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Research article

# Fabrication of highly hydrophilic filter using natural and hydrothermally treated mica nanoparticles for efficient waste oil-water separation

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#### ABSTRACT

For the effective oil/water separation, a novel superhydrophilic (underwater superoleophobic) filter is fabricated with the naturally and hydrothermally treated mica particles. To fabricate a double layered filter, hydrothermally treated mica particles were initially electrodeposited on a stainless steel mesh and a natural mica particles were sprayed on the first hydrothermally deposited mica layer. The double layered mica coated membrane showed superamphiphilic and superhydrophilic/superoleophobic (contact angle >159°) characteristics in air and underwater respectively. The membrane can separate range of oil-water mixtures with oil/water separation efficiency over ~99%. Properties of double layered mica membrane were investigated and noted that the surface adhesion properties of mica is enhanced by the hydrothermal treatment of mica and the higher roughness of the mica layer is maintained by the natural mica.

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## 1. Introduction

In the modern world, water which is one of the scarcest commodities is polluting by several ways in every second. Among the different methods of water pollution, oil spill is one of the major negative contributions to the environment from large number of industries, especially in automobile service stations (Fried et al., 1979; Mazumder and Mukherjee, 2011; Reed et al., 1998). It is known that the prompt water pollution occurs when oil passes in to the water sources, rivers and sea water and the water pollution by oil is considered to be a greater threat to the humans, marine life, animals and to the entire ecosystem (Fosberg, 1974; Nomack, 2010).In past few decades, the following water treatment techniques have been used; (a) physical treatment methods such as adsorption of dissolved organics on activated carbon (Gur-Reznik et al., 2008), organoclays (Doyle and Brown, 2000), copolymers and resins, (Jan and Reed, 1989) sand/stone filters, organics evaporating methods (Fakhru'l-Razi et al., 2009), electrodialysis methods (Fakhru'l-Razi et al., 2009), and filtering through oil/water separating membranes, (Kota et al., 2012); (b) chemical/electrochemical treatment methods such as coagulation and flocculation methods (Bratby, 1980), advanced chemical oxidation methods (Bautista et al., 2008), electrochemical methods (Ma and Wang, 2006) and photocatalytic treatment methods (Chong et al., 2010; Teng et al., 2015; Gunatilake et al., 2017) and (c) *biological treatment methods* (Fakhru'l-Razi et al., 2009; Sugano et al., 2008; Teng et al., 2015). The major disadvantages of most of these conventional techniques are that these methods are not economical as well as they cannot separate oil/water emulsions efficiently. As a result, the scientists are looking forward to capitalize the cheap and efficient methods to remove oil spills from water.

Contrary to the conventional oil/water separation techniques mentioned earlier, extremely high special wetting solid material surfaces can be used to separate oil and water more selectively and easily (Feng and Jiang, 2006; Li et al., 2016; Sun et al., 2014; Xue et al., 2014). If wetting properties are considered, materials having different affinities towards oil and water would be the best choice for designing of efficient oil/water separation filters. In this respect, materials with both hydrophobic/oleophilic and oleophobic/hydrophilic properties were actuated a broad attention in last few years to invent novel oil/water separation systems (Bellanger et al., 2014; Darmanin and Guittard, 2014; Xue et al., 2014). However, superhydrophobic materials are unsuitable for the separation of oil/water under gravity due to formation of a water barrier layer on superhydrophobic layer preventing







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penetration of oils as water has higher density than most of the common oils (Zhang et al., 2014). On the other hand, underwater superoleophobic and superhydrophilic solid surfaces allow water to penetrate through the membrane while repelling the oil outwards from the membrane allowing separation of oil/water effectively. Going through these theories, various materials such as polyacrylamide hydrogel coated mesh (Xue et al., 2011), Cu(OH)<sub>2</sub> covered mesh (Liu et al., 2013), photo-induced TiO<sub>2</sub> thin films, Sawai et al., 2013) polyelectrolyte/clay hybrid film (Xu et al., 2013), PANI (Polyaniline) nanowire film (Ding et al., 2012), polypyrrole nanowire mesh (Ding et al., 2012), have been fabricated to separate oil/water.

