Bioinspired oil–water separation approaches for oil spill clean-up and water purification

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Water contamination is one of the major environmental and natural resource concerns in the twenty-first century. Oil contamination can occur during operation of machinery, oil exploration and transportation, and due to operating environment. Oil spills occasionally occur during oil exploration and transportation. Water contamination with various chemicals is a major concern with growing population and unsafe industrial practices of waste disposal. Commonly used oil–water separation techniques are either time consuming, energy intensive and/or environmentally unfriendly. Bioinspired superhydrophobic/superoleophobic and superoleophilic/superhydrophilic surfaces have been developed which are sustainable and environmentally friendly. Bioinspired oil–water separation techniques can be used to remove oil contaminants from both immiscible oil–water mixtures and oil–water emulsions. Coated porous surfaces with an affinity to water and repellency to oil and vice versa are commonly used. The former combination of affinity to water and repellency to oil is preferred to avoid oil contamination of the porous substrate. Oil–water emulsions require porous materials with a fine pore size. Recommended porous materials include steel mesh and cotton fabric for immiscible oil–water mixtures and cotton for oil–water emulsions. A review of various approaches is presented in this paper.

This article is part of the theme issue ‘Bioinspired materials and surfaces for green science and technology (part 2)’.
1. Introduction

Water contamination is one of the major environmental and natural resource concerns in the twenty-first century [1–5]. Contamination by oil can occur during operation of machinery, oil exploration and oil transportation, and due to operating environment. Oil is commonly used as a lubricant in machinery and can leak and produce contamination. Oil spills occasionally occur during oil exploration and transportation. They will continue to occur as long as society is dependent upon oil [3,4]. The Deepwater Horizon oil spill in the Gulf of Mexico in 2010 was the worst accidental offshore oil spill in history. It spilled about 200 million US gallons of oil (figure 1). The partial clean-up by British Petroleum took several years and full clean-up was never accomplished. Oil spills cause damage to the environment and contaminate sources of potable water. Another source of contamination stems from the emergence of fracking in the US, where water-based fluids (containing sand and chemicals) are injected under high pressure to fracture rocks to release oil and gas, which lead to oil-contaminated wastewater. Water contamination with a variety of chemicals is another major concern with growing world population and industrialization with unsafe practices of waste disposal. Various organic contaminants present in contaminated water pose health risks. It is estimated that more than 800 million people do not have access to ‘clean’ water [3].

In water contaminated with oil, oil and water are not soluble or miscible. Oil–water mixtures present can be divided into immiscible mixtures and emulsions (figure 2). Immiscible oil–water mixtures are common in water contamination and oil spills. Oil–water emulsions are common in some liquid waste. In the immiscible oil–water mixture, mixtures are somewhat stratified by densities of oil and water. An emulsion is a type of colloid formed by combining two liquids that normally do not mix. It is a more intensive mix type in which microdroplets (less than a micrometre to a few micrometres) of one liquid are dispersed in the other. Emulsions normally require mechanical agitation and the use of emulsifiers (surface-active agents). Emulsifiers are used to prevent the suspended droplets from coalescing and breaking up the emulsion. Based on dispersed phases, oil–water emulsions fall into two types: oil-in-water and water-in-oil emulsions [6,7]. An example of an oil-in-water emulsion would be milk and water-based paint. An example of water-in-oil emulsion would be margarine and mayonnaise.

Next, commonly used oil–water separation and water purification techniques are described, followed by bioinspired surfaces which can be used for oil–water separation and water purification, and the objective of the paper.

(a) Commonly used oil–water separation and water purification techniques

Oil–water separation techniques are of interest in industrial applications and important for environmental sustainability. To separate immiscible oil–water mixtures, traditional physical methods, such as gravity separation, centrifuge, sedimentation and hydrocyclone separation, are widely used [2,4,7]. These methods are either time-consuming or energy intensive. For the more complex emulsions, thermo/chemical demulsifiers and electrolytic demulsification methods are commonly used. However, the complexity and the high energy consumption add to the cost.

For oil spill remediation, various methods are used by the oil industry [3,4]. Toxic dispersants are used in which chemicals reduce the interfacial tension between oil and water to facilitate the breakup of the oil into smaller droplets. However, the toxicity and poor biodegradability of both dispersants and the resulting dispersed oil makes using such chemicals undesirable. Skimming of the oil from the surface of the water with absorbent booms is another method of oil removal; however, this is dependent upon favourable conditions including calm waters and slow oil speeds. Other methods for the collection of the oil use other absorbent materials such as zeolites and organoclays, or natural fibres such as straw, cellulose, wool or human hair. However, many of these materials also have a tendency to absorb water, which can lower their efficiency. Additionally, the absorbed oil must be removed from the material, making such methods incompatible with continuous flow systems [3].
For water purification, separation filters and membranes that repel one liquid phase while allowing the other to pass through also exist. These are commonly designed for maximum permeation, at the cost of some degree of selectivity.

(b) Bioinspired surfaces for oil–water separation and water purification

Bioinspired surfaces may provide optimum solutions for oil–water separation and water purification, which are sustainable and environmentally friendly.

(i) Lessons from nature

In nature, the lotus leaf is known to be water repellent [4,8–11]. Lotus leaves are found in muddy ponds, and yet the leaf surface is typically clean. Water droplets falling on the leaf are found to exhibit high contact angles and a low contact angle hysteresis or tilt angle due to formation of air pockets (referred to as the Cassie–Baxter state of wetting). Therefore, droplets roll off the surface, moving easily across the leaf, collecting debris as they go and keeping the leaf clean for photosynthesis. The superhydrophobic nature of the leaf surface is a result of its chemistry and surface roughness. It is composed of a hierarchical structure of microbumps formed by convex papillae epidermal cells, covered with three-dimensional epicuticular wax which self-assemble in the form of nanotubes (figure 3a). The nanotubules are made of a hydrophobic wax and, when
combined with the micropapillae, result in a superhydrophobic surface with low contact angle hysteresis or tilt angle [4].

Oils have a lower surface tension than that of water [3,4]. It is therefore possible to design surfaces that repel water but have an affinity for oils. Inspiration can be taken from the lotus leaf to create hierarchically structured surfaces with relatively low surface energy, lower than surface tension of water but higher than that of oil. The low surface energy will make the surface hydrophobic and the hierarchical roughness will result in a superhydrophobic surface with high water contact angle and low oil contact angle. Oil–water separation can be achieved when the coating is applied to a porous substrate. The oil will pass through the porous structure and water will be collected on the top surface.

