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TiO₂ encapsulated cross-linked polystyrene-polyacrylic acid membranes for waste oil-water separation



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ABSTRACT

Special wetting polystyrene (PS) based superhydrophobic material has been investigated as a potential costeffective and efficient oil-water separation membrane to remediate the oil spills. However, superhydrophobic properties of polystyrene based materials are susceptible to harsh physical or chemical conditions and their superhydrophobic properties can be diminished easily. To address the stability of polystyrene based superhydrophobic membranes, polystyrene was cross-linked with the acrylic acid (AA) either by ex-situ or in-situ polymerization on the TiO₂ nanoparticles. Membranes fabricated either by ex-situ or in-situ polymerization of styrene-acrylic acid on the TiO₂ nanoparticles exhibited enhanced oleophilic properties having the oil contact angles of $\sim 0^{\circ}$. The water contact angles of different membranes varied in the range 141 $\sim 155^{\circ}$ demonstrating the variation of hydrophobic properties of different membranes fabricated by controlling the styrene-acrylic acid co-polymer coating method. Membranes fabricated with co-polymerized PS-polyacrylic acid(PAA)/TiO2 NPs can be used to separate for both highly viscous and light oils having exceptional oil-water separation efficiencies of \sim 99%. The in-situ co-polymerized PS-PAA/TiO₂(NP) membranes separate high and low density oils from water with a separation efficiency of over \sim 99% with a flux of \sim 50,000–60,000 L m⁻² h⁻¹ under gravity driven process and a flux of \sim 7500–9000 L m⁻² h⁻¹ under antigravity driven process due to excellent oil-wetting properties. It was demonstrated that the oil-water separation efficiency, reusability, durability and hydrophobicity of the styrene-acrylic acid co-polymer coated TiO2 membranes can be enhanced by using appropriate membrane fabrication methods.

1. Introduction

The rapid industrial growth has increased the demand for oil exploration, transportation and industrial use of petroleum oil in several ways resulting in the exponential increase in wastewater that contaminated with oil. Contamination of natural water bodies by petroleum and non-petroleum oils, such as vegetable oils and animal fats pose threats to public health and the environment as they have toxic properties and produce harmful physical effects, i.e. oil spills may harm sea grasses and kelp beds and also, can harm birds and mammals by physical contacts of toxic substances [1,2]. Skimming, coagulation-flocculation, gravity separation, adsorption and biological degradation methods etc., are the conventional methods that have been used for decades for the removal of oil from the oil-contaminated wastewater [3–6]. The major shortcomings of such conventional methods are that these methods are economically unproductive due to higher energy consumption, limited adsorption capacity and poor separation selectivity and also due to the

treated water do not satisfy the stipulated water quality standards [7,8].

On the other hand, separating oil and water from the oil-water mixture using the selective oil-water filtering membrane fabricated with the special wetting materials is of great interest due to their better separation efficiency and the cost-effectiveness compared to conventional methods [9-16]. Thus, by using special wetting super hydrophobic-oleophilic membranes in treating oil-contaminated wastewater may help to address some of the major problems and difficulties that arise when using those conventional methods to separate oil-water. A number of methods and materials have been used to fabricate super hydrophobic-oleophilic membranes, i.e. spray deposition, template method, electrospinning, composite coatings, sol-gel method, layer by layer (LBL) method, chemical vapor deposition (CVD), dip coating method lithography are some of the methods used to fabricate hydrophobic surfaces while commonly used materials are polystyrene (PS), polyvinylidene fluoride (PVDF), fluorinated hydrocarbons, polymer composite nanoparticles etc [17-20].

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Among these materials, PS which possesses a long chain organic molecule with a benzene ring on it is a highly suitable material for the separation of the oil-water mixture owing to the surface free energy of PS lies between the surface free energies of water and oil [21]. Additionally, it is inexpensive and possess good chemical stability [22]. Superhydrophobic surfaces with a contact angle of $\sim 150^{\circ}$ have been reported with PS dissolved in DMF or paraffin wax [23,24]. Similarly, temperature-induced capillary template wetting method has been used to tune the contact angel of PS based membranes [25]. The poor mechanical stability is the major problem in polymer-based super wetting membranes. In recent investigations, the stability of polymer-based membranes has been enhanced by incorporating nanoparticles in polymer- membranes [26-28]. The effect of the incorporation of nanoparticles in polymer-based membranes on the mechanical strength, hydrophilicity, permeability, selectivity and antifouling property of hydrophobic polymer membranes has been reported recently by Wang et al. [27] and Rabajczyk et al. [29]. On the other hand, to enhance the stability of the PS based superhydrophobic membranes, chemical modification [20], surface treatment and incorporation of nanomaterials in PS have been investigated.[30-33] i.e. incorporation of Fe₂O₃ and SiO₂ nanopartices in PS have been reported to strengthen the resistance towards water jet impact and self-cleaning properties of the superhydrophobic membranes fabricated with PS [34,35]. In a recent investigation, Wang et al. reported the enhancement in salt resistance and acid/alkali stability by moulding of PS with polyacrylamide and the porous structure on the fiber surface has been reported to be controlled by the content of PAM [32]. Similarly, a polystyrene-based microfiber membrane with hierarchically tunable structure with excellent hydrophobicity-oleophilicity properties has been fabricated by the incorporation of cellulose acetate, silica nanoparticles and hydrophobic silica nanoparticles in PS [33].

