A Self-supporting, Surface Carbonized Filter Paper Membrane for Efficient Water-in-Oil Emulsion Separation

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Abstract Due to the important role of oil source in our life, the separation of water-in-oil emulsion is urgent and necessary. Membrane separation technology has been an efficient and widely used method in separating oil-water separation. Herein, we report a versatile approach to fabricate surface carbonized membranes with self-standing property from biomass-derived precursor by synergistic charring of phytic acid, arginine and filter paper. The obtained membrane exhibited superhydrophobicity in oil, excellent fouling resistance, and self-supporting ability. The membrane can be cycle-used at least 12 times with high permeation flux (up to 1380 L·m⁻²·h⁻¹) and separation efficiency (up to 99.4%).

Keywords Water-in-oil emulsion separation; Filter paper membrane; Surface carbonized; Self-supporting

INTRODUCTION

Oil has been one of the most important resources that human being depends on during the period of social and economic development.¹ Moisture in oil will raise problems such as the damage of oil quality, corroding of equipment and even severe safety accidents.² It becomes harder to separate water/oil mixture once water is emulsified in small droplet form in the presence of amphiphilic impurities such as surfactant. Membrane separation technology has the advantages of high separation efficiency, simple operation, no secondary pollution, low energy consumption and so on,³ which has already been widely used in the field of oil-water separation. Under-oil superhydrophobicity of membrane is the requisite for separating water-in-oil emulsion. Except that, good stability of the membranes under physical or chemical treatment also plays a key role in their practical applications. Conventional membranes include polymeric membranes, metal-mesh membranes, ceramic membranes and so on. Polymeric membranes have the advantages of low cost, good flexibility and easy processing.⁴⁻⁵ However, the susceptibility to oil pollution of polymer-based membrane inevitably leads to sharp attenuation in separation performance after long-term application. Metal-mesh membranes have excellent physical stability but relatively poor chemical stability,⁶ which may gradually be corroded by those components in emulsion. As for ceramic membranes,⁷ they can be used under harsh conditions with both good physical and chemical stability, but the fabrication of the membranes requires complex preparation process together with expensive cost.

Comparing with those conventional membrane materials above-mentioned, carbon materials are superior in inherent hydrophobicity, oil-fouling resistance, chemical inertness, good thermostability, abundant pore structure, and therefore have been recognized as a promising material for purification of water contaminated oil.⁸⁻¹¹ However, it is very hard to prepare highly carbonized materials into self-supporting membranes owing to their fragile nature,¹² which therefore limits their practical applications in oil/water separation.

Herein, we demonstrated a novel strategy to prepare carbonized separation materials with self-supporting property by controlled surface carbonization rather than integral carbonization, which endowed the material with both desirable under-oil superhydrophobicity and certain flexibility. Moreover, all raw materials, i.e. filter paper (FP) and polyelectrolyte complex (PAAg) from phytic acid (PA) and arginine (Arg), for preparing the precursor membrane (PAAg@FP) are biomass-derived materials or compounds. Owing to the synergistic charring effect of PAAg, surface-carbonized FP membrane (C-PAAg@FP) was obtained by heat treatment of PAAg@FP. Benefiting from the formation of compact char layer on FP surface, the inner structure of FP fibers and porous structure of FP membrane had been well-preserved in a certain extent. As a consequence, the C-PAAg@FP membrane exhibited both self-supporting property and under-oil superhydrophobicity, which makes it a promising candidate...
for separating water-in-oil emulsion. Besides, the C-PAArg@FP membrane could be cycle-used at least 12 times without separation performance attenuation because of its good oil-fouling resistance and structural stability during separation.

**EXPERIMENTAL**

**Materials**

Commercially available cellulose filter papers were supplied from Fushun, Minzheng Filter Paper Manufactures, and were sieved by water flux and quality before test. Phytic acid (70 wt% in aqueous) and arginine were supplied from America, Aladdin Industrial Corporation. Dimethylbenzene, toluene, and chloroform were purchased from Tianjin, Zhiyuan Chemical Agent Company, and Span-80 was purchased from Chengdu, Kelong Chemical Plant. Ultrapure water was obtained in laboratory.