An alternative method that once again is inspired by nature, is to use a surface that is oil repellent when underwater. Examples of oil repellency in nature are generally limited to underwater oil repellency [4]. As mentioned earlier, the top of the lotus leaf is superhydrophobic due to wax nanotubules. However, the underside of the leaf has no such structures and is superhydrophilic and superoleophilic. When floating on water, the underside of the leaf is superoleophobic (figure 3b). In another example, shark skin is superhydrophilic and superoleophilic in air but superoleophobic underwater (figure 4) [4,14,15]. Water soaks into the skin and forms a thin water layer. The oil droplets sit on top of the water layer to result in superoleophobicity. It should be noted that the surface is only superoleophobic underwater and that can be a major limitation in application.
oil droplet underwater and apparent contact angle for shark skin

conceptual mechanism of samples (underwater)

actual

153°

Figure 4. Optical images of water droplet in air and oil droplet underwater for shark skin replicas [14,15].

(ii) Superliquiphobic/philic porous surfaces

Surfaces that are superoleophobic in air are also superhydrophobic due to water having a higher surface tension. Such surfaces would therefore be unsuitable for oil–water separation since the interactions with both liquids is similar. Coated porous surfaces that attract one liquid (-philic) and repel the other liquid (-phobic) are suitable for oil–water separation. Bioinspired roughness-induced surfaces which attract one liquid and repel the other liquid have been fabricated by various researchers [4,16–20]. A multi-scale hierarchical roughness structure with a functional coating is used to provide various combinations of water and oil repellency and affinity.

To fabricate a roughness-induced superhydrophobic/superoleophilic surface, a non-fluorinated silane layer can be deposited on a surface with hierarchical roughness. Coated porous structures can be used for oil–water separation with oil passing through and water being collected on the top surface. To fabricate a superoleophobic/superhydrophilic surface, a fluorosurfactant layer can be used, which contains a high surface energy head group and a low surface energy tail group. After deposition, the fluorinated tails segregate at the air interface, resulting in a low surface energy barrier that repels oils. However, when droplets of water are placed on the surface, they are able to penetrate down through the tail groups to reach the high surface energy polar head groups below. The coating therefore appears hydrophilic while also being oleophobic. Therefore, porous structures coated with fluorosurfactants can be used for oil–water separation with water passing through and oil being collected on the top surface.

Re-entrant geometries are used for improved repellency of very low surface tension liquids. Re-entrant geometries are shapes that have overhanging structures in which the surface features become narrower at the base [4,21,22]. These geometries are necessary for repelling low surface tension liquids, and particularly surfactant-containing liquids such as shampoos and laundry detergents due to their low tension components and active groups.

For superoleophilic porous surfaces, after absorbing a certain amount of oil, the separation efficiency of these surfaces reduces as the filter surface retains oil. In all superoleophilic porous surfaces, oil contamination is of concern, and porous materials must be cleaned or replaced are use. Therefore, superoleophobic/superhydrophilic porous surfaces are preferred in which the water passes through the porous material and the oil is repelled. Additionally, water is denser than oil and tends to sink to the bottom of a mixture, meaning that hydrophobic/oleophilic materials are not suitable for certain applications, such as gravity-driven separation.

Porous structures commonly used include stainless steel mesh, fabric, filter paper, sponge and compressible cotton. The stainless steel mesh can have pore size (opening) as low as about 25 µm. Woven cotton fabrics can also have pore size as low as about 25 µm [23]. However, cotton can have very small pore size (on the order of fraction of 1 µm to about 10 µm) dependent upon compressibility. Different porous structures are used for separation of different oil–water mixtures. For immiscible oil–water mixtures, stainless steel mesh is commonly used. Cotton fabric is also occasionally used. For oil–water emulsions, the pore size of steel meshes and cotton fabrics
is generally too large and compressible cotton is preferred. Cotton fabric can be used in some oil–water emulsions with relatively large liquid droplets of one liquid dispersed in the other. Photographs of various porous surfaces are shown in figure 5.

Unlike absorbent materials, in the coated porous material techniques, both phases are immediately separated with no additional steps required to remove one phase from the material. It is envisioned that such a device could be used upstream of the conventional purification membranes. This ensures that the majority of the contaminant phase is removed before further purification and processing, resulting in greater efficiency of the more selective membranes.

(c) Objective

In this paper, a review of various bioinspired approaches for fabrication of superliquiphobic/philic porous surfaces with affinity to water and repellency to oil or vice versa is presented. Details of fabrication and characterization of superliquiphobic/philic stainless steel mesh, cotton fabrics and cotton are presented. Applications of bioinspired oil–water separation techniques to oil spill clean-up and water purification are discussed.

2. Coated stainless steel mesh for separation of immiscible oil–water mixtures

Superhydrophobic/superoleophilic and superoleophobic/superhydrophilic stainless steel mesh surfaces having multi-scale roughness with low surface energy coatings have been developed. In an early example of fabrication of superhydrophobic/superoleophobic mesh surfaces, only a low surface energy coating was used to repel water. A polytetrafluoroethylene (PTFE) emulsion was spray coated onto stainless steel meshes with various pore diameters [24]. The resulting coated mesh was superhydrophobic and superoleophilic with contact angles of about 150° for water and about 0° for diesel oil. When oil was added to the mesh, it quickly spread and permeated the mesh and was collected on the other side, while water added to the mesh remained on top.
Later, bioinspired approaches were developed for fabrication of superhydrophobic/superoleophobic mesh surfaces. Brown & Bhushan [16,17] used a nanoparticle/binder layer to create hierarchical roughness by using a so-called, layer-by-layer technique. The nanoparticles also increase the coating hardness, resulting in a durable coating. Two polyelectrolyte layers were used to support a silica nanoparticle layer by electrostatic attraction on a stainless steel mesh surface. They deposited a silane layer on the top to produce a surface which was superhydrophobic and superoleophobic. Bhushan & Martin [18] used a spray coating of silica nanoparticles and methyphenyl silicone binder to produce a low surface energy surface with hierarchical roughness. Both coated mesh surfaces demonstrated that hexadecane oil goes through the mesh and water is collected on the top. Both deposition techniques are facile.

