Preparation and properties of phosphinic acid–functionalized polyacrylonitrile hollow fiber membrane for heavy metal adsorption

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Abstract
In this study, phosphorylated polyacrylonitrile hollow fiber membrane was synthesized by reacting aminated polyacrylonitrile hollow fiber membrane with phosphinic acid in a Mannich reaction. The batch single-factor measurements revealed that the phosphorylated polyacrylonitrile (PPAN) membrane had an outstanding ability for $\text{Hg}^{2+}$ adsorption. Thermodynamic investigations indicated that the adsorption process was homogenous, and the theoretical maximum adsorption capacity predicted by the Langmuir model was 371.75 mg·g$^{-1}$. The PPAN membrane was able to successfully chelate $\text{Hg}^{2+}$ ions and attain saturation in 4 h, demonstrating that the reaction was chemically controlled by the adsorption kinetics. Based on the FT-IR and XPS spectral characterization data, successful phosphinic acid group grafting was proven, and a plausible mechanism for $\text{Hg}^{2+}$ adsorption by PPAN membranes was presented. Furthermore, the five adsorption–desorption cycle experiments revealed that PPAN hollow fiber membranes had outstanding reusability, indicating a possible use for removing heavy metal ions from wastewater.

Keywords Polyacrylonitrile · Hollow fiber membrane · Modification · Selectivity · Adsorption · Recyclability

Introduction
Heavy metal ions in water are hazardous to public health and the environment due to their significant biological toxicity and carcinogenicity, even at low concentrations (Muhmmad et al. 2011; Srivastava and Majumder 2008; Sarkar and Paul 2017). Therefore, it is crucial to create dependable adsorbents with great adsorption effectiveness in order to remove these heavy metal ions. Chemical precipitation (Fu and Wang 2011), electrochemical processes (Khandegar and Saroha 2013), ion exchange (Hadi et al. 2016), chemisorption (Tan et al. 2017), and membrane separation (Rao et al. 2017) are the most extensively researched approaches. Due to the substantial benefits of simplicity, safety, high adsorption capacity, and reusability, membrane separation is one of the approaches that is most affordable and practicable.

The interaction between the adsorbent’s functional groups and heavy metal ions greatly influences adsorption efficiency, which is also an important indicator for determining adsorption capacity. Numerous functional groups, including carboxylate, sulfate, hydroxyl, phosphate, and amino groups, are capable of efficiently chelating and adsorbing metal ions (Kampalanonwat and Supaphol 2011; Xu et al. 2017; Li et al. 2013; Lou et al. 2018; Huang et al. 2013; Yang et al. 2016; Ndayambaje et al. 2016). Hollow fiber membranes made of polyacrylonitrile (PAN) with a wide surface area and a fast adsorption equilibrium are efficient water purification materials. Additionally, the abundant nitrile groups on the membrane surface have remarkable modification potential and can be easily changed into certain functional
moieties, considerably expanding its applications (Li et al. 2011).

There are numerous publications on the adsorption of heavy metal ions by polyacrylonitrile with functional groups. Chaúque et al. (2016) designed a modified polyacrylonitrile nanofiber (EDTA-EDA-PAN) that efficiently adsorbed Cd$^{2+}$ (32.68 mg·g$^{-1}$) and Cr$^{3+}$ (66.24 mg·g$^{-1}$) from wastewater. Lee et al. (2017) prepared a functionalized nanofiber network by hydrolytic oxidation of polyacrylonitrile (H-PAN). The adsorption of H-PAN is chemically regulated and can selectively adsorb Pb$^{2+}$ (116.2 mg·g$^{-1}$) and Cd$^{2+}$ (85.7 mg·g$^{-1}$). Although these functionalized PAN compounds are effective at adsorbing some metal ions in wastewater, their Hg$^{2+}$ adsorption performance is poor. The phosphate modification of the adsorption material and the inclusion of functional groups such as P–O or P$\equiv$O can substantially enhance the material’s chelating activity for metal ions, resulting in strong complexation with Hg$^{2+}$ (Huang et al. 2017). However, the aqueous solutions of phosphorylated compounds are irreversibly harmful to organisms, and this is obviously not allowed for adsorbents. The safety of use can be considerably increased by immobilizing phosphorus compounds on solid support to prevent the material from dissolving in water (Gao et al. 2017; Notni et al. 2014; Zhao et al. 2015). For instance, Notni et al. (2014) prepared chelating agents that can adsorb Ga(III) by phosphonic acid functionalization of polyazacycloalkane, which can be utilized for radiological diagnostics and therapy.