**Preparation of PAArg@FP**

Typically, with the molar ratio of Arg:PA=3:1, PA (1.43 g) was dissolved in ultrapure water and formed 100 mL of aqueous solution. Arg (0.86 g) was then added into solution and dissolved after stirring with glass rod for a while. The electrolyte complex of PAArg was therefore obtained through ionic exchanging. After that, a filter paper was immersed in solution PAArg complex for 1 h. After drying under vacuum, the weight content of PAArg loaded on FP was calculated and listed in Table S1 (in the electronic supplementary information, ESI), and the corresponding membrane was recorded as PAArg\_x@FP, where x is the weight content of PAArg in PAArg@FP.

**Preparation of C-PAArg@FP**

The C-PAArg@FP was obtained by heat treatment of PAArg@FP in tube furnace from 40 °C to 250 °C under the atmosphere of air. The schematic illustration of the preparation process of C-PAArg@FP is shown in Fig. 1.

![Fig. 1](image.png)

The schematic diagram of the preparation process of C-PAArg@FP.

**Characterization**

The scanning electron microscopy (SEM) images were obtained by a JSM-7500F (JEOL, Japan) field-emission scanning electron microscope at 15.0 kV. The thermogravimetric (TG) curves were obtained by a TG 2901 F1 (NETZSCH, Germany) thermogravimetric analyzer from 40 °C to 700 °C with the rate of 10 °C·min\(^{-1}\) under the atmosphere of nitrogen. The Fourier transform infrared spectra (FTIR) were obtained by a Nicolet 6700 (THERMO FISHER, America) Fourier transform infrared spectroscopy analyzer. The X-ray photoelectron spectra were obtained by a XSAM800 (KRACHTOS, UK) X-ray photoelectron spectroscopy analyzer to characterize element of C, O, N, P. The water contact angles under oil were measured by JC2000D2H (ZHONGCHEN, China) contact angle measurement with 5 µL droplet on the surface of materials. The test of oil-adhesive force under water of different materials was carried out by a DCAT25 (DATAPHYSICS, Germany) surface tension measurement with dynamic approach-compress-detach test. The particle size of water-in-oil emulsion and filtrate were tested by a Zetasizer Nano ZS90 (MALVERN, UK) particle size and zeta potential analyzer. The content of moisture in filtrate was tested by a ZDU-Z5 (XIANQU WEIFENG, China) Cartesian moisture measurement.

**Preparation of Water-in-Oil Emulsion**

The water-in-oil emulsion with 1 wt% oil content was prepared by mixing 247.5 g of oil, 2.5 g of ultrapure water and 0.5 g of Span-80 under stirring of 2×10\(^{-3}\)·r·min\(^{-1}\) for 20 min.

**Separation of Water-in-Oil Emulsion**

The separation was performed with a vacuum filtration device using the C-PAArg@FP membrane under gravity within 1 min. And the effective area of membrane was approximately 2.0 cm\(^2\). The membrane was washed by ethanol and water, respectively, and then dried in oven after use so that the cycle-use process was carried out.

**RESULTS AND DISCUSSION**

**Preparation of C-PAArg@FP Membrane**

Phosphorous/nitrogen flame retardant, which is usually made up of three parts: acid source, gas source and carbon source, has been recognized as one of most effective synergistic systems for promoting charring.\[13\] With the increase of temperature, the acid source was decomposed to generate a dehydrating agent which may esterify with carbon source. After that, the generated ester compounds dehydrated and crosslinked to form the compact char layer. The as-formed char layer can block the heat delivery and the contact of oxygen. At the same time, the gas source generates a large amount of non-flammable gas that dilutes the flammable oxygen to stop further oxidation. Inspired by this flame retarding mechanism, the polyelectrolyte from PA and Arg was prepared and loaded on FP surface, which could respectively serve as acid source, gas source, and carbon source to conduct controllable surface carbonization. PA is a kind of organic acid with six phosphoric acid groups, which exists in the roots, stems and leaves of many plants. When dissolved in water, the phosphate groups of PA dissociate into phosphate ions with negative charge. Meanwhile, Arg will charge positively in water because of protonation of amino and guanido groups. Therefore, when mixing the water solution of PA and Arg, polyelectrolyte complex of PAArg was formed through electrostatic interaction and ion exchange.\[14\]