Nanda et al. [25] developed another facile method. They chemically etched steel mesh to create flower like microstructures, then coated the etched surface with hexadecyltrimethoxysilane (HDTMS) to produce a superhydrophobic and superoleophilic surface. They demonstrated that kerosene–water and n-hexane–water mixtures can be separated with kerosene or n-hexane going through the filter with a high separation efficiency.

In an early example of fabrication of underwater superoleophobic surfaces, these were created by immersing stainless steel mesh into an acrylamide solution. The acrylamide was polymerized by UV irradiation to form a hydrogel, a water-swollen polymer network [26]. When placed underwater, the treated hydrophilic mesh exhibited oil contact angles of 153° and droplets were found to roll easily from the tilted surface. When an oil–water mixture was poured onto the mesh, the water permeated through the mesh while the oil remained on top. Although this configuration helps to reduce the impact of oil fouling, the fact that the surface is only superoleophobic underwater limits its application.

Brown & Bhushan [17] created a superoleophobic/superhydrophilic mesh surface by combining the chemistry of the fluorosurfactant with hierarchical roughness using the layer-by-layer technique described earlier. Bhushan & Martin [18] used the nanoparticle/binder coating with an over layer of fluorosurfactant. The fluorosurfactant provides oil repellency and water affinity, while the roughness enhances these properties to result in oil contact angles of greater than 150° and water contact angles of less than 5°. When this coating is applied to a stainless steel mesh and an oil–water mixture is poured over it, the water penetrates through the mesh while the oil remains on top and can be easily rolled off by tilting. By inclining the mesh at an angle, the two liquids can be separated and collected simultaneously. A nanoparticle/binder composite coating technique is found to work with a variety of substrates with desired performance [18]. It requires a minimum number of processing steps, which is desirable [27].

Such superoleophobic/superhydrophilic surfaces represent the ideal scenario for oil–water separators. Their oil-repellent nature means they are less prone to oil fouling than devices where the water phase is being repelled. In addition, their water affinity makes them more compatible with gravity-driven separation, where the water phase will end up at the bottom of the mixture, or in scenarios where water is the dominant phase.

Fabrication techniques for superliquiphobic/philic stainless steel meshes and selected characterization data and their application for oil–water separation will be presented next.

(a) Fabrication technique

Schematic of fabrication methods to produce superhydrophobic/superoleophilic and superoleophobic/superhydrophilic coatings are shown in figure 6. Coatings consisting of hydrophobic SiO₂ nanoparticles and a binder of methylphenyl silicone resin with or without functional layers to obtain combinations of superhydrophobic/philic and superoleophobic/philic properties have been fabricated [4,12,18]. Methylphenyl silicone resin binder is commonly selected because it is known to be durable and offers strong adhesion between the nanoparticles and substrate. Hydrophobic, 10 nm SiO₂ nanoparticles are selected because they have high hardness for wear resistance and high visible transmittance for transparency. For a superhydrophobic/superoleophobic surface, the nanoparticle/binder mixture is deposited
Figure 6. Schematics of fabrication methods. For superhydrophobic and superoleophilic surfaces, hydrophobic nanoparticles and methylphenyl silicone binder is applied to provide nanoroughness. For superhydrophobic and superoleophilic surfaces, nanoparticle/binder coating is treated by ultraviolet–ozone light to activate the surface and then fluorosurfactant is deposited as the last step. (Online version in colour.)

by a spray method on various substrates. For superoleophobic/superhydrophilic surfaces, the nanoparticle/binder coating is irradiated with ultraviolet–ozone (UVO) treatment followed by spin/spray deposition of fluorosurfactant (aqueous anionic fluorosurfactant, Capstone FS-50).

For the coating mixture, 375 mg of hydrophobic silica nanoparticles (10 nm diameter, Aerosil RX300, Evonik Industries) were dispersed in 30 ml of 40% tetrahydrofuran (THF, Fisher Scientific) and 60% IPA by volume. This mixture was sonicated using an ultrasonic homogenizer (20 kHz frequency at 35% amplitude, Branson Sonifer 450A) for 15 min. Then, 150 mg of methylphenyl silicone resin (SR355S, Momentive Performance Materials) was added for a particle-to-binder ratio (p-b ratio) of 2.5 for optimum wettability with highest value of CA and lowest value of TA. The mixture was then sonicated for an additional 15 min to form the final mixture. One millilitre of the coating mixture was deposited via spray gun (Paasche \textsuperscript{®}) from 10 cm away with compressed air at 210 kPa. The sample was transferred to an oven at 70°C for 5 min to remove the remaining solvent. The coated surfaces were superhydrophobic/superoleophilic [4,12,18].

For superoleophobic/superhydrophilic surfaces, a fluorosurfactant coating was applied on top of the nanoparticle/binder coating. To prepare an active surface, the underlayer was first irradiated using UVO treatment with the samples placed 2 cm underneath the lamp source for 60 min. The UVO exposure was generated from a U-shaped, ozone producing, ultraviolet lamp (18.4 W, Model G18T5VH-U, Atlantic Ultraviolet Co.). It is reported that this lamp puts out a total of 5.8 W of 254 nm light, 0.4 W of 185 nm light, and 1.6 g h\textsuperscript{−1} of ozone in ambient conditions. The lamp was placed in an enclosure and was connected to an electronic ballast (120 v, Model 10-0137, Atlantic Ultraviolet Co.) in order to provide the proper electrical conditions [18]. Next, 1 ml of a fluorosurfactant solution (Capstone FS-50, DuPont) diluted with ethanol to an overall fluorosurfactant concentration of 45 mg ml\textsuperscript{−1} was spin coated or spray coated onto the sample [4,12,18].
Characterization data of nanoparticle/binder coatings with and without fluorosurfactant on glass substrates is presented. The glass substrate is a commonly used substrate in scientific studies.

(i) Surface morphology

To study surface morphology, scanning electron microscope (SEM) and atomic force microscope (AFM) images of a superoleophobic coating on glass substrates were taken (figure 7) [18]. SEM images show the multi-scale roughness structure of the coating. From the AFM measurements, root mean square (RMS) roughness of the coating was about 1 µm with a Peak-to-Valley (P-V) distance of 5.5 µm.

The coating thickness was obtained by measuring the step height of the coating deposited on part of the substrate. The measured coating thickness at particle-to-binder (p-b) ratio of 2.5 was about 3 µm.