However, superhydrophobic properties of PS based materials are susceptible to harsh physical or chemical conditions and their superhydrophobic properties can be diminished easily [36] i.e. it has been reported the loss of nonwetting properties of PS based membranes due to flexing, bending, or abrasion [37]. In this report, PS was cross-linked with the grafted PAA on $\mathrm{TiO}_2\mathrm{NPs}$ to address the stability of PS based superhydrophobic membranes. The novelty of this investigation is that it was demonstrated that by using chemically coated PAA and further cross-linking of PAA with PS enhances the adherence of PS membrane to the surface and that would enable to withstand the harsh physical and chemical conditions while maintain the superhydrophobic properties of PS. Furthermore, in recent studies it has proven that highly oriented surfaces and surfaces with more surface roughness are the ideal for achieving the superhydrophobicity [38]. Hence, in order to enhance the surface roughness, the strengthen and the instability of the coated layers, co-polymerized styrene-AA/TiO2 composites were fabricated on the Stainless steel (SS) meshes by (a) ex-situ co-polymerized styrene-AA coated TiO₂ NPs, (b) in-situ co-polymerized styrene-AA on TiO₂ NPs and (c) in-situ co-polymerized styrene-AA on TiO2 coated stainless steel mesh. Despite all the membranes fabricated with the above methods exhibit high water contact angle with superoleophilicity, in-situ co-polymerized polystyrene (PS)-polyacrylic acid (PAA)/TiO2 NPs found to be possessed superior wetting and efficient oil-water separation properties.

2. Experimental

2.1. Materials

Potassium persulfate 99 + %, A.C.S reagent from Aldrich, TiO₂ P25 from Degussa, AA (stabilized with 200 ppm MEHQ) from Daejung, Styrene reagent plus (contains 4-tert-butylcatectechol as a stabilizer, \geq 99% from Sigma Aldrich), Acetone, Distilled water, Tetrahydrofuran (contains 250 ppm BHT as an inhibitor, puriss.p.a. ACS reagent, \geq 99%), Engine oil (SAE 15W-40), Kerosine, 1-Octadecane, stainless steel meshes (#120–100 µm opening) were used as received without further purification.

2.2. Fabrication of AA – styrene co-polymer coated TiO₂ nanoparticles

As shown in Fig. 1, membranes with polystyrene (PS)-polyacrylic acid (PAA) co-polymer coated TiO_2 nanoparticles were fabricated either by in-situ or ex-situ copolymerization of styrene and AA on TiO_2 NPs. As described in Sections 2.2.1, 2.2.2 and 2.2.3, three different membranes were fabricated.

2.2.1. Preparation of ex-situ copolymerized styrene-AA/TiO₂ NPs. (filter A)

In the ex-situ method, AA and styrene were pre-polymerized together and the co-polymerized AA-styrene was coated on TiO₂ nanoparticles. For the polymerization, 0.01 mol of AA was added to 100.0 ml of distilled water and stirred for 1 hr and ultrasonicated further for 20 min and finally 0.03 mol styrene was added to the solution and stirred for another 1 h. The solution was kept in a hot water bath at $75-80^{0}$ C and N₂ was purged for 30 min to remove dissolved O₂. To initiate the radical polymerization reaction, 50.0 mg of K₂S₂O₈ initiator was added and the solution was stirred for 8 h until the polymerization complete. As synthesized polymer was filtered, washed with distilled water to remove unreacted monomers and then dried in a vacuum drving oven for 3 h. The PAA-PS coating on TiO2 was carried out by mixing 200.0 mg of PAA-PS co-polymer and 200.0 mg of TiO₂ in 20.0 ml of acetone followed by 20 min ultrasonication and stirring for 2 h. To fabricate the filter membrane, the PAA-PS coated TiO₂ (PAA-PS/TiO₂) was sprayed onto pre-cleaned and 130 °C heated SS mesh on a hot plate using an airbrush spraying tool. Stainless steel meshes (#120/100 µm opening width, size $2'' \times 2''$) were pre-cleaned by ultrasonication of SS mesh in acetone and then rinsed with ethanol and deionized water.