In the present investigation, phosphorylated polyacrylonitrile (PPAN) hollow fiber membranes were generated by a Mannich reaction. This was accomplished by the efficient grafting of phosphinic acid segments to the surface of amidated polyacrylonitrile (APAN) membranes. The modified PPAN membranes were then utilized for adsorbing a variety of heavy metal ions in order to purify water. As illustrated in Scheme 1, based on the concepts of hard and soft acids and bases (Pearson 1969), mercury, as a soft acid, can preferentially form a coordination complex with the PPAN membrane. Herein, the optimum conditions for adsorption as well as the water flux and mechanical properties of the PPAN membrane were analyzed. Moreover, adsorption isotherms and kinetics were also researched to further illuminate the adsorption mechanism of heavy metal ions. The pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion models (Ramasamy et al. 2017) were used to study the adsorption kinetics, and the experimental data was fitted using the classic Langmuir and Freundlich isotherm models (Wang et al. 2017). Finally, the reusability of the PPAN hollow fiber membrane was determined by performing 24 h of dynamic adsorption and five adsorption–desorption cycles.

Scheme 1 Adsorption mechanism of Hg$^{2+}$ on PPAN hollow fiber membrane
**Experimental**

**Materials**

Polyacrylonitrile and dimethylformamide (DMF) were provided by Kemiou Chemical Reagent Co., Ltd., Tianjin. Sulfonated polyethersulfone (SPES) was made in the laboratory. NaOH, triethylenetetramine (TETA), Pb(NO₃)₂, Ni(NO₃)₂, and CuSO₄·5H₂O were purchased from Chen Fu Chemical Co., Ltd., Beijing. KCl, anhydrous ethanol, and isopropyl alcohol were purchased from Yong Hua Chemical Co., Ltd., Jiangsu. HCl (36%), HNO₃ (69%), and formaldehyde were purchased from Guangzhou Chemical Reagent Factory. Standard solutions of chromium and mercury were obtained from the Shanghai Chemical Reagent Factory. All chemical reagents were of analytical grade and were used directly in the synthesis of materials.

**Preparation**

The synthesis of PPAN hollow fiber membranes requires sequential amination and phosphorylation modification of the PAN membranes, and Scheme 2 illustrates the synthetic process.

**Step 1: synthesis of the PAN membrane**

First, 10 wt% PVA and 1 wt% SPES were dissolved in 69 wt% DMF and stirred at 60 °C to form a homogeneous solution. Next, 20 wt% dried PAN was added to the flask and the mixture was agitated consistently for 4 h with condensed reflux. The solution was then moved to the spinning tank, where it was stirred at a steady speed for a period of 10 h. After defoaming for 24 h, the slurry was placed into hollow fiber spinning machines to produce PAN hollow fiber membranes.

**Step 2: synthesis of the APAN membrane**

Dried PAN membranes (2.5 g) were added to 100 mL of TETA, which was then agitated at 90 °C with reflux for 12 h. Following the reaction, the APAN membrane was rinsed with hot deionized water (65–70 °C) until neutral, then immersed in deionized water for preservation.

**Step 3: synthesis of the PPAN membrane**

In a 250-mL flask, dried APAN membrane (2 g), phosphinic acid (10 g), and 40% formaldehyde (20 mL) were added, followed by the addition of 50 mL of ethanol and deionized water. The flask was filled with nitrogen, and the mixed solution was swirled at 90 °C and refluxed for 5 h. Then, the unbonded molecules were then eliminated by repeatedly washing the functionalized membrane with deionized water and extracting it with ethanol (boiling point 78 °C) for 12 h. For reserve, the PPAN hollow fiber membrane was soaked in water.

**Characterization**

The scanning electron microscope (JSM-7600F, Koehler Corporation of Japan) was used to determine the surface and cross-sectional morphologies of the hollow fiber membranes. Fourier transform infrared spectroscopy (FT-IR) spectra were acquired using a Bruker Vertex 70 spectrometer with a wavenumber ranging from 4000 to 400 cm⁻¹. On a Kratos AXIS Ultra DLD spectrometer, the X-ray photoelectron spectra with binding energies ranging from 0 to 1000 eV were examined. The zeta potential was measured using a potentiometer (Supaar-3, Odinga, Austria) on a solid surface.