(ii) Wettability

Contact angles and tilt angles were measured using a standard automated goniometer. Optical images and measured contact angle (CA) and tilt angle (TA) values for water and hexadecane droplets on the glass substrate and with two coatings are shown in figure 8 [18]. Untreated glass has a water CA of $55 \pm 2^\circ$ and a hexadecane CA of $27 \pm 1^\circ$. By applying the coatings to these substrates, superhydrophobic/superoleophilic and superoleophobic/superhydrophilic properties were obtained. The nanoparticle/binder coating resulted in water CA of $165 \pm 2^\circ$, water TA $\leq 1^\circ$, and wetting with hexadecane. The nanoparticle/binder and fluorosurfactant coating results in wetting with water, hexadecane CA of $157 \pm 2^\circ$, and hexadecane TA of $2 \pm 1^\circ$. 

Figure 7. SEM and AFM images of superoleophobic coating with an optimum p-b ratio of 2.5 on a glass substrate (adapted from Bhushan & Martin [18]).
Figure 8. Optical images and measured CA and TA values of water and hexadecane droplets on glass substrates and coated samples to show repellency and wetting with the two liquids (adapted from Bhushan & Martin [18]). (Online version in colour.)

Figure 9. Optical micrographs after wear experiment using ball-on-flat tribometer using a 3 mm diameter sapphire ball with 10 mN load on superoleophobic coating. There was slight burnishing but the coating was still able to repel hexadecane (adapted from Bhushan & Martin [18]).

(iii) Wear resistance

Wear resistance on the macroscale of the superoleophobic coating on glass substrate was investigated by performing wear tests using a ball-on-flat tribometer [28,29]. For the wear test, a 3 mm diameter sapphire ball was slid against the samples in a reciprocating mode. The test was carried out at 10 mN for 100 cycles. The optical images of the samples after wear experiments showing the wear track are shown in figure 9 [18]. Burnishing of the coatings was observed. The coating was still able to repel hexadecane over the burnished region suggesting that the coating was not destroyed.
wear experiment using AFM on superoleophobic surface

Figure 10. AFM surface height maps and surface profiles (locations indicated by arrows) before and after AFM wear experiments with 15 µm radius borosilicate glass ball at a load of 10 µN over 50 × 50 µm on superoleophobic coating. After AFM test, there was no burnishing of the coating (adapted from Bhushan & Martin [18]).

Figure 11. Photographs of oil and water droplets on superoleophobic/superhydrophilic stainless steel mesh. Oil droplet remained on the mesh surface, whereas water droplet spread quickly and penetrated through the mesh in a fraction of a second.

To study wear resistance on the microscale, the superoleophobic coating was scanned with an AFM using a 15 µm radius borosilicate glass ball mounted on a rectangular lever at a normal load of 10 µN over 50 × 50 µm region [30]. Figure 10 shows AFM images over 100 × 100 µm scan area before and after the AFM wear experiments. After the AFM test, there was no burnishing of the
Figure 12. Photographs of the superoleophobic/superhydrophilic and superhydrophobic/superoleophilic coated stainless steel meshes acting as oil–water separators. On the superoleophobic/superhydrophilic coated mesh, oil collects on top of the mesh while water passes through. In contrast, on the superhydrophobic/superoleophilic coated mesh, oil passes through the mesh while the water remains on the top surface. If the meshes are placed at an angle, oil or water sitting on the mesh can be collected simultaneously in separate beakers. Red oil and blue water dyes were used to enhance contrast (adapted from Brown & Bhushan [17] and Bhushan & Martin [18]).

(c) Characterization of coated stainless steel mesh surfaces for oil–water separation

Stainless steel meshes (#400) were cleaned with acetone and 2-propanol (Fisher Scientific) until they were found to be hydrophilic. They were then coated with nanoparticle/binder coating and some with fluorosurfactant coating as well to produce superhydrophobic/superoleophilic and superoleophobic/superhydrophilic meshes, respectively.

To study repellency to oil and affinity to water droplets on a superoleophobic/superhydrophilic stainless steel mesh, droplets were placed on the coated mesh, as shown in figure 11. Oil droplets remained on the mesh. The sequence of photographs of the water droplet on the coated mesh shows that the water droplet spreads quickly and penetrates through the mesh in a fraction of a second (F Li 2019, personal communication).
Nets featuring bioinspired coated mesh trap oils while allowing passage of water. Oil can easily be recovered from nets via pumping. Oil-repellent nature of mesh reduces need for cleaning.

Figure 13. Schematic showing bioinspired nets connected to a boat for oil-spill clean-up. When to boat is driven in an oil spill region, nets will capture the oil, where it can be recovered by pumping, while allowing water to pass through (adapted from Bhushan [4]). (Online version in colour.)

To demonstrate oil–water separation capability in continuous flow systems, agitated, immiscible oil–water mixtures were poured onto coated stainless steel meshes suspended horizontally over beakers as shown in figure 12. In both cases, the -philic component quickly passed through the mesh, while the -phobic component remained on top of the mesh. When the mesh was tilted, the -phobic component rolled across the top of the mesh and was collected in another beaker [4,16–18].

As indicated earlier, the use of oleophobic/hydrophilic coated surfaces is preferable to using hydrophobic/oleophilic coated surfaces because surface contamination by oil and other oil-based contaminants is common, and the porous material must then be cleaned or replaced, resulting in a drop in the separation efficiency.

(d) Applications to oil spill clean-up and water purification

Oil–water separation is of interest in oil spill clean-up and water purification. Methods commonly used for oil spill clean-up include the use of toxic dispersants to break up oil globs into smaller droplets, controlled burning which is not eco-friendly, solvents to soak up oil on contact (very slow method), and skimmer and booms. An environmentally friendly and fast approach would be to use coated steel nets that are superoleophobic/superhydrophilic which should allow oil–water separation in a continuous flow [3]. Figure 13 shows a schematic of how these bioinspired nets can be incorporated into currently used booms on a boat [3]. When the boat is driven in the oil spill region, the bioinspired nets will capture the oil, where it can be recovered by pumping, while allowing water to pass through. These nets can be used repeatedly.

The bioinspired nets can also be used for water purification by removing organic contamination in water.

(e) Summary

For fabrication of superliquiphobic/philic surfaces, the nanoparticle/binder coating method is attractive due to its ease of deposition, flexibility in substrate application and desirable properties. The nanoparticle/binder coating method can be used for fabrication of
superhydrophobic/superoleophobic and superoleophobic/superhydrophilic steel meshes for oil–water separation capabilities.

