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Description of membrane fouling characteristics during ultrafiltration of organic foulants contained in sweetwater solutions

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ABSTRACT

The characterization and the filtration behavior of commercial ultrafiltration (UF) membranes used in the removal of triglycerides (TG) and combined mixtures (TG–fatty acid) from glycerol–water solution were examined. Flat sheet ultrafiltration (UF) polyethersulfone and polyvinylidenfluoride membranes were used for comparison. Glycerol–water solutions were synthesized as feed and the influences of membrane surface chemistry and pH solutions were studied. Fouling behavior of TG and TG–FA were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform spectroscopy (FTIR), contact angle and surface energy measurement. Results from this work reveal that hydrophobic surfaces are more prone to TG and FA deposition than less hydrophobic surfaces in glycerol–water mixture. SEM morphologies and cross structure as well as FTIR spectrums revealed that the membranes were severely fouled with TG (oil droplets) instead of TG–FA. Further, contact angle measurements obtained in this work showed that the angles tended to decrease with oil wetted material and in acidic conditions.

Introduction

Glycerin is a valuable and highly appreciated product in the oleochemical industry, which is currently contained in sweetwaters. Sweetwaters are abundant sources of glycerin; nevertheless, they contain impurities such as free fatty acids, unreacted mono-, di-, and triglycerides, inorganic salts and a variety of "matter organic non-glycerol" (MONG) [1,2] in the hydrolysis process. The removal of these impurities, especially for the unreacted glycerides, is of commercial importance due to severe membrane fouling during the pretreatment. Ultrafiltration (UF) processes are effective and promising ways to treat the triglycerides (TG) and fatty acids (FA). However, they have been limited by fouling, which is caused by the deposition of oil droplets. A great number of studies have reported on the use of ultrafiltration for the removal of triglycerides, but most of the studies have focused on the treatment in solute–solvent systems [3–8] and less attention has been paid in aqueous (solute–water) systems.

To our knowledge, membrane filtration has been extensively used to treat oil/water contained in wastewater from various process industries such as food processing, petrochemical and textile [9,10]. However, less consideration has been applied to TG (oil droplets) removal from edible and oleochemical industries. Numerous studies have demonstrated the ability of several kinds of filtration processes including ultrafiltration and nanofiltration for oil separation [11–13]. Previously, Faibish and Cohen [14] and Wang Shu et al. [15] developed a ceramic supported polymer ultrafiltration membrane that resists fouling to treat oil in water. More recently, Del Colle et al. [16], have synthesized porous ceramic tubes made of α-alumina to demulsify sunflower oil in water through the tangential filtration process. The literature also demonstrated the separation of fatty acids and linear hydrocarbons using reverse osmosis [17]. They noticed that the chemical nature of the solutes, its molecular weight, and influence of solvent type might affect the membrane performance. Ohya et al. [18], investigated the role of pore size on permeate flux and oil rejection during the oil separation in water using microfiltration membranes. The suitable selection of the membrane material may improve the performance of oil separation, which concerns the chemical nature of the solutes, wettability and resistance to various conditions such as pH, temperature, and oil concentrations [9,19–21]. On the other hand, the fouling characterizations of UF membranes after removal of TG and FA in a water system using analysis methods such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), contact angle (CA) and surface energy (SE) are still scarce in the literature. Tres et al. [8] used FTIR, DCS and SEM–EDS to analyze the changes that have occurred to polymeric membranes after oil-solvent separation. Hu et al. [22] used the FTIR spectrums to analyze the composition of oil adsorbed on the membrane surface after ultrafiltration

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of oil in water emulsions. Xu et al. [23] visualized the oil fouling during the use of SEM corroborated by ultrasonic reflectometry.

Previous work has shown flux reduction during the removal of TG and FA in glycerol–water solutions [24]. However, their contribution to the membrane fouling is incompletely understood due to the limited characterization of them as foulants. The aim of the present study was, thus, to characterize the membranes used in the treatment and to visualize oil droplet deposition on the membrane surface using SEM, AFM, FTIR, contact angle, and surface energy in order to determine membrane changes after fouling during the pretreatment process. Another main objective of this study was to elucidate the nature of fouling after being exposed to the TG and TG–FA mixtures.

Experimental

Membrane selection and characterizations

The membranes selected for this study (i.e., polyethersulfone (PES) and polyvinylidenfluoride (PVDF) membrane) were purchased from Sterlitech. The properties of the membranes exhibited in Table 1. Samples of UF membranes after fouling were characterized by SEM, FTIR, and contact angle measurements. Analysis with SEM (Gemini model SUPRA, 55VP-ZEISS, Germany) following previously published methods [25], was used to observe the morphological changes on the membrane surface and to compare the cross-structural differences between clean and fouled membranes.

The pore reduction was approximately calculated according to Eq. (1) based on the mean pore diameter of the fouled membrane (Eq. (2)):

$$\text{Pore reduction} = \left(1 - \frac{d_{m,f}}{d_{m,o}}\right) \times 100 \quad (1)$$

$$d_{m,f} = \left(d_{m.o}^2 . \frac{R_m}{R_f}\right)^{0.5} \quad (2)$$

where $d_{m,o}$ and $d_{m,f}$ indicate the mean pore diameter of clean and fouled membranes, while R_m and R_f show the resistance of the clean and fouled membrane (m^{-1}), respectively.