Here, we report the fabrication of a novel superhydrophilic and underwater superoleophobic filter to repel and separate oil under water efficiently by using natural mica mineral particles coated stainless steel mesh. The superhydrophilicity nature and micro hierarchical rough particles layered arrangement of the mica particles leads to enhance the underwater superoleophobicity of the filter. The fabricated filter selectively and effectively repel not only low dense oils but also high dense organic oils from oil/water mixtures such as engine oil, crude oil, gasoline, diesel, vegetable oil and forth on. The oil-water separation filter described in this investigation is a low cost method as the main chemical substrate (mica) is taken from a natural source directly. Interestingly, the double layered electrodeposition and spray techniques makes the mica coated mesh more stable under high peeling off forces. Additionally, the cleaning of the mesh is very easy with the help of non-polar solvent at the high contamination levels.

## 2. Experimental

## 2.1. Materials

Stainless steel meshes were purchased from Benny the Stoog, USA. Acetone, sodium hydroxide pellets, absolute ethanol, 1,2dichloroethane,1-octadecene, hexane, and potassium bromide were purchased from Sigma Aldrich chemicals Pvt. Limited, USA. Silicon oil (commercial grade), kerosene (commercial grade), engine oil (SAE 10W-30), rapeseed oil (commercial grade) was purchased commercially and mica flakes were obtained from mica deposit found in Matale, Sri Lanka.

#### 2.2. Fabrication of mica coated stainless steel mesh

Natural flake mica (from Matale, Sri Lanka) was finely ground from ring mill crusher and sieved to collect <50 µm size mica particles. For electrodeposition of mica, mica particles were hydrothermally treated to make them negatively charged. For hydrothermal treatment, 5.0 g of mica was stirred with 55.0 ml of 10 M NaOH for 30 min and the mixture was transferred to a 73.0 ml capacity Teflon chamber with a stainless steel hydrothermal vessel and treated at 160 °C for 12 h. The highly basic (pH ~13) hydrothermally modified mica particles were separated at room temperature by washing with water several times till pH of the solution reaches ~ 10.0-11.0. Stainless steel meshes (#125/100 µm opening width, size  $2^{"} \times 2^{"}$ ) were ultrasonically cleaned in acetone and then rinsed with ethanol and deionized water. For electrodeposition of hydrothermally modified mica, 20 ml of methanol was mixed with 40 ml of hydrothermally modified mica suspension solution. Then two cleaned stainless steel meshes were used as anode and cathode with one inch space difference and 30 V was supplied for 3 min each for both sides of anode mesh. On top of the electrodeposited mica layer, a second mica layer which was prepared by dispersing 1.0 g of natural mica particles in 30 ml of ethanol followed by ultrasonication (15 min) and stirring for 1 h, was deposited by spray

method. Finally, the mesh was sintered at 650 °C for 1 h and cooled to room temperature. Finally the mica coated mesh was rinsed with deionized water to remove excess loosely bound mica particles. In this study, three different underwater superoleophobic filters were fabricated; (1) natural mica was sprayed on stainless steel mesh (filter-a), (2) hydrothermally treated mica was electrophoretically deposited on stainless steel mesh (filter-b) and (3) bi-layer filter containing electrophoretic deposited hydrothermally treated mica on stainless steel mesh and sprayed mica layer on the electro-deposited mica layer (filter-c).

## 2.3. Oil/water separation experiments

The oil/water separation apparatus was made by fixing mica coated stainless steel mesh into a PVC union setup. The oil/water mixture was prepared by mixing 10.0 g of engine oil and 35.0 g of water. The mica mesh was pre-wetted with water and the water/oil mixture (3.5:1 w/w) was poured to the filtration set up (1.0 inch diameter filtering area) at the rate of 1.5 ml/s under the gravity. Water was collected by a beaker under the PVC union setup. To check the stability of the mesh, the filtration was done continuously for several days. After every filtration step, the mica mesh was rinsed by distilled water to remove the trapped oil droplets from the mesh. The separation efficiency was calculated by  $\vartheta = \frac{m \text{ remains}}{m \text{ initial}} \times 100\%$  where,  $m_{\text{ remains}}$  and  $m_{\text{ initial}}$  is the mass of the oil before and after the separation. For the calculation of  $m_{remain}$  in the filter, oil remain in the filter was collected to a beaker and the oil residues on the column was wiped with a solvent carefully and weight of the oil was taken after evaporation of the solvent. This procedure was repeated for several oils to get the efficiency of each and the recycle efficiency was checked for 20 cycles with engine oil (SAE 10W-30).

