

Article

Biodegradable Nanofiber Membrane with Designed Beaded Structure for High-Efficiency Oil–Water Separation

Linlin Yan ^{1,2,3}, Jinglin Hong ¹, Jialing Zhang ¹, Yanying Zhao ¹, Yuqian He ¹, Kai Wang ^{1,2}, Yuhua Gao ⁴, Zongli Xie ⁵ and Xiquan Cheng ^{1,2,*}

¹ State Key Laboratory of Urban-Rural Water Resource and Environment, School of Marine Science and Technology, Harbin Institute of Technology, Weihai 264209, China

² Shandong Sino-European Membrane Technology Research Institute Co., Ltd., Weihai Key Laboratory of Water Treatment and Membrane Technology, Weihai 264209, China

³ Weihai Jinhong Group Co., Ltd., Weihai 264209, China

⁴ Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, China

⁵ CSIRO Manufacturing, Private Bag 10, Clayton South MDC, VIC 3169, Australia

* Correspondence: chengxiquan@hit.edu.cn

Abstract

Membrane separation technology has been extensively applied to treat oily effluent given its high performance and ease of operation. However, conventional polymer membranes are resistant to natural degradation after use, leading to severe environmental concerns. Consequently, the development of biodegradable membranes that combine satisfactory oil–water separation performance with ecological safety has emerged as a critical research priority. In this work, we fabricated a biodegradable membrane consisting of chitosan (CS), sodium methacrylate (SMa) and polyvinyl alcohol (PVA) via electrospinning, with anionic super-hydrophilic polyacrylamide (PAM) incorporated to enhance wettability. No toxic chemicals were used throughout the fabrication process. The resulting membrane with an interpenetrating network and beaded structure not only rendered the cross-linked nanofiber more hydrophilic but also improved the porosity of membranes, which significantly enhanced the separation performance and fouling resistance of the membrane. Specifically, the CS/PVA/SMa-PAM membrane achieved a separation flux of $2.7 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for oil–water emulsions. After 20 emulsion separation cycles, the flux of the modified membrane was stable at $2.5 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Benefiting from its excellent anti-fouling properties, high separation efficiency, eco-friendly biodegradability, and toxic-reagent-free fabrication, the as-prepared CS/PVA/SMa-PAM membrane offers a promising and sustainable option for oily wastewater treatment.

Keywords: biodegradable membrane; non-toxic; hydrophilic modification; oil–water separation; anti-fouling performance

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1. Introduction

Since the rapid development of industrialization, the shortage of potable water resources globally has become a severe concern [1–4]. The demand for industrial oil–water separation is continuously increasing, and the treatment of daily catering wastewater urgently requires advanced oil–water separation technologies [5–8]. Especially with increasingly stringent environmental policies, the sustainable application and promotion of oil–water separation technology should be further accelerated to provide technical support

for environmental remediation and water resource recovery [9]. Compared with traditional oil–water separation technologies [10,11], membrane separation technology endows a unique superior advantage in the domain of water purification with its low energy demand and superior filtration performance [12–15]. With the in-depth research on optimizing the hydrophilicity, anti-fouling performance and separation efficiency of membrane materials, many new coating materials, composite membrane materials and post-treatment technologies continue to emerge, promoting the widespread application of membrane technology in water treatment and other fields [16].

Electrospun nanofibrous membranes exhibit tunable structures and flexible preparation processes, enabling high permeability for water treatment [17]. By combining surface modification with electrospinning technology, nanofiber membranes with tunable interface properties can be achieved [18,19]. Chen et al. directly transesterified whole sugarcane bagasse without complex fractionation to improve its solubility and hydrophobicity, enabling electrospinning into porous nanofiber membranes for efficient oil–water separation [20]. Ge et al. fabricated a bioinspired nanofibrous surface with super wettability on an electrospun fibrous membrane via synchronous electrospraying and electrospinning [21], with ultrahigh flux and efficiency under gravity-driven conditions. However, these materials are expensive, and involving them requires the use of organic solvents such as dimethylformamide (DMF) and acetone [22]. Meanwhile, most of the aforementioned membranes are synthesized from non-renewable resources and are hardly biodegradable after disposal. Furthermore, the frequent use of these materials can lead to secondary environmental pollution. [23]. In contrast, natural biomass-derived green membranes can reduce “white pollution” and are comprehensively superior to synthetic polymer membranes in terms of sustainability and cost-effectiveness [24–26]. Developing green and degradable membrane materials [27] that enable efficient oil–water separation without the involvement of toxic reagents remains an important and urgent research priority.

CS, a polysaccharide material obtained via the deacetylation of crustacean or insect exoskeletons [28,29], is non-toxic, low-cost, and biocompatible, and has great commercial potential [30]. However, due to the ionic groups on its backbone, chitosan undergoes electrostatic repulsion in acidic solutions, making electrospinning difficult. PVA, as a non-toxic and stable hydrophilic polymer with excellent chemical stability and mechanical properties [31,32], can be blended with CS [33,34]. Nevertheless, CS/PVA nanofibrous membranes typically require crosslinking with glutaraldehyde (GA) to enhance stability [35], which often leads to decreased hydrophilicity, reduced permeation flux, and increased membrane fouling. Currently, research on stable chitosan-based nanofiber membranes for water treatment remains limited, and the inherent hydrophilicity of chitosan is insufficient for satisfactory oil–water separation. Therefore, developing efficient and sustainable chitosan-based materials is crucial. In particular, the introduction of non-toxic crosslinking reagents is needed to avoid the drawbacks of conventional toxic crosslinkers such as glutaraldehyde, which tend to reduce hydrophilicity and flux [36,37].

Herein, a novel PAM/SMA-reinforced CS/PVA nanofibrous membrane with an interpenetrating network was fabricated via electrospinning without toxic organic solvents or hazardous crosslinkers [38,39]. A superior hydrophilic interpenetrating crosslinked network was constructed through covalent crosslinking reactions. SMA chemically crosslinks with CS and PVA to construct an interpenetrating network backbone, while PAM interacts with the network components via hydrogen bonding and electrostatic interactions. Notably, the incorporation of PAM improved spinnability, resulting in an abundance of bead-on-string structures in the interpenetrating network fiber membrane, which reduced the fiber packing density and increased the porosity. The resulting CS/PVA/SMA-PAM membrane combines high flux, superior anti-fouling, and biodegradability, offering an innovative and sustainable pathway for future oily wastewater treatment.

