

Tannic Acid-Assisted Surface Coating of Peptides on the Poly(vinylidene fluoride) Membrane for Oil/Water Emulsion Separation

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The membrane separation of oil/water emulsions has drawn much attention in recent years. The goal of present work is to develop a facile, cost-effective modification method to improve the hydrophilicity and antifouling of polyvinylidene fluoride (PVDF) membrane. Inspired by the plant polyphenol with strong anchoring ability on the various substrates, we report a two-step polyphenol chemistry strategy to achieve the hydrophobic-to-hydrophilic transformation of PVDF membrane via coordination assembly of tannic acid and Fe³⁺ ion followed by grafting of glutathione (GSH). The successful coating of GSH onto the PVDF membrane was confirmed by X-ray photoelectron spectroscopy. The modified PVDF membrane has good wettability (the water contact angle is 24.8 ° and the underwater oil contact angle of 144.4 °) and high antifouling ability (the BSA rejection ratio is 87.7 %). More importantly, the modified membrane has a high water filtration flux up to 5,822 L m⁻² h⁻¹ at 0.09 MPa, and the separation efficiency is more than 99 % for the various surfactant stabilized oil-in-water emulsions. It is also successfully used to separate the high viscous crude oil-in-seawater emulsion, achieving a separation efficiency of > 95 %. The results showed that the simple and versatile method is promising for the modification of PVDF membranes with the ability of emulsion separation.

1. Introduction

The effective treatment of oil-in-water emulsions, especially for surfactant-stabilized oil-in-water emulsions (droplet size less than 20 μm) is highly desired, yet still challenging. Some useful technologies have been developed for the treatment the oily wastewater, such as coagulation, centrifuges, dissolved air floatation, and filtration (Tanudjaja et al., 2019). Among these methods, membrane filtration was acknowledged as one of the most advanced technologies for oil/water emulsions separation. However, most of the membranes are vulnerable to suffer from fouling and plugging by oil droplets during the emulsion separation process (Huang et al., 2018), which significantly decreases the permeation flux, shortens the operating life and increases the maintenance cost (Stoller et al., 2016). It is highly desired to develop a suitable membrane to address the fouling issue.

Polyvinylidene fluoride (PVDF) membranes with excellent chemical resistance, high mechanical strength and suitable pore size have been widely used for separation. Unfortunately, PVDF membranes are intrinsically hydrophobic, which also cause the membrane fouling easily (Shi et al., 2016). Many studies have focused on improving the hydrophilicity and antifouling performance of PVDF membranes. For example, Zin et al. (2019) reported a PDA/PEI coated PVDF microfiltration membrane with high oil rejection (> 98 %) and significantly reduced irreversible fouling by oily wastewater. Zhang et al. (2018) prepared a zwitterionic nanohydrogel-grafted PVDF membrane via surface grafting, which shows excellent antifouling performance and gravity-driven separation of crude oil-in-water with a high removal efficiency of 98.7 %. However, the use of zwitterionic polymers and macromolecule polymer, which composed of the complex surface modification process, limits its practical industrial applications.

In our previous work, polydopamine was used to form an adhesive layer for grafting a peptide on the PVDF membrane (Wu et al., 2018). However, the self-polymerization of dopamine in aqueous result in the aggregation

of nanoparticles, and then the membrane pores are blocked (Luo et al., 2017). As an alternative to dopamine, tannic acid (TA), is a natural polyphenol and can be extracted from tea, red wine and other natural plants (Sileika et al., 2013). TA has abundant catechol and galloyl groups coordinating with Fe^{3+} ion to form a highly stable octahedral complex, which is able to coat on various substrates via covalent and/or noncovalent bonding.

In this study, we developed a simple, mild and green dip-coating strategy to transform the hydrophobic PVDF membranes into hydrophilic ones. The coating of TA/Fe complex layer was performed and followed by the grafting of GSH, leading to enhanced pure water flux and antifouling performance of PVDF membrane. The morphology, surface composition, and wettability of the modified PVDF membrane were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy and contact angle measurement. The water flux, antifouling and separation performances of the membranes were evaluated.