## 2.4. Instrumentation and characterization

Scanning electron microscope (SEM) images and EDX were taken by Carl Zeiss EVO LS15 scanning electron microscope, Fourier transform infrared spectroscopy (FTIR) was recorded from Thermo Nicolet 6700 FTIR machine. Contact angle images were captured from 8-megapixel iSight camera and contact angles were measured using simple geometric angle measuring Protractor. Crystallographic data was taken from Ultima IV x-ray diffractometer.

## 3. Results and discussion

## 3.1. Characterization of natural and hydrothermally modified mica

Mica is a phyllosilicates mineral which forms as layer silicates comprising of Si–Al–O tetrahedral sheets between M-O and OH octahedral sheets, where M is usually  $Al^{3+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$  or  $Mg^{2+}$ . It mostly exists as Biotite K(Mg,Fe)<sub>3</sub>(AlSi<sub>3</sub>O<sub>10</sub>) (OH)<sub>2</sub>, Lepidolite K(Li,Al)<sub>3</sub>(AlSi<sub>3</sub>O<sub>10</sub>) (O,OH,F)<sub>2</sub>, Phlogopite KMg<sub>3</sub>(AlSi<sub>3</sub>O<sub>10</sub>) (OH)<sub>2</sub> and Muscovite KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>) (OH)<sub>2</sub> structures (Laoot et al., 2011; Rickwood, 1981). High in silica, the mica group sheet silicate minerals include several closely related materials having nearly perfect basal cleavage which can be split or delaminated into thin sheets usually causing foliation in rocks. Mica is a lightweight mineral having dielectric and hydrophilic characteristics. More importantly, mica is chemically inert material and can resist nearly all mediums like chemicals, acids, gasses, alkalis and oils which makes it an ideal material for the fabrication of oil-water separation filters (Christenson, 1993).

Strong bonding between mica and steel mesh is a prerequisite for the fabrication of durable filter for the separation of water and oil. However, it was noticed that a filter made of natural mica by spraying method is not long-lasting as mica particles get detached easily from the mesh after very few separation cycles. To overcome this problem, electrophoretic deposition method is employed. As natural mica particles cannot be electrophoretically deposited on steel mesh due to its dielectric nature, hydrothermal treatment with NaOH<sub>(aq)</sub> is an essential step to obtain a fine suspension of mica particles at the pH of 10.0–11.0 with a net negative surface charge on mica particles. Hydrothermally treated mica particles can be easily electrodeposited on steel mesh with strong bonding between mica and the mesh.