2.2.2. Preparation of in-situ copolymerized styrene-AA/TiO2 NPs. (filter B)

In the in-situ method, AA and styrene were co-polymerized directly on TiO₂ particles. Styrene, AA, and TiO₂ suspensions were pre-prepared separately as follows; P25 TiO₂ 200.0 mg was added to 100.0 ml of distilled water and stirred for 30 min followed by 20 min of ultrasonication. The solution was kept in a hot water bath at 75–80 $^\circ$ C and N₂ was purged for 30 min to remove dissolved O2. The AA solution was prepared by adding 0.03 mol of AA into 10.0 ml of distilled water followed by 20 min of ultrasonication and stirring for 30 min. The AA solution was also degassed for 20 min using N2 gas. To prepare a styrene solution, 0.03 mol styrene was dissolved in 10.0 ml of THF followed by 20 min of ultrasonication and stirred for 30 min and finally degassed with N2. As a first step, the pre-prepared AA solution was added dropwise into the pre-prepared TiO₂ solution while stirring and then the pre-prepared styrene solution was added drop wisely to the AA/TiO₂ solution mixture. The solution mixture was stirred for 2 hr followed by 20 min N₂ purging. To initiate the radical polymerization, 50.0 mg of K₂S₂O₈ initiator was added and the solution was stirred for 2 hrs until the polymerization complete. The in-situ AA-styrene co-polymer coated TiO2 NPs were extracted into CHCl3 solvent and dried in a vacuum drying oven. To fabricate the filter membrane B, a solution containing 100.0 mg of in-situ polymerized AA-PS/TiO2 in 20.0 ml of acetone was prepared and sprayed on to the SS mesh as explained in the Section 2.2.2.

2.2.3. Preparation of in-situ copolymerized styrene-AA on the TiO2 NPs coated SS mesh. (filter C)

In fabricating of filter C, TiO_2 nanoparticles were coated initially on the SS mesh and AA was pre-reacted or adsorbed on the TiO_2 surface and polymerization was carried out in the presence of styrene in the solution. To prepare TiO_2 coated SS mesh, 400.0 mg of P25 TiO_2 was dispersed in 40 ml of acetone followed by 30 min ultrasonication and stirring for 1 hr and then the prepared solution was sprayed on to the pre-cleaned SS mesh using an airbrush spraying tool. The TiO_2 coated mesh was



Fig. 1. (1) fabrication methods of different membranes; ex-situ AA – styrene co-polymer TiO₂ NPs (filter A), in-situ AA – styrene co-polymer TiO₂ NPs. (filter B) and in-situ AA – styrene co-polymer TiO₂ NPs coated on SS mesh (filter C).

sintered at 450 °C for 30 min and cool down to room temperature. For the polymerization process, 0.01 mol AA was dissolved in 100.0 ml of distilled water followed by 30 min ultrasonication and the solution mixture was stirred for 2 hr followed by 20 min N₂ purging to remove dissolved O₂. Styrene (0.03 mol) was added to the above solution and stirred for another 1 h followed by 30 mins of N₂ purging. For copolymerization, pre-prepared TiO₂ coated SS mesh was immersed in the co-polymerization solution and the whole set up was kept in a hot water bath that at 70 °C and 50.0 mg of K₂S₂O₈ was added to initiate the polymerization. The solution was stirred vigorously until the polymerization is completed. The polymer coated SS mesh was removed from the solution, washed with distilled water and dried at 110 °C for 2 h under air.

2.3. Instrumentation and characterization

For surface morphology analysis, Scanning electron microscope (SEM) images were taken by Carl Zeiss Evo 18 - Research scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) was recorded from the Thermo Nicolet iS50 FTIR spectrometer in the range $400-4000 \text{ cm}^{-1}$. The surface wettability and contact angle images of the AA-PS/TiO₂ coated SS membranes were detected using (Powereach JCD 2000 model Standard Contact Angle Goniometer) by sessiledrop technique at room temperature. For water contact angle measurement, with an automated syringe pump, $10 \,\mu$ l of water droplet is deposited on the surface of the membrane and the water contact angle was measured. For each membrane, this step was repeated for five times and the average value is reported. The surface wettability and contact angle images of the AA-PS/TiO₂ coated SS membranes were detected using (Powereach JCD 2000 model Standard Contact Angle Goniometer) by set images and the average value is reported. The surface wettability and contact angle images of the AA-PS/TiO₂ coated SS membranes were detected using (Powereach JCD 2000 model Standard Contact Angle Goniometer)

by sessile-drop technique at room temperature. The crystallographic data was taken using a Rigaku Ultima IV X-ray diffraction with Cu K α ($\lambda = 1.540^{\circ}$ A) radiation, angle range from 5 to 65°.

2.4. Oil/water separation experiments

The oil-water separation apparatus and the details of the synthetic water/oil mixture preparation are given in the SI. The source of oil used and their properties are given in Table S1.

3. Results and discussion

3.1. Fabrication of the membrane and the mode of coordination in PS-PAA/TiO₂ coated SS membrane

The PS-PAA/TiO₂-SS membrane was prepared by copolymerization of styrene and AA in the presence of TiO₂ NPs in the polymerization solution or immobilized TiO₂ on the SS mesh. As the wetting and adherence properties of PS-PAA/TiO₂-SS membranes are found to be highly dependent on the method of polymerization, i.e. ex-situ or in-situ method, fabricated membranes were characterized to distinguish the dependence of wetting properties with the mode of polymerization.