2. Materials and methods

2.1 Materials

The PVDF membrane with an average pore size of $0.22\ \mu\text{m}$ was purchased from Merck Millipore Ltd., Ireland. Glutathione (GSH, 97 %), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), hexadecyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), tween-60 and humic acid were available from Heowns Biochemical Technology Co. Ltd. (Tianjin, China). Tannic acid (TA, analytical reagent), bovine serum albumin (BSA), tris-(hydroxymethyl) aminomethane (Tris, 99 %), n-hexadecane (98 %), toluene and anhydrous ethanol were supplied by Aladdin Chemistry Co. Ltd. (Shanghai, China). Diesel oil and crude oil were obtained from a local supermarket. The solution pH was measured on an MP 220 pH meter (Mettler Toledo, Switzerland). The water used during experiments was purified with a three-stage Millipore Mill-Q Plus 185 purification system (Millipore Corp., Bedford, MA). All chemicals were used as received without any further purification.

2.2 Preparation of hydrophilic PVDF membranes

The PVDF membranes were completely soaked in ethanol for 2 h and then washed with ultrapure water several times. The pre-treated PVDF membranes were firstly immersed in 2 mg/mL TA Tris-buffer (pH = 7.8, 50 mM) solution for 4 h under mild shaking at room temperature. Then, the membranes were transferred into FeCl_3 solution (0.15 mg/mL) for 5 min. After that, the obtained membranes were rinsed with ultrapure water three times and named as PVDF@TA/Fe. The PVDF@TA/Fe membranes were submerged in 10 mg/mL GSH Tris-buffer solution (pH = 7.8, 50 mM) for 2 h. The as-prepared membranes were then washed thoroughly with ultrapure water three times and named as PVDF@TA/Fe-GSH. Finally, the obtained membranes were placed in ultrapure water or dried under a stream of nitrogen gas for further use.

2.3 Characterization

The surface morphology of the pristine and as-prepared PVDF membranes was characterized by SEM (Hitachi S-4800). The chemical composition of the samples was determined using XPS (ULVAC-PHI, Japan) with $\text{Al-K}\alpha$ as the radiation source. The water contact angle (WCA) and underwater oil (1,2-dichloroethane) contact angle (UOCA) were measured with SL200KS optical measuring device (Kina, America), and at least three different points on each sample with a drop size of $2\ \mu\text{L}$ to get a reliable average value.

2.4 Preparation of the surfactant stabilized oil-in-water emulsions

The surfactant-stabilized oil-in-water emulsions, including SDS/toluene/water, SDS/n-hexadecane/water, SDS/diesel oil/water, CTAB/crude oil/water, SDS/crude oil/water, Tween 60/crude oil/water and humic acid/crude oil/water, were prepared by mixing oil and water at a volume ratio of 1:100 with the addition of 0.02 mg surfactant per ml of emulsion under high-shear stirring at a speed of 20,000 rpm for 15 min. After emulsification, the floating oil was removed. All above-mentioned emulsions before use were stabilized for 24 h in a laboratory environment.

2.5 Evaluation of separation and antifouling performance

A vacuum filter apparatus with an effective filtration area of $11.53\ \text{cm}^2$ was adopted to evaluate the separation efficiency and antifouling performance of the modified membrane. For each filtration cycle, 50 mL of feed solution was permeated through the membrane under 0.09 MPa. The permeated water was collected, and the oil concentration of the filtrate was measured using a total organic carbon analyzer (TOC, Shimadzu TOC-VCPH, Japan). The micrographs of the emulsion and filtrate solution were recorded by an optical microscope. The flux J ($\text{L m}^{-2}\ \text{h}^{-1}$) was calculated by Eq(1) as follows:

$$J = \frac{V}{A\Delta t} \quad (1)$$

where V (L) is the volume of collected filtrate, Δt (h) represents the permeation time and A (m^2) is the effective filtration area of the membrane.

The separation efficiency R (%) was calculated as given in Eq(2).

$$R(\%) = \left(1 - \frac{C_2}{C_1}\right) \times 100\% \quad (2)$$

where the C_1 (mg/L) and C_2 (mg/L) are the oil concentration of feed and filtrate solution.

The flux recovery ratio (FRR) was employed to evaluate the antifouling ability of the membranes. It is worth noting that a larger FRR value indicates the better fouling resistance ability. The FRR value was calculated using Eq(3).

$$FRR(\%) = \left(\frac{J_2}{J_1}\right) \times 100\% \quad (3)$$

where J_1 ($L\ m^{-2}\ h^{-1}$) and J_2 ($L\ m^{-2}\ h^{-1}$) refer to the pure water flux before and after filtration of feed solution containing BSA ($1\ mg\ mL^{-1}$) or oil-in-water emulsions.

