Electron Microscopic Study. The surface and cross-sectional views of PAN, PAN-NH₂, and PAN-NH₂-La0.3 membranes are shown in Figure 2. The surface of PAN
and PAN-NH2 membranes shows uniformly distributed pore structures; however, a slightly denser surface is observed for the PAN-NH2 membrane at a larger magnification, as shown in the inset image of Figure 2c. This indicates that the pore size is reduced after the amination, which is due to the introduction of amine and carboxylate groups on the PAN membrane.33,34 The introduction of carboxylate groups on the PAN membrane that was hydrolyzed by NaOH causes the pore size reduction, as reported by Muthumareeswaran et al.33 On the other hand, Qin et al. reported that the thermal treatment during the amination resulted in the radial shrinkage of the membrane matrix and the decline in the pore size.34 The existence of new functional groups after the amination and reduction of pore size are further discussed later.

After the modification of the PAN-NH2 membrane by La, it can be seen that the La particles are scattered and slightly aggregated on the membrane surface, as shown in Figure 2e. Most of the particles are ellipsoid with the length and diameter of approximately 1.34 and 0.61 μm, respectively, while a minority of them are irregularly shaped.

As shown in Figure 2b,d,f, all membranes consist of an asymmetric structure with a thin dense layer on the top and a thick porous layer below. Besides, fingerlike macropores are observed at the cross section of each membrane, due to the solvent–nonsolvent exchange during phase separation.35

3.1.2. FTIR, XRD, and XPS Studies. The functional groups and crystalline structure of PAN, PAN-NH2, and PAN-NH2-La0.3 membranes were determined by an ATR-FTIR spectrometer and XRD, respectively, with the results shown in Figure 3a,b. According to the FTIR spectra, two characteristic bands are observed for the PAN membrane; the bands at 2243 and 1738 cm\(^{-1}\) are attributed to the stretching vibration of the nitrile group (\(-\text{C}≡\text{N}\)) and the C=O bond, respectively.29,36 After the amination, the intensity of these two peaks become less with the appearance of new functional groups; the peaks at 1577 and 1645 cm\(^{-1}\) can be assigned to the stretching vibration band of the amide group (\(-\text{CONH}\)) and the bending vibration band of the amine group (N–H), respectively. The change in the functional groups indicates that the nitrile group was first hydrolyzed to the amide group and then reacted with DETA for the formation of the amine group. The amine group can act as the active site for La metal via a Lewis acid–base pair. After the incorporation of La, the lattice vibration of the La–O bond is observed at the peak of 515 cm\(^{-1}\).37

The identification of La particles on the membrane surface was further made by analyzing XRD spectra, with the results given in Figure 3b. No obvious difference is detected between the XRD patterns of PAN and PAN-NH2 membranes; the amorphous phase of the PAN membrane is maintained after the amination. After the modification with La, the characteristic peaks (2\(θ\) = 8.8, 16.2, 26.7, 27.8\(^{\circ}\)) of lanthanum hydroxide are detected, indicating that La particles on the membrane surface are lanthanum hydroxide.12

The chemistry of the PAN membrane before and after the modification was determined by XPS. As shown in Figure 3c, the relative content of the amine group is increased after the amination, from 14.34 to 45.83%; this shows that the amine group was successfully introduced into the PAN membrane. Furthermore, the La species is detected on the PAN-NH2-La0.3 membrane through the XPS study, as shown in Figure 3d; this indicates that La was effectively incorporated into the PAN-NH2 membrane. La species on the membrane will help in removing phosphates during filtration, which will be demonstrated in the later section.

3.1.3. Other Important Physical Properties. The PZC values of PAN-NH2 and PAN-NH2-La0.3 membranes were determined, as they are important to understand the surface charge properties of membranes during adsorption. The PZC result is demonstrated in Figure 4a. The PZC of the PAN-NH2
membrane is approximately 6.26, while it increases slightly to 6.55 after the La modification on the membrane. The increase in the PZC would enhance the adsorption of phosphates since the membrane surface is positively charged in a larger pH range. In addition, the PAN-NH2-La0.3 membrane causes a larger pH change below PZC compared to that of the PAN-NH2 membrane; this suggests a larger charge density on the surface of the PAN-NH2-La0.3 membrane, which may cause better adsorption of phosphates due to electrostatic attraction.