2. Methods and Materials

2.1. Fabrication of Interpenetrating-Network CS/PVA/SMa-PAM Nanofibrous Membrane

First, 3 g of CS was dissolved in 97 g of 80% aqueous acetic acid to obtain a CS solution with a mass fraction of 3 wt.%, and the solution was stirred for 5 h. Then, an appropriate amount of PVA was dispersed in deionized water to formulate an 8 wt.% PVA solution (8 g PVA in 92 g deionized water), which was stirred at 85 °C in a water bath for 40 min. The CS solution and the PVA solution were mixed at a volume ratio of 3:7 (30 mL CS solution and 70 mL PVA solution). Then, 2.4 wt.% of SMa (2.4 g per 100 g of total polymer mass) was added as a crosslinking modifier, along with 0.2 wt.% ammonium persulfate (0.2 g per 100 g of total polymer mass) as an initiator, and stirred for 4 h. Subsequently, 1.5 wt.% PAM (1.5 g per 100 g of total polymer mass) was further introduced to enhance the crosslinking network. After leaving this solution to stand to remove bubbles, the spinning solution was obtained. An amount of 10 mL of the spinning solution was drawn into a syringe and fixed onto the electrospinning apparatus. Electrospinning was performed at a voltage of 18–20 kV, a scanning rate of 0.4–0.5 cm/s, a tip-to-collector distance of 22–25 cm, a feeding rate of 0.0006–0.0008 mm/s, and a drum rotation speed of 100–400 rpm, with a spinning time of 8–12 h. After electrospinning, the membrane was placed in an oven and thermally treated at 60 °C for 2 h to obtain the PAM-enhanced CS/PVA-SMa membrane. Detailed information on the materials, including their sources and purities, is provided in Table S1 in the Supplementary Information.

2.2. Properties and Performance of Separation Membranes

2.2.1. Preparation of Oil-in-Water Emulsion

The emulsion was first prepared applying SDS as a surfactant. Tween 80 and CTAB were additionally used as surfactants when investigating the effect of different charges. During the procedure, 0.05 g of SDS was dispersed in 495 mL of water and stirred at 1000 rpm for 40 min [40,41]. Subsequently, 5 mL of n-octane dyed with Oil Red O (50 ppm) was added to the solution [42], stirring at 1000 rpm for 12 h to form the oil-in-water emulsion [43,44].

2.2.2. Permeation Flux Test

The membrane (diameter 1.475 cm, effective area 1.71 cm²) was wetted with water, then sandwiched between two ground glass tubes, which were fixed with small iron clips. Emulsion separation was carried out under gravity, and the liquid column height was maintained constant at 10 cm (~1 kPa, 0.01 bar) [45]. The schematic diagram is illustrated in Figure S12, and the actual device is shown in Figure S9. During the experiment, the volume of permeated emulsion collected within 5 min was recorded. The flux (J , L·m⁻²·h⁻¹·bar⁻¹) of the membrane was calculated using Equation (1):

$$J = V / (A \times \Delta t \times P) \quad (1)$$

where J is the permeate of the emulsion (L·m⁻²·h⁻¹·bar⁻¹); V is the volume of the filtrate (L); A is the filter membrane area (m²); Δt is the filtration time (h); and P is the operated pressure (bar).

2.2.3. Determination of Separation Efficiency

The standard curve between oil droplet concentration and absorbance was plotted by employing a TU-1810PC UV-Vis spectrophotometer (Beijing Purkinje General Instrument, Beijing, China). On the basis of this calibration curve, the oil contents of the original emulsion and filtered permeate were quantitatively analyzed. The oil–water separation rejection was calculated via Formula (2) and (3):

$$R = (1 - C_p/C_f) \times 100\% \quad (2)$$

$$A = 0.0085c + 0.0012 \quad (3)$$

where C_p is the oil droplet content in the retention (%), C_f is the oil droplet content in the feed solution (%), A is the absorbance, and c is the oil concentration (mg/L).

2.2.4. Cyclic Performance Test

For assessing the reusability and anti-fouling performance of the membrane [46], a total of 20 consecutive filtration runs were carried out on the self-assembled oil–water separation device. Each filtration cycle lasted 5 min, and deionized water was adopted for backwashing the membrane after every cycle [47]. After each separation cycle, the membrane was rinsed with deionized water to remove residual oil on the surface. Then, the membrane was placed in the filtration setup in reverse orientation (active layer facing the permeate side), and deionized water was filtered through the membrane from the permeate side to the feed side under gravity-driven conditions with a constant liquid column height of 10 cm (hydrostatic pressure ~0.01 bar) for 10 min. Finally, the membrane was reoriented to its normal position for the next cycle. The permeation flux and oil rejection rate were measured and documented for each filtration run.

2.3. Anti-Fouling Performance Test

To explore the anti-fouling behavior of the membrane, the initial pure water flux was firstly determined. Subsequently, the membrane was applied for emulsion separation testing. After the filtration process was finished, deionized water was used to perform backwashing treatment on the membrane [48], and pure water flux was tested every 3 min for a duration of 3 h. Four typical evaluation indices were adopted to compare the anti-fouling properties [49]: the flux recovery ratio (FRR), total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}). These values can be calculated via Equations (4), (5), (6), and (7), respectively:

$$FRR = J_3/J_1 \times 100\% \quad (4)$$

$$R_t = (1 - J_2/J_1) \times 100\% \quad (5)$$

$$R_r = (J_3 - J_2)/J_1 \times 100\% \quad (6)$$

$$R_{ir} = (J_1 - J_3)/J_1 \times 100\% \quad (7)$$

where J_1 , J_2 , and J_3 represent the pure water flux before initial fouling [50], the initial permeation flux during separation, and the pure water flux after cleaning [51], respectively ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$).

2.4. Characterizations of the Membrane

The chemical composition of the membrane was analyzed via X-ray photoelectron spectroscopy (XPS) using a PHI-1600 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with an Al $K\alpha$ X-ray source. The water contact angle of the membranes was

conducted using a SL200KS goniometer (KINO Industry Co., Ltd. New York, NY, USA) via the pendant drop method. The pore size distribution of the membrane was determined via BSD-PB pore size analyzer (Beishide, Beijing, China). The surface and cross-sectional morphologies of the prepared membranes were observed using field emission scanning electron microscopy (SEM) [52,53]. The morphology, chemical structure, wettability, and mechanical properties of the membranes were characterized by various instruments. The models and manufacturers of the instruments are summarized in Table S2 in the Supplementary Materials.

