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Full Length Article

Separation of asphaltene-stabilized water in oil emulsions and immiscible oil/water mixtures using a hydrophobic cellulosic membrane

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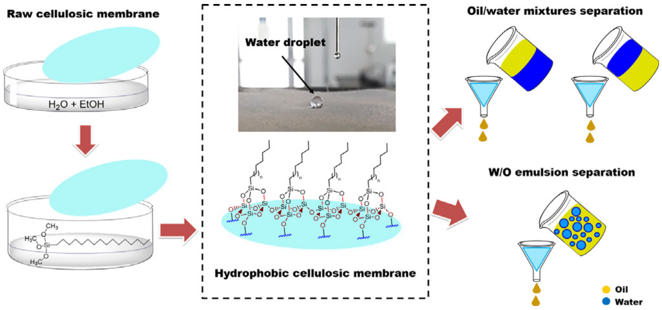
GRAPHICAL ABSTRACT



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ABSTRACT

We present a two-step method to prepare a hydrophobic cellulosic membrane involving a SiO_2 sol-gel process, to increase surface roughness, followed by grafting of hexadecyltrimethoxysilane groups to chemically enhance the membrane's water repellency. The modification processes induced morphological and chemical changes as observed by scanning electron microscopy and infrared spectroscopy, respectively. The hydrophobic membrane was used to separate immiscible oil/water mixtures with efficiencies over 99%. In addition, we tested the material for breaking an asphaltene–stabilized water in oil emulsion and registered separation efficiencies from 75% to 95%. The demulsification process depends on membrane surface hydrophobicity, emulsion viscosity and dispersed droplet size. The hydrophobic/oleophilic cellulose membrane was efficiently reused over 18 times to break a water/oil (50% water) emulsion. This facile solution for breaking low viscosity w/o emulsions and immiscible water/oil mixtures could be easily scalable and used to develop efficient separation methods driven solely by gravity.

1. Introduction

The chemical composition of oil and formation water in oil reservoirs is variable, mostly depending on source rock. Recently we have shown that some chemical components in asphaltenes behave as surface active materials. For instance, in a recent publication we have shown that asphaltenes contain polar molecules with abundant heteroatoms, such as $N_nO_oS_s$, N_nO_o, O_o, that not only can stabilize emulsions but also form aggregates [20]. As crude oil contains native surfactants and is normally processed along with formation water, stable emulsions are formed during pumping operations due to the shear stress experienced in valves and pipelines [2,16,17,27,28,58,67]. Single and multiple

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emulsions are common to the petrochemical industry; the former are of the water in oil (w/o) or oil in water (o/w) types if the continuous phase is either oil or water, respectively; the latter can be of the o/w/o or w/o/w types if an immiscible oil layer exists between two water layers (o/w/o) or *vice versa* [30]. It is widely known that w/o emulsions behave like non-newtonian fluids; upon emulsion formation an increase in oil viscosity ensues, together with changes in rheology that can dramatically affect transport operations in pipelines [1,15]. Conventional heating, chemical additives and electrocoalescers are some of the most common ways to break these emulsified crude oil streams. In many 7cases, although there is a reduction in the water content, phase separation is not completely achieved [21] when using these alternatives individually; thus a combination of these methods can improve the results however at the expense of increasing operational and maintenance costs [6].

Reducing operational costs and increasing profitability during crude oil processing requires the use of efficient strategies to separate or inhibit the formation of w/o emulsions. Nowadays, demulsification using membranes has gained more attention due to low energy consumption when relying on gravity for the separation; additionally, the fact that oil and water are not contaminated by chemical additives after separation and that the process does not require extra safety cautions in contrast, for instance, with high voltage demulsification [14,60,71]. The membranes used for the separation of mixtures and emulsions are made of materials with high chemical, thermal and mechanical stability. In addition, modifications on the surfaces of these materials are oriented towards the improvement of the separation efficiency, either by modifying the porosity to achieve a higher flux or by providing anti-fouling properties to avoid clogging issues [31]. For instance, o/w nanoemulsions, stabilized by surfactants are separated via ultrafiltration using hydrophilic membranes with nanoporous surfaces between 2 and 50 nm of pore size. In this way, oil droplets dispersed with a typical size between 0.1 and 10 μm will not permeate the membrane and the water can be separated without oil impurities [8]. Conversely, for the separation of water in oil emulsions, the membrane's surface is generally modified with hydrophobic compounds to retain water allowing permeation of oily phases [60].