As shown in Fig. 2, the formation of the PS-PAA co-polymer can be described as follows [39,40]: According to Ríos-Osuna et al. and Lessard et al., during the polymerization reaction, ionomers or copolymers can be formed by the chain of free radical polymerization reactions between monomers of styrene and AA in the presence of an initiator [39,40]. In the case when the membrane is formed by the ex-situ polymerization (filter A), the co-polymer PS-PAA is formed initially by the polymerization of styrene and AA and later co-ordinated with the TiO₂NP while



Fig. 2. Free radical polymerization reactions between monomers of styrene and AA in the presence of initiator in the fabrication of filters A, B and C.

in the case of in-situ polymerization (filter B), TiO_2NP co-ordinated with the PS-PAA co-polymer during polymerization of styrene and AA. On the other hand, in the case of the membrane is formed by the in-situ copolymerization of AA–styrene on TiO_2 NPs coated SS mesh (filter C), AA is initially adsorbed on the TiO_2 NP and co-polymer PS-PAA is formed on the AA-coated TiO_2 NP. As the isoelectric point of TiO_2 (P25) is 6.47, AA and PS-PAA can easily get grafted to the positively charged TiO_2 particles under acidic conditions as demonstrated for titanium dioxide encapsulated poly(styrene-co-butyl acrylate-co-acrylic acid) [41].

The functional structures and the mode of coordination of PS-PAA to TiO₂ NP were characterized by using FTIR spectroscopy and the spectra of PS-PAA and PS-PAA co-polymer coated TiO₂ NP are shown in Fig. 3 while FTIR spectra of PS and PAA are shown in Fig. S1. In the FTIR spectra of pure PS, peaks at 3061 and 3026 due to aromatic C-H stretching vibration, three absorption peaks at 1605, 1492 and 1452 cm⁻¹ are due to aromatic C⁼C stretching vibrations and peaks at 756 and 698 cm⁻¹ are due to C–H out-of-plane bending vibrations. The absorption peak at the 3446 cm^{-1} is for the stretching vibration of adsorbed water. The IR spectrum of polyacrylic acid shows that characteristic band at 1714 cm⁻¹ which, could be assigned to the stretching vibrations of the carbonyl group of the carboxylic group of the monomer and the broadband having a medium value at 3429 cm^{-1} is characteristics for y CH aliphatic chain. While the bands between 1108 and 1330 cm⁻¹ are assigned to (CO) stretching and (OH) bending vibrations. The band 1446 cm⁻¹ is assigned to δ (CH2) and the band at 629 cm⁻¹ is assigned to δ (C=O, trans) [42,43]. The IR spectra of PS-PAC co-polymer coated TiO₂ NP are shown in spectra b (membrane A), c (membrane B) and d (membrane C) in Fig. 3. The appearance of well-defined characteristic bands of both styrene (i.e. 1605 cm⁻¹, stretching of benzene ring) and AA (i.e. 1704 cm⁻¹, carbonyl bond) in all FTIR spectra of co-polymers formed by ex-situ and in-situ methods, confirm the copolymer PS-PAC composed of polystyrene and polyacrylic acid.

To investigate the binding nature of the co-polymer and TiO₂ NP, the change in the carbonyl vibrations in PS-PAA is scrutinized as carboxylic groups have the ability to form coordination bonds with the metal ions. It has been reported that the reaction between polyacrylic acid and a metal oxide would be the formation of polymer-metal complexes [42]. Hence, the binding nature of the copolymers with the metal ions could be the coordinating interaction of the carboxylic groups of PAA in PS-PAA copolymer and Ti metal ions in TiO₂. As shown in Scheme 1, monodentate, bidentate bridging or bidentate chelating can be formed between the carboxylic group and Ti metal. In PS-PAA copolymer, carbonyl bond in the carboxylic group appears at 1704 cm⁻¹ (symmetric stretch) and 1734 cm⁻¹ (asymmetric stretch) while C–O stretching vibration appears in the range 1108–1132 cm⁻¹. After binding of the PS-PAA copolymer with TiO₂ NPs, the absence or weaken C–O stretching vibration at 1108–1132 cm^{-1} and the presence of C=O peak in the FTIR spectra of PS-PAA/TiO2 NP is noted. According to Fahmiati et al., if bidentate bridging or bidentate chelating is formed between PS-PAA and TiO₂ NP, a peak that corresponds to carboxyl group cannot be appeared at it coordinated with the Ti metal as shown in Scheme 1b and c [42]. Hence, after binding of the PS-PAA copolymer with TiO₂ NPs, the absence or weaken C–O stretching vibration at 1108–1132 cm⁻¹ and the presence of C=O peak in the FTIR spectra of PS-PAA/TiO2 NP is an indication of monodentate interaction between copolymer and -TiO2 NP. Additionally, as shown in Fig. 3, in all the PS-PAA/TiO₂ NP copolymers, the appearance of a new peak at 1322 cm^{-1} that corresponds to monodentate chelating of C-O with the metal and absence of



Fig. 3. FTIR spectra (i) of co-polymer PS-PAA, (a) free PS-PAA, (b) ex-situ AA – styrene co-polymerized PS-PAA/TiO₂ NPs (filter A) (c) in-situ AA – styrene co-polymerized PS-PAA/TiO₂ NPs (filter B) and in-situ AA – styrene co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C). (ii) figure shown in the below is the magnified FTIR spectra of the upper figure.

bidentate bridging or bidentate chelating peaks (1241 and 1225 cm⁻¹) is strong evidence for the formation of monodentate interaction between copolymer and TiO₂ NP [44].