2.5. Biodegradability Test

The biodegradability of the CS/PVA/SMa-PAM membrane was evaluated using the soil burial method. Agricultural soil was collected from the top layer (0–20 cm depth) of a farmland in Weihai, China. The soil was air-dried and sieved through a 2 mm mesh to remove debris. The membrane samples were cut into rectangular pieces ($2 \times 2 \text{ cm}^2$), dried to a constant weight at 60°C , and weighed (W_0). The samples were then buried in plastic boxes containing the agricultural soil at different depths: 0 cm (surface), 3 cm, 5 cm, 7 cm, and 9 cm. The boxes were kept in a closed, dark environment at room temperature ($25 \pm 2^\circ\text{C}$) to avoid light exposure. At predetermined time intervals (10, 20, 30 days), the membrane samples were carefully retrieved from each depth, gently cleaned with deionized water to remove adhered soil particles, dried at 60°C to a constant weight, and weighed (W_t). The degradation rate can be calculated via Equation (8):

$$\text{Degradation Rate (\%)} = (W_0 - W_t)/W_0 \times 100\% \quad (8)$$

where W_0 and W_t are the weights of the membrane sample before and after degradation, respectively.

3. Results and Discussion

3.1. Membrane Preparation and Morphological Analysis

The strong hydrogen bonding between PVA and amino ($-\text{NH}_2$) [54] and imino ($-\text{NH}-\text{R}$) groups can effectively improve fiber formation during the electrospinning process [55,56]. Under the initiation of the APS initiator, the double bonds of SMA participate in free radical polymerization. Meanwhile, the carboxyl groups provided by SMA undergo condensation polymerization with the amino groups of CS, leading to the construction of a hydrophilic closed-loop crosslinked network. Moreover, the H-bond interaction between PAM and CS as well as PVA also leads to a high-strength interpenetrating cross-linked network. The schematic mechanism of the fabrication of the membrane with an interpenetrating polymer network is illustrated in Figure 1. The resulting CS/PVA/SMa-PAM nanofibrous membrane fabricated by electrospinning exhibits excellent permeability. Notably, it not only achieves significantly enhanced separation performance but also possesses environmentally friendly biodegradability.

The morphological evolution of CS/PVA-SMa nanofibrous membranes enhanced with varying concentrations of PAM is shown in Figure 2a–d. The CS/PVA-SMa membrane without PAM exhibited a relatively smooth fiber surface. Upon the introduction of PAM, abundant beaded structures gradually appeared on the fiber surfaces at the microscopic level, indicating that the incorporation of PAM promoted the interaction among the nanofibers. To more intuitively analyze the microstructure of the membranes [57], the cross-sectional morphologies of the interpenetrating-network CS/PVA-SMa membrane and the CS/PVA/SMa-PAM membrane were characterized by SEM. As shown in Figure 2e,f, after the PAM-enhanced modification, the thickness of the membrane rose from $43.3 \pm 2.2 \mu\text{m}$ to $44.9 \pm 1.8 \mu\text{m}$ due to the presence of the beaded structure incorporated into the nanofibrous layer. The CS/PVA-SMa membrane exhibited a porous layered structure

(Figure 2e), while the CS/PVA/SMa-PAM membrane showed a dense non-woven morphology (Figure 2f). This transition is attributed to the addition of PAM, which decreased the solution viscosity and increased its conductivity. Lower viscosity weakens resistance to jet elongation, leading to compact deposition, while higher conductivity enhances electrostatic stretching, accelerating solvent evaporation and promoting dense film formation. Overall, the introduction of PAM not only optimized the membrane's chemical composition to form an interpenetrating crosslinked network but also increased the packing density of the nanofibers, resulting in a more compact membrane structure. Nevertheless, the membrane maintained excellent hydrophilicity and high separation performance due to the abundant hydrophilic groups introduced by PAM and SMa.

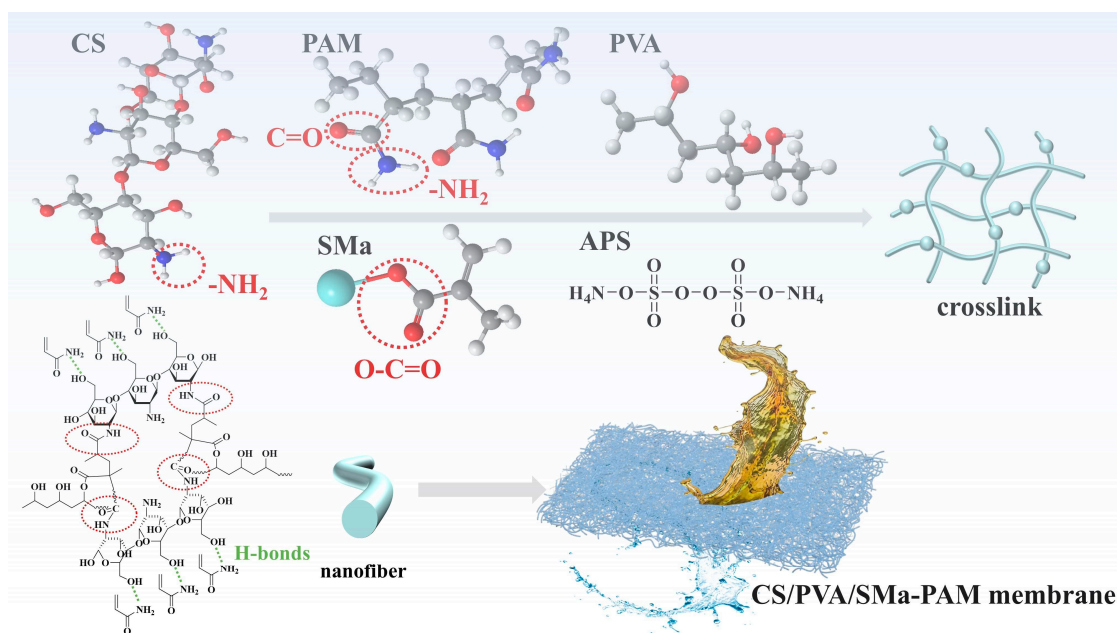


Figure 1. The fabrication of the CS/PVA/SMa-PAM nanofibrous membrane.

