Performance of tannic acid/tetraethylenepentamine coated polymeric membrane for the separation of different surfactant-stabilized oil in water emulsions

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Abstract. The present research reported on the surface coating of PVDF membrane with polyphenolic-amine, which improves the hydrophilicity and underwater oleophobic properties. The separation efficiency and antifouling property of emulsion oil by pristine PVDF and polyphenolic-amine coated PVDF microfiltration membranes were evaluated. The performance of pristine and coated membrane was compared using three different types of surfactant-stabilized oil droplets (T80/Diesel/H₂O, SDS/Diesel/H₂O and CTAB/Diesel/H₂O) in terms of flux recovery ratio (FRR) and removal efficiency. The continuous cycle using cross-flow filtration mode was also investigated. The filtration experiments indicated that modifying the surface properties of the PVDF polymer membrane by polyphenolic-amine coating method can significantly improve the antifouling properties compared to unmodified polymeric membranes.

1. Introduction

Oily wastewater consists of different forms of oils, including free-floating oils, unstable dispersed oils and stable emulsified oils. The dispersed types tend to coalesce into the free floating oils which make both of these types easily separated using conventional methods (gravity, skimming and flotation) [1]. In contrast, emulsified oils with an aqueous phase are rather stable due to the presence of surfactants. The stable emulsified oils which have tiny droplet size (< 10 μm) are effectively treated by membrane filtration methods due to energy efficiency with higher separation quality [2].

Generally, on the membrane market, polymeric membranes such as polyvinylidene fluoride, polysulphone and polyacrylonitrile are most dominant materials used as the commercial membrane that are mainly for the water and wastewater treatment [3]. The focus attention to the improvements of membrane surfaces because of the fouling issues due to its hydrophobic properties resulting in poor flux and rejections as well as cleaning problems [4]. Moreover, the separation of the emulsion was influenced by surfactants depends on the surface charges and types [5]. For examples, Wu et al. reported the effect of membrane surface charges towards cationic and anionic surfactants emulsion [6].

Among the surface modification strategies, surface coating is the most convenient and facile method to be applied on a large scale [7,8]. To address these challenges towards the scalable

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modification techniques of commercial polymeric membrane for oil/water separation, this study report on the improvements of membrane surfaces with hydrophilic and underwater oleophobic properties with low oil adhesion. Inspired by mussel surface chemistry [9], the alternative of polydopamine [10] which showed high similarities in structure and have adhering efficiency with a lower cost are required [11].

In this study, the tannic acid, plant polyphenols with abundant of phenolic hydroxyl groups, will be used. It also tends to be oxidized under alkaline conditions and react with amine groups to form stable hydrophilic coated membrane surfaces. Then, the comparison of fouling ability of pristine and coated membranes was analysed using different types of surfactant-stabilized emulsions. Furthermore, the influences of different surfactant types onto the coated membrane were evaluated.

2. Experimental

2.1. Materials
Tannic acid (TA) and tetraethylenepentamine (TEPA) were supplied by Merck (Darmstadt, Germany). Tris(hydroxymethyl)aminomethane, Tween 80 (T80) and sodium dodecyl sulfate (SDS) were purchased from Friendemann Schmid Chemical and cetyltrimethyl ammonium bromide (CTAB) supplied by Nacalai Tesque. PVDF microfiltration (flat sheet, 0.22 μm pore size) were purchased from Merck Millipore, which was prewetted in 25% isopropanol for 24 h and soaked overnight with deionized water (DI) prior to the modification process.

2.2. Preparation of Surfactant-Stabilized Emulsion Oil Solution
A diesel oil (Shell Malaysia) emulsion was used as the foulant in crossflow filtration studies. Three types of surfactant-stabilized diesel in water emulsions with the concentration of 1500 ppm (9:1 ratio of oil: surfactant) were prepared including T80/diesel, SDS/diesel and CTAB/diesel in 3L of deionized water. The solutions were emulsified using homogenizer (Ultra Turrax T-50, IKA) operated at 6000 rpm for 30 – 45 min.

2.3. Modification of Membrane
TA (0.2 g) and TEPA (1.2 mL) were dissolved in 50 mM Tris-HCl solution (pH 9, 100 mL). Then, the prewetted pristine PVDF membrane (M1) was stirred into the solution using the open container for 6 h at 30°C. Then, the coated membranes were named as M2 after this procedure was rinsed by isopropanol for 30 min and soaked overnight in deionized water to remove the redundant solution. Finally, M2 was dried in an air-drying oven for 3h at 45°C.