3. Results and discussion

The preparation process and a possible reaction of PVDF@TA/Fe-GSH membrane are shown in Figure 1. Firstly, an ultrathin metal-polyphenol layer is formed on the PVDF membrane by a two-step coating process. In this process, we found that the colour of PVDF membrane was changed, indicating the formation of a layer of TA/Fe complex. Subsequently, the GSH was covalently introduced into the PVDF@TA/Fe membrane via the Michael addition reaction between thiol and catechol groups of TA.

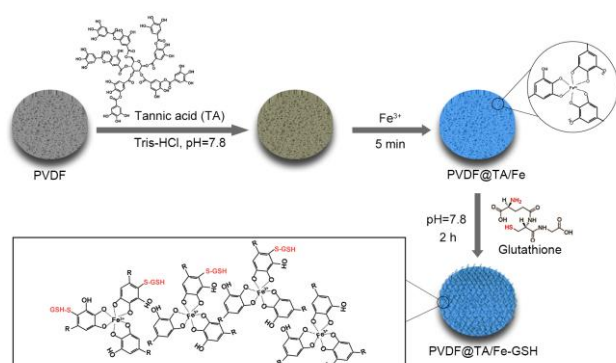


Figure 1: Schematic illustration of the preparation of the PVDF@TA/Fe-GSH membranes.

The surface morphology the original PVDF, PVDF@TA/Fe and PVDF@TA/Fe-GSH membrane were revealed by SEM (Figure 1). As presented in Figure 2a, d, the original PVDF membrane exhibits relatively smooth with many large pores on the membrane. The PVDF@TA/Fe and PVDF@TA/Fe-GSH display slightly different surface with a few particles, which is probably due to the deposition of TA/Fe thin film onto the PVDF membrane. As expected, the coating layer on the surface is too thin to block the pores.

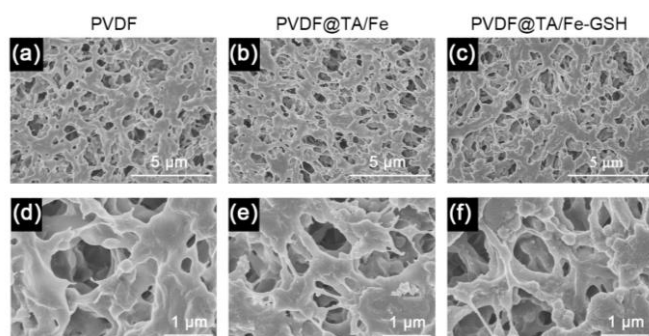


Figure 2: Surface morphology of (a,d) PVDF, (b,e) PVDF@TA/Fe, and (c,f) PVDF@TA/Fe-GSH

Successful coating of GSH onto the PVDF@TA/Fe-GSH membrane was further confirmed by X-ray photoelectron spectrometry (XPS) analysis. The XPS spectra of the membranes are shown in Figure 3. Compared with the original PVDF membrane, the new peaks of Fe 2p and S 2p appeared in the spectrum for PVDF@TA/Fe-GSH (Figure 3b, d), indicating that the TA/Fe complexes were coated onto the PVDF membrane and the GSH was also grafted on the surface.

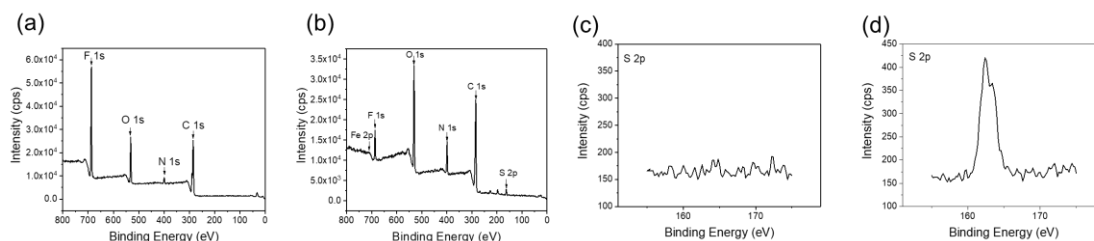


Figure 3: XPS wide and S 2p high-resolution spectra of (a,c) PVDF and (b,d) PVDF@TA/Fe-GSH