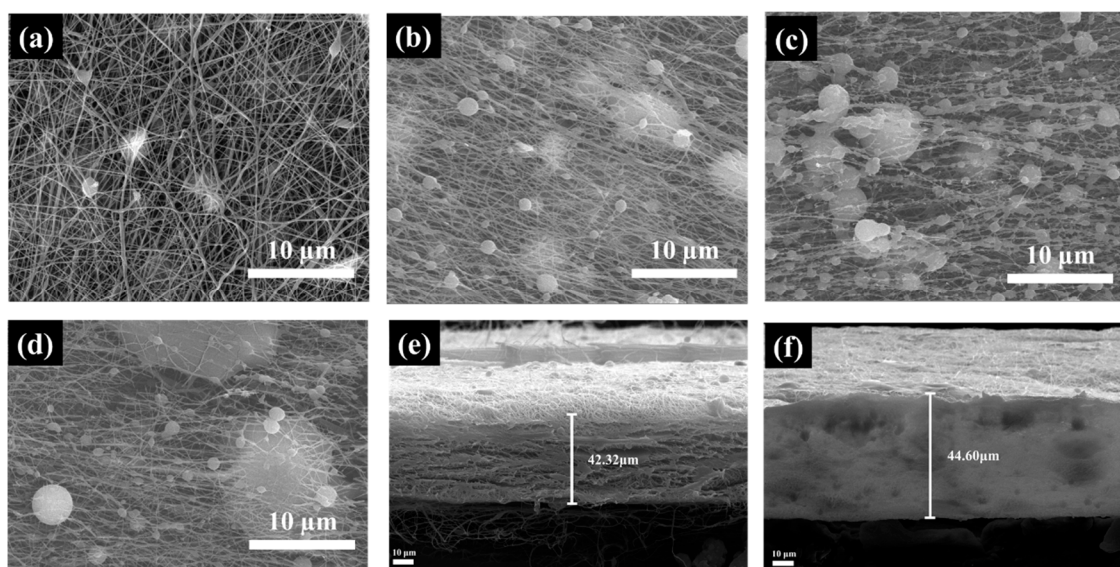


Figure 2. Effect of PAM amount on the surface morphology of (a) the CS/PVA-SMa membrane; (b–d) modified membranes with PAM added in amounts of 0.5%, 1.0%, and 1.5%, with a cross-sectional SEM of different nanofibrous membranes; (e) the CS/PVA-SMa membrane; (f) the CS/PVA/SMa-PAM membrane.

3.2. Membrane Surface Chemical Characterization and Wettability

To gain insights into the effects of PAM-enhanced modification on the chemical composition and reaction mechanism of the nanofibrous membranes, XPS characterization was performed on the membranes after enhancement. The corresponding results are presented in Figure 3a,b. The C 1s spectra showed four peaks of the C–C (284.8 eV), C–N (285.6 eV), C–O (286.7 eV), and O–C=O (288.5 eV) functional groups [58]. The C–N peak confirms the presence of amino groups from CS and amide groups from PAM. The C–O peak belongs to the hydroxyl groups and ether linkages of CS and PVA. Moreover, the O–C=O peak confirms the formation of amide/ester bonds between SMa and CS/PVA, evidencing successful crosslinking. High-resolution XPS N 1s analysis was conducted on the CS/PVA/SMa-PAM membrane. The N 1s spectrum (Figure 3b) exhibits the C–N peak at 399.9 eV. The FTIR spectrum of the CS/PVA/SMa-PAM membrane is presented in Figure S10, providing further evidence for the successful reaction following the XPS analysis. The characteristic absorption bands of all components are clearly observed. The peak at around 1650 cm^{-1} is assigned to the amide I (C=O stretching) vibration, which originates from two sources: one from the amide groups of PAM, and the other from the amide bonds formed via the crosslinking reaction between CS and SMa. The peak at approximately 1560 cm^{-1} corresponds to the asymmetric stretching vibration of carboxylate ($-\text{COO}^-$) groups from SMa. These findings confirm the successful incorporation of CS, PVA, SMa and PAM within the nanofibrous membrane, which ultimately constructed a well-formed interpenetrating network structure. As can be observed from Figure 3c, the pore diameter of membrane reached 1.74 μm after incorporating 1.5% PAM. Such structural features help diminish flow resistance in separation, further enhancing the membrane permeation flux. In the inset of Figure 3c, the tensile strength of the CS/PVA/SMa-PAM nanofibrous membrane was approximately 8 MPa, and the elongation at break was about 15%, which meets the mechanical strength requirements of nanofibrous membranes in practical applications.