3. Coated cotton fabric for separation of immiscible oil–water mixtures

In addition to stainless steel mesh, cotton fabric can be used for immiscible oil–water separation. Superhydrophobicity of cotton fabric is achieved by introducing multi-scale roughness and coating with low a surface energy material [4]. Treatment of the cotton fabric surfaces is challenging due to the inherent heterogeneous roughness with low thermal stability. Several methods such as dip coating [31,32], solution immersion coating [19,33,34], sol-gel based coating [35], wet chemical process [36] and spray coating [37] have been used to make cotton fabric superhydrophobic. Physical and chemical durability has been a concern. Chauhan et al. [19] reported that wettability was maintained after physical and chemical abuse and demonstrated high durability. Chauhan et al. [19] fabricated superhydrophobic cotton fabric by simple immersion in non-fluorinated hexadecyltrimethoxysilane (HDTMS) solution. Their coating repelled oils with surface tension as low as 47.70 mN m\(^{-1}\) (ethylene glycol). Tudu et al. [34] fabricated superhydrophobic cotton fabric by simple immersion in perfluorodecyltriethoxysilane (PFDTS) solution. Their coating repelled oils with surface tension as low as 27.05 (hexadecane). Both Chauhan et al. [19] and Tudu et al. [34] demonstrated that coated fabric can be used for oil–water separation as long as surface tension of oil in the mixture was low enough that it wetted the coated surface.

A facile fabrication technique and selected characterization data for superhydrophobic/superoleophilic cotton fabric and their applications for oil–water separation will be presented next [19].

(a) Fabrication and characterization techniques

To fabricate superhydrophobic cotton fabric, as received treated cotton fabric was cleaned ultrasonically to remove wax and other impurities with distilled water and ethanol for 30 min and subsequently dried at 70°C for 1 h. A 5% (v/v) HDTMS was dissolved in ethanol and stirred for 1 h at room temperature to obtain a homogeneous solution. Subsequently, cleaned cotton fabric was immersed in HDTMS solution for 5 h and then dried at 120°C for 6 h in a hot air oven to remove the solvent. Finally, it was left in air for drying [19].

Surface morphologies of as received and treated cotton fabric were examined with SEM. The wettability of the treated cotton fabric was studied by measuring contact angles with a 3–5 µl droplet of water and liquids (with surface tension greater than 47 mN m\(^{-1}\)) such as tea, honey, milk and ethylene glycol. Surface tension values of selected liquids are given in table 1. Chemical stability of the treated cotton fabric was examined by immersing samples in saline water (3.5% w/v NaCl) and organic solvents (chloroform, toluene and dimethyl carbonate). At regular intervals of immersion, contact angles were measured to observe any changes in wettability. A thermal stability test was performed by heating the samples at various temperatures (120, 140, 160, 180 and 200°C) for 1 h. After cooling the samples, the contact angles were measured [19].

To evaluate the self-cleaning performance, as received and treated cotton fabric were immersed in muddy water for 10 min. The treated cotton fabric was difficult to immerse in the muddy water due to the high liquid repellence property, so it was immersed by application of force. Afterward, the effect of mud on the surfaces was characterized by photographing samples before and after soaking in mud [19].

For oil–water separation studies, before conducting an experiment the treated cotton fabric was dipped in oil (organic solvents). The wetted treated cotton fabric was placed on top of a funnel. Later, the oil–water mixture was poured onto treated cotton fabric which repelled the water (blue colour) and was collected on its surface and the oil penetrated the fabric by gravity. Next, n-hexane, kerosene, and ethylene glycol were used as oils in the oil–water mixtures.
as received cotton fabric

![Image](https://example.com/image1.png)

WCA = 0°

superhydrophobic cotton fabric

![Image](https://example.com/image2.png)

WCA = 157 ± 5°, TA = 7°

**Figure 14.** SEM images of as received and superhydrophobic/superoleophilic cotton fabric. Water contact angle and tilt angles are also presented (adapted from Chauhan *et al.* [19]). (Online version in colour.)

**Table 1.** Surface tension values of various liquids and whether superhydrophobic/superoleophilic cotton repels liquid or not (adapted from Chauhan *et al.* [19]).

<table>
<thead>
<tr>
<th>liquid</th>
<th>surface tension (mN m⁻¹)</th>
<th>treated cotton repels or not</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>71.99</td>
<td>repel</td>
<td>Rumble [38]</td>
</tr>
<tr>
<td>glycerol</td>
<td>63.40</td>
<td>repel</td>
<td>Takamura <em>et al.</em> [39]</td>
</tr>
<tr>
<td>milk</td>
<td>55–60</td>
<td>repel</td>
<td>Chandan [40]</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>47.70</td>
<td>repel</td>
<td>Rumble [38]</td>
</tr>
<tr>
<td>kerosene</td>
<td>approximately 30</td>
<td>does not repel</td>
<td>Speight [41]</td>
</tr>
<tr>
<td>benzene</td>
<td>28.80</td>
<td>does not repel</td>
<td>Harkins &amp; Brown [42]</td>
</tr>
<tr>
<td>n-hexane</td>
<td>18.43</td>
<td>does not repel</td>
<td>Rumble [38]</td>
</tr>
</tbody>
</table>

Separation efficiency was calculated by dividing volumes of water after the separation process by volumes of water before the separation process [19].

**b** Surface morphology and wettability

The surface morphologies of as received and treated cotton fabric were observed by using SEM as shown in figure 14 [19]. The SEM images show no significant differences due to the formation of HDTMS monolayers; however, both surfaces show the hierarchical morphology.

Wettability of as received and treated cotton fabric was examined by measuring contact angles. Water contact angles and tilt angles are presented in figure 14. It was found that as received cotton fabric exhibits superhydrophilic and superoleophilic behaviour with a contact angle of approximately 0°. After modification of cotton fabric with HDTMS, it displays water repellency
Images of various liquid droplets on treated cotton fabric are shown in figure 15 and observations on whether the fabric repels or not selected liquids along with their surface tension values are presented in table 1. Liquids whose surface tension is equal to or more than 47 mN m\(^{-1}\) (tea, coloured water, milk, lemon, turmeric, honey, glycerol and ethylene glycol) show good repellency for the treated cotton fabric with contact angles more than 150°, revealing the superoleophobic nature [19].