The total porosity, mean pore size, contact angle, and PWF were determined, with the results given in Figure 4b. The porosity, mean pore size, and PWF follow the decreasing order of the PAN > PAN-NH2 > PAN-NH2-La0.3 membrane. The pore size and porosity of membranes are reduced after the amination due to the radial contraction of the membrane matrix during thermal treatment, which subsequently led to a decline in the PWF. After the La loading, the pores and surfaces of membranes are partially filled with La particles, thus further resulting in even smaller pore sizes, lower porosity, and PWF, although the hydrophilicity of membranes is improved. Nevertheless, the PWF of the PAN-NH2-La0.3 membrane is higher than that of nanofiltration membranes, NF200 and NF90, which are 2.84 and 6.48 LMH/bar, respectively, reported in the literature. It can be categorized as an ultrafiltration membrane based on the characteristics shown above. The PAN membrane becomes more hydrophilic after being aminated, as proven by the reduction of water contact angle, while the similar hydrophilicity is retained after the incorporation of La since La has a minimal influence on the surface wettability of the membrane.

3.2. Phosphate Uptake Study. 3.2.1. Effect of La Concentration. The effect of La concentration during the fabrication of adsorptive membranes was evaluated in terms of adsorption capacity. As demonstrated in Figure 5, the La content within the membrane increases gradually with the La precursor concentration. Because of the increasing number of free La available to be adsorbed onto the PAN-NH2 membrane, a higher content of La particles is detected within the modified membrane as the La precursor concentration is increased.

As shown in Figure 5, the PAN-NH2 membrane shows a low adsorption capacity (~10 mg/g) for phosphate uptake due to less reaction strength and weak electrostatic attraction between the protonated amine group and negatively charged phosphate anions in the aqueous solution. The mechanism for the uptake of phosphates due to the amine functional group was illustrated in the literature. For example, Shen et al. reported that an amine-functionalized polymer adsorbent could adsorb phosphates via the electrostatic attraction.

After the modification of the PAN-NH2 membrane with 0.05 M La, the phosphate uptake is doubled and then enhanced gradually by 20–30% as the La precursor concentration is increased from 0.05 to 0.3 M. However, the adsorption capacity is improved only by 6.8% when the concentration of the La precursor is 0.4 M. This could be explained by the saturation of La loading within the membrane. Even though the La content is increased, the aggregation of La particles within the membrane reduces the adsorption sites and thus leads to low increment in phosphate uptake. Therefore, 0.3 M La concentration is the optimum synthesis parameter and was used in the fabrication of adsorptive membranes for the following experiments.

3.2.2. Adsorption Kinetics. As shown in Figure 6a, 80% of ultimate adsorption occurs within 4 h of contact time, followed by a gradual increase in the adsorption capacity over time until equilibrium is reached. The initial fast adsorption rate is attributed to the great availability of active sites and the high driving force due to the concentration gradient of phosphates. The adsorption equilibrium is achieved in about 8 h, which is relatively faster than by other reported adsorbents.

To evaluate the mechanism of adsorption based on the kinetics data, the pseudo-first-order kinetics equation, the pseudo-second-order kinetics equation, and the intraparticle diffusion equation were used to simulate the experimental data. The mathematical equations are demonstrated as follows:

Pseudo-first-order kinetics equation:

\[ q_t = q_e (1 - e^{-kt}) \]  

(9)

Pseudo-second-order kinetics equation:

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

(10)
Intraparticle diffusion equation:

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

(11)

where \( q_t \) and \( q_e \) are the adsorption capacities (mg/g) at any time \( t \) (h) and at equilibrium, respectively; \( k_1 \), \( k_2 \), and \( k_{id} \) represent the adsorption constants associated with the pseudo-first-order kinetics equation, the pseudo-second-order kinetics equation, and the intraparticle diffusion equation, respectively; and \( \alpha \) is the boundary layer or mass transfer effect.