## 3.1.1. XRD analysis

X-ray diffraction patterns of natural mica, natural mica heated at 650 °C, hydrothermally treated mica and hydrothermally treated mica heated at 650 °C are shown in Fig. 1. As shown in Fig. 1a, the natural mica contains mainly Vermiculite [(Mg,Al)<sub>3</sub>(Si,A-1)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O] and phlogopite [KMg<sub>3</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>] forms of mica. The characteristic diffractions peaks of Vermiculite at 6.1°  $(d = 14.4773), 31.1^{\circ} (d = 2.8788), 24.8^{\circ} (d = 3.5986), 37.5^{\circ}$  $(d = 2.3964), 18.43^{\circ} (d = 4.8014), 35.2^{\circ} (d = 2.5542), 60.2^{\circ}$  $(d = 1.5356), (d = 4.6136), 54.6^{\circ} (d = 1.6768) and 12.4^{\circ} (d = 7.1582)$ [JCPDS 340166, JCPDS 760847] are clearly distinguishable in Fig. 1a. Also diffraction patterns at 8.8° (d = 10.1185), 26.4° (d = 3.3647), 54.8° (d = 1.6770), 33.9° (d = 2.622), 60.0° (d = 1.537) and 54.5° (d = 1.6784) [JCPDS 100493] are due to phlogopite forms of mica. These results confirm that the mica contains mainly Vermiculite and phlogopite structures. Also, other forms of mica such as Lepidolite and Zinnwaldite are absent in mica used in this investigation. When the natural mica is hydrothermally treated with NaOH, Vermiculite and phlogopite forms of natural mica is converted to Clinochlore [(Mg,Al)<sub>6</sub>(Al, Si)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>]and Saponite [Na<sub>0,33</sub> Mg<sub>3,00</sub>(Al<sub>0,33</sub>Si<sub>3,67</sub>)O<sub>10</sub>(OH)<sub>2</sub>] crystal structures as evidenced by the diffraction patterns of hydrothermally treated mica particles shown in Fig. 1c. The X-ray diffraction patterns of hydrothermally treated mica which is shown in Fig. 1c matched well with the Clinochlore diffraction peaks at  $6.2^{\circ}$  (d = 14.3763), 24.5° (d = 3.6243), 12.2° (d = 7.2210), 18.2° (d = 4.8301), 19.0° (d = 4.6264), 30.9° (d = 2.9143), 59.7° (d = 1.5454), 44.5° (d = 2.0488) [JCPDS 100183] and Saponite diffraction peaks at 6.9° (d = 12.7696), 19.2° (d = 4.5958), 33.9° (d = 2.6378)) [JCPDS 120157] indicating that when the natural mica is hydrothermally treated at 150 °C for 12 h, natural mica is converted to Clinochlore and Saponite. The Clinochlore crystal structure is one of the most hydrophilic forms of mica structures which contained eight hydroxyl groups compared to two hydroxyl group in Vermiculite and phlogopite forms (Wong-Ng et al., 1983).

In the process of fabricating mica layer on stainless steel mesh, mica coated mesh was subjected to heating to enhance the adherence properties of mica on mesh. The X-ray diffraction patterns of heat treated natural mica and hydrothermally treated mica are shown in Fig. 1b and d respectively. After heat treatment at 650 °C, natural mica containing Vermiculite is converted to Pyrophyllite [Al<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] and Talc [Mg<sub>3</sub>Si<sub>4</sub> O<sub>10</sub>(OH)<sub>2</sub>] where diffraction peaks seen at  $9.6^{\circ}$  (d = 9.1674),  $29.4^{\circ}$  (d = 3.0325),  $19.3^{\circ}$  $(d = 4.5671), 26.6^{\circ} (d = 3.3459), 55.9^{\circ} (d = 1.644) [JCPDS 020613)]$ matched with Pyrophyllite while the peaks appear at 19.5°  $(d = 4.5556), 34.5^{\circ} (d = 2.5964), 36.3^{\circ} (d = 2.4777), 41.05^{\circ}$  $(d = 2.1994), 43.1^{\circ} (d = 2.0925), 60.5^{\circ} (d = 1.5230)$  [JCPDS 030887] matched well with Talc form. Also, hydrothermally treated mica containing Clinochlore form is converted to Hydrogen Aluminum Silicate  $[H_{0.32}Al_{0.32}Si_{95.68}O_{192}]$ , {peaks at 8.0° (d = 11.0454), 8.9°  $(d = 9.8866), 23.0^{\circ} (d = 3.8584), 14.0^{\circ} (d = 6.3355)$  [JCPDS 420024] matched with to Hydrogen Aluminum Silicate}, Talc [Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>] [JCPDS 030887] and Saponite [Na<sub>0,33</sub> Mg<sub>3,00</sub> (Al<sub>0.33</sub> Si<sub>3.67</sub>) O<sub>10</sub> (O H)<sub>2</sub>] forms(Wong-Ng et al., 1983).