2.4. Characterization
The M2 membranes were characterized by field-emission scanning electron microscope (FESEM, Quanta FEG 650) to ascertain structural morphology and element mapping. The droplet size distribution and zeta potential of each type of emulsion were measured using the Zetasizer Nano Series (Nano-ZS).

2.5. Filtration Studies
Cross-flow filtration mode was used to evaluate the separation performance of the membrane. Prior to the filtration process, the pristine membrane was wetted using 25% IPA, while DI water used for the coated membrane to prevent the surfactant wetting effect during the filtration cycles. Then, the prewetted membrane was compacted at 2 bar for 20 min prior to the filtration process. The pure water flux ($J_0$) of deionized water was measured at TMP of 1 bar for 60 min, then the feed was replaced by emulsion solution at the same TMP for 60 min. The permeate mass (m) was recorded by a computer-recorded electronic balance (EK3000i, A&D Company) at an interval of 1 min (t) which was used to calculate permeate flux ($J_P$) according to following formulae:
\[ J_p = \frac{\Delta m}{\rho_w A \Delta t} \]  

(1)

where \( \rho_w \) is the density of water, and \( A \) is the effective filtration area. Then, the membrane was cleaned using the flushing method of 0.005 M HCl solution for 5 min followed by 10 min of deionized water. Finally, the pure water flux \( (J_C) \) were measured again for 60 min. The concentration of permeate flux was then measured using UV-Vis spectrophotometer (DR 6000, Hach). The flux recovery ratio \( (\text{FRR}) \) was calculated using the following equation:

\[ \text{FRR} = \frac{J_C}{J_0} \times 100 \]  

(2)

The continuous cycle of emulsion separation was also evaluated for 30 min and the same cleaning steps was done for each interval. The normalized flux for each cycle \((n)\) was calculated as follows:

\[ \text{Normalized flux} = \frac{J_n}{J_0} \]  

(3)

3. Results and Discussion

3.1. Characterization

The properties of the emulsion solution were evaluated using Zetasizer to determine the charges and mean diameter of droplet sizes for each type. The results were presented in Table 1. The emulsion stabilized by CTAB emulsion was positively charged due to the ammonium groups, while the T80 and SDS were negatively charged. These charges represent the types of surfactant used which CTAB as cationic type, while SDS as anionic surfactant. While, the slightly negative charge of T80 surfactant was attributed to the ionization of polar oil [12]. The droplet size of the emulsion types is in the range of 0.10 - 10 \( \mu \)m with approximately similar mean diameters. The charge of coating solution was -3.96±0.5 mV as illustrated in Figure 1 represented the negative charge of coated surface was dominant by OH groups of catechol units on polyphenolic components [13].

| Table 1. Properties of emulsion solution |
|----------------------------------------|
| **Emulsion Types** | **Surfactant Types** | **Zeta potential (mV)** | **Mean diameter (μm)** |
|---------------------|----------------------|--------------------------|------------------------|
| T80/Diesel/H2O      | Nonionic             | -25.5±0.9                | 3.67±0.02              |
| SDS/Diesel/H2O      | Anionic              | -79.8±1.2                | 3.52±0.23              |
| CTAB/Diesel/H2O     | Cationic             | 69.2±3.5                 | 3.74±0.29              |

Figure 1. Zeta potential of coating solution (triplicate data)
The surface morphologies of pristine (M1) and coated (M2) membranes are shown in Figure 2 and Figure 3. In comparison on the cross-sectional morphology of both membranes as shown in Figure 2b and 2c, the coated membrane (M2) has denser and compact layer throughout the pore walls. It can be observed that some deposition on the wall of the pores resulting in the increase of roughness on the M2 membrane surface as displays in Figure 3. The EDX elemental mapping on the top surface of M2 indicating that the presences of O and N elements distributed well which were ascribed to the TA/TEPA coating solution. The functional groups between the pristine and coated membrane using FTIR and XPS analysis already reported details in our previous studies [14].

**Figure 2.** Surface morphology of (a) top surface; (b) cross-section for pristine membrane (M1) and (c) cross-section for coated membrane (M2)

**Figure 3.** Surface morphology and element mapping for additive of O and N elements on the coated membrane (M2) surface

**Figure 4.** Photograph of water permeation (a) and underwater oil droplets (b) on top of coated membrane (M2) surface
The effect of hydrophilicity and underwater oleophobicity is shown in Figure 4 by dropping the water and oil droplet (1,2-dichloroethane as model oil), respectively on top of the M2 surfaces. It shows that the coated membrane improved the surface hydrophilicity due to the appearance of the hydroxyl and amine group and successfully coated on the membrane surfaces [15]. Also, the roughness surface with micro/nanostructure created by the coating solution helps the trapped water molecules prevent the permeation of oil onto the membrane surface [16].