The experimental data fitted by the three models are demonstrated in Figure 6a, and model constant values are summarized in Table S1. Both pseudoequations fit the experimental data well; a careful comparison shows that the pseudo-first-order kinetics equation does a slightly better job in fitting of the experimental data at a higher correlation coefficient \( \rho^2 \) of 0.9931, different from that of lanthanum hydroxide particles reported in the literature.47 The difference could be possibly due to additional resistance induced by the membrane substrate to the flow of the solute from the membrane surface to the adsorbent surface. Besides, the adsorption capacity at equilibrium obtained from the pseudo-first-order kinetics equation is close to the experimental value (59 mg/g).

On the other hand, the single linearity is obtained from the intraparticle diffusion model, indicating that the adsorption is governed mainly by intraparticle diffusion.48 As some of the La particles reside within the membrane, the membrane pore size is influential for the diffusion of the solute from the bulk solution into the membrane for adsorption. Therefore, the process is primarily affected by the intraparticle diffusion before the adsorption occurs.

3.2.3. pH Effect. An important parameter in controlling the adsorption process is the pH of aqueous medium since it can influence the surface properties of adsorbent and the speciation of the adsorbate. Therefore, it is important to evaluate the effect of pH on phosphate removal by the PAN-NH2-La0.3 membrane. Batch adsorption experiments were conducted in the pH range of 2–10. As seen in Figure 6b, the adsorption capacity increases from pH 2 to 6 and then slowly decreases as the pH increases above pH 7.

According to the PZC value, the surface of the membrane is positively charged at pH below 6.55, which is favorable for adsorption of negatively charged phosphate ions. However, a lower phosphate uptake is observed at pH 2 and 3 compared to other acidic pH values due to dissolution of La particles. Despite that, the membrane is stable as no dissolution of La is detected at pH beyond 3, indicating that it can be utilized in most of the wastewater treatment.

Better adsorption performance is observed in the acidic pH region due to the favorable reaction as well as the electrostatic attraction. The surface of the membrane is negatively charged in the alkaline pH region, and the predominant species of phosphates is HPO\(_4^{2-}\) ions in the pH range of 7.2–12.3. Under such a situation, the chemical reactions between these two negatively charged entities are less favorable. Furthermore, the great repulsion between both entities exists and causes a lower intensity of the uptake of phosphorus.49 Besides, the abundance of hydroxide ions in the solution would cause the competition for active sites with the negatively charged phosphorus, eventually leading to the decline in the adsorption.

The optimum pH for the uptake of phosphates is pH 4 and 5 without the pH control and with the pH control (throughout the process), respectively. After adsorption, the pH increases for all the cases, as shown in Figure S1. The increase in pH is attributed to the release of hydroxyl groups possibly in exchange with the phosphate ions during the uptake. Therefore, the adsorption capacity with the pH control is higher than that without the pH control as the released hydroxide ions are neutralized in the case of the pH control. This membrane demonstrates a wide operating pH range, which may extend the application of adsorptive membrane in water industries.

3.2.4. Adsorption Isotherm. The experimental data for the adsorption isotherm at pH 5 and 7 are shown in Figure 6c. Two isotherm models, Langmuir and Freundlich isotherm models, given below were used to fit the experimental data.

Langmuir isotherm:

\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \]  

(12)
Freundlich isotherm:

\[ q_e = k_f C_e^{1/n} \]  

(13)

where \( q_e \) and \( C_e \) are the adsorption capacity (mg/g) and concentration (mg/L) of phosphates at equilibrium, respectively; \( q_{\text{max}} \) is the maximum adsorption capacity (mg/g); \( b \) is the Langmuir isotherm coefficient associated with the strength of adsorption (L/mg); \( k_f \) is the Freundlich constant of relative adsorption capacity [(mg/g)/(L/mg)\(^{1/n}\)]; and \( n \) is the affinity constant.