## 3.1.2. FTIR analysis

Surface bonding properties of natural and hydrothermally treated mica particles were characterized by FTIR analysis. In Fig. 2, the FTIR spectra of natural, hydrothermally treated and sintered mica particles are shown by finger patterns of a, b and c respectively. As shown in Fig. 2, some significant changes in surface



Fig. 1. XRD analysis of (a) natural mica (b) natural mica at 650 °C (c) hydrothermally modified mica (d) hydrothermally modified mica at 650 °C. [Notation-v(Vermiculite), pl(Plogophie), py (Pyrophyllite), t (talc), c (Clinochlore), s (Saponite), a (Hydrogen Aluminum Silicate)].



Fig. 2. (a) FTIR spectra of natural mica particles. (b) FTIR spectra of hydrothermally modified mica particles. (c) FTIR spectra of the 650 °C sintered mica particles.

properties of natural, hydrothermally treated and sintered mica particles can be observed. In FTIR analysis of natural mica, the strong peak observed at 1640 cm<sup>-1</sup> is due to-OH bending vibrations while the peak at 3418 cm<sup>-1</sup> could be assigned to -OH stretching vibration and adsorbed H-O-H. The other peaks seen at 1400, 1012, 812, 684 and 456 cm<sup>-1</sup> can be assigned to K-O or Na-O (vibrational bond), Si-O (stretching vibrational bond), Al-OH (bending vibrational bond), Si-O-Al/Mg (bending vibrational bond) and Si-O (bending vibrational bond) respectively. As shown in curve a in Fig. 2, an additional vibration peak seen at 3702 cm<sup>-1</sup> is due to presence of highly crystalline Al-OH in natural mica (Bishop et al., 2008).

Comparison of FTIR spectra of the hydrothermally modified mica particles and natural mica particles indicates some few changes in hydrothermally treated mica particles. Compared to the natural mica particles, for hydrothermally mica particles, a strong peak at 1427 cm<sup>-1</sup>can be observed and it could be due to incensement of K-O or Na-O bonds due to hydrothermal process. Interestingly, after hydrothermal treatment of natural mica, two stretching crystalline OH peaks at 3475 and 3573 cm<sup>-1</sup> were noted and this could be due to the addition of the O-H groups from the hydrothermal process. On the other hand, stretching crystalline OH peaks observed at 3475 and 3573 cm<sup>-1</sup>are characteristic to Clinochlore form where it shows broad peaks near  $(3560-3586 \text{ cm}^{-1})$ and (3400-3436  $\text{cm}^{-1}$ ) due to the interlayer OH groups. These results further confirm that the natural mica is converted to Clinochlore form when natural mica is subjected to hydrothermal treatment. Furthermore, enhancement in relative intensities of OH peaks at 3418 and 1640 cm<sup>-1</sup> also can be observed in hydrothermally treated sample compared to natural mica.

Significant changes in surface properties of mica were observed when natural and hydrothermally treated mica were subjected to heat treatment. As shown in Fig. 2, curve c, OH bending and stretching peaks are diminished while crystal Al–OH peak at  $3702 \text{ cm}^{-1}$  is absent in 650 °C heated hydrothermally treated mica particles. Additionally, it can be noted that the intensities of almost all other peaks due Si–O (stretching vibrational bond ~ 1012 cm<sup>-1</sup>),K–O or Na–O (vibrational bond ~1400 cm<sup>-1</sup>), Si–O (bending vibrational bond ~456 cm<sup>-1</sup>), Si–O–Al/Mg (bending vibrational bond ~ 684) and Al–OH (bending vibrational bond ~812 cm<sup>-1</sup>) have been reduced significantly due to high temperature treatment. (Corma et al., 1994; Góra-Marek et al., 2005; Handke and Mozgawa, 1993; Laoot et al., 2011; Miller and Wilkins, 1952; Saikia and Parthasarathy, 2010).