3.2. Characterization and morphology of the PS-PAA/TiO₂ coated SS mesh

The crystal structures of PS-PAA/TiO2 membranes fabricated by

three different methods were analyzed by XRD technique. Fig. 4 shows the X-ray diffraction patterns of PS-PAA-A, PS-PAA-B and PS-PAA-C in which, the observed week and wide peak at 2θ of around $15-17^{\circ}$ can be attributed to amorphous hybrid copolymer [43,45]. The XRD patterns and SEM image of pure TiO₂ are shown in Fig. S2a and S2b respectively. As shown in Fig. 4 and Fig. S3a, for TiO₂ P25 the peaks at 2θ at 25.31 (101)) and 20 at 27.41 (110) are characteristic diffractions of anatase and rutile respectively and the incorporation of TiO₂ NP in the copolymer is confirmed by the presence of diffraction peaks that correspond to TiO₂ P25 [46]. Also, other characteristic peaks observed at 20 positions of 38.28, 48.21°, 54.35°, 55.61° and 63.25°, correspond to the (004), (200), (105), (211) and (204) crystalline planes of the anatase phase and the diffraction peaks detected at θ positions of 27.48, 36.28, and 41.48 correspond to the (110), (101), and (111) crystalline planes of the rutile (R) phase are well agree with the reported diffraction patterns of TiO₂ [46].

As the texture and the polarity of the surface are the main deciding factors of the wettability of any surface, the surface morphology and the polarity of filters A, B and C were analyzed by SEM and contact angel measurements respectively. In superoleophilic-superhydrophobic surface, a highly textured surface and nonpolar surface trap a thin air layer between the solid surface and the liquid leading to lowering of the interaction between the solid surface and the liquid droplet and hence water droplets an easily slide away without wetting the surface [47,48].

To distinguish the morphology variations of the different membrane fabrication methods, the surface morphology of the copolymer coated



Fig. 4. XRD patterns of (A) ex-situ co-polymerized PS-PAA/TiO₂ NPs (filter A) (B) in-situ co-polymerized PS-PAA/TiO₂ (filter B) and (C) in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C). The magnified image in the 2θ angle of 10–20 is shown in the inset.



Scheme 1. Possible coordinating interactions of the carboxylic groups of PAA in PS-PAA copolymer and Ti metal ions in TiO₂. (a) monodentate, (b) bidentate bridging or (c) bidentate chelating.

 TiO_2NP (PS-PAA-filter A, PS-PAA-filter B and PS-PAA-filter C) membranes were investigated by SEM and shown in Fig. 5a, b and c respectively while the respective magnified SEM images are shown in Fig. 5d–f. The cross-section images of filter B is shown in Fig. 6a and b while the uncoated stainless steel mesh surface is illustrated in Fig. S4. The comparison of the SEM image of the bare SS mesh (Fig. S4) together with SEM images of polymer coated TiO_2NPs (Fig. 5a–c), clearly indicates that the smooth stainless steel surface is completely covered with the co-polymer coated TiO_2 NPs resulting in a highly rough surface.

However, in the magnified SEM images of PS-PAA/TiO₂NP coated mesh (Fig. 5d–f), micro and nanoscale surface roughness in all three membranes can be observed and that would enhance the super-hydrophobicity in PS-PAA/TiO₂NP which, prevents wetting of these surface by water. Importantly, TiO₂NP are totally and smoothly covered by the PS-PAA co-polymer and an extra PS-PAA not observed in the magnified image of filter B. However, in the magnified images of filters A and C, TiO₂NP are not fully covered by the PS-PAA co-polymer and

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also patches of extra PA-PAA layers can be clearly seen. Importantly, surface morphologies of all three membranes indicate a nonhomogeneous distribution of copolymer on the surface of the SS mesh resulting in a highly rough surface and the relative surface roughness of the membrane surface increases in the order PS-PAA-C < PS-PAA-B < PS-PAA-A. Hence, considering the surface roughness alone, relatively an enhanced superoleophilicity can be expected in the filter A than the filters B and C. The incorporation of titanium (TiO₂) in PA-PAA/TiO₂NP in the membrane is confirmed by the EDX results of PS-PAA/TiO₂NP (filter B) shown in Fig. S5 in which, the presence of Ti (atomic 1.1%) due to TiO₂ and C (atomic 25.0%) due to PS-PAA is confirmed. From the cross-section image of filter B (Fig. 6a and b), the full coverage of bare SS mesh with the PS-PAA/TiO₂NP layer is clearly noticeable and the calculated PS-PAA/TiO₂NP layer thickness on the SS was found to be ~11.0 μ m.

The nonpolar surface and textured surface structure are the essential features of a superhydrophobic membrane that control the oil-water



Fig. 5. low magnification SEM images of (a) ex-situ co-polymerized PS-PAA/TiO₂NPs (filter A), (b) in-situ co-polymerized PS-PAA/TiO₂NPs (filter B) and (c) in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C) and their high magnification images are d, e and f respectively.