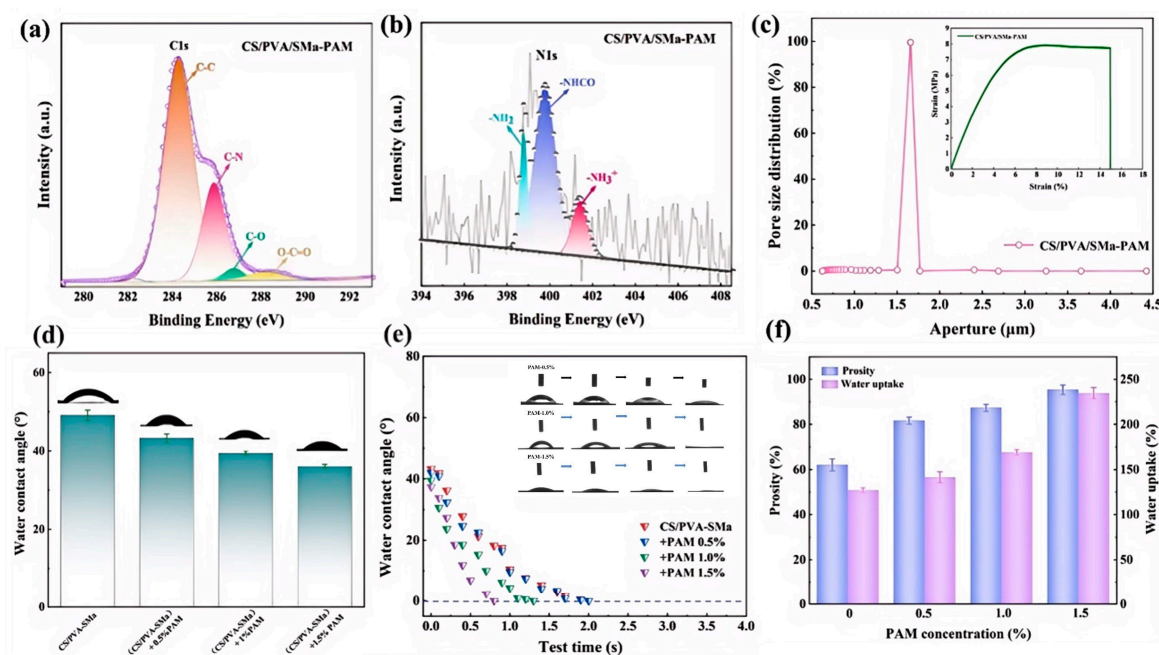


Figure 3. XPS spectra of CS/PVA/SMa-PAM: (a) C 1s spectrum; (b) N 1s spectrum; (c) pore size distribution and mechanical properties of CS/PVA/SMa-PAM; (d) variation in contact angle with different amounts of PAM added after modification; (e) variation in dynamic contact angle at different PAM concentrations; (f) porosity and water absorption of nanofibrous membranes with different amounts of PAM added.

To ascertain the influence of PAM modification on the wettability of the nanofibrous membranes, water contact angle measurements were conducted. As observed in Figure 3d, with the increase in the amounts of PAM added, the water contact angle decreased, reaching a minimum of 37° . A possible explanation is that the introduction of PAM increased the content of hydrophilic groups (such as $-\text{NH}_2$ and $-\text{NHCO}$) in the interpenetrating network structure, thereby enhancing the overall hydrophilicity of the membrane [59]. Importantly, owing to the synergistic effect introduced by PAM, the dynamic wetting performance of the membrane remained favorable (Figure 3e). The membrane with 1.5% PAM added allowed the droplet to rapidly penetrate within 0.75 s, achieving a fully wetted state. The improved wettability also affected the water absorption of the membrane, which rose from 134% to 235% upon an increase in the amount of PAM added, to 1.5%, corresponding to an enhancement of approximately 230% (Figure 3f). After the addition of PAM, the interpenetrating crosslinked network was enriched with more hydrophilic groups, including amino and carbonyl groups, enhancing the water absorption capacity of the membrane within a short period. In addition, due to the beaded structure reducing the packing density of the fibers, the porosity of the membrane elevated from 65.0% to 95.3% as the PAM concentration increased from 0 to 1.5%.

3.3. Physicochemical Properties of the Spinning Solutions

To reveal the mechanism underlying the formation of beaded structures, the properties of the spinning solutions were investigated, including the surface tension, viscosity, density, and conductivity of the pristine and modified solutions (Figure 4). As a result, the surface tension of the pristine CS/PVA-SMa spinning solution was $0.118 \text{ mN}\cdot\text{m}^{-1}$. After the introduction of PAM, the surface tension decreased to $0.117 \text{ mN}\cdot\text{m}^{-1}$. With the addition of PAM, the surface tension finally decreased to $0.110 \text{ mN}\cdot\text{m}^{-1}$ (Figure 4a). This decreasing trend indicates that the hydrophilic groups (e.g., $-\text{NH}_2$, $-\text{CONH}_2$) introduced by PAM effectively reduced the surface energy of the spinning solution. The viscosity of the spinning solution gradually decreased from 406 mPa·s for the pristine solution to 322 mPa·s for the CS/PVA-SMa + 1.5% PAM sample (Figure 4b), which would have been conducive to the formation of a beaded structure. Similarly, the density of the spinning solution increased stepwise from $1.034 \text{ g}\cdot\text{mL}^{-1}$ to $1.047 \text{ g}\cdot\text{mL}^{-1}$ (Figure 4c), further confirming the densification of the crosslinked network structure after PAM-enhanced modification. The conductivity also increased significantly from $5.7 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$ to $19.0 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$ (Figure 4d), attributed to the introduction of anionic PAM, which increased the ionic concentration and charge density. This higher conductivity was favorable for stabilizing jet stretching during electrospinning, thereby promoting the formation of uniform nanofibers. In summary, the incorporation of PAM effectively tailored the physicochemical properties of the spinning solutions, providing favorable conditions for the subsequent fabrication of a high-porosity and highly hydrophilic interpenetrating-network nanofibrous membrane.