#### 3.1.3. Adhesion test

The major problem with natural mica is that it does not firmly bind to the stainless steel due to lack of binding sites in both natural mica as well as stainless steel. However, hydrothermally treated mica contains fair amount of binding sites that can be bound to both stainless steel as well as natural mica. This way mica can be firmly bound to stainless steel mesh. However, some loosely bound spray deposited mica particles can be easily detached from the membrane. As mentioned earlier, we employed the electrophoretic deposition method to obtain a strongly bonded and homogeneous hydrothermally treated mica layer on stainless steel mesh. The electrophoertic deposition of mica via electric charge ensures firm binding of charged mica particles on the charged stainless steel mesh. The required thickness of the deposited layer was obtained by varying the applied voltage and deposition time. The adhesion property of mica on stainless steel mesh was tested by adhesive tape method and the adhesion properties of different filters made of natural mica, hydrothermally treated mica and bi-layered mica are given in Table S1 in SI. As expected, a higher adhesion property was noticed with the filter made of hydrothermally treated mica compared to sprayed mica filter. The results presented above clearly demonstrate that the enhancement of hydroxyl groups in hydrothermally treated mica particles enhances the adhesion property of mica onto steel mesh compared to natural mica.

## 3.1.4. Surface morphology characterization

Surface morphology of natural and hydrothermally treated mica



Fig. 3. SEM images of low magnification (a) Hydrothermally modified mica electrodeposited mesh, (b) natural mica sprayed mesh, (c) Sprayed layer on top of the electrodeposited layer, (d) 10 kx magnified image of random area of SEM image c.

was investigated by SEM. The SEM images of natural and hydrothermally treated mica on steel mesh are shown in Fig. 3 a and b respectively in which natural mica was spray deposited on mesh while hydrothermally treated mica was electrodeposited on mesh. SEM images clearly indicate a higher surface roughness for natural mica compared to hydrothermally treated mica indicating hydrothermal treatment results in smooth surface on mica (For further details, see the SEM images of Fig. S1 in SI). However, enhanced surface roughness is a prerequisite for better oil-water separation. Hence to increase the surface roughness of hydrothermally mica, on top of the electrodeposited mica layer, a thin layer of natural mica layer was sprayed. The SEM images of mica layer on electrodeposited mica containing double layered mica coated mesh shown in Fig. 3c and the magnified image of natural mica (Fig. 3d) clearly demonstrate an enhanced surface roughness for double layered mica filter. Hence, with the additional rough mica layer, contact angle of the oil can be increased under the water and hence enhanced oil water separation can be expected.

#### 3.1.5. Wetting behaviour of the membrane

The wettability of the filter is an important parameter for efficient oil-water separation. The uncoated mesh has a water contact angle of ~96° in air. The hydrophilicity of mica coated mesh is very high in comparison to the wettability of uncoated stainless steel mesh. Their static contact angles are lying in  $0-2^\circ$  and after 2 s the droplet almost spreads. When the water droplet is contacted with the filters made of natural mica, hydrothermally treated mica and double layered mica containing both natural and hydrothermally treated mica in air, an instant wetting is noted in all three filters indicating that all the filters made of mica on mesh enhances the water

wettability greatly, water can be easily seeped down by the filter made of mica. As shown in Fig. 4, mica coated mesh exhibits oleophilic property in air with silicon oil and several different other oils also behave in similar manner. However, oleophilicities of filters made of mica, hydrothermally treated mica and double layered mica containing both natural and hydrothermally treated mica showed slightly different oleophilicity where mica and double layered mica exhibited least and most dynamic oleophobicity respectively as shown in Fig. 4. In addition, the observed superhydrophilicity of filter can be understood as follow; The Clinochlore form is converted to Hydrogen Aluminum Silicate, Talc and Saponite after the heat treatment. (650 °C). Dehydroxylation of the hydroxyl groups of the inter layers is possible around 500-600 °C and the dehydroxylation temperature depends on the particle sizes. After sintered, the dehydroxylated interlayer sheet is divided into areas enriched in MgO and porous areas with a deficit in MgO. Microspores are then formed in these MgO deficient regions. When the sample comes to room temperature it has ability to absorb water to these microspores enhancing the superhydrophilicity. (Villieras et al., 1994).