FTIR spectra of PAArg@FP and FP are shown in Fig. 2(a). For FP, the absorption band at around 3336 cm\(^{-1}\) was attributed to stretching vibration of −OH of cellulose including inter- and intra-molecular hydrogen bonds; the band at 1646 cm\(^{-1}\) was assigned to vibration of water molecules absorbed in cellulose, while the band at 1054 cm\(^{-1}\) was attributed to characteristic stretching vibration of C—O of cellulose.\[13\] After loading with PAArg, new absorption at 1628 cm\(^{-1}\) was observed, which corresponded to stretching vibration associated with O−P−O of PA,\[16,17\] indicating the formation of ionic complexation between positively charged Arg and negatively charged PA. Meanwhile, the stretching mode of (PO\(_3\))\(^{3−}\) associated with NH\(_3\)\(^+\) at around 1057 cm\(^{-1}\) was overlapped by C—O stretching vibration of cellulose.

https://doi.org/10.1007/s10118-020-2492-9
The thermostability of PAArg@FP was investigated (Fig. 2b), and the specific data obtained from TG and DTG curves are listed in Table S2 (in ESI). For PAArg, its $T_{5\%}$ (the temperature at 5 wt% of mass loss) was around 229.4 °C, while $T_{5\%}$ of FP was 249 °C. After loaded with different contents of PAArg, $T_{5\%}$ values of PAArg@FP showed certain decrease owing to the lower decomposition temperature of PAArg. Moreover, with the increase of PAArg content, $T_{5\%}$ of PAArg@FP decreased gradually. With the decomposition of PAArg, acidic phosphorous compounds and inflammable gases were produced, then synergically inducing dehydration and carbonization of FP in condensed phase. As shown in Fig. 2(b), the weight loss rate of PAArg@FP decreased sharply just after 300 °C, and its char residue was also much higher than that of FP under 700 °C. Remarkably, for those PAArg@FP samples with higher PAArg content (PAArg10%@FP, PAArg20%@FP and PAArg30%@FP), their residue weight was almost as high as that of neat PAArg, suggesting that the synergistic charring process at surface also effectively suppressed the decomposition of inner part of FP fibers. However, excessive loading of PAArg (PAArg30%@FP) did not result in further increase in char residue because the charring process mainly occurred at the surface of the FP fibers. Based on the results of TGA, the surface carbonization temperature for PAArg@FP was set at 250 °C.

The micro-structure of FP and PAArg@FP was also investigated by SEM. As shown in Figs. 2(c) and 2(d), randomly stacked FP fibers with wrinkled surface were observed for FP before modification. After loading with PAArg, some attachments corresponding to PAArg complex on fiber surface were observed for PAArg20%@FP under high resolution (Figs. 2e and 2f). The hole morphology displayed in Figs. 2(c) and 2(e) with size around dozens of micrometers was originated from the random stacking of cellulose fibers. Because of the wide size distribution and irregular stacking morphology of the cellulose fibers, the size and numbers of holes within local area were heterogeneous from the top view. The PAArg were mainly loaded on the wrinkled surface of cellulose fibers of FP as attachments rather than covering on the holes as films.
Therefore, the pore structures of FP were not changed after loading with PAArg.

Thermal treatment of FP and PAArg@FP under relatively low temperature (250 °C) was then conducted to prepare surface carbonized samples, i.e. C-FP and C-PAArg@FP, respectively. The micro-structures of carbonized samples are shown in Figs. 3(a)–3(d). For FP, since it had relatively good thermal stability under 250 °C (Fig. 2b), the fibers in it also showed no obvious change in shape and weight after thermal treatment. However, its brown color (inset of Fig. 3a) and porous surface (Fig. 3b) suggested it had already experienced extensive oxidation under such temperature. Although the oxidation did not result in obvious release of gaseous products, it caused decrease in molecular weight of cellulose in FP. As the consequence, the obtained C-FP was too brittle to be used as a free-standing membrane (Fig. S1 in ESI). As for C-PAArg@FP membrane, the weight loss around 250 °C (Fig. 2b) was attributed to decomposition of PAArg and its catalytic carbonization effect on FP, which therefore led to the formation of compact superficial char layer as shown in Figs. 3(c) and 3(d). Figs. 3(e) and 3(f) show distribution of C, O, N and P elements on the surface of C-FP and C-PAArg@FP, respectively. And except for the change in micro morphology, the weight contents of N and P elements distributed on surface of PAArg@FP were obviously higher than those of C-FP (Fig. 3g), suggesting the synergistic carbonation of PAArg@FP. The small amount of N and P elements on C-FP surface could be attributed to the nitrogen adsorption and residue in filter paper fibers, respectively. However, when extra PAArg was loaded on the FP surface, it did not show further enhancement on carbonization of FP and only some rough and loose attachments were found on the surficial char layer (Fig. S2 in ESI), suggesting that the surficial char layer had a condense structure and therefore effectively prevented the reaction of extra PAArg with inner part of FP fibers. The tensile test also indicated that the C-PAArg@FP membrane had much better