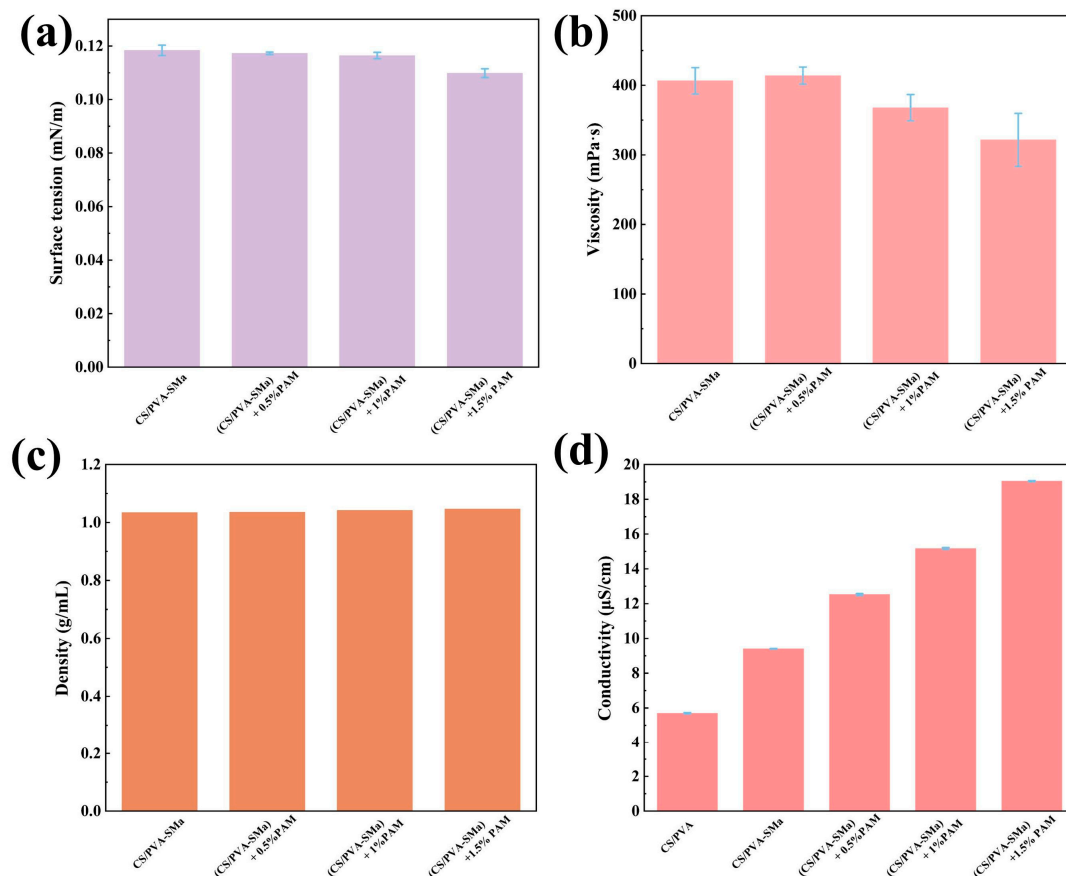


Figure 4. Effect of PAM incorporation on the properties of the spinning solutions: (a) surface tension; (b) viscosity; (c) density; (d) conductivity.

3.4. Separation Performance

The separation effect of the membrane on the oily emulsion was further investigated. Owing to the stable construction of the crosslinked network, the PAM-optimized membrane tended to effectively intercept oil droplets. With the addition of PAM, the separation flux gradually exceeded $1.80 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, representing a significant improvement, and the maximum flux reached $2.7 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ (Figure 5a). The abundant hydrophilic groups in PAM promoted water molecule diffusion and wettability on the membrane surface, thereby reducing the resistance to liquid permeation and increasing the water flux, with a separation efficiency above 99.5%. The separation efficiency of the nanofibrous membrane for oil-in-water emulsions with different types of surfactants was further investigated. As shown in Figure 5b,c, the CS/PVA/SMa-PAM membrane achieved a flux of $2.7 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for the CTAB-stabilized emulsion, which is higher than that for the SDS-stabilized emulsion, and significantly exceeds the fluxes of the unmodified membrane. This resulted from the enhanced negative charge of the membrane surface after PAM incorporation, which electrostatically attracted the positively charged CTAB emulsion, promoting demulsification and rapid water permeation. Notably, the rejection was above 99.5% for all of the measured emulsions, demonstrating excellent separation performance. The zeta potentials of the membranes and the solution containing three different surfactants were measured and are shown in Figure S8. After PAM modification, the negative charge on the membrane increased from -2.8 mV to -5.8 mV , resulting in electrostatic attraction with the positively charged CTAB emulsion ($+58 \text{ mV}$), repulsion with the negatively charged SDS emulsion (-97.7 mV), and no interaction with the neutral Tween80 emulsion (-1.3 mV). These results show that the membrane surface

charge has a significant effect on the emulsion permeation flux, and that electrostatic attraction can effectively improve the flux. As shown in Figure 5d, the order of droplet sizes in the permeate was SDS (about 106 nm) < Tween 80 (122–164 nm) < CTAB (220–295 nm). The negatively charged SDS emulsion exhibited the smallest droplet size, whereas the positively charged CTAB emulsion exhibited the largest. This is consistent with the previous speculation that the surface of different PAM-modified membranes is negatively charged, and its electrostatic effect can repel SDS emulsion, inhibit droplet aggregation and retain smaller droplets; on the contrary, the electrostatic attraction of CTAB emulsion promotes the coalescence of droplets to form larger droplets [60]. As shown in Figure 5e, the PAM-modified membrane showed a higher FRR value and lower RIR value, indicating that its anti-pollution performance was improved. The flux recovery ratio (FRR) after separation was calculated to be 88.2%. The 20-cycle stability test (Figure 5f) showed that the flux remained at the level of $2.5 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ because of the reduction in oil droplet pollution on the membrane surface during the cycle. The introduction of PAM improved the surface charge density and anti-pollution ability, which not only helped to maintain outstanding separation efficiency, but also remarkably enhanced the long-term stability and durability of the membrane. Therefore, PAM-enhanced membranes should demonstrate superior performance in actual oil–water separation applications, with the key advantages summarized in Table 1.

Table 1. Performance comparison between the CS/PVA/SMa-PAM membrane and those reported in the literature for oil–water separation.

Membrane	Flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)	Rejection (%)	Toxic Reagents Involved	Ref.
m-PVDF	6.9×10^2	99.5%	Glutaraldehyde	[61]
GO/g-C ₃ N ₄ @TiO ₂	4536	99.9%	DMAc-	[62]
M-CoOOH@ZIF-67	425.72	98.4%	DMF	[63]
PVDF@TP	955	99%	DMF	[64]
U1gFx	8081.9	95%	DMAc and DMF	[65]
CS/PVA/SMa-PAM	2.7×10^4	99.5%	-	This work