The fitting of experimental data and the summary of isotherm constants are demonstrated in Figure 6c and Table S2, respectively. The Langmuir isotherm better fits the experimental data at a higher correlation coefficient than the Freundlich isotherm, suggesting monolayer adsorption on the homogeneous surface of the adsorbent.\(^{41}\) Moreover, the maximum adsorption capacities at pH 5 and 7 are 50 and 44.64 mg/g, respectively, which are higher than that of the reported adsorbents.\(^{50,51}\)

3.2.5. Competitive Adsorption. As natural water or wastewater consists of several types of co-existing anions, it is imperative to investigate the potential impact of such anions on the performance of membranes. It is well known that monovalent ions (F\(^-\), Cl\(^-\), NO\(_3\)\(^-\)) and divalent ions (SO\(_4\)\(^{2-}\), CO\(_3\)\(^2-\)) commonly exist in the phosphate-containing water. As such, we use them to study the individual effect on the adsorption.

As demonstrated in Figure 6d, the presence of anions except fluoride ions does not have a significant negative impact on adsorption. This phenomenon is similar to the adsorption performance of lanthanum hydroxide particles in the presence of co-existing anions.\(^{47}\)

On the contrary, the existence of fluoride ions retards the adsorption by 65% at the fluoride concentration of 10 mM. According to the literature, La shows higher affinity toward fluorides and good adsorption of fluorides in aqueous solution.\(^{52,53}\) Therefore, fluorides compete with phosphates for the similar active sites on the membrane. On the other hand, the concentration of fluorides in natural water is typically very low. As such, it is not an issue of concern for phosphate removal by the membrane. In the case of treatment of wastewater that contains both fluorides and phosphates, our membrane would outperform other materials as it can do a good job for simultaneous removal of these two contaminants. Therefore, the PAN-NH2-La0.3 membrane can be applied to most types of water due to high selectivity toward phosphates.

It is noted that NF, RO, and even some of UF may work well in the removal of phosphates from the water. However, the retention (removal) is based on the physical effect and they do not have better selectivity. On the other hand, the membrane in this study has a better selectivity and thus outperforms the aforementioned membranes.

3.3. Filtration Study. 3.3.1. Effect of Pressure. The effect of transmembrane pressure on the removal of phosphates by PAN, PAN-NH2 and PAN-NH2-La0.3 membranes at three influent phosphate concentrations (1, 10, and 20 mg/L) is presented in Figure 7. At an influent concentration of 1 mg/L, the flux of the PAN membrane increases linearly with an increase in the pressure; however, the removal of phosphates is less than 50% at 1 bar and decreases tremendously as the pressure is further increased since the contact time between phosphates and the membrane becomes shorter at a higher pressure. Due to no chemical interaction between the PAN membrane and phosphate ions, the slight removal of phosphates is merely attributed to physical separation. On the other hand, both PAN-NH2 and PAN-NH2-La0.3 membranes can achieve nearly 100% removal of phosphates at all of the tested pressures, while the PAN-NH2 membrane has a slightly higher flux than that of the PAN-NH2-La0.3 membrane. Due to the poor performance of the PAN membrane, it was not tested in the following experiments.

At the influent phosphate concentration of 10 mg/L, a higher removal of at least 95% can be attained by the PAN-NH2-La0.3 membrane, even though at the highest transmembrane pressure of 3 bar. On the contrary, the PAN-NH2 membrane shows an obvious decline in the removal of phosphates when the pressure is increased from 1 to 1.5 bar; the performance for the removal remains consistent at 70% as the pressure is increased to 3 bar.

