

Fabrication of PAN/PHCS Adsorptive UF Membranes with Enhanced Performance for Dichlorophenol Removal from Water

Yan Gao, Yuan Qiao, Sen Yang

Department of Environmental Science and Engineering, College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, People's Republic of China
Correspondence to: S. Yang (E-mail: syang@cau.edu.cn)

ABSTRACT: A series of novel polyacrylonitrile (PAN) adsorptive UF membranes were prepared via the nonsolvent induced phase inversion method using adsorbent-amphiphilic porous hollow carbonaceous microspheres (PHCSs) as additive. The resulted PAN/PHCS membranes were demonstrated to have better mechanical strength than the pure PAN membrane. The water fluxes of the PAN/PHCS membranes were slightly decrease; however, the rejections to pepsin were maintained at a high level (81–86%). The properties of the PAN/PHCS membranes for 2,4-dichlorophenol removal from water were investigated. The results showed that 2,4-dichlorophenol could be rapidly removed from water via adsorption mechanism by PAN/PHCS membranes, and the maximum reduction efficiency was up to 70%. The adsorption of 2,4-dichlorophenol to the membranes was reversible and the membranes could be regenerated facilely by water washing. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40837.

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INTRODUCTION

Recently, with the water quality regulations becoming more and more rigorous, organic micropollutants with potential biological effects have attracted increasing attention. And there is an urgent need for efficient and cost-effective methods to mitigate organic micropollutants from water.¹ Membrane-based separations have been extensively used in water treatment due to their high efficiency and environmentally benign nature.^{2–4} It is found that high removal performance for organic micropollutants can generally be achieved by nanofiltration (NF) and reverse osmosis (RO).^{5–7} However, these processes are limited by energy intensiveness, low flux and membrane fouling.^{1,8,9} Ultrafiltration (UF) and microfiltration (MF) membranes, with larger pore size than NF or RO membranes, permit a relatively high flux at low pressure, but can not remove micropollutants effectively. Alternatively, coupling of UF unit with adsorption unit could work effectively.^{10–12} The performance of the combination of adsorption-UF process is mainly depends on the properties of the membrane, the characteristics of the adsorbent, the reactor configuration, as well as the nature of the adsorbate.¹⁰ Moreover, this method owns significant and intrinsic defects such as high cost and difficulty of scale up since the UF and adsorption work separately. Developing novel and effective UF-based technique is necessitated.

In fact, besides size exclusion and charge repulsion, adsorption is one important way for compound removal by membrane separa-

tion.^{13–15} In some cases, the UF or MF membrane itself could lead to removal of low molecular weight contaminants via adsorption at a very high level.^{13,16–18} For example, Dong et al.¹⁸ reported that bisphenol could be removed effectively from drinking water by hollow fiber MF membrane, and they believed that adsorption plays a significant role. As reported by Chang et al.,¹⁹ estrone could be removed almost completely by hollow fiber MF membrane for a wide range concentrations tested. Since the pore size of the membranes was several orders of magnitude larger than the estrone molecules, the authors attributed this high degree of removal to a result of adsorption rather than membrane sieving. Studies on estradiol removal had also demonstrated the high level (up to 80%) of estradiol retention could be achieved by polyethersulfone UF membrane (100 KD), and the retention mechanism was attributed to adsorption.²⁰ These studies indicate that removal of organic micropollutants may be performed by UF/MF membranes via adsorption.⁸ However, due to the low adsorption capacities of most polymer membranes,²¹ modifications with other components are desirable. Indeed, employing amphiphilic graft glycopolymer as additive, Shi et al.²² obtained an improvement in boron adsorption capability of PSF membranes. Entrapping TiO₂ nanoparticles in PVDF, Zhang et al.²³ had observed a promoted adsorption and elution efficiency over the PVDF/TiO₂ hybrid membranes compared with the pristine PVDF film. And an enhancement of removal of endocrine disrupting plasticizer EDCs has been reported by polysulfone hollow fiber membranes functionalized with amphiphilic

β -cyclodextrin.⁹ Unfortunately, there are only limited reports about effective hybrid adsorptive membranes for removal of organic micropollutants.

It has been recognized that finely dispersed particles are effective additives for membrane modification, and synergism properties between the polymeric materials and particles can usually be generated.^{24–28} To obtain a hybrid adsorptive membrane with high removal performance for organic micropollutants, the adsorptive particles should be carefully selected. First, it should disperse finely in the polymeric matrix and even could enhance the membrane performances; second, it should have not only high adsorption capacity but also rapid adsorption speed to allow treatment of large quantities of water per unit time; lastly, the most important is that facile regeneration could be realized once the adsorption is saturated.