(c) Physical and chemical durability

Treated cotton fabrics should work indoors as well as in harsh environments such as high temperature, UV irradiation, acidic/alkaline/organic contact and washing. The durability after washing was evaluated by immersing superhydrophobic cotton fabric into a detergent solution, organic solvent (benzene) and hot water (80°C), and then it was ultra-sonicated for 1 h. Afterward wettability behaviour of the dried fabric was examined by measuring the contact angle. Data are shown in figure 16 [19]. It was observed that contact angles of all washed fabrics remained at more than 150° and water droplets rolled off the surface, exhibiting the washable nature of the surface without any damage. This test indicates that the HDTMS-treated cotton fabric maintained wettability properties after washing.

The chemical stability of the treated cotton fabric was examined by immersing the samples in organic solvents (chloroform, toluene and dimethyl carbonate) for 7 days and in saline water (3.5% w/v NaCl) for 24 h. After immersion, water droplets on the surface formed spherical shapes as shown in figure 17 [19]. Contact angles were found to remain more than 150°, displaying superhydrophobic nature. Thus, treated cotton fabric was suitable for organic solvents, as well as the saline water, which is important for industrial purposes.
after 7 days in chloroform
WCA = 156°

after 7 days in toluene
WCA = 155°

after 7 days in dimethyl carbonate
WCA = 156°

after 12 h in saline water
WCA = 157°

Figure 17. Optical images of water droplets on treated cotton fabric after immersion in chloroform for 7 days, toluene for 7 days, dimethyl carbonate for 7 days, and saline water for 12 h. Inserts are contact angle images. Water contact angles are also presented. Chemical stability is demonstrated (adapted from Chauhan et al. [19]). (Online version in colour.)

Figure 18. Contact angle of treated cotton fabric after heating for 1 h at different temperatures. Thermal stability of treated cotton fabric is demonstrated below 150°C (adapted from Chauhan et al. [19]). (Online version in colour.)

The thermal stability of the treated cotton fabric was studied by heating the sample at various temperatures (120–200°C) for 1 h in a hot air oven. The data are shown in figure 18 [19]. The superhydrophobicity, with water contact angle of 157 ± 5° of the treated cotton fabric, was maintained after heating up to 120–150°C, exhibiting thermal stability of the treated cotton fabric below 150°C. The contact angle of the cotton was 141° after heating to 160°C and the
superhydrophobicity turned into hydrophobicity due to the decomposition of the HDTMS (boiling point, 155°C) which resulted in the removal of low surface energy material from the surface [19].

(d) Self-cleaning properties

The self-cleaning properties of the treated cotton fabric were examined by immersing as received and treated cotton fabric into muddy water for 10 min, as shown in figure 19 [19]. It was observed that the treated cotton fabric did not immerse easily in mud and remained floating on the muddy water surface due to its high water repellence property. Therefore, it was forcefully immersed into the muddy water. After immersion, as received cotton fabric was found to be wetted with muddy water and it remained polluted even after cleaning and drying. On the other hand, treated cotton fabric was fully clean when it was removed from the muddy solution, showing its excellent self-cleaning property [19].

(e) Separation of immiscible oil–water mixtures

Droplets of water and liquids with a surface tension more than 47 mN m$^{-1}$ could not penetrate through the superhydrophobic cotton fabric surface whereas low surface tension oils could. Therefore, coated cotton fabric can be used for oil–water separation with oils having surface tension equal to or less than 47 mN m$^{-1}$. Oil (n-hexane = 18.43 mN m$^{-1}$), kerosene (approx. 30 mN m$^{-1}$) and ethylene glycol (47.70 mN m$^{-1}$) were used to separate from their mixtures. All mixtures consisted of a 1:1 ratio. Figure 20a shows optical images of n-hexane–water mixture before, during and after oil–water separation [19]. It can be seen that oil is separated by its own gravity. After separation, no water trace (blue colour) is visible within the penetrated oil (n-hexane), showing excellent oil–water separation efficiency. Separation efficiency of oil–water (n-hexane–water and kerosene–water) and oil–liquid (benzene–ethylene glycol) mixture was measured and is presented in figure 20b. It was found to be about 99%. After a few cycles, the separation process became slow due to adsorption of the oil on the cotton surface. Afterward, oil
adsorbed cotton fabric was cleaned with acetone and water. It was found that the cleaned cotton fabric showed a contact angle more than 150° and could be re-used for the oil–water separation process [19].

(f) Summary

Superhydrophobic cotton fabric was produced by using a simple immersion technique in non-fluorinated HDTMS solution [19]. Treated cotton fabric exhibited repellency with water and liquids with surface tension equal to or more than 47 mN m\(^{-1}\), such as tea, honey, glycerol, ethylene glycol and milk. Wettability was maintained after machine washing in detergent solution, benzene and hot water at 80°C, after immersion in chloroform, toluene and dimethyl carbonate, and in saline water, as well as exposure to high temperature (approx. 150°C). The treated cotton exhibited self-cleaning properties. Treated cotton fabric could separate the oil from its oil–water (n-hexane–water, kerosene–water) and oil–liquid (benzene–ethylene glycol) with high separation efficiency of about 99%.

4. Coated cotton for separation of oil–water emulsions

The mesh-based materials with opposite wettability towards oil and water are used in separating immiscible oil–water mixtures. Separation efficiency is dependent upon the pore size. The mesh-based materials are impractical for separating emulsions, because the microdroplets dispersed...
in emulsions can easily pass through the mesh whose apertures are larger than about 25 µm. To separate emulsions, one of the effective approaches is to decrease the pore size of the substrates. Attempts have been made to accomplish the separation of emulsions by selecting specially made mesh or membrane substrates whose pore sizes are several micrometres [31,43]. The efforts of decreasing the pore sizes resulted in some success in emulsion separation, but were not efficient for separation of immiscible oil–water mixtures with high flux.

To separate both immiscible oil–water mixtures and emulsions, a compressible soft material which has small pore structures would be desirable. The use of cotton makes it possible to separate immiscible and emulsified mixtures. A superhydrophobic/superoleophilic three-dimensional porous structure with fine pore size was used to separate oil from immiscible oil–water mixtures as well as from water-in-oil emulsions [44]. However, a porous structure of this kind is easily contaminated and the pores become blocked by oil. Li et al. [20] developed superoleophobic/superhydrophilic cotton for oil–water separation. The coated cotton provided oil-repellency and water-wetting behaviour in ambient atmosphere. It was capable of separating both immiscible oil–water mixtures and oil-in-water emulsions. Since the cotton pores do not get blocked by oil, this approach is attractive.