**Study on the properties of hollow fiber membranes**

The reaction time and temperature have a significant impact on the phosphorylation degree, water flux, and mechanical strength of PPAN hollow fiber membranes. Exploring the appropriate synthesis conditions is beneficial for subsequent adsorption investigations.

The degree of phosphorylation modification was measured using the weighing method (Pan et al. 2018), and the conversion rate (α, %) could be attained by utilizing Formula (1):
1 3

where \( w_1 \) and \( w_2 \) refer to the weights (g) of the dried PAN and PPAN hollow fiber membrane, respectively.

At an operating pressure of 0.1 MPa, the volume of water that flowed through the hollow fiber membrane over time was recorded, and the water flux \( J \) (L·m\(^{-2} \)·h\(^{-1} \)) was calculated using Formula (2):

\[
J = \frac{V}{A \times \Delta t}
\]

where \( V \) (L) represents the permeate volume throughout the test, \( A \) (m\(^2\)) is the effective permeation area of the hollow fiber membrane, and \( \Delta t \) is the test duration (h).

The tensile strength of the PPAN membrane was measured using an electromechanical universal testing machine (Instron 5565, Instron Corporation of America). The tensile strength of hollow fiber membranes with a length of 70 mm was tested at a speed of 10 mm·min\(^{-1} \).

Ion adsorption experiment

Dried PPAN hollow fiber membrane samples (15 mg) were introduced to flasks containing 30 mL of various heavy metal ion solutions (Cd\(^{2+}\), Hg\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\), pH = 5), each of which had an initial concentration of 50 mg·L\(^{-1}\). After 24 h of adsorption, the hollow fiber membranes were removed and the leftover metal ions in each adsorption solution were determined using an ICP spectrometer. Dilute HNO\(_3\) or NaOH was used to adjust the acidity of the solution, and the interaction between the adsorption capacity of the PPAN membrane for Hg\(^{2+}\) and pH value was investigated. Then, 50 mg of PPAN hollow fiber membrane was immersed in 30 mL of Hg\(^{2+}\) solution (initial concentration = 50 mg·L\(^{-1}\)) and stirred at a steady speed at 25 °C for 24 h. The Hg\(^{2+}\) concentration was estimated using the ICP spectrometer before and after the process.

The adsorption kinetics and isotherm of Hg\(^{2+}\) on PPAN hollow fiber membranes were studied. For the kinetics studies, 50 mg of PPAN membrane was immersed in 30 mL of Hg\(^{2+}\) solution (pH = 5) with an initial concentration of 100 mg·L\(^{-1}\), and the Hg\(^{2+}\) content was measured at regular intervals. For the adsorption isotherm experiments, the dried PPAN samples (50 mg) were put into solutions with different Hg\(^{2+}\) concentrations for 24 h, and the remaining Hg\(^{2+}\) content was then determined using an ICP spectrometer.

Dynamic adsorption and reusability experiments

For the dynamic adsorption experiments, the Hg\(^{2+}\) solution with an initial concentration of 10 mg·L\(^{-1}\) was passed through the PPAN membrane at a uniform speed, and the Hg\(^{2+}\) content in the filtrate was monitored hourly. During the reusability tests, 50 mg of PPAN hollow fiber membrane was added to 30 mL of 100 mg·L\(^{-1}\) Hg\(^{2+}\) solution and stirred at the optimum pH. The metal ion-PPAN complex was immersed in 30 mL of 0.2 mol·L\(^{-1}\) HNO\(_3\) solution, agitated for 24 h to desorb Hg\(^{2+}\) ions, and washed with excess distilled water until the filtrate was neutral. The amount of Hg\(^{2+}\) that was adsorbed and desorbed during the dynamic adsorption experiment was measured over the course of five successive cycles.

Results and discussion

Synthesis of the PPAN membrane

Reaction time and temperature are essential factors affecting the degree of amination (Zhang et al. 2009). Appropriate amination can be beneficial to subsequent phosphonic acid modification, but excessive amination will dramatically reduce the membrane performance. Hence, the APAN membrane with a weight gain of 10.86% (Table 1, entry 2) was employed for the further phosphorylation modification. The weight of the PPAN membrane grew quickly for the first 5 h before beginning to level off, and the weight gains were 10.06%, 15.94%, 16.26%, 16.43%, and 16.66% after 1 h, 3 h, 5 h, 7 h, and 12 h of the contact time (Table 1, entries 3–7).