![Fig. 3](https://doi.org/10.1007/s10118-020-2492-9)
mechanical properties than C-FP (Fig. S1 in ESI) owing to the low degree of oxidation of inner part of cellulose fibers. Although the surface carbonized samples exhibited deteriorated mechanical properties comparing to FP, they still had enough self-standing property for separation under gravity.

To confirm the acceleration of PAArg on surface charring of FP during heat treatment, the chemical structure of C-PAArg@FP was analyzed. FTIR spectra of C-FP, C-PAArg@FP, surface and inner part of C-PAArg@FP are shown in Fig. 4(a). Comparing with that of FP, the new weak absorptions at approximately 1701 and 1620 cm\(^{-1}\) in spectrum of C-FP, which belong to the stretching vibration of C=O and C=O, respectively, suggesting the oxidation and dehydration reaction of FP during heat treatment. Meanwhile, the absorption bands around 2850–2950, 1360 and 1425 cm\(^{-1}\) attributed to saturated –CH and –CH\(_2\) bonds also proved that a part of FP surface did not experience oxidation or carbonization yet under such temperature.\(^{[18,19]}\) Comparatively, only characteristic absorption bands corresponding to C=C and C=N (1562 cm\(^{-1}\)) rather than saturated C–H were observed in spectrum of sample C-PAArg@FP, indicating the formation of condensed char layer with
aromatized structure.\textsuperscript{[20]} Furthermore, C-PAArg@FP surface showed absorption bands around 1173 cm\(^{-1}\) corresponding to P=O,\textsuperscript{[16,17]} and 962 cm\(^{-1}\) corresponding to P―O―P, indicating that the phosphorous participated in the charring process.\textsuperscript{[18]} Comparing with C-FP and C-PAArg@FP surface, the inner part of PAArg\textsubscript{20\%}@FP showed obvious absorption bands of C―H, which indicated the low degree of oxidation of it. And the absorption bands located at approximately 1074 and 880 cm\(^{-1}\) belonged to the crosslinking structure P―N―C, which was an intermediate structure between dehydration and aromatization. Besides, the absorption bands of P=O and P―O―P were also obvious in the spectra. All these results proved the low degree of carbonization of inner part. The well preservation of inner structure of cellulose fibers explained why C-PAArg@FP retained self-supporting property together with good flexibility. As for FTIR spectra of C-
PAArg@FP with different mass of PAArg loading, the intensity of absorption band at around 1700 cm\(^{-1}\) decreased with the increase of loading mass as well, which also represented the decrease in oxidation degree owing to the increase of synergetic charring effect. Meanwhile, the absorption bands at 1074 and 880 cm\(^{-1}\) also increased with the loading mass of PAArg, again confirming that P=\(\equiv\)N–C crosslinking structure was the intermediate structure during charring. The compact surficial carbon layer effectively prevented the oxidation of the inner part, endowing FP with both under-oil superhydrophobic surface and self-supporting interior.

XPS was carried out to further investigate the crosslinking and aromatized structure as shown in Fig. 4(c) and Fig. S3 (in ESI). The bands representing C, O, N, and P elements all existed in C-PAArg\(_{20\%}\)@FP while only C and O elements in FP and C-FP.\(^{[21]}\) P2p spectra were fitted in Fig. 4(d). The binding energy belonging to polyphosphate and/or pyrophosphate located at around 134.2 eV,\(^{[22]}\) while the binding energy belonging to P–O and O=\(\equiv\)P–O–C groups located at approximately 133.4 and 135.0 eV owing to the existence of P–O–C crosslinking structure, which proved the charring reaction of PAArg and FP. Raman spectra (Fig. 4e) also suggested that amorphous carbon together with a few of graphitized carbon was formed on the C-PAArg@FP surface, while almost no carbon was detected for C-FP.

