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Omega-3 PUFA concentration by a novel PVDF nano-composite membrane filled with nano-porous silica particles

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ABSTRACT

In this study, polyvinylidene fluoride (PVDF) and nano-porous silica particle were used to fabricate an asymmetric nano-composite membrane. Silica particles enhanced the thermal stability of PVDF/SiO_2 membranes; increasing the decomposition temperature from 371 °C to 408 °C. Cross sectional morphology showed that silica particles were dispersed in polymer matrix uniformly. However, particle agglomeration was found at higher loading of silica (i.e., 20 by weight%). The separation performance of nano-composite membranes was also evaluated using the omega-3 polyunsaturated fatty acids (PUFA) concentration at a temperature and pressure of 30 °C and 4 bar, respectively. Silica particle increased the omega-3PUFA concentration from 34.8 by weight% in neat PVDF to 53.9 by weight% in PVDF with 15 by weight% of silica. Moreover, PVDF/SiO_2 nano-composite membranes exhibited enhanced anti-fouling property compared to neat PVDF membrane. Fouling mechanism analysis revealed that complete pore blocking was the predominant mechanism occurring in oil filtration.

Industrial relevance: The concentration of omega-3 polyunsaturated fatty acids (PUFA) is important in the oil industries. While the current methods demand high energy consumptions in concentrating the omega-3, membrane separation technology offers noticeable advantages in producing pure omega-3 PUFA. Moreover, concentrating omega-3 via membrane separation produces products in the triacylglycerol form which possess better oxidative stability. In this work, the detailed mechanisms of fouling which limits the performance of membrane separation were investigated. Incorporating silica particles to polymeric membrane resulted in the formation of mixed matrix membrane with improved anti-fouling behaviour compared to the neat polymeric membrane. Hence, the industrial potential of membrane processing to concentrate omega-3 fatty acids is enhanced.

1. Introduction

Concentration of fatty acids, especially omega-3 PUFA has become important in edible oil industries. The high content of docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA) in different oils has significant role in disease prevention. Fish oils are one of the main sources of DHA and EPA, thus concentration of fish oil with significant content of DHA and EPA has gained more interest in the food industry. Conventional methods including hexane extraction, urea crystallization and vacuum distillation are widely used to extract and purify the omega-3 PUFA. However, developing a suitable commercial method with a proper efficiency in concentrating omega-3 PUFA has been the topic of several studies (Rodriguez et al., 2010; Tengku-Rozaina & Birch, 2013; Simopoulos, 1991; Shahidi & Wanasundara, 1998; Kapoor & Patil, 2011; Liu, Zhang, Hong, & Hongwu, 2006).

Membrane separation processes with advantages of low energy consumption, compact structure, working at low temperature and lower investment cost have broadly been used in the oil and fat industries (Abedini, Mousavi, & Aminzadeh, 2012; Nematollahi, Saeedi Dehaghani, & Abedini, 2016; Castro-Muñoz, Yáñez-Fernández, & Fíla, 2016; Mereddy, Chan, Fanning, Nirmal, & Sultanbawa, 2017). Performance of membranes was evaluated based on deacidification and degumming of oils, colour reduction and solvent recovery (Linder, Matouba, Fanni, & Parmentier, 2002; Kumar & Bhowmick, 1996).

Polymeric membranes have been widely used in membrane separation processes due to their low cost, ease of fabrication and flexibility. However, lack of thermal, chemical and mechanical stability limits their application. In contrast, ceramic membranes have shown proper thermal and chemical resistance through poor membrane forming, brittle and high costs that have so far

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restricted the usage of these membranes. On the other hand, composite membrane can mingle basic properties of polymeric and ceramic membranes known as organic-inorganic material with better separation performance as well as good thermal and chemical stability (Dorosti, Omidkhah, & Abedini, 2015; Malomo & Aluko, 2015; Zhu & Mhemdi, 2016; Aliasghari Aghdam, Mirsaeedghazi, Aboonajmi, & Kianmehr, 2015).

Polyvinylidene fluoride (PVDF) is one of the polymeric materials that is extensively used for membrane fabrication because of its superior thermal and mechanical strength. However, its separation capability does not respond to the level of industrial demand. Many studies have examined the various techniques such as chemical grafting, surface modification and physical blending to improve the separation performance of PVDF. Among these studies, blending with inorganic particles is interesting due to the inherent properties of organic-inorganic compounds (Azmi et al., 2015; Bai, Wang, Zhou, & Zhang, 2012).

Metal oxides such as alumina (Al_2O_3), titanium dioxide (TiO_2), and silica (SiO_2) are the main inorganic materials that are used to blend with PVDF membrane to enhance its separation characteristics. Among the several inorganic materials, silica has been widely used owing to its high thermal resistance and proper reactivity and chemical properties (Bai et al., 2012; Abedini, Omidkhah, & Dorosti, 2014; Azmi et al., 2015)

In this work, the PVDF/silica composite flat sheet membrane is prepared by a phase separation procedure. Rice hull is used as a precursor for the synthesis of nano-porous silica particles and the membranes are characterized by means of FTIR (Fourier transform infrared spectroscopy), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The main objective of this study was to concentrate the omega-3 PUFA of Lantern fish oil. The effect of silica particles on the performance of PVDF composite membranes was evaluated, specifically oil flux and omega-3 PUFA concentration. Moreover, the created fouling on the membrane surfaces due to oil filtration was studied.