### Table 1 The weight gain of functional membranes and their water flux and tensile strength

| Entry | Hollow fiber membrane | Reaction time (h) | Weight gain (%) | Water flux (L·m\(^{-2} \)·h\(^{-1} \)) | Tensile strength (MPa) |
|-------|-----------------------|-------------------|-----------------|-------------------------------------|------------------------|
| 1     | PAN                   | –                 | –               | 77.30                               | 4.23                   |
| 2     | APAN                  | 12                | 10.86           | 130.15                              | 3.50                   |
| 3     | PPAN\(_{10.06}\)     | 1                 | 10.06           | 138.54                              | 2.16                   |
| 4     | PPAN\(_{15.94}\)     | 3                 | 15.94           | 165.26                              | 2.45                   |
| 5     | PPAN\(_{16.26}\)     | 5                 | 16.26           | 176.15                              | 2.60                   |
| 6     | PPAN\(_{16.43}\)     | 7                 | 16.43           | 180.94                              | 2.69                   |
| 7     | PPAN\(_{16.66}\)     | 12                | 16.66           | 183.55                              | 2.75                   |

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respectively. These findings confirm that the grafting sites on the membrane surface gradually attain saturation at the conclusion of the reaction, indicating the successful modification of the phosphonic acid.

Table 1 lists the water flux and tensile strength of PAN, APAN, and PPAN hollow fiber membranes with varying degrees of phosphorylation. The water flux of the APAN membrane dramatically increased as compared to the raw PAN membrane, rising from 77.30 to 130.15 L·m⁻²·h⁻¹, but the tensile strength was reduced from 4.23 to 3.50 MPa (Table 1, entries 1 and 2). The water flux of the PPAN membrane was significantly enhanced following functionalized modification, reaching 176.15 L·m⁻²·h⁻¹ after 5 h of reaction time. However, the primary chain of polyacrylonitrile molecules was gradually destroyed after the amination and phosphorylation modifications. Compared to the APAN membrane, the tensile strength of the PPAN membrane decreased from 3.50 to 2.60 MPa (Table 1, entries 2 and 5). Despite a reduction in tensile strength following phosphate modification, the PPAN membrane’s strength was still more than 50% of its initial strength. These results show that the PPAN membrane is a kind of adsorbent material with excellent water flux and tensile strength.

FT-IR

Figure 1 depicts the FT-IR spectra of pure PAN, APAN, and PPAN hollow fiber membranes. In the infrared spectra of APAN and PPAN hollow fiber membranes, a reasonably significant absorption peak (N–H stretching vibrations) developed at around 3400 cm⁻¹ after amination and phosphorylation modification. The bending vibration of N–H corresponded to the absorption peak at approximately 1595 cm⁻¹, indicating the presence of reactive amine sites on the modified membrane. Compared to the APAN infrared spectra, three new absorption peaks appeared in the PPAN infrared spectra at around 1160 cm⁻¹ (–PO₂ stretching vibrations), 1054 cm⁻¹ (–PO₂ stretching vibrations), and 910 cm⁻¹ (P–OH stretching vibrations), which confirmed the existence of –PO₂ and P–OH groups (Ma and Qiao 2014). The FT-IR infrared spectra of PAN, APAN, and PPAN membranes proved that the phosphinic acid groups were successfully grafted onto the APAN hollow fiber membranes.

Zeta potential analysis

Figure 2 shows the zeta potentials of APAN and PPAN hollow fiber membranes at different pH values. The isoelectric point of the PPAN membrane shifted to the left as compared to the APAN membrane, and the isoelectric points of the two membranes were at pH values of 7.4 and 4.3, respectively. Grafting a significant number of phosphinic acid groups onto PPAN hollow fiber membranes resulted in a fall in isoelectric point pH, dramatically raising opposing charges and eventually leading to a left shift of the isoelectric point (Zhao et al. 2019).