In a previous study, we reported a facile method for fabricating amphiphilic porous hollow carbonaceous spheres (PHCSs) in the size range 2.0–4.0 μm from yeast cells via mild hydrothermal treatment.²⁹ The surfaces of these hollow spheres were covered with both hydrophobic and hydrophilic functional groups and could be well dispersed not only in water but also in nonpolar solvents. Most interestingly, the PHCSs exhibit high capacity, rapid adsorption, and facile regeneration for organic pollutants.³⁰ This inspired us to speculate that it may be potential additive to fabricate effective hybrid adsorptive membranes. In this study, we report the fabrication of novel polyacrylonitrile (PAN) adsorptive UF membranes using PHCSs as additive via nonsolvent induced phase inversion method. The effects of the addition of PHCSs on the membrane morphology, properties and performance have been investigated. 2,4-Dichlorophenol has been selected as the model of low molecular weight contaminant to test the removal efficiency of the adsorptive UF membranes. And membrane reusability was examined using distilled water as regenerant at room temperature.

EXPERIMENTAL

Materials

PAN was purchased from Shanghai Jinshan Chemical Industry Factory and dried in an oven at 80°C for 24 h, and then kept in a desiccator before use. *S. cerevisiae* cells were obtained from Angel Yeast, China. Dimethylsulfoxide (DMSO) was obtained from Beijing Chemical Industry Factory in reagent grade purity and used as received. Pepsin (TBO, Tokyo), albumin egg (Sigma) and bovine serum albumin (BSA, Sigma) were used in the retention test. Distilled water was used for all the experiments.

Synthesis of PHCSs

PHCSs were synthesized via mild hydrothermal treatment of yeast cells as described in our previous studies.²⁹

Viscosity Studies

The viscosity of casting solutions with 0–3 wt % of PHCSs was investigated by a NDJ-1B Digital Viscometer (Shanghai Changji, China) at 25°C controlled by water bath.

Preparation of PAN/PHCS Adsorptive Membranes

The adsorptive UF membranes were prepared by a nonsolvent induced phase inversion process. The casting solution which consisted of 0–3 wt % of PHCSs and 15 wt % of PAN in

DMSO was cast on a glass plate by spreading them between thin wires with a glass knife to control the thickness of the film without a preceding dry phase inversion in atmosphere; and then the film was immediately immersed in distilled water at 25°C. After coagulation, the membrane was rinsed with distilled water to remove the solvent and wet stored until tested.

Membrane Characteristics

Membrane Structure. The morphology of the prepared membrane was inspected with field emission scanning electron microscopy (FESEM, AMARY, and 1910FE). For this purpose, all samples were soaked in 40 vol % glycerol aqueous solution for 24 h, dried in vacuum, frozen in liquid nitrogen, and fractured. After plated with gold, they were transferred into the microscope.

Flux and Separation Experiments. A common UF cell was used to measure pure water flux and protein rejection of membrane. The obtained membrane sheets were cut into circle membrane species of 3.25 cm diameter and compacted at 150 kPa with distilled water for 2 h before measurement. The pure water flux and protein rejection were measured at 100 kPa, room temperature and 150 rpm. Three sets of membrane samples were made for each casting condition specified in this paper and the total effective area of the membrane was 92 cm². The rejection tests were carried out with (i) pepsin (500 $\mu\text{g}/\text{mL}$), (ii) egg albumin (500 $\mu\text{g}/\text{mL}$), and (iii) BSA (1 mg/mL) solutions prepared in distilled water. The protein concentrations in the feed and permeate samples were determined using a spectrophotometer (Persee, TU-1810) at 280 nm. The average flux and the rejection of proteins data were reported. After each run the whole test apparatus was rinsed thoroughly with distilled water and membrane was washed to remove any deposition. The permeation flux and rejection of proteins (R) was calculated by the following formulae (1) and (2), respectively:

$$J = \frac{Q}{S \times T} \quad (1)$$

$$R_{\text{rej}} = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \quad (2)$$

where J is the pure water flux of membrane ($\text{L}/\text{m}^2 \cdot \text{h}$), Q is the volume of permeate pure water (L), S is the effective area of membrane (m^2), and T is the permeation time (h). R_{rej} is the rejection of protein (%). C_P and C_F is the permeate concentration and the feed concentration, respectively.

Membrane Water Content and Pore Statistics. Membrane water content test was using a conventional procedure.³¹ Membranes were dipped in distilled water for 24 h immediately weighed after drying the surface of species by filter paper. After that, the membranes were dried at 50°C for 24 h and weighed again. Water content and porosity was calculated by the following formulae (3) and (4). To reduce the errors, this test was repeated six times.

$$\text{Water content (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (3)$$

$$P_m = \frac{W_w - W_d}{\rho \times V} \times 100\% \quad (4)$$

where W_w and W_d is the weight of a membrane at the wet, swelling, and dry state respectively, P_m is the membrane

porosity, ρ is the water density (0.998 g/cm^3), and V is the volume of membrane.

From the protein rejection studies, the average pore radius, surface porosity, and pore density of the membranes were calculated.^{32–34} The average pore radius was found using the following formulae (5).

$$\bar{R} = \frac{\bar{\alpha}}{R_{\text{rej}}} \times 100 \quad (5)$$

where \bar{R} is the average pore radius (\AA) of the membrane; $\bar{\alpha}$ is the average solute radius (\AA), and the average solute radius of the pepsin, egg albumin, and BSA is 28.5, 33.0, and 45.0 \AA , respectively.³⁵ R_{rej} is the rejection of protein (%).

