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Fabrication of non-fluorinated hydrophilic-oleophobic stainless steel mesh for oil-water separation

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ABSTRACT

Oil-water separation is a worldwide concern due to the increasing emissions of oil-contaminated industrial water, frequent oil spills and the general shortage of clean drinking water. In this study, hydrophilic/underwater superoleophobic stainless steel (SS) meshes were fabricated via a one-step solution-based coating method using methyltrimethoxysilane (MTMS). The dimensions of the meshes were varied to study their effect on wettability and separation efficiency. Coated meshes were then used for gravity-driven oil/water separation with oil-water mixtures and oil-water emulsions in which water passed through the meshes while oil was retained. Contact angles, fluid flux and separation efficiency were evaluated to determine the optimum mesh dimensions. XPS and ATR-FTIR were performed on the coated stainless steel surface to confirm the presence of silanol groups that are accountable for the resultant unique wetting properties. After sand impact durability testing, the treated meshes were still able to separate oil-water mixtures with high separation efficiency and water recovery rates, despite the presence of residual sand particles.

1. Introduction

Recent oil spills in Alaska, the Gulf of Mexico, France and many other locations have highlighted the risks of environmental pollution that accompanies the development of industry and society [1,2]. The difficulties that were encountered during oil spill cleanup and the general challenges associated with post-treatment of increased volumes of oil-contaminated industrial wastewater underscore the critical need for energy-efficient systems to separate oil-water mixtures. Extensive investigations on the fabrication of porous substrates with special wetting properties have inspired the idea of separating oil-water mixture without applying high amounts of external energy [3–8].

Numerous studies have been performed on the surface modification of porous materials to achieve special wettability properties that can be used for oil-water separation. Various hydrophobic-oleophilic material structures, including metal meshes, have been reported as potential oil-water separation solutions [9–11]. In these materials, the oil contaminant is absorbed, while water is rejected. The primary challenge for the application of these types of materials is fouling [12,13]. Throughout the separation process, oil penetrates into the material and blocks the pores, which often results in a significant decrease in flux and overall performance after several operating cycles. More importantly, these materials are not suitable for *in situ* oil removal where the oil phase does not have sufficient contact with the hydrophobic-oleophilic separation system underneath because the higher density water forms a barrier layer between the oil phase and the oleophilic substrate. The prevailing substrates that have been explored are fabrics, sponges, metal meshes, foams, paper, carbon-based aerogels and powdered materials [14–18]. Although it is bio-degradable, paper lacks the mechanical strength necessary for large scale oil-water separation. For common bulk materials like sponges and foams, the urgent concern is their limited volume for absorption of oil or water [19]. When considering absorption capacity, carbon-based aerogels ranked the highest among these common materials [19,20]. However, the preparation processes for these materials are often complicated and cost intensive, and absorbent-based processes are usually batch-wise, which inherently limits fluid handling capacity.

The problems discussed above have drawn attention to the design of an alternative system that uses hydrophilic-oleophobic materials where the denser water passes through the substrate as filtrate in a continuous separation process, while oil is left in the retentate stream for collection and further processing [21–

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23]. Although the concept has many merits, finding suitable materials is challenging. Since oils commonly have lower surface tension than water, a hydrophilic surface usually also shows affinity to oil; similarly, oleophobic surfaces generally also repel water. Nevertheless, researchers have found several ways to design substrates with these unique hydrophilic-oleophobic wetting characteristics [24–26]. Among the materials listed above, metal meshes have the advantages of reliable mechanical strength as well as easy recycle after use through remolding. Thus the fabrication of hydrophilic-oleophobic metal meshes with durable surface coatings and high water flux represents a very promising approach for oil-water separation.

Extensive research has demonstrated that surface wettability is determined by the synergistic effect of surface chemistry and morphology [27–30]. In addition, the existence of "re-entrant" surface structures has been found to be essential for establishing high repellency towards low surface tension liquids (e.g. oils) [31–33]. Materials with cylindrical geometries such as metal meshes are therefore of particular interest; they have naturally occurring re-entrant structures due to the curvature of the bottom half of the filaments (fibers) that comprise the mesh. Good mechanical strength and well-defined, homogenous weave patterns are additional factors that make metal meshes a superb substrate for liquid-liquid separations.