**Separation Performance of C-PAArg@FP**

The water contact angle (WCA) under oil (UOWCA, in dimethylbenzene) of thermal treated samples with different PAArg loading mass is shown in Fig. S4 (in ESI) and Fig. 5(a), respectively. For C-FP sample, which had no surficial char layer, it had an under-oil superhydrophobic surface and self-supporting interior. With the increase of PAArg amount loaded on FP surface, the UOWCA of carbonized samples increased first and then decreased. When 20% PAArg was loaded, the UOWCA of C-PAArg\(_{20\%}\)@FP achieved the highest value of 157.5°, suggesting its optimal loading ratio of PAArg for constructing under-oil superhydrophobic surface. All C-PAArg@FP membranes’ surfaces were super-oleophilic in air. The oil droplet on the surface of the C-PAArg@FP membrane could spread easily and permeate into the membrane within several seconds. Meanwhile, the surfaces of C-PAArg@FP membranes were hydrophobic in air with WCA around 90°–110°, which increased with the loading amount of PAArg, as shown in Fig. S4 (in ESI).

The droplet approach-compress-detach test was conducted for evaluating the wettability of samples (Fig. 5b). For FP without modification, the oil droplet quickly penetrated into the membrane. When the oil droplet was compressed on the surface of C-FP, it would partially adhere to the surface. As for C-PAArg@FP, the oil droplet only slightly deformed from circle to oval during compression, and it could be lifted up completely without obvious deformation and attachment. This phenomenon indicated that the surface of C-PAArg@FP had very low adhesion to oil in water despite its strong lipophilicity, endowing it with excellent anti-pollution ability to oil during separation.

Fig. 5(c) displays the images of separation device, emulsion and filtrate, respectively. The white emulsion was stable with particle size around 400 nm (Fig. 5d). After separation, the filtrate was transparent and the particle size was approximately 20 µm. (Fig. 5e). The permeation flux and separation efficiency of C-PAArg\(_{20\%}\)@FP after separation.

Fig. 6 The permeation flux and separation efficiency of C-PAArg\(_{20\%}\)@FP within 12 times of cycle-use in separating water-in-demethylbenzene emulsion (a); Digital photographs (b, c) and SEM images (d, e) of C-PAArg\(_{20\%}\)@FP after separation.
separation efficiency (99.5%, Fig. 5f). However, the C-FP exhibited a low separation flux because its poor fouling resistance to oil (Fig. 5b). With the increase of PAAArg content, the fouling resistance to oil of C-PAArg@FP increased obviously, resulting in an enhanced separation flux (Fig. 5f).

The recyclability of C-PAArg20%/FP was evaluated by a cyclic filtration test. Owing to the very low adhesion of C-PAArg@FP surficial char layer to both oil and water, the membrane after separation could be easily decontaminated and then recycled by rinsing with a few amounts of ethanol and water, respectively. As shown in Fig. 6(a), the C-PAArg@FP could be recycled and reused at least 12 cycles of separation without any attenuation in separation performance. Moreover, the morphological observation on membrane both in macroscopic (Figs. 6b and 6c) and microscopic (Figs. 6d and 6e) views suggested that the C-PAArg@FP had excellent structural stability with almost no differences between the unused sample. The recovered sample after 12 separation cycles still exhibited compacted char layer and excellent self-standing property.

CONCLUSIONS

In summary, a self-supporting, surface carbonized filter paper membrane original from all biomass precursor was fabricated by a versatile method based on the synergistic charring effect of phosphorus/nitrogen flame retardant. The surface carbonization endowed the C-PAArg@FP membrane with under-oil super-hydrophobicity, super-oleophilicity in air and very low adhesion to oil. When used for separation of water-in-oil emulsion, the super-hydrophobic membrane in oil could be cycle-used at least 12 times with high permeation flux (up to 1380 L·m⁻²·h⁻¹) and separation efficiency (up to 99.4%).

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2492-9.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21875147 and 51991351) and the Fundamental Research Funds for the Central Universities.

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https://doi.org/10.1007/s10118-020-2492-9