Assuming the membrane to be asymmetric type, the surface porosity, and the pore density of the membrane was found using the following formulae (6) and (7), respectively.

$$\varepsilon = \frac{3\pi\eta_w J_w}{R \times \Delta P} \quad (6)$$

$$n = \frac{\varepsilon}{\pi \times \bar{R}^2} \quad (7)$$

where ε is the surface porosity; η_w is the viscosity of the deionized water (Pa s); J_w is the pure water flux (cm/s) and ΔP is the applied pressure (Pa); n is the pore density of the membrane (pores/cm²).

Mechanical Properties. Mechanical properties of membranes were measured by a material test machine (INSTRON5565) at a loading velocity of 2 mm/min. The report values were measured three times for each sample and then averaged.

Static Adsorption Experiment of BSA and Antifouling Property of Membrane. To investigate the protein resistant property, the static adsorption of BSA on the membrane was tested. The membrane with about 40 cm² of external surface area was first soaked in distilled water for 24 h, cut into 1 × 1 cm square specie, and then placed into bottle that contained 5 mL, 0.1 mg/mL of BSA solution. Bottles were shaken with a shaking water bath at 25°C for 20 h. The static adsorption capacity was calculated by the formulae (8):

$$Q = \frac{(C_0 - C_e) \times V \times 1000}{S} \quad (8)$$

where Q is the adsorption capacity ($\mu\text{g/cm}^2$), C_0 and C_e are the concentration of adsorbate before and after adsorption experiments (mg/mL), respectively. V is the solution volume (mL). S is the membrane surface area (cm²).

After 60 min of UF of 1 g/L BSA solution in PBS (pH = 7.0), the membranes were washed with deionized water for 20 min and the water flux of the cleaned membranes was measured (J_2) at 100 kPa. To evaluate the fouling-resistant ability of the membranes, the flux recovery ratio (FRR) was calculated by using the following equation:

$$\text{FRR} = \frac{J_2}{J_1} \times 100\% \quad (9)$$

2,4-Dichlorophenol Removal Performance

Static Adsorption Experimental of 2,4-Dichlorophenol. The membrane with about 40 cm² of external surface area was first soaked in distilled water for 24 h, cut into 1 × 1 cm² specie,

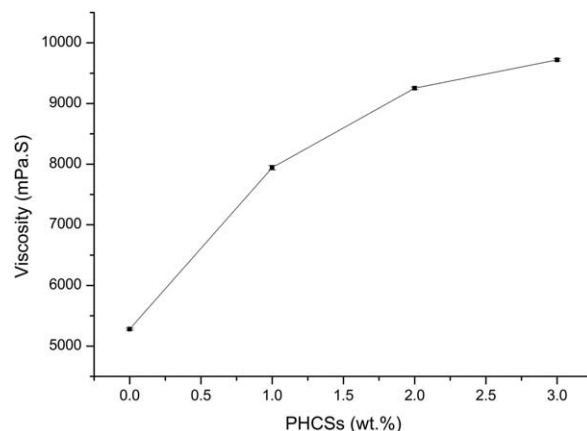


Figure 1. Effect of PHCSs concentration on the viscosity of PAN casting solutions.

and then placed into bottle that contained 15 mL, 34 mg/L of 2,4-dichlorophenol solution. Bottles were shaken with a shaking water bath at 25°C for 2 h. The 2,4-dichlorophenol concentrations were determined by a UV-visible spectrometer at the maximum adsorption wavelength of 2,4-dichlorophenol (284 nm). The 2,4-dichlorophenol amount adsorbed per unit area of membrane was calculated by the formulae (8).

2,4-Dichlorophenol Adsorption Filtration. Filtration experiments were carried out using a 50 mL UF cell. In a typical filtration experiment, 2,4-dichlorophenol solution (20 mg/L) was filtered at the constant flow rate of 1.5 mL/min, room temperature, and 150 rpm. The permeate 2,4-dichlorophenol concentrations were measured at regular time intervals (every 5 min for 20 min). The reduction of 2,4-dichlorophenol was calculated according to the formulae (2).

Membrane Reusability. The membrane was placed in 50 mL UF cell to repeat the removal test using of 2,4-dichlorophenol solution (20 mg/L) as feed. The removal of 2,4-dichlorophenol with time was recorded every 5 min. After 30 min of 2,4-dichlorophenol filtration, the membrane was washed with 10 mL distilled water at 50 KPa and room temperature. This procedure was sequentially performed for eight times.