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was conducted on APAN and PPAN hollow fiber membranes, and the wide-scan spectra are depicted in Fig. 3. The full spectrum of the PPAN membrane (Fig. 3b) revealed that carbon (284.82 eV), nitrogen (398.4 eV), and oxygen (530.15 eV).
all have separate distinctive peaks. In comparison to the XPS spectra of the APAN membrane (Fig. 3a), the phosphinic acid modification resulted in the appearance of a phosphorus peak at about 130 eV. The PPAN spectra of carbon (C1s), nitrogen (N1s), oxygen (O1s), and phosphorus (P2p) are shown in Fig. 3c–f. The C1s spectra of the PPAN membrane showed three distinct peaks at 284.13 eV, 285.25 eV, and 286.87 eV (Fig. 3c), which were associated with C–C (C–H), C–O, and C–N bonds, respectively. In addition, the characteristic peak at 285.05 eV corresponds to the C–O (PO) bond of the phosphinic acid group (Xiong et al. 2018). Figure 3d shows the N1s spectra of the PPAN membrane, and three peaks at 396.61 eV, 398.53 eV, and 400.25 eV corresponded to NR₂ (R = CH₂H₂PO₂), –NH, and O = C–N bonds (Yuan et al. 2013), respectively. In the O1s spectra of the PPAN membrane (Fig. 3e), two additional peaks at 529.49 eV and 530.57 eV represented O = C/P = O and C–O/P–O bonds, respectively. As can be seen from Fig. 3f, after modification with phosphinic acid, two new peaks belonging to P–C and P–O/P=O were generated at 131.49 eV and 132.03 eV (Viornery et al. 2002). In addition, the percentage content of atoms on the hollow fiber membranes is summarized in Table S1, and the content of phosphorus atoms increased with the progress of phosphorylation modification, which confirmed the effective grafting of phosphate groups on the membrane surface. As a result, the XPS tests revealed that new distinctive peaks developed on the PPAN hollow fiber.

Fig. 3 The XPS spectra of APAN and PPAN. a The full spectrum of APAN. b The full spectrum of PPAN. c–f The spectra of C1s, N1s, O1s, and P2p on PPAN.
membrane, confirming the efficacy of the phosphinic acid modification.

**Scanning electron microscopy**

SEM was used to examine the morphologies of PAN and PPAN membranes, and cross section and surface images are shown in Fig. 4. Both the PAN and PPAN membranes had a three-layer structure when seen through their respective cross sections. In addition, it could be clearly seen from the enlarged pictures of the cross sections (Fig. 4d–f) that the finger-like pores in the middle layer became more prominent with the deepening of phosphorylation, which was conducive to reducing the mass transfer resistance and improving the water flux. As shown in Fig. 4g–i, the original PAN hollow fiber membranes were smooth and uniform. With the increasing phosphorylation, the surfaces of the membranes were rougher, and the pore size was more extensive due to swelling. The rough surface and the enlarged pore size increased the contact area of the membrane with water, which led to an increase in the water flux. These phenomena well confirm the previous experimental results, indicating that phosphorylation modification could effectively improve the performance of hollow fiber membranes. In addition, Fig. S1 displays the SEM images of the PPAN membrane following saturated adsorption of Hg$^{2+}$. The morphology of the PPAN membrane did not alter considerably, and its three-layer structure remained unchanged. However, the membrane surface grew rougher and the number of particles increased after the adsorption reaction, indicating that Hg$^{2+}$ ions were effectively deposited on the surface of the PPAN membrane.

**Adsorption of heavy metal ions by PPAN hollow fiber membranes**

Equilibrium adsorption capacity and removal efficiency are essential parameters to measure adsorption properties. The equilibrium adsorption capacities ($Q_e$) of the PPAN membranes are calculated using the formula $Q_e = \left[\left|C_0 - C_e\right| \times V\right]/m$, and the removal efficiencies ($R$) of the heavy metal ions can be computed using the formula $R = \left[\left(C_0 - C_e\right) / C_0\right] \times 100\%$, where $C_0$ and $C_e$ represent the metal ion concentrations in solution at the beginning and end of the adsorption reaction, respectively. $V$ represents the volume (mL) of the adsorption solution, whereas $m$ is the weight (g) of the PPAN membranes. For the adsorption experiments, the PPAN hollow fiber membrane with the highest phosphorus content (17.64% conversion rate) was employed.