Fig. 5 shows the underwater contact angle of 1,2- dichloroethane with filters a, b, c where the underwater oil wettability of the mesh was evaluated by immersing the mica coated mesh in aqueous media. (filter-a, natural mica was sprayed on stainless steel mesh, filter-b, hydrothermally treated mica was electrophoretically deposited on stainless steel mesh, filter-c bi-layer filter containing electrophoretic deposited hydrothermally treated mica on stainless steel mesh and sprayed mica layer on the electrodeposited mica layer). The estimated underwater contact angels of filters a, b and c with 1,2- dichloroethane are given in Table 1. As given in Table 1, contact angel measurements indicate that all the filters made of



Fig. 4. Wetting properties of oil (silicon oil) in air [continues images taken within 100 s after oil touching to the mesh] (a) sprayed mica mesh (b) electrodeposited mica mesh (c) bilayer of electrodeposited and sprayed mesh.



**Fig. 5.** Images of oil droplet (1,2 dichloroethane) under water (a) oil droplet on stainless steel mesh (b) oil droplet on mica sprayed (650 °C) (c) oil droplet on modified mica electrodeposited (650 °C) (d) oil droplet on both electrodeposited and sprayed mica layers (650 °C).

## Table 1

Static contact angles of oil (1.2-dichloroethane) in the medium of water.

Mesh type	Stainless steel	(a) Mica sprayed (650 °C)	(b) Modified mica electrodeposited (650 °C)	(c) Both electrodeposited and sprayed mica layers (650 °C)
Contact angle of oil droplets in water (deg)	66.8 ± 4.7	164.7 ± 2.9	159.5 ± 2.0	163.0 ± 1.9

mica exhibit underwater oleophobic property allowing separation of oil and water. However, underwater superoleophobicity property of all three mica coated meshes varies in the order (a) > (c) > (b) which could be due to the variation of surface roughness of the mica surfaces as shown previously by SEM images. The uncoated stainless steel mesh exhibited underwater oleophilic property with a contact angel of ~68° with 1,2- dichloroethane.

According to the static contact angle of the mica surfaces, it can be clearly expressed that the hydrophilic surfaces of mica in the air is automatically converted to superoleophobic solid surfaces under water. It is known that aluminosilicate mica mineral consists of



Fig. 6. Water/oil separation process (a) complete setup for the separation (mesh fixed inside the union) (b,c) oil/water separation process (d) separated oil and water (right side - oil, left side - water).

Al–Si–O tetrahedral sheets sandwiched by Mg, Fe, Li trioctahedral sites and altogether it's surrounded by OH crystalline bonds. Hence, the atomic composition and arrangement makes mica to possess higher surface energy with compared to other mineral groups. To get a clear logical mechanism of the underwater superoleophobicity of mica particles it should have to consider the theories of Young's equation(Young, 1805). The contact angle of water ( $\theta w$ ) and oil ( $\theta o$ ) in air can be given as,

$$\cos\theta w = \frac{\gamma sa - \gamma sw}{\gamma wa} \tag{1}$$

$$\cos\theta o = \frac{\gamma sa - \gamma so}{\gamma oa} \tag{2}$$

where,  $\gamma sa$ ,  $\gamma sw$ ,  $\gamma wa$ ,  $\gamma so$  and  $\gamma oa$  are the surface tension of solid-air, solid-water, water-air, solid-oil, oil-air interfaces respectively. This Young's equation can be extended to an underwater oil droplets in solid surfaces as oil/water/solid systems. (Cai et al., 2014) In such cases underwater oil contact angle ( $\theta ow$ ) can be expressed as,

$$\cos\theta ow = \frac{\gamma sw - \gamma so}{\gamma ow}$$
(3)

$$\cos\theta ow = \frac{\gamma oa\cos\theta o - \gamma aw\cos\theta w}{\gamma ow}$$
(4)