RESULTS AND DISCUSSION

Viscosity of the Casting Solution

Viscosity of the casting solution can influence the exchanging rate of solvent and nonsolvent during phase inversion process, and therefore, it is an important parameter to determine the precipitation kinetics, the formation of microstructures and performances of the membranes.³⁶ The viscosity of the casting solution was measured and the results are shown in Figure 1. It can be seen that the viscosity of 15 wt % of PAN in DMSO is about 5280 mPa s. Once 1 wt % of PHCSs was added into the solution, the viscosity significantly increased to 7942 mPa s. Clearly, the viscosity of PAN casting solution increased with the increment of PHCSs concentration, as 9252 and 9720 mPa s for 2 and 3 wt % of PHCSs addition, respectively. Similar viscosity trends have also been observed for many inorganic

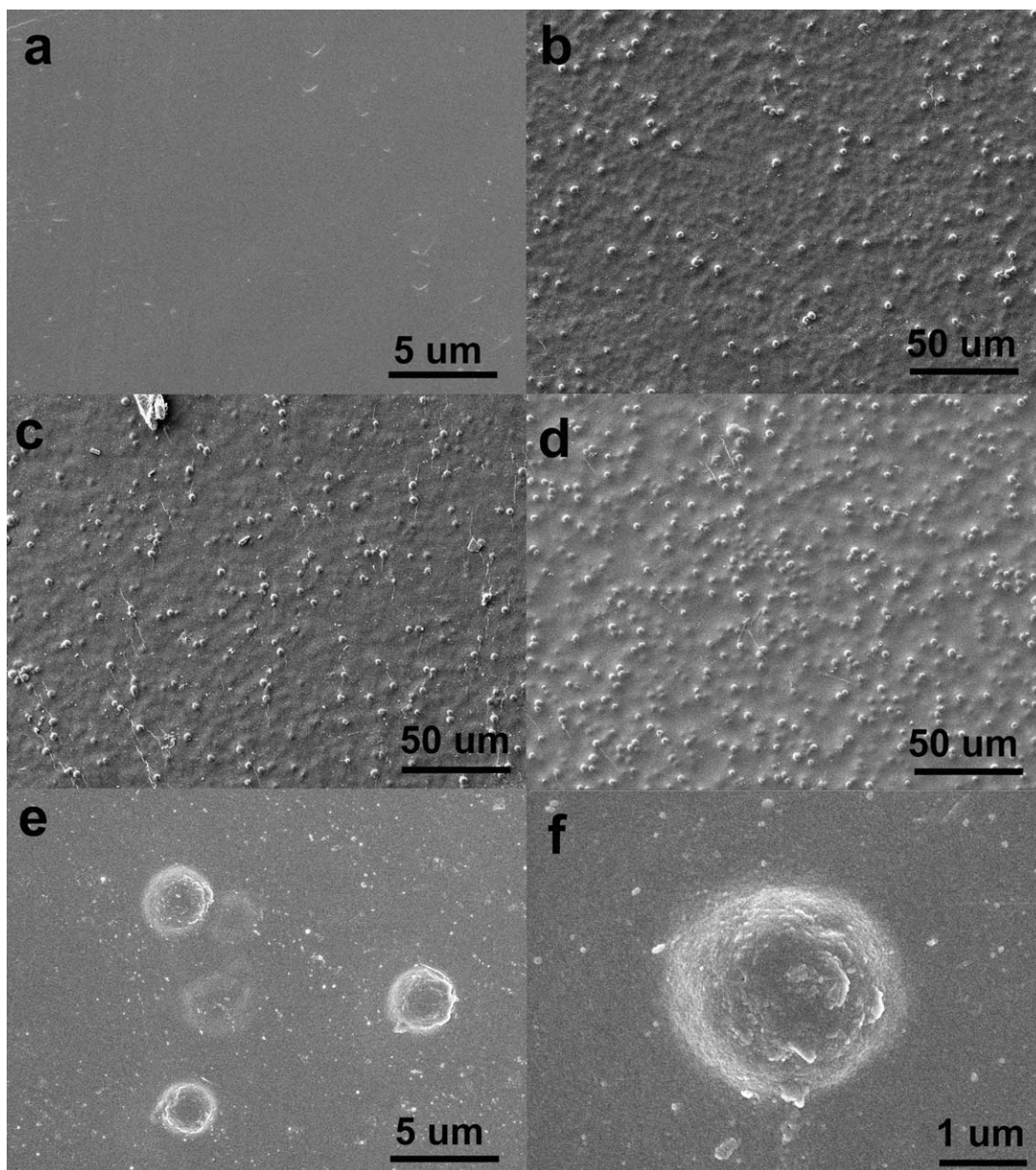


Figure 2. The FESEM pictures of the membrane surfaces. (a) PAN-0, (b) PAN-1, (c) PAN-2, (d) PAN-3, and (e) and (f) PAN-1 with high magnification.

nanoparticle additives such as ZnO, SiO₂, and Zeolite, and the reason was attributed to intensify the interaction force among macromolecules by the high specific surface area of inorganic nanoparticles.^{24,25,37} Aerts et al.³⁸ also reported the similar result; however, they attributed the increased viscosity to the formation of a suspension by the adsorption of polysulfone at the hydroxyl groups of the SiO₂ spheres. PHCSs are the hydrothermal treatment products of yeast, which composed of aromatic furan ring and oxygenated functional groups, including hydroxyl^{29,30}; and they could be well dispersed in DMSO, which means PHCSs has strong interaction with DMSO. Thus, the increased viscosity maybe due to the intensified interaction force among macromolecules or/and the decreased solvating power of DMSO for PAN by pHCSs.^{39,40}