**Selective adsorption for Hg$^{2+}$**

Excellent selective adsorption is a desirable attribute of adsorbents, and this property of the PPAN hollow fiber membrane was evaluated. Firstly, the selective adsorption capacity of different ions (Cd$^{2+}$, Hg$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, and Cu$^{2+}$) was investigated at a high concentration (50 mg·L$^{-1}$). As shown in Fig. 5, based on the statistical analysis, the as-prepared PPAN membranes exhibited a high adsorption capacity (63.77 mg·g$^{-1}$) for Hg$^{2+}$ at equilibrium, which
was significantly higher than the adsorption of other metal ions (Cd\(^{2+}\) < Ni\(^{2+}\) < Cu\(^{2+}\) < Pb\(^{2+}\) < Hg\(^{2+}\)). Furthermore, the adsorption capacities of PAN and APAN were tested at the same Hg\(^{2+}\) concentration (50 mg·L\(^{-1}\)) and pH (5), and the results are shown in Fig. S2. When compared to PAN and APAN membranes, PPAN membranes were much better at absorbing Hg\(^{2+}\). This showed that phosphorylation increased the affinity of the adsorbent for Hg\(^{2+}\). Scheme 1 depicts the adsorption of Hg\(^{2+}\) on the PPAN membrane. On the one hand, when the phosphate groups remove H\(^{+}\), there may be an ion exchange reaction with Hg\(^{2+}\) (Lin et al. 2018). On the other hand, Hg\(^{2+}\) was adsorbed by coordination complexation with the phosphate groups on the PPAN membrane (Xiong et al. 2018). Furthermore, FT-IR and XPS characterization results revealed that the –NH– and –NH\(_2\) functional groups were still present on the PPAN membrane. Due to the presence of lone pair electrons in the N atom, it is easy to enter the empty orbital of the metal ion to create a coordination bond. Consequently, the N-containing functional groups on the PPAN membrane may additionally coordinate and complex Hg\(^{2+}\), thereby facilitating the adsorption reaction. According to the theory of hard and soft acids and bases, the N, O, and P atoms in PPAN belong to the soft base category, which readily combine with soft metal ions. Table S2 lists the radii and softness of several metal ions (Parr and Pearson 1983; Pearson 1988; Shannon 1976). Hg\(^{2+}\) ions have a more suitable softness and radius, allowing them to form better complexes with soft bases (Li et al. 2012). Hence, the PPAN hollow fiber membrane has the highest affinity and selectivity for adsorbing Hg\(^{2+}\).

**Effects of pH on adsorption capacities**

The acidity of the aqueous solution has a significant impact on the chemical characteristics of the adsorbent and its ability to adsorb metal ions. As a potential adsorption material, functional hollow fiber membranes must be suitable for mercury-containing wastewater in a wide pH range. Figure 6 demonstrates the adsorption capacity of PPAN hollow fiber membranes for heavy metal ions in solutions of pH 3–9. According to the statistical analysis results, the adsorption capacity of the PPAN hollow fiber membrane for Hg\(^{2+}\) showed a peak-like trend with the increase of solution pH and exhibited excellent adsorption performance (100.78 mg·g\(^{-1}\)) at around pH 5. The main reason for the above results was that the acidity of the solution changed how well the phosphinic acid groups on the PPAN membrane worked. In the high acidity solutions, the positive charges on the membrane surface produced electrostatic repulsion with Hg\(^{2+}\), and the presence of a large amount of H\(^{+}\) also competed with Hg\(^{2+}\) for adsorption sites, resulting in a reduction in removal effectiveness (Ge et al. 2016). In the low-acidity solutions, however, Hg\(^{2+}\) would be complex with OH\(^-\) and generate Hg(OH)\(_2\) (Venkateswarlu and Yoon 2015). Excessive Hg(OH)\(_2\) hindered the formation of Hg-PPAN complexes and reduced the adsorption capacities of PPAN membranes for Hg\(^{2+}\). Even so, the adsorption capacities were still 56.60 mg·g\(^{-1}\) and 35.29 mg·g\(^{-1}\) with the unfavorable conditions of pH 3 and 9, indicating that the PPAN hollow fiber membrane has a strong affinity for Hg\(^{2+}\). Besides, relevant research has documented the amide bond
grafting technology (Deng et al. 2015; Shandil et al. 2017), which demonstrates that the amide group has good stability, so the functional groups in PPAN can be stable in acidic or alkaline solutions.