The wettability of the original and modified PVDF membrane was further investigated. As shown in Figure 4, the WCA of the original PVDF membrane was about 119.4° and no obvious change was observed in 60 s, demonstrating its high hydrophobicity. The WCA of PVDF@TA/Fe-GSH sharply decreased to 24.8° , which is much lower than the original PVDF membrane and PVDF@TA/Fe. This is attributed to the formation of a hydration layer on the surface because GSH can bind a large number of water molecules through electrostatic and hydrogen bonding interactions. For TA/Fe modified membranes, the WCA values slowly decreased from 31.7° to 0° within 46 s, while the value for the PVDF@TA/Fe-GSH became almost 0° within 10 s. The results provide direct evidence in support of the improvement in hydrophilicity of the GSH-modified membranes. The UOCA of the original PVDF membrane was 48.7° , while the underwater oil droplets on the PVDF@TA/Fe-GSH membrane surface were nearly spherical (Figure 4d) with a high UOCA of 144.4° , indicating that the modified membrane possesses underwater oleophobicity.

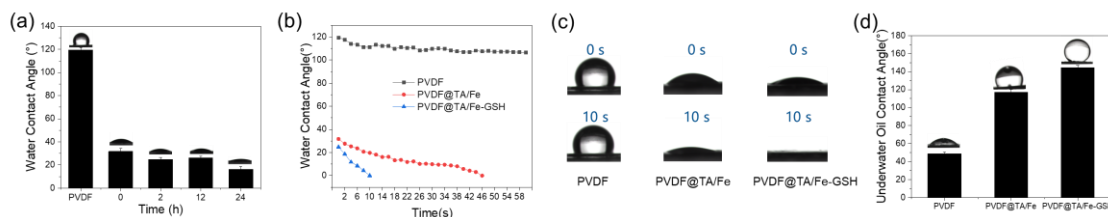


Figure 4: (a) Water contact angles of PVDF membranes with different GSH coating time. (b,c) Water CAs of different membranes with different drop time (the time of GSH treatment was 2 h). (d) Underwater oil CAs of different membranes

Pure water flux is an important parameter for membrane separation. As shown in Figure 5a, the pure water flux of the original PVDF membrane at 0.09 MPa was $0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, indicating that water can not penetrate the membrane because of its hydrophobicity. In comparison, the pure water fluxes of PVDF@TA/Fe and PVDF@TA/Fe-GSH under the same pressure increased to $8,448 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $8,475 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

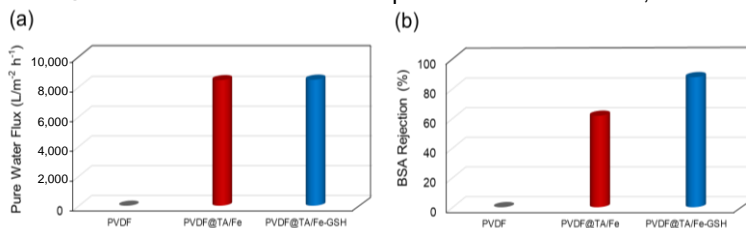


Figure 5: (a) Pure water flux of different membranes under 0.09 MPa. (b) BSA rejection ratio of various membranes under 0.09 MPa

Antifouling ability, as an important parameter to evaluate the separation performance of the PVDF membranes, plays an important role in the service life of the membrane. The fouling resistance of the membranes was investigated by using the representative substance BSA, and the results were shown in Figure 5b. After the filtration of the BSA feed solution, the BSA rejection ratios (*FRR*) of PVDF, PVDF@TA/Fe and PVDF@TA/Fe-GSH are 0 %, 61.7 % and 87.7 %. The results indicated that the BSA rejection ratio of the membrane was significantly improved after the modification of TA-Fe and GSH. Due to the coating of TA/Fe complex and the GSH layer on the surface (including the inside pores) of the PVDF membranes, the enhancement of the hydrophilicity is able to prevent the non-specific adsorption of BSA on the PVDF surface.