Moreover, atomic force microscopy (AFM) was used to observe the changes in roughness of the membranes after fouling and the method is described elsewhere [25].

FTIR analysis was carried out using a PerkinElmer (Lambda 35, Malaysia) spectrophotometer within the range of 4000–500 cm^{-1} in order to provide the information about the changes in functional groups after the removal of TG and TG–FA. Contact angle measurements and surface charge analysis were done by using a drop shape analysis system (Easy Drop KRÜSS, GmbH, Germany). About 3 μL of water drops were injected using stainless steel micro-syringe needles onto the membrane surface at the rate of 30 μL/min. The water drop was captured and recorded for 90 readings; then the mean angle (left and right angle) was determined. The analyses are repeated 3 times in different areas for the average reading. The solid–liquid surface energy (ΔG_{SL}) was determined from the Owens–Wendt–Rabel–Kaelble equation:

$$\Delta G_{SL} = \frac{[0.5\ (1 + \cos\theta)] \times \gamma_L}{\sqrt{\gamma_D}} \quad (3)$$

Eq. (3) must be solved using measured contact angles from one nonpolar and polar liquid, respectively, with known values of membrane surface tension, γ.

All membranes for all characterizations were dried overnight at room temperature before the analysis in order to eliminate the effect of capillary penetration.

Permeation experiments

Ultrafiltration processes were carried out using synthesis of glycerol–water solutions plus a single foulant (TG) or combined foulants (TG–FA). Glycerin (USP, 92.09 g/mol) and oleic acid (282.46 g/mol) were purchased from Merck (Malaysia), and commercial TG (RBD Palm Olein, 870 g/mol) was obtained from a local hypermarket (Malaysia). Mixtures of 15% glycerin, 1% (v/v) TG, and 0.003 g/L oleic acid were synthesized and used as a feed solution. The pH of the feed solution varied between pH 3 and 10 with a few drops of 0.1 M HCl or 0.1 M NaOH and measured with a pH meter (Mettler, Toledo, Malaysia).

Results and discussion

The effectiveness of the UF process during the removal of single solutes and mixed solutes (TG–FA mixtures) in glycerin-rich solutions depends on membrane characteristics and operating conditions applied. Results of the experiments conducted to validate the effect of membrane characteristics and the feed characteristic on the permeate flux, are reported below.

Analysis of functional groups (FTIR spectrums)

The functional groups present in the surface layer after treatment could be identified by FTIR analysis. Fig. 1(a) and (b) reveals the FTIR spectrums of PES25 and PVDF membranes fouled with TG and TG–FA mixtures, respectively. It was found that the bands at 2916, 2848, and 2846 cm^{-1} correspond to C—H stretching vibrations of the CH_2 group, which are the typical peaks of hydrocarbons. A similar trend was observed in Fig. 1(b). Two small bands associated with stretching vibration of symmetrical and asymmetrical CH_2 scissors present at 2925 and 2854 cm^{-1} represent the unsaturated fatty acid chains [26,27]. There is no band corresponding to the C ═O stretching around 1690–1750 cm^{-1} for fouled PES25 membranes with TG as well as TG–FA mixtures, even though the C ═O groups could be found for the fresh PES25 membrane. The absence of the band in our spectrums could be due to the heterogeneously distributed solutes on the membrane surface. Nevertheless, it can be noted that the spectrum of PVDF membranes (as exhibited in Fig. 1b) exhibits the presence of a band characteristic of the carbonyl group (C ═O) in the region between 1745 and 1714 cm^{-1} as evidence of the deposition of residual oil on the membrane surface after the separation test [8]. Moreover, an additional absorption band at 1470–1370 cm^{-1} corresponds to C—H bending [28], while the small peak at wavenumber 718 cm^{-1} for both foulants can be attributed to the out-of-plane –CH and ring bending [29]. These two spectra revealed that the typical characteristic of common triglycerides, which are the principal components of fats and oil, consequently dominate the spectrum of fats and oil [30]. As a matter of fact, the peaks suggest the presence of oil on the top surface and susceptibility to fouling.

On the other hand, the strong fingerprint region, which is illustrated in frequency from 1250 to 1150 cm^{-1} (as shown in Fig. 1a), can be ascribed to the symmetrical vibration of the sulfonic groups (S ═O) and is characteristic of polyethersulfones [31,32]. However, it should be noted that no characteristic peaks of polyethersulfone were detected on PES25 membranes fouled neither with TG nor TG–FA mixtures, meaning that the fouling was probably due to pore blockage.

Analysis of surface morphology (SEM)

Effects of membrane surface chemistry and the nature of the solutes

The phenomenon of pore plugging and cake formation, which contributed to membrane fouling were observed qualitatively using SEM images of the surface morphologies for fouled PES25 membranes (Fig. 2b and c). The solution used in this part is original condition