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Fig. 6. cross section images of (a) PS-PAA(filter B) (b) and its high magnification image of the same.

separation efficiency. To gain a more complete understanding of the surface wetting properties of the different membranes, water contact angles (WCA) in air and rolling angles were measured and measured contact angels of different filters are shown in Fig. 7. All three filters

fabricated with ex-situ AA – styrene co-polymer TiO_2 NPs (filter A), insitu AA – styrene co-polymer TiO_2 NPs (filter B) and in-situ AA – styrene co-polymer TiO_2 NPs coated on SS mesh (filter C) methods exhibit superhydrophobicity-superoleophilicity and the respective water



Fig. 7. Water contact angles (WCA) of (A) ex-situ co-polymerized PS-PAA/TiO₂NPs (filter A), (B) in-situ co-polymerized PS-PAA/TiO₂NPs (filter B) and (C) in-situ co-polymerized PS-PAA/TiO₂NPs (filter C).

contact angels are $154\pm2^\circ,\,156\pm2^\circ$ and $141\pm4^\circ.$ Hence, the filter B exhibits enhanced oleophilicity than filters A and C despite the surface roughness increase in the order PS-PAA-C < PS-PAA-B < PAA-A indicating the surface roughness alone with the coverage of TiO_2NP by the copolymer PS-PAA plays a significance role in deciding the superoleophilicity.

Theoretically and experimentally, it has been reported that the contact angle hysteresis (CAH) which is highly related to the surface roughness and, chemical heterogeneities, can predict the dynamics of water droplets on superhydrophobic surfaces [49,50]. Hence, CAH is a good measurement of the surface roughness as well as the surface resistance to the movement of a droplet in which a low CAH indicates the higher hydrophobicity of the membrane [51]. The CAH for filters A, B and C were measured using a 10 μ l water droplet. Filter A and B showed a CAH of ~2–5° while with the filter C, a CAH of ~7–10° is noted. The observed low CAH is a clear indication of the superior hydrophobicity of all three filters while filters A and B exhibit better hydrophobicity than the filter C.

The mechanical stability of filters plays significant role in deciding the long-term use of the membrane under real conditions. It has been noted that the solid interaction between the coating and the substrate is crucial to achieve a reliable and robust polymer coating on the substrate that would retain the separating function of the membrane intact. In recent study, it has been demonstrated the enhanced durability and resistance to mechanical damage and chemical attack due to the intertwined cross-linking network and hydrogen bonds by the incorporation of ZnO in the HPVDF@ZnO/Ag membrane [27]. Hence, to demonstrate the enhanced mechanical stability of TiO2 incorporated PS-PAA co-polymer based membrane, the adhesion test was employed to test the robustness of the as-prepared superhydrophobicity filters as described in SI and Fig. S5. The adhesion test results indicated that the loosely bound or unbounded polymer materials are easily detached from the membrane i.e. up to cycle 4 and the after that the weight loss is negligible. Hence, the stability of the filters fabricated by three methods was confirmed by the adhesion test indicating that the underneath PS-PAA/TiO₂NP are firmly bound to the steel mesh. However, filter C which, was fabricated by in-situ AA - styrene co-polymer TiO2 NPs coated on SS mesh exhibited superior stability compared to the other two methods which, could be attributed to strongly bonded and cross-linked interactions between PS and PAA, and also due to enhanced bonding between both copolymer-TiO₂ and TiO₂-mesh. A similar robust and excellent mechanical stability has been noted for ZnO incorporated HPVDF membrane as a result of the formation of cross-linked polymer network and hydrogen bonding [27]. Such a strong mechanical stability of PS-PAA/TiO₂NP based membrane is an important parameter concerning prevention of leaching of TiO2 NPs to water. The National Institute for Occupational Safety and Health (NIOSH) Authoritative recommends exposure limits of 2.4 mg/m³ for fine TiO₂ and 0.3 mg/m³ for ultrafine (including engineered nanoscale) TiO₂, as time-weighted average (TWA) concentrations for up to 10 h per day" [52]. On the other hand, the calculated Ti and C atomic ratio in the film by EDX analysis is found to be 1.1% and 25.0% respectively indicating the amount of Ti is significantly lower than the NIOSH recommendation and hence even the presence of TiO₂ in the membrane has minimal effect even if it leached out of the membrane. It should me mentioned that no drastic physical changes (slight change in color was noted) or fouling were observed after long-term usage of PS-PAA/TiO2NP membranes. Significantly the membranes retain the separation efficiency while water contact angle and rolling angles were not enacted. These observations suggested the long-term stability of PS-PAA/TiO2NP membranes.