Adsorption experiments

During the adsorption kinetic studies, the PPAN hollow fiber membrane was immersed in a 100 mg·L\(^{-1}\) mercury-containing solution (pH = 5) at room temperature, and its adsorption rate for Hg\(^{2+}\) ions was determined. As depicted in Fig. 7a, the PPAN hollow fiber membrane absorbed Hg\(^{2+}\) ions rapidly in the first 20 min, resulting in a rapid drop in Hg\(^{2+}\) concentration from 100 to 30 mg·L\(^{-1}\). The whole adsorption reaction reached saturation after 4 h, and the concentration of Hg\(^{2+}\) in the solution maintained a dynamic equilibrium (11.29 mg·L\(^{-1}\)), which means that the PPAN hollow fiber membrane can remove about 90% of the Hg\(^{2+}\) in a short time.

According to the fitted data in Table 2, the pseudo-second-order model had the greatest correlation coefficient (\(R^2 = 0.9994\)) among the three kinetic models. These results indicated that the adsorption reaction was mainly limited by the chemical interaction, which was the complexation of Hg\(^{2+}\) with phosphinic acid groups on the surface of the PPAN membrane (Zhang et al. 2010; Li et al. 2015). Additionally, intraparticle diffusion is a significant element that plays a role in determining the adsorption rate. The intraparticle diffusion equation (Fig. 7d) was separated into three portions, and particular fitting data are presented in Table 2. The adsorption processes of the three portions exhibited an excellent linear connection after piecewise fitting. The decreasing diffusion rate constant (\(k_p\)) during the adsorption process (6.9123 > 1.9041 > 0.5513) suggested that the adsorption process had three stages: quick adsorption on

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**Table 2** Fitting the kinetic data obtained from different adsorbents using the pseudo-second-order, pseudo-first-order, and intraparticle diffusion

| Adsorbents | Pseudo-second-order | Pseudo-first-order | Intraparticle diffusion |
|------------|---------------------|--------------------|-------------------------|
|            | \(k_2\) (g·mg\(^{-1}\)·min\(^{-1}\)) | \(R^2\) | \(k_1\) (min\(^{-1}\)) | \(R^2\) | \(k_p\) (mg·g\(^{-1}\)·min\(^{-1}\)) | \(R^2\) | \(C\) |
| PPAN       | \(1.34 \times 10^{-3}\) | 0.9994 | 0.023 | 0.9429 | All | 1.9155 | 0.7774 | 50.8880 |
|            |                     |        |         |        | Part 1 | 6.9123 | 0.9827 | 26.9538 |
|            |                     |        |         |        | Part 2 | 1.9041 | 0.9827 | 55.4963 |
|            |                     |        |         |        | Part 3 | 0.5513 | 0.7687 | 72.5676 |
the outer surface, slow adsorption in the particle, and final equilibrium. In summary, the adsorption process of Hg$^{2+}$ by PPAN membrane was mainly controlled by chemisorption and supplemented by intraparticle diffusion.

Adsorption performances of adsorbents can be efficiently analyzed using isotherm models, which can reflect the surface chemical characteristics of the materials and the affinities for metal ions. In this study, Langmuir and Freundlich isotherm models (Wang et al. 2017) were applied to the analysis of adsorption studies and the fitting of experimental data. As depicted in Fig. 8c, the equilibrium adsorption capacity of the PPAN hollow fiber membrane exhibited a logarithmic trend with the increase of Hg$^{2+}$ content in the solution, and the maximum adsorption capacity (269.24 mg·g$^{-1}$) was obtained as the adsorption sites on the membrane surface gradually reached saturation. Table 3 details the relevant experimental data for the two isotherm models. The Langmuir isotherm is a homogeneous adsorption that assumes that the adsorption sites on the adsorbent surface have equal affinity for metal ions. In contrast, due to the specificity of the adsorption sites or the various characteristics of the adsorbates, the Freundlich isotherm is viewed as heterogeneous adsorption (Bai et al. 2012). The Langmuir isotherm model has a better fit ($R^2 = 0.9952$, Fig. 8a), indicating that the adsorption sites are evenly distributed on the membrane surface and the reaction process is homogeneous. The theoretical maximum adsorption capacity is 371.15 mg·g$^{-1}$, which is higher than those reported for other absorbents such as iminodiacetic acid–functionalized polyacrylonitrile fiber (275.76 mg·g$^{-1}$) (Deng et al. 2015), aminophosphoric acid composite silica gels (303.03 mg·g$^{-1}$) (Wang et al. 2012), and phosphinic acid functionalized nanosilica (274.32 mg·g$^{-1}$) (Xiong et al. 2018). Although some other adsorbents may have greater adsorption capacity, it typically takes longer to reach adsorption equilibrium, such as thioamide group–chelating nanofibers (10 days) (Li et al. 2013) and thiol-functionalized Zn-doped biomagnetite particles (5 days) (He et al. 2012). These results indicate that the prepared PPAN hollow fiber membrane has great application in the treatment of mercury-containing wastewater.