When considering the design of porous substrates for liquid penetration or repellency, surface porosity and breakthrough pressure are important physical characteristics [34,35]. For meshes, the fiber diameter and inter-fiber spacing determine the surface porosity. While higher surface porosity yields higher permeation rates, the spacing cannot be infinitely large in order to repel low surface tension liquids. Choi et al. have introduced a dimensionless measure of surface robustness with design parameter A^* on a textured surface with cylindrical features [35]. The robustness factor A^* refers to the ratio of breakthrough pressure P_{BT} that is required for the transition from the composite interface to a fully wetted interface and a characteristic reference pressure P_{ref} which is defined as $P_{ref} = 2\gamma_{lv}/l_{cap}$ where l_{cap} is the capillary length of the liquid (defined below). This model has been used extensively to evaluate the substrate resistance to liquid permeation [32,34]. The robustness factor is defined by:

$$A^* = \frac{P_{BT}}{P_{ref}} = \frac{2Dl_{cap}}{G^2}\frac{1-\cos(\theta_{eq})}{1+2(D/G)\sin(\theta_{eq})} \tag{1}$$

where $l_{cap} = \sqrt{\gamma_{lv}/\rho g}$, γ_{lv} and ρ are the surface tension and density of the testing liquid, respectively. θ_{eq} refers to the equilibrium contact angle of the liquid on an ideal flat surface of the same chemical composition and is given by Young's equation [36], while D and G are the fiber diameter and inter-fiber gap respectively. In order for water to penetrate the surface but keep oil retained on top, $A^* \gg 1$ for oil and $A^* < 1$ for water.

To achieve the desired surface morphology needed for wettability modification, most studies have employed superhydrophilic-superoleophobic materials that were fabricated via careful construction of rough structures on the surface using methods such as spraying nanoparticles [37,38] and growing nanowires [39]. One problem with this approach is that the artificial hierarchical structure can easily be damaged or destroyed; this causes the substrates to lose their oil-water separation ability after abrasion or application of mechanical stresses.

Most surface wettability modifications, especially for hydrophilic-oleophobic surfaces, employ fluorinated chemicals. However, there are growing concerns about the risks that fluorocarbons may pose to the environment [40–43]. Unfortunately, it is difficult to achieve oleophobicity without the use of fluorinated materials and/or complicated surface texturing and coating processes. Cao has coated various substrates with non-fluorinated films (polydopamine and polyethylenepolyamine) to achieve hydrophilicity and oleophobicity for separating a mixture of water and hexane, but the coating process takes nearly two days to complete which limits large scale, low cost use [44]. Rohrbach demonstrated a successful separation of a hexane-water mixture using hydrophilic-oleophobic filter paper [45]. This process requires a long drying time and the water flux is low (89.6 L m^{-2} h^{-1}). A simple two-step dip coating process in paraffin wax and poly (dimethylsiloxane)-*b*-poly(ethylene oxide) (PDMS-*b*-PEO) diblock copolymer to fabricate functional filter paper was reported by Paul, but the water flux is too low (77 L m^{-2} d^{-1}) for most practical applications [46]. Moreover, paper is not a good candidate for large scale oil-water separation due to its low strength and susceptibility to fouling.

The goal of this study is to fabricate a mechanically stable stainless steel mesh for efficient oil-water separation using a non-fluorinated short chain silane via a simple immersion coating method. Previous studies on cellulose-based substrates have demonstrated that the presence of silanol groups on the coated cellulose surface can be controlled by adjusting sonication time of the liquid mixture before coating [18]. The premise of the manuscript is that this concept can be transferred to metal substrates: silanol groups from the hydrolyzed silane impart hydrophilicity to the surface, while the methyl groups lower the surface energy of the metal mesh and render the surface oleophobic. Thus, coated meshes can simultaneously display hydrophilicity and oleophobicity; these meshes can then be used to separate layered oil-water mixtures with high efficiency, and to pretreat oil-water emulsions to remove large oil drops. The relation between separation performance and the dimensions of the mesh is explored in detail to enhance fundamental understanding. Without complicated construction of hierarchical structures on mesh surfaces, the coated substrate can withstand abrasion tests without performance loss. This straightforward, quick and cost effective fabrication process on stainless steel mesh offers the potential for application in large scale oil/water separation for cleanup of oil spills and wastewater treatment.

2. Experimental methods

2.1. Coating procedure

Corrosion-resistant type 304 stainless steel (SS) meshes with mesh numbers 100, 200 and 400 were obtained from McMaster-Carr; the mesh number refers roughly to the number of openings per inch (see Fig. 1 for images and Table 1 for key dimensions). Meshes were rinsed with acetone, methanol and isopropanol and dried under a flow of dry nitrogen. Methyltrimethoxysilane (MTMS, Sigma Aldrich, deposition grade, ⩾98%) was mixed with 0.1 M hydrochloric acid (Fisher Chemicals, 37.3%) in a 4:1 ratio and sonicated in an ice-water bath (Fisher Scientific ultrasonic cleaner model FS20, 70 W, 42 kHz) for 5 min to induce hydrolysis. The cleaned meshes were immersed in the hydrolyzed MTMS solutions for 2 min. After removal from the solution, excess liquid was removed from the mesh by touching the liquid with a piece of tissue paper (KimWipe, Kimberly-Clark Co). The coated meshes were finally air-dried under ambient conditions for 1 h.

2.2. Contact angle measurements

All static contact angle measurements were performed by placing a 4 μL droplet of DI water, diiodomethane (Sigma Aldrich, reagent plus grade, 99%, surface tension 50.8 mN/m, density 3.32 g/mL, viscosity 2.8 mPa s at 20 °C) or motor oil (SAE 10W-