The PAN-NH2-La0.3 membrane shows a gradual decline in removal as the pressure is increased at the influent phosphate concentration of 20 mg/L but maintains 80% removal at 3 bar. In contrast, the performance of the PAN-NH2 membrane becomes worse and drops steeply to only 50% removal as the pressure is increased to 3 bar. The flux of both membranes increases linearly with pressure, and the trend is similar in all cases, regardless of the influent phosphate concentration. The
The removal of phosphates demonstrated by the ultrafiltration PAN-NH2-La0.3 membrane is compared to that of commercial nanofiltration membranes of NF90 and NF200, as shown in Table 1. Even at a higher influent concentration (10 mg/L), the PAN-NH2-La0.3 membrane is able to achieve at least 95% removal, compared to less than 90% removal demonstrated by both NF90 and NF200 membranes at a lower initial concentration of 7.66 mg/L during filtration. We would like to highlight that the PAN-NH2-La0.3 membrane can perform the removal at a higher permeance than that of nanofiltration membranes. This comparison shows that the PAN-NH2-La0.3 membrane is a promising material for phosphate removal through ultrafiltration; such operation under a lower pressure is more cost-effective and energy-saving than the nanofiltration. Note that the research was conducted with phosphate-spiked DI water. The permeance and removal performance of the aforementioned membranes would be different when the application is for the treatment of real surface water or wastewater, which contains a variety of suspended and dissolved substances. Further studies are needed to conclude the suitability of our developed membranes for advanced separation and water treatment.

3.3.2. Effect of Bed Volume. The removal performance and permeance of pristine and regenerated PAN-NH2-La0.3 membranes for synthetic 10 mg/L phosphate water are shown in Figure 8. Both membranes can treat nearly a similar volume of phosphate-contaminated water, from the influent concentration of 10 mg/L to the effluent concentration of below 0.15 mg/L, which meet the USEPA maximum allowable limits in the effluent. The pristine membrane can achieve 1819 BVs (equivalent to 0.32 L), while the regenerated membrane has 1930 BVs (equivalent to 0.34 L). According to Table S3, the regenerant, 2 M NaHCO₃, at 60 °C provides the best regenerative efficiency in recovering phosphates (68%) and retaining original adsorption capacity in the second cycle (87%). After the regeneration, the permeance of the membrane is slightly higher than that of the pristine membrane. Since the regenerant is an alkaline solution, the pore size of the membrane is increased as reported, thus resulting in a higher flux. Even though with the higher flux, the regenerated membrane is still able to achieve nearly the same performance as the virgin (pristine) membrane, showing a good reusability of the membrane for the filtration process. Besides, a negligible leakage of La is observed, namely, only 0.31 and 0.78% of total La within the membrane are detected in the effluent during the first and second filtration cycles, respectively; this suggests that the membrane and the embedded material are rather stable.

The reservoir water with a phosphate concentration of 11.6 mg/L was filtrated through the PAN-NH2-La0.3 membrane. As demonstrated in Figure 8b, the membrane shows a similar permeance over time, regardless of the type of feed water (synthetic phosphate solution or reservoir water). This indicates that the suspended solids in the reservoir water have an insignificant influence on the flux. Even at a slightly higher influent concentration of phosphates, the membrane is able to remove the phosphate content of reservoir water to a concentration of less than 0.15 mg/L in the effluent, which meets the USEPA standard limit in the effluent. Besides, the membrane can achieve 1706 BVs (equivalent to 0.30 L), which is slightly lower than that for the synthetic phosphate water.

3.4. Mechanism Study. The change in membrane properties in terms of the crystalline structure and functional group as a result of the adsorption was determined by the FTIR and XRD studies. After the adsorption, an asymmetric vibration band of the P−O bond at 1048 cm⁻¹ strongly appears, as shown in Figure 9a. Furthermore, a slight shift in the La−O band from 515 to 539 cm⁻¹ is observed; this indicates that the La−O bond becomes different after the adsorption as phosphate is adsorbed. Besides, the XRD peaks at 19.5, 28.2, 30.8, 37.4, and 41.5° correspond to the
lanthanum phosphate, as demonstrated in Figure 9b, showing the transformation of lanthanum hydroxide to lanthanum phosphate.12

The detailed mechanism of adsorption was further investigated by the XPS study. As shown in Figure 10a, the XPS wide-scan spectra demonstrate the main elements, C, La, O, and N, in both pristine and spent PAN-NH2-La0.3 membranes. After the adsorption, two new peaks assigned to phosphorus, P 2p and P 2s, appear, indicating successful adsorption of phosphates on the membrane. Besides, an observation of a slight shift of the O 1s peak suggests the possible interaction between the oxygen-containing group in the membrane and phosphate anions.