3.3. Oil-water separation performances of PS-PAA/TiO2

To assess the oil/water separation performance of membranes, the oil absorption efficiency of different members were tested by placing a known amount of oil droplet on the surfaces of filters A, B and C. As shown in Fig. 8, the oil droplet gets quickly absorbed by all the test filters indicating high oleophilicity. However, the oil absorption is comparatively faster in filter B than the filters A and C in which, the oil absorption efficiency is in the order of B > A > C. As it was noted that both water and oil passes through the bare SS mesh or TiO2NPs coated SS mesh, oil-water cannot be separated by using either by the bare SS mesh or TiO₂NPs coated SS mesh. Having demonstrated the superoleophilicity characteristics of the filters, membranes A, B and C were then tested for their oil/water separation capabilities as explained in SI. As shown in Fig. S1 a and b, oil-water separation was tested under gravitational force and underwater, anti-gravitational force. Different types of oil/water mixtures were passed through the membranes to check the feasibility of the separation including kerosene, 1-octadecene and engine oil and the individual separation efficiency of different oils can be seen in Fig. 9-i. As shown in Fig. 9-i, all three membranes achieved the separation efficiencies of ~99.0% with high and low viscous oil. Compared to the PS nanofiber membrane on a SS mesh, which can only separate low-viscous oil from water, the PS-PAA/TiO2 membrane can separate both low and high-viscous oils [21]. Also the PS nanofiber membrane on a SS mesh was found to be hydrophilic in the absence of oil layer while the PS-PAA/TiO₂ membrane does not show any hydrophilicity under similar condition. Despite polystyrene alone coated SS mesh exhibits oil-water (i.e. kerosene, octadecane, engine oil) separation efficiencies over 98%, the coated polymer layer detached very easily from the SS mesh and hence the delicate stability is the major issue when using polymer alone membrane [30,53]. On the other hand, the reusability of filters A, B and C was confirmed by the reusability test. The reusability of membranes for the separation of oil-water was tested by passing oil-water mixtures over 20 cycles and as shown in Fig. 9-ii, all three membranes retain over 98.5% separation efficiencies during test cycles confirming the excellent durability and the reusability of PS-PAA/TiO2 based films for effective oil-water separation.

In addition to the oil-water separation efficiency, the oil flux is also a significant factor that determined the performance of membrane. The oil flux was estimated by measuring the time taken to permeate a known amount of oil through the coated mesh and the flux value was calculated by F⁻V/St, where F is the flux, V is the oil volume passed through the membrane, S is the effective area of the membrane and t is the time taken to permeate V amount of oil [54]. To assess the oil flux performance of membranes, x ml of high and low viscous oil were passed through the filters under gravity or antigravity methods and the flow rates of oils were recorded. As shown in Fig. 11-i, the filter A demonstrated oil flux of 63455 \pm 2665, 36,468 \pm 1276, and 1260 \pm 12, L m $^{-2}$ h^{-1} for kerosene, octadecane and engine oil respectively under the gravity separation while the same oils demonstrated flux of 8042 \pm 96, 8035 ± 176 , and 1876 ± 18 , L m⁻² h⁻¹ respectively under the antigravity separation. Similarly, as shown in Fig. 11-ii, oil flux for filter B are $66,055\pm1981,~37,154\pm928,$ and $1990\pm69,~L\,m^{-2}~h^{-1}$ for kerosene, dodecane and engine oil respectively under the gravity separation while the same oil demonstrated flux of 8789 \pm 237, 8937 \pm 277, and 2595 \pm 23, L m $^{-2}\,h^{-1}$ respectively under the antigravity separation. As shown in Fig. 11-iii, the oil flux of filter C are $59,541 \pm 5299, 34$, 276 \pm 1679, and 1185 \pm 17, L m⁻² h⁻¹ for kerosene, octadecane and engine oil respectively under the gravity separation while the same oil demonstrated flux efficiencies of 7725 ± 77 , 7640 ± 91 , and 1422 ± 21 , L m⁻² h⁻¹ respectively under the antigravity separation. Hence, the oil separation rate of the filter B is comparatively higher than filters A and C and it was noted the oil separation rates follow the order of B > A > C. The oil separation rate of filter B is significantly higher than filters A and C for high viscous oil while for low viscous oil, the oil separation rate is marginally higher than filters A and C. The enhanced oil separation rate of filter B can be understood based on the superior wetting property of filter B (Fig. 8 that allows the facile passing of droplets through the superoleophilic membrane as shown in schematically in Fig. 10. Also the oil fluxes of PS-PAA/TiO₂ based membranes are



Fig. 8. Absorption of oil (engine oil) in air by (a) ex-situ co-polymerized PS-PAA/TiO₂NPs (filter A), (b) in-situ co-polymerized PS-PAA/TiO₂NPs (filter B) and (c) in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C). Images were taken continuously by 1.0 s intervals.



Fig. 9. separation efficiency (i) and the rates of separation retention(ii) of different oils with filter A: ex-situ co-polymerized PS-PAA/TiO₂NPs, filter B: in-situ co-polymerized PS-PAA/TiO₂NPs and filter C: in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh.

higher than the similar superhydrophobic membranes reported recently [55–57].