As described above, PVDF@TA/Fe-GSH has good hydrophilicity and antifouling ability, which endow the membranes with great potential for oil-in-water emulsions separation. To verify this point, a series of SDS-stabilized oil-in-water emulsions were prepared. The separation results of PVDF@TA/Fe-GSH toward various emulsions are shown in Figure 6. After filtration, the milky oil-in-water emulsion becomes transparent (Figure 6a), and no oil droplet is observed in the filtrate according to the optical microscope, suggesting the oil droplets have been intercepted by the membrane. In Figure 6b, the permeation flux is 5,822 L m⁻² h⁻¹, 3,033 L m⁻² h⁻¹ and 5,667 L m⁻² h⁻¹, for the toluene-in-water, n-hexadecane-in-water and diesel oil-in-water emulsions, and the oil rejection ratio is higher than 99 % for each emulsion (99.8 %, 99.5 % and 99.6 %). The results revealed the excellent separation efficiency of PVDF@TA/Fe-GSH membranes. In comparison with the other modified PVDF membranes, such as the TiO₂ (Shi et al., 2016), SiO₂ (Cui et al, 2019) and GSH (Wu et al., 2018) coated membranes modified by PDA-assisted methods, in which the flux of emulsion was 382 - 1,496 L m⁻² h⁻¹ and the separation efficiency was 98.7 % - 99.9 %, the PVDF@TA/Fe-GSH membrane exhibited a higher emulsion flux (5,822 L m⁻² h⁻¹) and comparable separation efficiency (99.8 %).

To further examine the separation performance of PVDF@TA/Fe-GSH membrane for the crude oil emulsions, four-kinds of surfactant stabilized crude oil-in-artificial seawater emulsions were passed through the membrane driven by vacuum under 0.09 MPa. As shown in Figure 6c, the membrane showed stable emulsion permeation with a flux of 520 L m⁻² h⁻¹ for CTAB/crude oil/artificial seawater, 3,996 L m⁻² h⁻¹ for SDS/crude oil/ artificial seawater, 6,355 L m⁻² h⁻¹ for Tween 60/crude oil/ artificial seawater and 1,189 L m⁻² h⁻¹ for humic acid/crude oil/ artificial seawater emulsions. The difference in the flux for the different emulsions is probably attributed to the different emulsification ability of surfactants and the different size of emulsion droplets. Besides, there is no obvious change in oil rejection with a value of approximately 95 %.

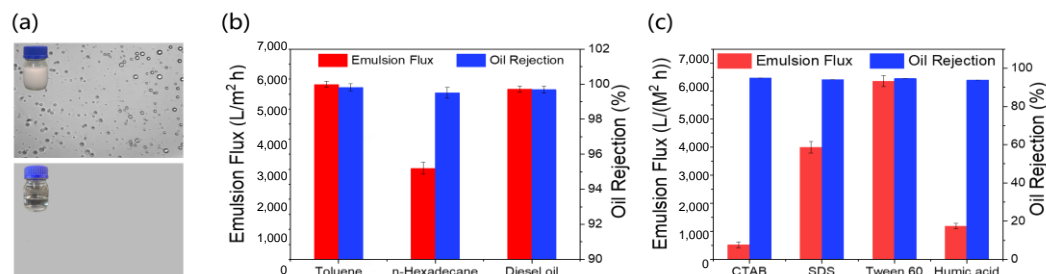


Figure 6: (a) Photograph and optical microscope images of SDS stabilized toluene-in-water emulsion and filtrate. (b) Emulsion flux and oil rejection of PVDF@TA/Fe-GSH for SDS stabilized emulsions. (c) Emulsion flux and oil rejection of PVDF@TA/Fe-GSH for different surfactant stabilized crude oil-in-seawater emulsions

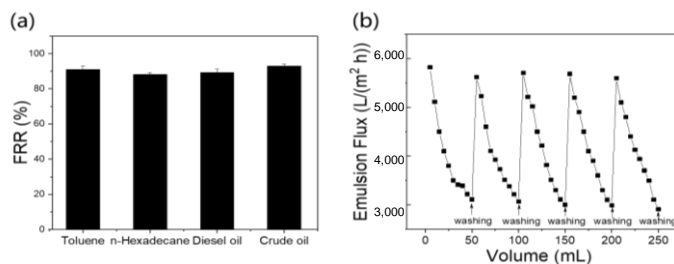


Figure 7: (a) Flux recovery ratio for various oil-in-water emulsions. (b) Flux recovery in the separation of SDS-stabilized toluene-in-water emulsion over five cycles under 0.09 MPa

The antifouling performance of the PVDF@TA/Fe-GSH membrane during the emulsion separation was investigated by the measurement of flux recovery ratio (*FRR*), divided by the pure water fluxes of PVDF@TA/Fe-GSH before and after filter the emulsion. As shown in Figure 7a, all the flux recovery ratios are greater than 88 %. The results indicated that the PVDF@TA/Fe-GSH membrane has good antifouling performance against from the non-specific adsorption of oil and surfactants.