The high-resolution La 3d spectra before and after the adsorption given in Figure 10b show that all peaks are shifted to the left. Two peaks corresponding to La 3d3/2 shift from binding energies of 834.3 and 838.1 to 834 and 837.6 eV, respectively; at the same time, we see that the peaks of La 3d5/2 shift from 851.2 and 855 to 850.9 and 854.5 eV, respectively. The shift of peaks suggests the transfer in the valence electrons of La 3d, which leads to the possible formation of the La–O–P inner complex.12 A similar observation reported by Fang et al. illustrates the shift of La 3d peaks after the adsorption of phosphates by the lanthanum hydroxide nanorod.12

The O 1s spectrum of the pristine membrane can be deconvoluted into three component peaks at binding energies of 530.35, 531.45, and 531.6 eV, which can be assigned to C–O, La–OH, and C––O, respectively. The C–O and C––O bonds originate from the membrane substrate (PAN-NH2), while the La–OH results from the lanthanum hydroxide particles within the membrane. After the adsorption, a new component peak can be seen at the binding energy of 529.4 eV, as illustrated in Figure 10c, which would be attributed to the P–O bond. The relative content of the P–O component after the adsorption is 14.75%, while the relative content of La–OH reduces significantly from 30.31 to 17.97% due to the formation of the La–O–P bond. The reduction indicates that an ion exchange reaction between the hydroxyl group of lanthanum and phosphate anions in water solution can be the major mechanism in the uptake. Since the relative contents of other components (C–O and C––O) remain nearly unchanged after the adsorption, the ratio of phosphates adsorbed to hydroxyls released is approximately 1. As the dominant species of phosphate anions in the pH range of 2.1–7.2 is H2PO4−, the hypothesized ion exchange reaction is therefore expressed as follows.

$$\text{La(OH)}_3 + 3\text{H}_2\text{PO}_4^- \rightarrow \text{La(H}_2\text{PO}_4)_3 + 3\text{OH}^-$$  (14)

The P 2p high-resolution XPS spectrum of the PAN-NH2-La0.3 membrane after adsorption is illustrated in Figure S3. A characteristic peak at a binding energy of 132.1 eV corresponds to P species, indicating the formation of lanthanum phosphate within the membrane after adsorption.22

4. CONCLUSIONS

In this research work, a La-modified aminated PAN (PAN-NH2-La0.3) membrane was developed for the phosphate removal from an aqueous solution. The La dosage for the fabrication of the membrane was first optimized. The resulting membrane showed promising performance for phosphate uptake through a series of batch adsorption and filtration studies. A rapid adsorption occurred in the first 4 h, and the equilibrium was achieved at the end of adsorption time of 8 h; the pseudo-first-order kinetics equation did a better job in...
fitted the experimental data; and the adsorption was mainly governed by the intraparticle diffusion. The membrane performed the best in the acidic pH region. The maximum adsorption capacities of 50 and 44.64 mg/g can be seen at pH 5 and 7, respectively. The Langmuir isotherm fitted the experimental data better than the Freundlich isotherm. The coexistence of anions except fluorides in water showed an insignificant influence on the phosphate uptake. The membrane showed at least 95% phosphate removal for the filtration of a 10 mg/L phosphate solution, even though at a higher operating pressure. The continuous filtration study revealed that the membrane with a surface area of 12.56 cm² was able to treat 0.32 L of 10 mg/L phosphate-contaminated water to meet the USEPA effluent requirement. The XPS study suggested that ion exchange between the hydroxyl and phosphate ions was the major mechanism. This study demonstrated that the PAN-NH₂-La₀.3 membrane is a promising ultrafiltration membrane for specific phosphate uptake and outperforms the nanofiltration membranes as a result of low material cost and energy consumption.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03573.

Kinetic model constants, isotherm model constants, regenerative performance of the membrane, change of pH after adsorption, La leakage during filtration, and P 2p XPS spectra (PDF)

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Notes

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