Fig. 8  a Fitted Langmuir and b Freundlich isotherm plots for the adsorption of Hg$^{2+}$ by PPAN hollow fiber membrane. c The effect of initial Hg$^{2+}$ concentrations on adsorption

Table 3  Fitting the equilibrium data using the Langmuir and Freundlich models

| Adsorbents | Langmuir | Freundlich |
|------------|----------|------------|
|            | $q_{max}$ (mg·g$^{-1}$) | $b$ (L·mg$^{-1}$) | $R^2$ | $1/n$ | $k$ | $R^2$ |
| PPAN       | 371.75   | $5.17 \times 10^{-3}$ | 0.9952 | 0.7641 | 0.0138 | 0.9787 |
Dynamic adsorption and reusability tests

For practical applications, the ability of the PPAN membrane to effectively remove Hg\(^{2+}\) in a flow process was examined. The flow rate of the 10 mg·L\(^{-1}\) Hg\(^{2+}\) solution (pH = 5) through the PPAN membrane was 3 mL·min\(^{-1}\), and the Hg\(^{2+}\) content in the filtrate was monitored hourly. As depicted in Fig. 9b, the functionalized membrane was able to effectively adsorb Hg\(^{2+}\) ions, with the removal rate remaining at 99.5% after 24 h. The mercury content in the adsorption solution within 5 h of dynamic adsorption was lower than the WHO drinking water standard, and it was still lower than the Chinese mercury-containing wastewater discharge standard after 24 h of adsorption (Fig. 9a).

Cyclic adsorption experiment results of the PPAN membrane are given in Fig. 10, and the adsorption capacity after each cycle was 100%, 96%, 84%, 80%, and 77% of the initial adsorption capacity. Although the retention rate has decreased, it is still 77% after 5 cycles of adsorption, indicating that the phosphorylation-modified PPAN hollow fiber membrane is regenerable and recyclable. These results demonstrate the potential of PPAN membranes in the treatment of mercury-containing wastewater.

Conclusion

Here, phosphorylated polyacrylonitrile (PPAN) hollow fiber membranes were prepared by surface chemical grafting. Compared with some common heavy metal ions such as copper (Cu\(^{2+}\)), lead (Pb\(^{2+}\)), nickel (Ni\(^{2+}\)), and cadmium (Cd\(^{2+}\)), the obtained functionalized membrane had higher selective adsorption of Hg\(^{2+}\) ions. The PPAN membrane rapidly captured Hg\(^{2+}\) in the first 20 min of the adsorption reaction and reached saturation after 4 h. In addition, there was chemisorption between the PPAN membrane and Hg\(^{2+}\), which was well confirmed by the pseudo-second-order kinetic model. The reaction appeared to be homogenous based on thermodynamic analyses, indicating a consistent distribution of adsorption sites on the membrane surface. The theoretical maximum adsorption capacity (371.15 mg·g\(^{-1}\)) was obtained using the Langmuir isotherm model, which exhibited the excellent adsorption performance of the material. Furthermore, the Hg\(^{2+}\) adsorption in solutions of varying acidity levels demonstrated that PPAN membranes were appropriate for mercury-containing wastewater treatment over a broad pH range (from 3 to 9). The PPAN membrane exhibited excellent performance in a flow adsorption process, and it could maintain a 99.5% mercury ion removal rate within 24 h. The modified membranes were reusable and maintained 77% removal efficiencies of Hg\(^{2+}\) after 5 cycles. These results demonstrate that PPAN hollow fiber membrane is an efficient and reusable material for mercury-containing wastewater treatment.
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Data availability  The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval and consent to participate  This article does not contain any study with human and animals performed by any of the author. Consent to participate is not applicable.

Consent for publication  The participant has consented to the submission of the study to the journal.

Competing interests  The authors declare no competing interests.

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