3.2. Comparison on Antifouling Properties of Membranes
The performances studies of nonionic (T80), anionic (SDS) and cationic (CTAB) surfactant-stabilized emulsion oil for pristine (M1) and coated (M2) membranes are shown in Figure 5. The enhancement of pure water fluxes of M2 membranes could be observed due to the hydrophilic surface, which makes water easily permeate through this membrane. The water affinity mainly attributed to the hydration effect between hydroxyl groups on coated membrane and water [17].

![Figure 5. Performances of antifouling studies on different types of surfactant-stabilized emulsion (a) T80/Diesel/H2O (b) SDS/Diesel/H2O (c) CTAB/Diesel/H2O for pristine (M1) and coated (M2) membranes](image-url)
The antifouling performances of the M1 and M2 membranes were evaluated using time-dependent fluxes. During emulsion filtration separation, the flux sharply reduced for both membranes due to oil deposition and cake formation. After the cleaning process, it could clearly be seen that the flux recovery for the M1 membrane is lower for all types of foulant due to the hydrophobic properties of membranes. Furthermore, for the M2 membranes, the flux recovery ratio (FRR) were significantly improved for all types of emulsion solutions. Among the surfactant types, the CTAB cationic gave higher FRR as 62% followed by anionic and nonionic emulsion types. However, the removal efficiency for cationic emulsion slightly lower due to the electrostatic interaction between the coated membrane with negative charges and CTAB with opposite charges. The separation efficiencies of T80 nonionic and SDS ionic surfactants were increased using M2 membranes. The coated membrane surface is hydrophilic and rough, which traps water molecules and decreases the contact area between the oil droplet and membrane surface. The improvement of separation efficiency and flux recovery after being subjected to the cleaning process indicates that coated membrane demonstrated low oil-adhesion behavior compared to the pristine membrane. Therefore, the M2 coated membrane exhibits the anti-fouling ability by hydrophilic and underwater oleophobicity properties [18].

3.3. Comparison on Different Separation of Surfactant-Stabilized Emulsion
The separation efficiency and reusability towards oil droplets with different surfactants were further evaluated with a continuous cycle separation by using the same cross-flow system. The normalized flux ratios for each cycle are collected and presented in Figure 6. For the CTAB cationic emulsion, the normalized fluxes after each cycle are 90% higher than SDS and T80 emulsions. It may due to the surfactant barrier effect that promotes the demulsification of oil droplets. Initially, the oil droplets tend to coalesce into larger droplets and stuck on the pore mouth and walls, which could prevent the penetration of tiny oil droplets into membrane pores. Therefore, it can be deduced that electrostatic repulsion reduced the fouling effects [6]. However, the static attraction effects between the cationic foulant and coated surface, resulting in the lower rejection (63%) and higher permeate flux values (~168 LMH) than negatively charge emulsions.

![Figure 6. Normalized flux and removal efficiency for five cycle of emulsion filtration process](image-url)
Besides, for the negatively charged emulsion, the normalized recovery ratio slightly lower for both types. It may due to the low demulsification effects, resulting in the penetration of tiny droplets into the membrane pores which could lead to serious irreversible fouling. The permeation fluxes of anionic and nonionic surfactants are slightly lower about 129 and 82 LMH, respectively. However, the rejection of T80 emulsion is 94% and 85% for SDS emulsion. It may due to the stronger electrostatic repulsion with the negatively charged membrane surface, which caused less surfactant adsorption on top of the membrane surface [19]. After 5-cycles, the coated M2 membrane still displayed the stable removal efficiency with slightly decrease the permeation fluxes.

4. Conclusions
In summary, the hydrophobic PVDF polymer membrane was successfully modified using polyphenolic-amine coating method. The hydrophilic and underwater oleophobic properties of coated membrane surface exhibited better antifouling ability compared to the pristine membrane for nonionic, anionic and cationic surfactant-stabilized emulsion solutions. In addition, the surfactants play the roles towards the demulsification of emulsions depends on the surface charge of the membrane. It was concluded that this coated membrane shows a potential application in oil/water separation.

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