Morphologies of the Membranes

Four membranes fabricated were named as PAN-0, PAN-1, PAN-2, and PAN-3, with the casting solution of only 15 wt % of PAN, additional 1, 2, and 3 wt % of PHCSs, respectively. To understand the influence of PHCSs on the final membrane structure, the membrane surfaces were observed by FESEM and typical images are shown in Figure 2. No pores could be observed on the surfaces of PAN-0 and other PAN/PHCS hybrid membranes even at a magnification of 20,000, indicating formation of dense surface layers for all the membranes. However, comparing with the pure PAN membrane (PAN-0), there are many PHCSs embedded on the surface of PAN/PHCS hybrid membrane without obvious aggregation. Interestingly, the PHCSs are protuberant rather than submersed in the polymer

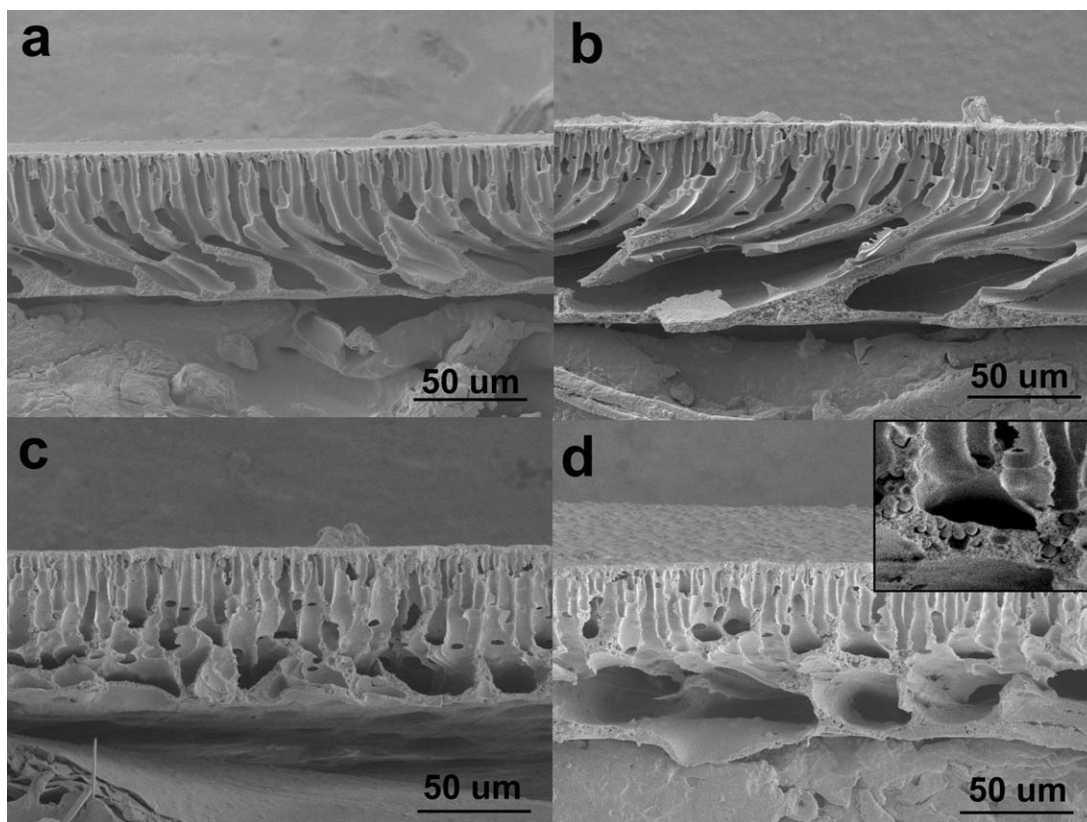


Figure 3. The FESEM pictures of the membrane cross-sections. (a) PAN-0, (b) PAN-1, (c) PAN-2, (d) PAN-3, and the inset shows the selected area with high magnification. Scale bar is 50 μm .

matrix. The reason may be that the PHCSs are amphiphilic and possesses the phase-transfer feature as we reported previously.²⁹ During the phase separation process, PHCSs would migrate from casting solution toward water bath so as to reduce the interfacial energy between these two phases.

It is well known that the compatibility between additive particles and polymer matrix has an intensive effect on the membrane performance and is one of the most prominent challenges in the formation of hybrid membrane.⁴¹ In fact, the compatibility between PHCSs and PAN matrix is desirable as shown in Figure 2(e,f), which reveal that the PHCSs are closely entrapped by PAN. The homogeneous distribution of the PHCSs within the hybrid membrane also can be observed from the cross-sectional FESEM images as shown in Figure 3. All membranes exhibits a typical asymmetric structure, composed of a thin and dense skin layer and a macrovoidal sublayer. The

same structure indicated that the addition of PHCSs did not significantly change the instant of phase separation. However, these pictures [Figure 3(a–d)] illustrate that all of PAN/PHCS membranes are thicker than the pure PAN membrane. This indicates a slower transport of solvent and nonsolvent during the membrane formation process when PHCSs are added. Another observation is the change of the macrovoids structure, depending on the amount of PHCSs present in the casting solution: from a long tear-shaped form to a more irregular and round shape. That is, the nonsolvent diffusion decreases. Similar effects were observed by Aerts et al.³⁸