For any membrane to be practical for oil/water separation it should be rigid for harsh conditions and as shown by the adhesion test, filters fabricated by three methods were found to be stable but the filter C which, was fabricated by in-situ AA - styrene co-polymer TiO₂ NPs coated on SS mesh exhibited superior stability compared to other two methods. The superior stability of the filter C could be due to the formation of strong bonding between TiO_2 NP and the SS as TiO_2 NPs were pre-attached to the SS surface prior to copolymerization of styrene and AA on the TiO₂ particles. The durability test of PS/PAA/TiO₂ membranes was investigated by using the same filer for several separation cycles of the oil-water mixture. The separation efficiency test was carried out using standard high and low viscosity oils. Even after 10 cycles of separation all three PS-PAA/TiO₂NP membranes have showed ~99% separation and no visible fouling on the filter material was observed. These oil-water separation results as well as stability tests clearly indicate that 99% separation and long-term stability can be achieved with all three PS-PAA/TiO₂NP membranes and importantly all of them exhibit superior oleophilic behavior with fairly high flux rates. Especially PS-PAA/TiO₂NP membranes demonstrate high separation ability for both high and low density oils compared to recently reported oleophilic membranes for the similar purpose [17,32,35,58]. Though all three PS-PAA/TiO₂NP membranes fabricated by different methods showed greater reusability for oil-water separation, further improvements are vital for practical uses.

The oil-water separation results clearly demonstrated the superior oil-water separation properties of filter B, which was fabricated by the in-situ copolymerization of styrene-AA on TiO₂NP. The better oil-water separation properties of filter B could be attributed to the formation of highly nonpolar surface by the in-situ copolymerization of styrene-AA on TiO₂NP. Furthermore, as shown by SEM images of Filter B, the insitu copolymerization of styrene-AA on TiO2NP resulted in complete and smooth coverage of TiO₂NPs by the PS-PAA than the other two methods. The higher water contact angle as well as the fast oil wetting properties of filter B additionally supports the superoleophilicity of filters B than the filters A and C. The superior oil-water separation properties of filter B can be explained as follows; The oil-water separation performance of a filter strongly depends on surface energy and surface roughness of the filtering material which, will lead either to repel water or attract oil vise-versa [59–61]. According to the Wenzel's model, if a surface is wetted by a liquid satisfactorily, the wetting of the surface by the liquid will be enhanced with the increase of the roughness and if the surface repel the liquid, it will enhance the repelling of the liquid [2]. Different fabrication methods employed in this investigation was intend to have different surface energy, surface roughness and the adhesion to the SS. i.e., in filter B, the in-situ copolymerization of styrene-AA on TiO₂NP permits a better modification of surface roughness and energy of





Anti-gravity filtration

Fig. 10. Schematic diagram of Flux efficiency of different oils with (1a) ex-situ co-polymerized PS-PAA/TiO₂NPs (filter A), (1b) in-situ co-polymerized PS-PAA/TiO₂NPs (filter B) and (1c) in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C), (2) Schematic of the oil/water separation in which, (2a) Oil-water mixture approaching to the modified mesh, (2b) Oil starts to absorb in to the modified mesh and (2c) oil passing through the superoleophilic membrane while blocking the water layer.

the filter B, over other two methods. On the other hand, in the filter C, the in-situ polymerization on immobilized TiO_2 NPs provides better adhesion properties but less surface properties modification function over the TiO_2 NP surface due to immobilization of TiO_2 NP. Hence, even the adhesion properties of the filter C is better than the filter B, surface modification is better on Filter B which, will lead to the better performance in separation efficiency.

4. Conclusion

Highly superhydrophobic membranes can be fabricated either by exsitu and in-situ copolymerization of styrene-AA on TiO_2 nanoparticles or in-situ copolymerization of styrene-AA on the TiO_2 coated stainless steel mesh for the effective separation of contaminated oil-water mixtures. All the membranes exhibited superhydrophobicity irrespective of the fabrication methods, however, the durability of the membrane was found to be highly dependent on the method of fabrication. Highly superhydrophobic membranes having a water contact angel of 154° and a rolling angel of ~ 2–5° was obtained for the membranes fabricated by in-situ copolymerization of styrene-AA on TiO₂ nanoparticles. Membranes can be used to separate both high and low viscous oil and a separation efficiency of over ~99% with a flux of ~50,000–60,000 L m⁻² h⁻¹ in under gravity driven process and a flux of or low viscous oils. All three membranes exhibit excellent durability with no visible fouling for over 20 oil-water separation cycles. However, an







Fig. 11. Flux efficiency of different oils in anti-gravity condition and undergravity condition with (i) ex-situ co-polymerized PS-PAA/TiO₂NPs (filter A), (ii) in-situ co-polymerized PS-PAA/TiO₂NPs (filter B) and (iii) in-situ co-polymerized PS-PAA/TiO₂NPs-SS mesh (filter C).

excellent durability was noted with the membrane fabricated by in-situ polymerization on immobilized TiO_2 NPs. Despite co-polymerized PS-PAA/TiO₂(NP) demonstrated exceptional separation and durability, further improvements on stability and durability of PS-PAA/TiO₂(NP) based membranes are necessary for a large scale application.

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CRediT authorship contribution statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. S.A. D.A.V.S conducted the major part of the experiments and B.D.K.K.T conducted and assisted in some experiments. J.B. designed the experiment and concept and the manuscript was mainly written by J.B. and all authors contributed to finalizing the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105394.

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