where  $\gamma oa$ ,  $\gamma sw$ ,  $\gamma aw$ ,  $\gamma so$ ,  $\gamma oa$ ,  $\gamma ow$  are the surface tension of oilair, solid-water, air-water, solid-oil, oil-air and oil-water interfaces respectively. It can be derived that, to be underwater superoleophobic,  $\cos \theta ow < 0$  which means  $\cos \theta w > 0$  and  $\theta w$  should be lower than 90°. Under such conditions, it can be expected that underwater superoleophobic materials could be hydrophilic in air. According to above verifications, hydrophilic materials in air should be suitable to prepare underwater superoleophobic solid surfaces. (Bellanger et al., 2014; Chen and Xu, 2013; Darmanin and Guittard, 2014; Waghmare et al., 2013). If the same theory is applied to our system, the bare stainless steel mesh should exhibit hydrophobic properties in air (contact angle ~ 96°) and oleophilic (contact angle ~  $67^{\circ}$ ) properties in under water. Mica coated steel mesh exhibits an underwater oil contact angle of  $163^{\circ}$ , making the underwater oleophilic bare steel mesh into underwater superoleophobic. Hence, the enhancement of the underwater superoleophobicity is due to the hydrophilicity of mica in air and the micro hierarchical structural behaviour of the coated mica layer which can be behave according to the Cassie Baxter model. (Cassie, 1948; Liu et al., 2009)

#### 3.1.6. Oil-water separation

The underwater superoleophobic mica filters were tested for the separation of oil and water mixture and the simple water/oil separation setup is illustrated in Fig. 6. In assembling the setup, mica coated filter mesh (filter c, #125 mesh pore size, containing electrodeposited under layer mica and over layer sprayed mica) is fixed in a PVC union joint and a mixture [1:3.5 ratio (w/w)] of water and commercial engine oil (SAE 10W-30) was passed through the filter. It was observed that the water permeated through the porous membrane without any blockage with the #125 mesh pore size. The separation of engine oil (yellow-brown colour) and the water (colourless) can be seen visibly in Fig. 6 indicating the underwater superoleophobic mesh can effectively separate oil and water without any extra force under gravity. It was noted that at the first separation cycle, it performs >99% separation efficiency.

The durability and the separation of different oils of mica coated mesh were tested and the results are shown in Fig. 7a and b respectively. For durability test, the filter was used for several cycles of oil-water separation and it was noted at each cycle, over 97.5  $(\pm 1.8)$ % separation efficiency was achieved where water in the mixture passed through the mesh quickly, and no visible oil was observed in the collected water. Interestingly it was noted that the oil-plugged in the mica coated mesh can be easily be removed by passing through a mixture of water and hexane through filter in air. The oil water separation ability of the filter c, (#125 mesh pore size) were tested for different oil types as shown in Fig. 7b. It was clearly observed an oil water separation efficiency of ~99.9% for high viscous oil (viscosity > 1 cP) while 90–95% oil water separation efficiency was observed for low viscous oil (viscosity < 1 cP) (Genereaux, 1930). The poor oil water separation of low viscous oils in the mesh with #125 pore size was due to penetration of less



Fig. 7. (a) Recycling ability of the mica coated mesh, (b) separation efficiency of the different oils.

viscous oil through the holes of the mesh which can be avoided by using small pore size mesh (i.e.> #175 pore size mesh). Despite over 99% water/oil separation could achieve under normal waste oil/water condition, 99% water oil separation may not be achieved for waste water containing excess oil due to loss of underwater oleophobicity as a results of lack of water layer. This could be a practical limitation and hence proper designing of the reactor may solve this problem.

#### 4. Conclusion

Underwater superoleophobic nature of natural mica and hydrothermally modified mica was demonstrated by coating mica on stainless steel mesh. Natural mica exhibited enhanced underwater superoleophobic properties but poorly adhere on the steel mesh. An adherence property of mica on steel mesh was improved by hydrothermal treatment of mica and electrophoretic deposition of hydrothermally modified mica on mesh. Hence by using modified and natural mica, a double layered mica filter was successfully fabricated on steel mesh by maintaining both adherence and underwater superoleophobic nature of mica. The membrane can separate range of oil-water mixtures with oil/water separation efficiency over ~99% due superamphiphilic and superoleophobic (contact angle >159°) characteristics in air and underwater respectively. The mica coated steel mesh is cheap and easy to handle while it could effectively separate water from the different oil-water mixtures.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.01.002.

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