Characteristics of the Membranes

The surface hydrophilicity of membranes can affect the flux and antifouling ability of membranes. And the contact angle is an important parameter for measuring surface hydrophilicity. The contact angles are in the range of 55–59° for all the prepared

Table I. Membrane Contact Angle, Water Content, and Pore Statistics

Membrane no.	Contact angle (°)	Water content (%)	Porosity (%)	Average pore radius, \bar{R} (Å)	Surface porosity, $\epsilon \times 10^{-4}$	Pore density, number of pores/cm ² , $n \times 10^9$
PAN-0	58.3 ± 0.8	384 ± 4	80 ± 0.8	34.10 ± 0.07	6.51 ± 0.01	1.78 ± 0.01
PAN-1	57.8 ± 1.2	377 ± 3	76 ± 0.6	34.87 ± 0.04	5.86 ± 0.01	1.54 ± 0.01
PAN-2	55.1 ± 0.8	354 ± 5	73 ± 1.0	33.83 ± 0.09	5.85 ± 0.01	1.63 ± 0.01
PAN-3	58.7 ± 1.1	336 ± 4	71 ± 0.8	33.70 ± 0.08	5.74 ± 0.01	1.61 ± 0.01

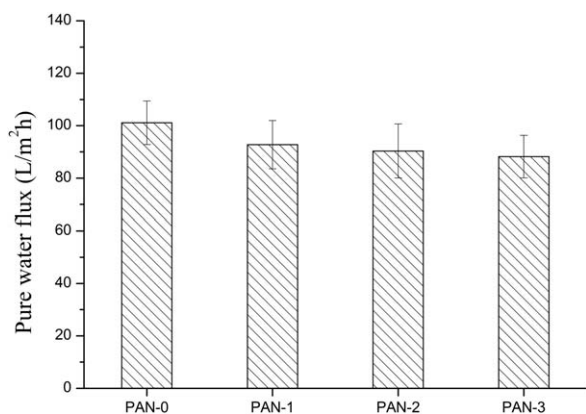


Figure 4. Effects of PHCSs content on the pure water flux of PAN membranes.

membranes as shown in Table I. These results demonstrated that the surface hydrophilicity of PAN membranes did not change significantly after modification with PHCSs.

Figure 4 shows the water flux characteristics of PAN/PHCS membranes and the base PAN membrane. The water flux of PAN-0 is 101 L/m²·h, and it slightly decreased to 93, 90, and 88 L/m²·h for PAN-1, PAN-2, and PAN-3, respectively. However, the pepsin, albumin egg, and BSA rejection of PAN/PHCS membranes and PAN membrane were kept unchanged and remained at a relatively high level as shown in Figure 5. In general, the pure water flux is determined by the porosity, pore size, hydrophilicity, and membrane thickness of the membrane, and the pore size and distribution of UF membrane could be deduced from the rejection property of membrane, and the results are presented in Table I. As shown in this table, the addition of the PHCSs does not have any significant effect on the average pore radius of PAN membranes, which indicates PHCSs did not aggregate and distributed evenly within the hybrid membrane.³² However, the surface porosity and pore density of PAN membrane decreased with the addition of PHCSs. In addition, as could be seen from Table I, the water content and porosity of PAN/PHCS membranes were lower than that of

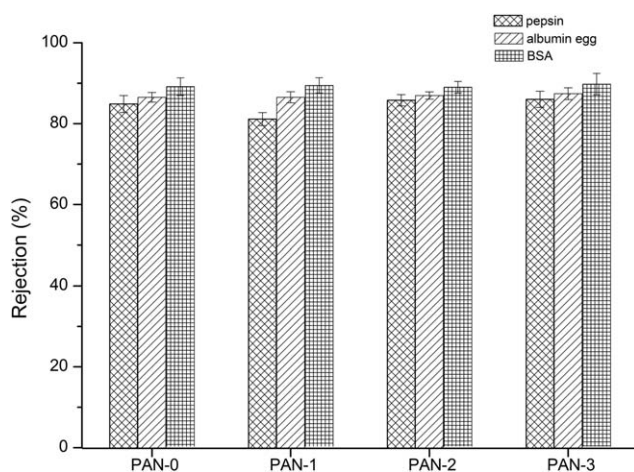


Figure 5. Effect of PHCSs content on the protein rejection of PAN membrane.

pure PAN membrane. Consequently, it is reasonable that the PHCSs has a negative impact on the pure water flux and the reason could be the less pore density and greater thickness of membrane due to the increased viscosity of casting solution by PHCSs.