A facile fabrication technique and selected characterization data for superoleophobic/superhydrophilic cotton and their applications for oil-in-water separation will be presented next [20].

(a) Fabrication and characterization techniques

(i) Fabrication technique

The fabrication process is shown in figure 21a [20]. Fluorosurfactant and hydrophilic Al₂O₃ nanoparticles were mixed in an ethanol solution with a magnetic stirrer and functionalized nanoparticles were formed by the attachment between the fluorosurfactant and Al₂O₃ particles in the process. Next, the cotton fibres were coated with the functionalized nanoparticles. The cotton fibres get attached to nanoparticles and fluorinated chains with low surface energy arranged at the air interface, as shown in figure 21b.

To determine an optimum concentration of fluorosurfactant, wetting properties were measured as a function of various concentrations. It was found that there was no effect on the superoleophobicity and superhydrophilicity when the concentration of the fluorosurfactant in ethanol solution was higher than 30 mg ml⁻¹. To prepare a fluorosurfactant–ethanol solution with a concentration of 40 mg ml⁻¹, 2 g fluorosurfactant (Capstone™ FS-50, Dupont) was dissolved in a 50 ml ethanol solution followed by 30 min of magnetic stirring. To determine the optimal concentration of Al₂O₃ nanoparticles, the superoleophobicity (contact angles and tilt angles of hexadecane droplets) of treated cotton was investigated by varying the Al₂O₃ concentration from 20 mg ml⁻¹ to 100 mg ml⁻¹. They found that the contact angle of hexadecane remained around 150° when the concentration was higher than 20 mg ml⁻¹, whereas the tilt angle was fairly high when the concentration was higher than 80 mg ml⁻¹ or lower than 40 mg ml⁻¹. The lowest tilt angle occurred at the concentration of about 60 mg ml⁻¹. Therefore, 3 g Al₂O₃ nanoparticles (30 nm, Aladdin Bio-chem) were added into the aforementioned solution so that the Al₂O₃ concentration was 60 mg ml⁻¹. The solution was magnetic stirred for another 20 min to improve mixing to produce a paint-like suspension [20].

Next, a piece of pristine cotton (approx. 0.5 g, Aladdin Bio-chem) was initially washed with ethanol and deionized water in succession, followed by 40 min of vacuum drying at 60°C. The cotton then was immersed in the suspension and ultrasonically cleaned for 20 min before being dried at atmospheric pressure at 80°C [20].

(ii) Preparation of emulsions

To prepare emulsions, diesel fuel (surface tension approx. 25.05 mN m⁻¹) and hexadecane oil (surface tension approx. 27.05 mN m⁻¹) were selected as the dispersed phase, and TWEEN60 (MW 1131, Aladdin Bio-chem) was selected as an emulsifier. TWEEN60, fuel or oil and deionized
water were mixed in a ratio of 1 : 10 : 100 by volume. Each solution was mixed with an ultrasonic homogenizer for 3 h. All emulsions appeared to be stable for more than 20 h under atmospheric conditions [20].

(iii) Wettability

Wettability was determined by measuring contact angles and tilt angles of the liquid droplets on the treated cotton. The droplet volume used was about 5 µl. Selected liquids of scientific and engineering interest were deionized water, diesel fuel, and octane, hexadecane and dichloroethane oils. Their surface tension data are presented in Table 2.

Table 2. Surface tensions, contact angles and tilt angles of liquids on superoleophobic/superhydrophilic cotton (adapted from Li et al. [20]).

<table>
<thead>
<tr>
<th>liquid</th>
<th>surface tension (mN m⁻¹)</th>
<th>contact angle (°)</th>
<th>tilt angle (0°)</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>deionized water</td>
<td>71.99</td>
<td>wetted</td>
<td>wetted</td>
<td>Rumble [38]</td>
</tr>
<tr>
<td>1, 2-dichloroethane</td>
<td>31.86</td>
<td>153 ± 0.5</td>
<td>4 ± 0.5</td>
<td>Rumble [38]</td>
</tr>
<tr>
<td>hexadecane</td>
<td>27.05</td>
<td>154 ± 1</td>
<td>4.5 ± 0.5</td>
<td>Rumble [38]</td>
</tr>
<tr>
<td>diesel</td>
<td>25–29</td>
<td>153 ± 0.5</td>
<td>5.5 ± 0.5</td>
<td>Li et al. [20]</td>
</tr>
<tr>
<td>octane</td>
<td>21.14</td>
<td>152 ± 1</td>
<td>4 ± 0.5</td>
<td>Rumble [38]</td>
</tr>
</tbody>
</table>
**Figure 22.** The schematic of the injector barrel for separation of emulsions. The treated cotton is pushed into the injector barrel and compressed as tightly as possible (density is about 0.28 g cm\(^{-3}\)), then the emulsions is poured into the barrel (adapted from Li et al. [20]).

**iv) Separation method of immiscible mixtures and emulsions**

To separate immiscible oil–water mixtures by a gravity-driven method, the treated cotton and a stainless steel mesh (#300) used as a support was pressed together between two glass tubes. The gap between the tubes was then sealed by silicone sealant (Silco RVT-4500). The combination was then set above the beaker with the cotton side up. For gravity driven separation, an immiscible oil–water mixture was poured into the top tube and the water penetrated the treated cotton and fell into the beaker [20].

For separation of emulsions, superoleophobic/superhydrophilic cotton (approx. 1 g) was pushed into an injector barrel as tightly as possible and the density of the compressed cotton was measured to be about 0.28 g cm\(^{-3}\). An oil-in-water emulsion was poured into the barrel, as shown in figure 22 [20]. During the separation, water will wet and penetrate the compressed cotton, while the microdroplets of oil will be rejected.

A 500 ml of emulsion feed was used for measurement of flux and separation efficiency of oil-in-water emulsions. The oil content in the feed and filtrate was measured by a total organic carbon analyser. The dispersion images of the emulsions were taken and the separated flux was calculated by dividing the volume of the separated emulsion divided by the product of the sectional area of the injector barrel and the time of the separation process. The efficiency of the emulsion-separation process was calculated by dividing the difference between concentrations of oil in the emulsion feed and filtrate, divided by the concentration of the oil in the emulsion feed [20].
(b) Surface morphology and wettability

The surface morphology of the cotton was characterized by SEM and the images are shown in figure 23 [20]. The fibres in the treated cotton were covered by the agglomerated fluorinated Al₂O₃ nanoparticles. Overlapping distributed fibres as well as the nanoparticles constitute a multi-dimensional roughness in both macro and micro scales. This multi-scale structure plays a dominant role in providing superoleophobicity and superhydrophilicity [4]. Surface roughness of the pristine and treated cotton was measured by using laser scanning confocal microscopy. The root mean square roughness, $R_q$, is presented in figure 23. Treated cotton is rougher than the pristine cotton.