To evaluate the reusability of the PVDF@TA/Fe-GSH membranes, a five-cycle filtration experiment was conducted using an SDS-stabilized toluene-in-water emulsion, and the membrane was washed by ultrapure water after each cycle. As shown in Figure 7b, for each cycle, the flux decreased in the process of filtration due to the oil retained on the surface or in the pore of membranes. But the flux of emulsion almost returned to its initial level after the washing with ultrapure water for 10 min, indicating the good stability of the coated TA/Fe-GSH layer on the membrane. The results suggest that the PVDF@TA/Fe-GSH membrane is a good candidate for practical use in separation of oil-in-water emulsions.

4. Conclusions

In summary, we demonstrate a tannic acid-assisted method to modify PVDF membranes, which converts PVDF membranes from hydrophobic to hydrophilic. We use GSH, an easily available material for use in oil-in-water emulsion separation, to modify the PVDF membrane and demonstrated its effectiveness. The modified PVDF@TA/Fe-GSH membranes show high pure water permeability and have good antifouling performance and reusability, which suit the membranes for long-term and efficient separation. PVDF@TA/Fe-GSH membrane also has good separation performance for the high viscous crude oil in seawater emulsions; so it is suitable for practical use in emulsion separation. Because of the green and simple fabrication procedure, the PVDF@TA/Fe-GSH membrane show great potential for practical application. In comparison with the polydopamine-assisted coating of zwitterionic polymers, the tannic acid-assisted surface coating of GSH has a lower cost. The WCA of the modified membrane is still more than 20 °, which is probably attributed to the low grafting density of GSH. A new approach for the enhancement of surface hydrophilicity is required in future.

References

- Cui J., Zhou Z., Xie A., Meng M., Cui Y., Liu S., Lu J., Zhou S., Yan Y., Dong H., 2019, Bio-inspired fabrication of superhydrophilic nanocomposite membrane based on surface modification of SiO₂ anchored by polydopamine towards effective oil-water emulsions separation, *Separation and Purification Technology*, 209, 434-442.
- Huang S., Li X., Jiao Y., Shi J., 2015, Fabrication of a superhydrophobic, fire-resistant, and mechanical robust sponge upon polyphenol chemistry for efficiently absorbing oils/organic solvents, *Industrial & Engineering Chemistry Research*, 54, 1842-1848.
- Huang S., Ras R.H.A., Tian X., 2018, Antifouling membranes for oily wastewater treatment: Interplay between wetting and membrane fouling, *Current Opinion in Colloid & Interface Science* 36, 90-109.
- Luo C., Liu Q., 2017, Oxidant-induced high-efficient mussel-inspired modification on PVDF membrane with superhydrophilicity and underwater superoleophobicity characteristics for oil/water separation, *ACS Applied Materials & Interfaces*, 9, 8297-8307.
- Sileika T.S., Barrett D.G., Zhang R., Lau K.H.A., Messersmith P.B., 2013, Colorless multifunctional coatings inspired by polyphenols found in tea, chocolate, and wine, *Angewandte Chemie International Edition*, 52, 10766-10770.
- Shi H., He Y., Pan Y., Di H., Zeng G., Zhang L., Zhang C., 2016, A modified mussel-inspired method to fabricate TiO₂ decorated superhydrophilic PVDF membrane for oil/water separation, *Journal of Membrane Science*, 506, 66-70.
- Stoller M., Ochando Pulido J.M., Sacco O., 2016, Optimized design of wastewater stream treatment processes by membrane technologies, *Chemical Engineering Transactions*, 47, 391-396.
- Tanudjaja H.J., Hejase C.A., Tarabara V.V., Fane A.G., Chew J.W., 2019, Membrane-based separation for oily wastewater: A practical perspective, *Water Research*, 156, 347-365.
- Wu W., Huang R., Qi W., Su R., He Z., 2018, Bioinspired peptide-coated superhydrophilic poly(vinylidene fluoride) membrane for oil/water emulsion separation, *Langmuir*, 34, 6621-6627.
- Zhang J., Zhang F., Wang A., Lu Y., Li J., Zhu Y., Jin J., 2018, Zwitterionic nanofibrous membranes with a superior antifouling property for gravity-driven crude oil-in-water emulsion separation, *Langmuir*, 35, 1682-1689.
- Zin G., Wu J., Rezzadori K., Petrus J.C.C., Di Luccio M., Li Q., 2019, Modification of hydrophobic commercial PVDF microfiltration membranes into superhydrophilic membranes by the mussel-inspired method with dopamine and polyethyleneimine, *Separation and Purification Technology*, 212, 641-649.