The static protein adsorption and FRR of membranes reflect the antifouling ability of membrane. The adsorption capacity of BSA onto the PAN and PAN/PHCS hybrid membranes was also shown in Table II. The adsorption capacity of BSA onto the pure PAN film was 8.0 μg/cm², and which for PAN-1, PAN-2, and PAN-3 were 6.5, 4.6, and 5.8 μg/cm², respectively. Higher FRR value reflected lower persistent protein adsorption to the membrane operated during the UF process.^{32,37} The FRR values are more than 60% for the PAN and PAN/PHCS membrane (Table II), meaning the BSA induced fouling is reversible. However, the high fouling resistance is only due to the hydrophilicity of PAN, since the effect of PHCSs on the surface hydrophilicity of membrane could be ignored.

The influence of PHCSs content on the mechanical strength including break strength, Young's modulus, and elongation at break are summarized in Table II. The break strength initially increased with the addition of PHCSs and reached the peak values at 2 wt % of PHCSs addition, and then declined with the further increase of PHCSs content to 3 wt %. And the elongation at break value was initially increased from 13.7 to 24.1% when the PHCSs content increased from 0 to 1% and then declined as the PHCSs content was further increased. The results indicate that the mechanical strength of PAN membrane enhanced with the addition of PHCSs. The analogous trend of tensile modulus have been reported for PVDF/ZnO, Cu₂₊-HNTs/PES, and PVDF/SiO₂ hybrid membrane.^{25,28,42} And the enhanced mechanical strength of membrane was attributed to the interactions between particle and membranes. Particles could act as a crosslinking point in composite membrane and increase the rigidity of polymer chain.

2,4-Dichlorophenol Removal

The static adsorption of 2,4-Dichlorophenol onto the PAN and PAN/PHCS membranes at 2 h were assessed firstly and the results are presented in Table II. It can be seen that PAN-1, PAN-2, and PAN-3 exhibit 155, 194, and 236% of the PAN-0 adsorption amount, respectively. The results show that the adsorption capability of PAN membranes can be increased linearly by increasing the content of PHCSs in the casting solution from 1 to 3 wt %. However, it should be noticed that the influence of addition of PHCSs on the 2,4-dichlorophenol and BSA adsorption properties of the membranes are quite different. The reasons maybe due to the smaller molecular size of 2,4-dichloropheno than that of BSA. As well known, most of BSA molecules would be blocked and adsorbed at the surfaces of the membranes. However, since the molecular size of 2,4-dichloropheno is several orders of magnitude smaller than the pore size of the membranes, adsorption could occur in the membrane surface, skin layer, support layer, and the membrane pores.¹³

Then, combining adsorption-UF removal of 2,4-dichlorophenol was tested and the results are shown in Figure 6. All the membranes exhibit the similar adsorption-filtration characters: the

Table II. Adsorption Capacity of BSA and 2,4-Dichlorophenol, FRR, and Mechanical Properties of PAN/PHCS UF Membrane

Membrane no.	BSA adsorbed amount ($\mu\text{g}/\text{cm}^2$) ^a	2,4-Dichlorophenol adsorbed amount ($\mu\text{g}/\text{cm}^2$) ^b	FRR (%)	Break strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PAN-0	8.0 ± 0.3	9.5 ± 0.1	62 ± 2	2.91 ± 0.05	153.5 ± 3.5	13.7 ± 0.5
PAN-1	6.5 ± 0.2	14.7 ± 0.2	63 ± 2.9	3.13 ± 0.06	165.0 ± 2.3	24.1 ± 0.1
PAN-2	4.6 ± 0.1	18.5 ± 0.1	65 ± 3.2	3.46 ± 0.12	164.5 ± 1.5	15.3 ± 0.3
PAN-3	5.8 ± 0.2	22.4 ± 0.3	63 ± 3	3.01 ± 0.10	161.3 ± 3.1	15.3 ± 0.1

^aInitial concentration = 0.1 mg/mL, pH = 7.0, $T = 25^\circ\text{C}$.

^bInitial concentration = 34 mg/mL, pH = 7.0, $T = 25^\circ\text{C}$.

2,4-dichlorophenol removal efficiency is highest at the start of the filtration and then gradually decreases. This is a common phenomena in pollutants removal via adsorption mechanism by membrane material.^{9,17} The 2,4-dichlorophenol removal efficiency increased in the order PAN-0 < PAN-1 < PAN-2 < PAN-3, that is, the 2,4-dichlorophenol removal efficiency increased considerably with the amount of PHCSs added, and the maximum reduction was 240% higher than that of the base PAN membrane. This apparent correlation between 2,4-dichlorophenol removal and PHCSs content further suggests that the adsorption capability of PHCSs plays a significant role.

However, compared with size exclusion membrane process, once the adsorption is saturated, the membrane will no longer adsorb 2,4-dichlorophenol from the influent and retention will cease. Therefore, ease of regeneration is a key criterion for assessing the usability of adsorption-based membrane processes. In fact, PHCSs are carbonaceous materials composed of the carbonized organic matter and the noncarbonized organic matter, and PHCSs that sorb phenol primarily by a partition process was described by facile regeneration property.³⁰ Experiments were carried out with PAN-3 to assess the membrane reusability. After 30 min of 2,4-dichlorophenol filtration of each cycle, the membrane was washed with 10 mL distilled water at 50 KPa and room temperature and subjected to the next cycle. As

shown in Figure 7, the reduction of 2,4-dichlorophenol is down from 70 to 58% after the first cycle. This may be due to some strong adsorption that could not regenerated by water washing. However, the reduction maintained a nearly consistent adsorption capacity during the next seven cycles of reuse. The pure water permeability and pepsin rejection of PAN-3 kept unchanged. These results indicate that the adsorption of 2,4-dichlorophenol to the membranes is reversible and the adsorbed 2,4-dichlorophenol would be substantially desorbed by water.