To assess the superoleophobicity and superhydrophilicity of the treated cotton, contact angles and tilt angles of fuel, oil and water were also measured. Data are summarized in table 2 [20]. Images of droplets of various liquids on the treated cotton are shown in figure 24a [20]. Diesel fuel and various oils with different surface tensions were repelled by the treated cotton without sticking or wetting. On the other hand, water droplets wetted and permeated the cotton upon immediate contact with the fibres. The hexadecane oil droplets were even able to slide freely on the treated cotton with low contact angle hysteresis, which demonstrated the oil repellent behaviour of the treated cotton as shown in figure 24b [20].

(c) Separation of oil–water mixtures

(i) Immiscible oil–water mixtures

The treated cotton could separate many immiscible oil–water mixtures by a simple gravity-driven pouring method. Figure 25 shows that the water, dyed blue, continuously passed through the cotton and hexadecane, dyed red, was restrained on the surface without any penetration. This treated cotton is expected to be superior to superhydrophobic/superoleophilic materials during which the material is easily blocked by viscous oil.

(ii) Oil-in-water emulsions

The superoleophobic/superhydrophilic cotton could also be used for the separation of oil-in-water emulsions due to its superoleophobicity and superhydrophilicity. A schematic of separation
of oil-in-water emulsion is shown in figure 26 [20]. For separation of oil-in-water emulsions, the continuous water phase easily wets the superhydrophilic fibres and permeates the cotton, whereas, the continuous water phase as well as the wetted fibres on the top surface form an obstructive layer towards oil and thus the micro oil droplets were rejected at the surface of the compressed cotton. Since the oil droplets do not stick on the cotton surface, the oil should not block the pores of the compressed cotton.

To test the separation properties, optical micrographs of the emulsion feed and filtrate before and after separation were taken, as shown in figure 27 [20]. Diesel-in-water and hexadecone-in-water emulsions were used as emulsion feeds. The figure shows that oil droplets were randomly dispersed in both emulsion feeds, while there were no droplets detected in the filtrates after separation.

To quantify the separation properties, the separated flux and the separation efficiency were measured, as shown in figure 28 [20]. High separated flux was observed which varied from
oil-in-water emulsion

Figure 26. Schematic of separation of oil-in-water emulsion. During the separation, the water phase wetted and permeated the compressed cotton, and the dispersed oil droplets were rejected (adapted from Li et al. [20]). (Online version in colour.)

diesel-in-water emulsion feed filtrate

hexadecane-in-water

Figure 27. Optical images of the emulsion feeds and filtrates before and after separation. Diesel-in-water and hexadecane-in-water emulsions were used as emulsion feeds.

520 l m\(^{-2}\) h\(^{-1}\) to 650 l m\(^{-2}\) h\(^{-1}\). The separation efficiency was higher than 98% for continuous separation of both diesel-in-water and hexadecane-in-water separation. High efficiency provides a practical approach in low-cost and effective separation of different stabilized emulsions in both industrial and domestic areas.

(d) Summary

A superoleophobic/superhydrophilic cotton was developed by immersion in a solution of fluorosurfactant and hydrophilic alumina particles in ethanol [20]. The treated cotton, which exhibited oil-repellent and water-wetting behaviour, can be used in separating various immiscible
Figure 28. The separated flux and separation efficiency for diesel-in-water and hexadecane-in-water emulsions (adapted from Li et al. [20]).

Table 3. Summary of filtration techniques suitable for immiscible oil–water mixtures and oil-in-water and water-in-oil emulsions. Filtration in immiscible mixture is dependent upon liquid surface tensions. Filtration in emulsion is dependent upon continuous phase and dispersed phase.

<table>
<thead>
<tr>
<th>Filtration Technique</th>
<th>Porous Material and Its Wettability</th>
<th>Mixture to Be Filtered</th>
<th>Oil–Water Mixture</th>
<th>Oil–In-Water Emulsion</th>
<th>Water–In-Oil Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stainless Steel Mesh/Cotton Fabric</td>
<td>Superhydrophobic/</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Superoleophilic</td>
<td>(Oil Contamination</td>
<td>(Oil Contamination of</td>
<td>Continuous Phase (Oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Superhydrophilic</td>
<td>of Porous Material)</td>
<td>Cotton)</td>
<td>Penetrates and Oil Gets Rejected</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Water) Does Not</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Penetrate and Oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gets Rejected As It</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td>Travels Through</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>The Thickness</td>
</tr>
</tbody>
</table>

oil–water mixtures without oil contamination. In addition, the treated cotton can also be used for separating oil-in-water emulsions with high flux and high efficiency without oil contamination.

5. Closure

Oil contamination can occur during operation of machinery, oil exploration and transportation, and due to operating environment. Water contamination with various chemicals is another major concern with growing population and unsafe industrial practices of waste disposal.
Commonly used oil–water separation techniques are either time consuming, energy intensive and/or environmentally unfriendly.

Bioinspired superhydrophobic/superoleophilic and superoleophobic/superhydrophilic porous surfaces have been developed for oil–water separation which are sustainable and environmentally friendly. Stainless steel mesh and cotton fabric as porous materials are used for immiscible oil–water mixtures, and cotton for oil–water emulsions. In superoleophilic/superhydrophobic porous surfaces, oil contamination is of concern, and porous materials must be cleaned or replaced. Therefore, superoleophobic/superhydrophilic porous surfaces are preferred. Furthermore, for separation of oil-in-water emulsions, only superhydrophilic/superoleophilic porous surfaces can be used. Whereas, for separation of water-in-oil emulsions, only superoleophobic/superhydrophilic porous surfaces can be used.

Table 3 presents a summary of various filtration techniques for immiscible oil–water mixtures and emulsions with some comments. These filtration techniques can be used for various applications including oil spill clean-up, water purification and emulsion separation.

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Competing interests. We declare we have no competing interests.

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