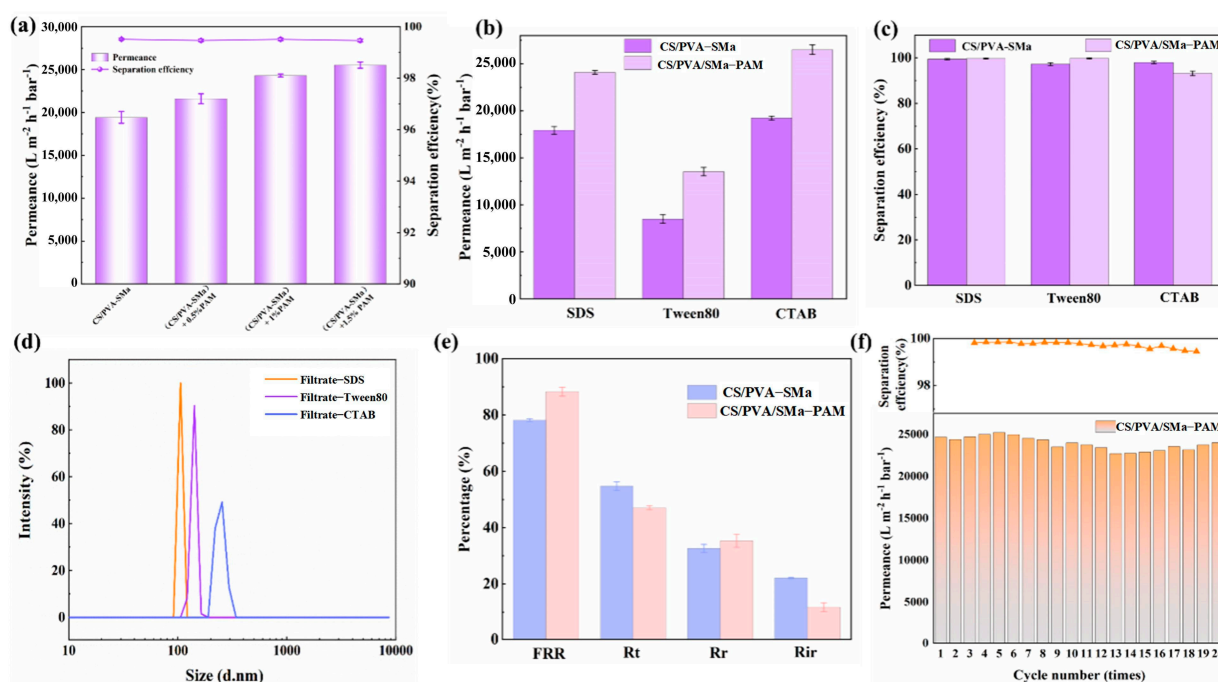


Figure 5. (a) Oil–water separation performance of membrane with different PAM contents, and the influence of emulsions containing different surfactants on membrane separation performance; (b)

oil water separation permeability; (c) separation efficiency; (d) particle size distribution of emulsion retention solution stabilized by different surfactants; (e) evaluation of anti-fouling performance before and after membrane modification; (f) cyclic stability of PAM-modified membrane.

The membrane stability was evaluated by monitoring the normalized flux (J/J_0) as a function of cumulative permeate volume per unit membrane area (Figure 6a). The J/J_0 value remained relatively stable at 0.98–1.02 up to a cumulative volume of $\sim 183 \text{ L}\cdot\text{m}^{-2}$, then gradually decreased to 0.92 at $\sim 297 \text{ L}\cdot\text{m}^{-2}$, and partially recovered to 0.93–0.97 in the subsequent stages. This recovery is likely attributed to the removal of loosely attached oil droplets during intermediate washing steps. Notably, even after a cumulative throughput of $458.79 \text{ L}\cdot\text{m}^{-2}$, the J/J_0 value remained above 0.92, indicating that the CS/PVA/SMa-PAM membrane possesses satisfactory operational stability and fouling resistance. The influence of feed oil concentration on membrane performance was examined over a range of 200 to 10,000 mg/L n-octane. As shown in Figure 6b, the permeation flux stayed nearly constant across all tested concentrations (200–10,000 mg/L), staying consistently above $2.5 \times 10^4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. Oil rejection remained around 99.5% for every concentration tested, indicating good concentration adaptability. The CS/PVA/SMa-PAM membrane showed high surface roughness (Figure 6c, $S_a = 5.432 \mu\text{m}$), which is typical for electrospun fibrous membranes. Since these membranes are intrinsically hydrophilic, such roughness likely promotes water spreading and retention [66], which helps reduce oil adhesion during use [67,68]. The TGA curve of the CS/PVA/SMa-PAM membrane (Figure 6d) exhibited an initial weight loss of $\sim 0.3\%$ below 100°C due to moisture evaporation, followed by a gradual loss of $\sim 3.3\%$ between 100 and 200°C from bound water and residual solvents. The major decomposition occurred at 200 – 400°C with a $\sim 43\%$ weight loss, corresponding to the degradation of CS, PVA, and PAM backbones. The onset temperature (5% weight loss) was $\sim 193^\circ\text{C}$, and the residual mass at 800°C was $\sim 21.0\%$, indicating good thermal stability for ambient applications. Membrane surfaces before and after filtration were observed by optical microscopy (Figure 6e). No obvious oil residue or surface change was found after repeated use, confirming good anti-fouling performance. The SEM image of the used membrane (Figure 6f) showed no obvious oil residue or structural change compared with the pristine membrane, further confirming good anti-fouling performance.

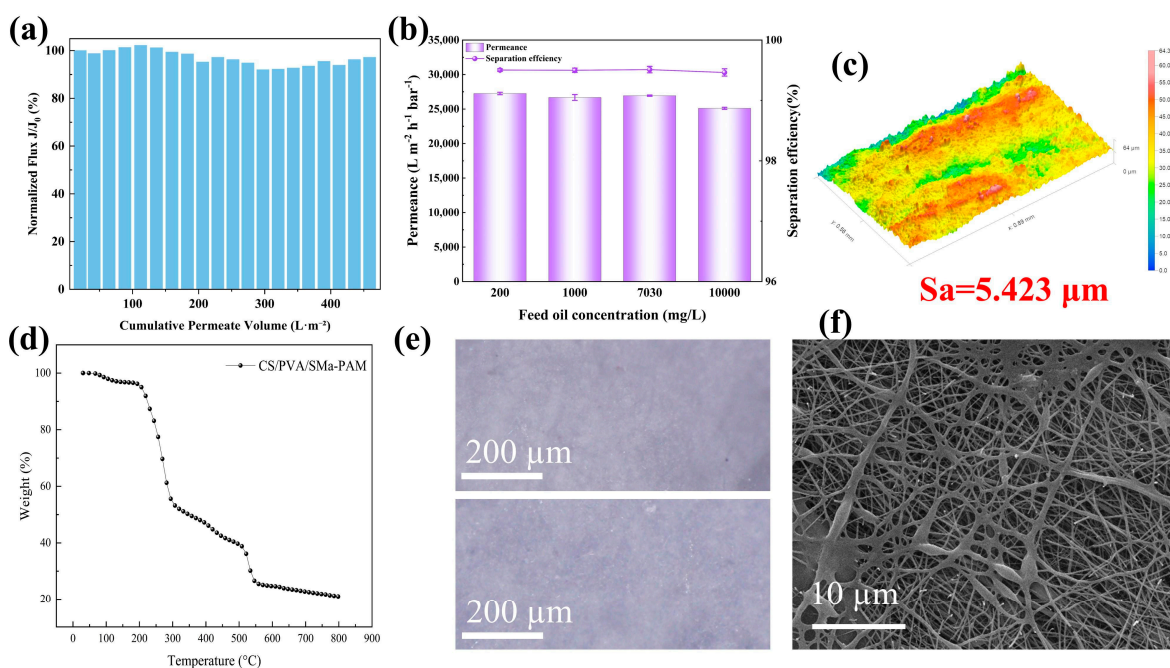


Figure 6. (a) Normalized flux (J/J_0) as a function of cumulative permeate volume per unit membrane area ($\text{L}\cdot\text{m}^{-2}$) of the CS/PVA/SMa-PAM membrane during multiple filtration cycles. J_0 is the initial

permeation flux ($246.78 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). (b) Separation performance at different feed oil concentrations. (c) AFM surface roughness of the CS/PVA/SMa-PAM membrane. (d) TGA curve. (e) optical microscopy images of the membrane surface before and after use. (f) SEM image of the membrane after use.