2. Materials and methods

2.1. Materials

Lantern fish oil was used as a source of omega-3 PUFA, supplied by Qeshm Fish Process Company in South of Iran. To analyze the fatty acids composition of fish oil, hexane, methanol, sodium hydroxide (NaOH) and boron trifluoride (BF_3) – all with purity of 99.9% – were purchased from Merck Company (Kenilworth, USA). Polyvinylidene fluoride (PVDF) with molecular weight of 275,000 Da – supplied by Sigma-Aldrich Chemical Company (St Louis, MO, USA) – was used as a polymer former for membranes. N-methyl-2-pyrrolidone (NMP) with an analytical purity of 99.9% was supplied by Merck Company (Darmstadt, Germany) and de-ionized water as a non-solvent agent were used to prepare a polymer solution.

2.2. Fatty acid methyl esters (FAME) analysis

The FAME analysis of Lantern fish oil was performed as reported by Metcalfe, Schmitz, and Pelka (1996) which was also described in a previous work (Ghasemian, Sahari, Barzegar, & Ahmadi Gavlighi, 2015).

2.3. Nano-porous silica synthesis

The acidified rice hull ash (RHA) was prepared using the 1.0 M HNO_3. The rice hull (RH) was obtained from a rice mill in the Rice Research Center (Amol, Iran). The RH was placed in a furnace (M110 Muffle, Thermo Scientific™, MA, USA) and heated up to 400 °C and 700 °C for 1 h and 4 h, respectively. The obtained ash was sieved through 500 mesh and then collected. The rice hull ash (RHA) was stirred in 1.0 M HNO_3 for 24 h at the room temperature. The resulting ash was washed with de-ionized water to remove extra acid and then dried in an oven at 50 °C for 24 h. The dried RHA was stirred in 50 ml of 6.0 M HCl for 4 h under reflux condition. Afterwards, the resulting ash was washed again with de-ionized water and dried in an oven at 50 °C for 24 h. The RHA was then stirred with 50 ml of 2.50 M NaOH for 24 h. After wards, concentrated sulphuric acid was added (about 5–6 cc) carefully to set the pH in the range of 7.5–8.5. The final solution was allowed to be sequestrated. Finally, the sample was washed with warm de-ionized water to remove the extra NaOH and then dried in an electrical furnace at 700 °C for 4 h (Monshizadeh, Rajabi, Ahmadi, & Mohammadi, 2011).

2.4. Membrane fabrication

A dry/wet technique was employed to prepare the asymmetric PVDF/silica mixed matrix membrane (MMM). In general, MMMs fabricated using a high boiling point solvent such as N-Methyl-2-pyrrolidone (NMP) (i.e., b. p = 204 °C) are free of surface defect and holes which attributed to the low rate of solvent evaporation. However, the high boiling point solvents suffer from problems such as inorganic filler sedimentation, higher evaporation time and larger energy consumption. Thus the membrane fabrication procedure should be combined with controlled particles dispersion. In this regard, NMP was used as a solvent for PVDF due to fast formation of a uniform polymer/filler solution. First, both PVDF and silica particles were preheated at 60 °C for 6 h in a vacuum oven to remove any moisture. After that, a specified amount of silica was added to NMP and stirred for 24 h to mix with NMP as the solvent. To obtain a more homogenous mixture, the prepared suspension was sonicated for 10 min. Thereafter, 10% of the total PVDF was added to the silica/NMP suspension which was further stirred for 12 h. The aim of this step was to form a thin layer coating of PVDF around the silica particles in a dilute and low viscosity polymer solution. The extra amount of PVDF was then added to form a 15 by weight% solution and the final mixture was allowed stirring for 24 h at the room temperature to form a uniform solution. The final solution was casted by means of film applicator with a thickness of 300 μm on a glass plate. The first stage of dry/wet technique was the thin dense layer formation on the top layer of the casted film. For this purpose, the casted film was placed in a vacuum oven at 150 °C for 2 min. The diminutive solvent evaporation of top surface of casted film can create a thin dense layer. The second stage was followed by immersing the casted film in the coagulation bath of de-ionized water at 0 °C for the phase separation induced by immersion precipitation. After primary phase separation, the membrane was stored in the same new bath for 24 h to assure complete phase separation. Finally, the formatted mixed matrix membrane (MMM) was placed in a vacuum oven at 60 °C for 24 h to obtain a dried membrane. To prepare the heat treated membrane, the fabricated MMM was placed in a vacuum oven at 120 °C for 48 h for slow initial heating and final cooling rates.

2.5. Characterization

To evaluate the chemical composition of silica particles and MMMs, FTIR-ATR was performed using a Perkin-Elmer Spectrometer, Frontier model, Version 10.03.06 (Perkin-Elmer Instruments, Norwalk, Waltham, MA, USA) in a range of 400–4000 cm^{-1}. The spectrum of each specimen was taken at an occurrence angle of 458° with 32 scans at a wave number resolution of 4 cm^{-1}.