Limitations and Further Work

The adsorptive UF membrane provides a potential strategy to rapidly remove a large number of chemically very different micropollutants from water. Partitioning PHCSs, that exhibit rapid sorption, no competition sorption and facile regeneration property, are suitable for environmental applications involving multiple contaminants. In this work, PAN/PHCS membrane could rapidly remove 2,4-dichlorophenol, and particularly, the membrane could be regenerated by water washing *in-situ*, which may significantly decrease the overall cost of the process. This adsorption capacity is similar to molecularly imprinted polymers (MIPs) membrane prepared by hybridization of MIP particles with cellulose acetate and polystyrene.⁴³ Compared with CS/ACF/TiO₂ composite membrane, the adsorption capacity of PAN/PHCS membrane is low (when the concentration of 2,4-DCP was

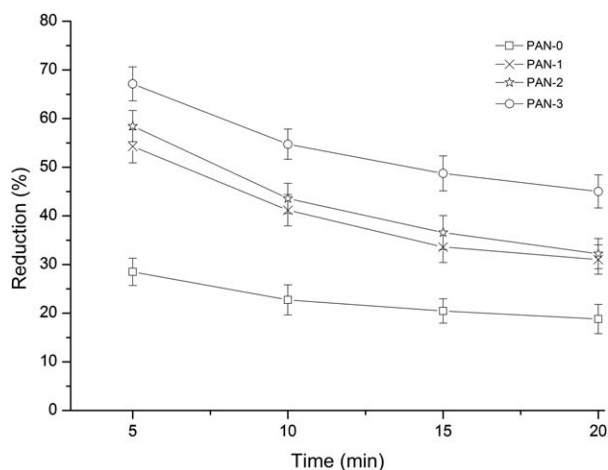


Figure 6. Removal of 2,4-Dichlorophenol from water by PAN and PAN/PHCS UF membrane (3.25 cm of diameter) at room temperature. Feed concentration: 20 mg/L; flux: 1.5 mL/min.

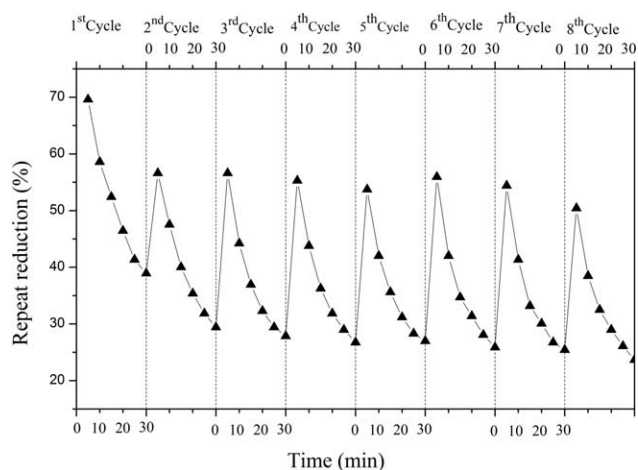


Figure 7. Removal of 2,4-Dichlorophenol from water by reusing one PAN-3 UF membrane (3.25 cm of diameter) for 8 cycles at room temperature. Feed concentration: 20 mg/L; flux: 1.5 mL/min.

50 mg/L, the adsorption capacity was about 85 mg/g).⁴⁴ However, the protein rejection of CS/ACF/TiO₂ composite membrane was not reported and the regenerated method is the chemical oxidation process. The reverse adsorption means the separation process should be controlled carefully to avoid undesired desorption from membrane. There are several important aspects influencing the removal efficiency, such as membrane permeability, membrane fouling, membrane regeneration, and solution characteristics (pH value, solute concentration, ionic strength, temperature, et al.), should be further studied to make the membrane and removal process more amenable to practical use. These issues will be discussed in future research.

CONCLUSION

In this work, novel adsorptive-UF PAN membranes were successfully fabricated by the nonsolvent induced phase inversion method using PHCSs as additive. The results showed that the addition of PHCSs would slightly decrease the water flux of the membrane, while maintaining the rejection to pepsin at a high level, and the membrane mechanical strength were enhanced. The adsorption capability of PAN membrane was increased significantly by addition of PHCSs. 2,4-Dichlorophenol could be rapidly removed from water via a adsorption mechanism, and the maximum reduction efficiency was up to 70%. The adsorption of 2,4-dichlorophenol to the membranes was reversible and the membranes could be regenerated facilely by water washing. The PAN/PHCS membrane showed highly consistent adsorption capacities for 2,4-dichlorophenol during a eight-cycle reusability test.

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