3.5. Degradation Performance

The biodegradability of membrane materials is a key index with which to evaluate their environmental friendliness. In order to evaluate its degradation characteristics, the membrane materials were buried in soil at different depths (0–9 cm), and their weight changes were recorded. As shown in Figure 7a, the degradation rate rose with the extension of the culture time at all tested depths. The most significant increase occurred at a depth of 0 cm: about 33.3% on the 10th day, 86.7% on the 20th day, and 89.3% on the 30th day. With the increase in depth, the rise in the degradation rate slowed down gradually; at a depth of 9 cm, the growth rate was the slowest and the range was the smallest: the degradation rate was about 11.0% on the 10th day, 36.7% on the 20th day and 39.0% on the 30th day. These results show that the degradation rate is highly dependent on time and depth, and the degradation efficiency is higher in surface soil samples. This difference can be attributed to the more suitable aerobic conditions and higher microbial activity of topsoil, where microorganisms such as bacteria (e.g., *Bacillus*, *Pseudomonas*) [69,70], actinomycetes (e.g., *Streptomyces*) [71], and fungi (e.g., *Aspergillus*) [72] are known to promote the biodegradation of polymeric materials. As the degradation process proceeds, the membrane size continues to decrease (Figure 7b), indicating that CS/PVA/SMa-PAM membrane has excellent biodegradability in the soil environment. The morphological changes after 30 days are shown in the SEM image (Figure 7c). Compared with the smooth and continuous fibrous structure before degradation, the boundaries between neighboring fibers became progressively indistinct, and the initially discrete, well-separated fibrous network transitioned into a merged morphology, resembling a fused or coalesced structure, with some regions showing breakage and collapse, further confirming the occurrence of the degradation process. In summary, the membrane possesses good environmental friendliness and biodegradation potential.

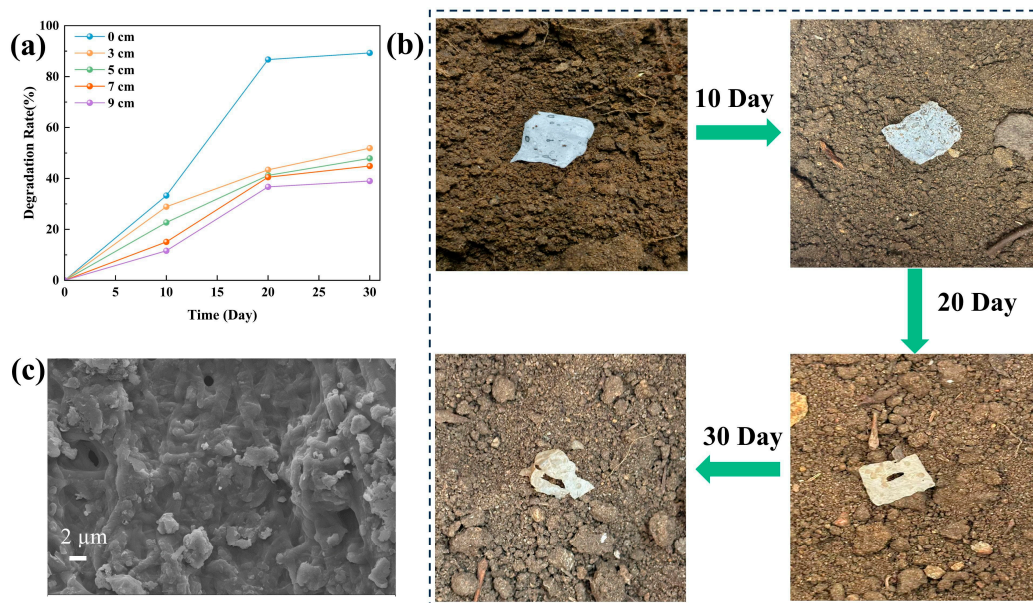


Figure 7. (a) Degradation rate profiles over time at different depths (0–9 cm), (b) degradation process of the membrane over 30 days, and (c) SEM of membrane after 30-day degradation.

4. Conclusions

In this work, a biodegradable interpenetrating network of CS/PVA/SMa-PAM was successfully constructed for high-efficiency oil–water separation. The interpenetrating crosslinked network, enriched with hydrophilic functional groups, contributed to a maximum water absorption of 230%. After 20 cycles of emulsion filtration, the steady-state flux remained at $2.5 \times 10^4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Furthermore, the membrane exhibited favorable biodegradability in soil, with significant weight loss and structural disintegration after 30 days. Based on the results above, the PAM-enhanced CS/PVA/SMa-PAM nanofibrous membrane is a potential candidate for high-flux, anti-fouling, biodegradable, and environmentally friendly oil–water separation, with exceptional potential for realistic wastewater treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations13070204/s1>. Table S1: Chemical reagents used for the preparation of the CS/PVA/SMa-PAM membrane; Table S2: List of instruments used for membrane characterization; Text S1: analysis and characterization methods; Figure S1: Effect of different injection rates on the microstructure of CS/PVA/SMa-PAM nanofibrous membranes; Figure S2: Effect of different injection rates on membrane performance; Figure S3: Surface morphology of CS/PVA/SMa-PAM membranes at different drum rotation speeds; Figure S4: Effect of different drum rotation speeds; Figure S5: Surface morphology of CS/PVA/SMa-PAM membranes at different electrospinning times; Figure S6: Effect of different electrospinning times; Figure S7: XPS spectra of the CS/PVA/SMa-PAM membrane; Figure S8: Zeta potential of (a) different types of membranes and (b) oil-water emulsions containing different surfactants; Figure S9: Oil-water emulsion separation process; Figure S10: FTIR spectra of the CS/PVA/SMa-PAM membrane; Figure S11: Optical microscopy images of the oil red O-stained n-octane-in-water emulsion before and after static standing for 2 h; Figure S12: Schematic diagram of the experimental setup.

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