Electrochemical deposition, electrochemical etching, vapor phase deposition, self-assembly, dipping, sol/gel processes and electrospinning techniques are among the most common procedures to confer superhydrophobicity/superoleophilicity and superhydrophilicity/superoleophobicity to composite materials. These properties are achieved by means of either increasing surface roughness and reducing surface energy or both [18,19,37,57,66]. Altering surface roughness, in the field of membrane design, is related to a change on surface topography. The introduction of roughness in soft materials, such as cellulose, is usually achieved by chemical grafting, sol gel dipping, nanoparticle deposition and chemical vapor deposition, among others [22,34,43]. Surface energy reduction is generally accomplished by adding low surface energy compounds such as alkyl chains, silicone and fluorine compounds which provide hydrophobic properties to the membrane [49]. Once these compounds are deposited on a surface, only liquids with equal or lower surface tension than the membrane can wet out and permeate it. This explains why water, with surface tension of 72.1 mN/m, is repelled by hydrophobic substrates, which typically exhibit a low surface energy. For this reason, organic solvents such as octane ($\gamma = 21.6$ mN/m) and hexadecane ($\gamma = 27.5$ mN/m) can permeate easily hydrophobic substrates due to similar intermolecular interactions with the functionalized surface [9,38].

Different approaches have been used to provide hydrophobic properties to membranes made of cellulosic materials [10,34,56,61]. For instance, a cotton fabric with a bi functional modification was used for the separation of hexadecane-water emulsions. One side of the membrane was treated with a polyamine polymer (poly (N,N-dimethyl aminoethyl methacrylate)) to increase the surface roughness and the other was grafted with a hydrophobic polymer. In this way, the side with the amine polymer helped coalesce oil droplets whereas the hydrophobic side allowed selective permeation of the oil, facilitating the separation. Although this approaching allowed rapid and efficient separations of o/w emulsions, fabrication is not simple limiting practical applications [64]. In another study, a filter paper functionalized with polytetrafluoroethylene nanoparticles was used as a membrane to separate o/w mixtures with high efficiency (99%) and good recyclability [13]. Increasing surface roughness of cellulose was achieved by adhering nano-amorphous titanium dioxide (TiO_2) and an epoxy resin to the surface. Also, modification of cellulose, by immersion in an ethanolic solution of octadecyltrichlorosilane, conferred hydrophobicity to the material which was used to separate oil/water mixtures thanks to its high oil absorption capacity [18]. Hydrophobic/oleophilic properties were given to a filter paper through a bi-silanization process that enabled separation of diesel-water and gasoline-water mixtures [62]. Recently, o/w nanoemulsions were separated by ultrafiltration employing porous membranes made of cellulose nanosheets, formed from a solution of cellulose through freeze/drying, with thickness between 80 and 220 nm. This hydrophilic/oleophobic membrane exhibited a decrease in flow rates as the thickness of the membrane increased, which is a serious drawback [72]. On the other hand, hydrophobic magnetic cellulose was used to separate oil/water mixtures and a toluene in water emulsion. In this case, magnetic and roughness properties were achieved by the introduction of a thin layer of Fe_3O_4 nanoparticles on the cellulose surface, while hydrophobicity was provided by self-assembly of a hexadecyltrimethoxysilane layer on the nanoparticle's surface or directly over the cellulose by reaction with the hydroxyl groups [42]. Finally, a hexane in water emulsion stabilized by sodium dodecyl sulfate was successfully separated using a cellulose filter paper with hydrophilic/oleophobic wettability properties. The cellulosic substrate was coated with a layer of nanofibrillated cellulose hydrogel through a dipping/drying process. The hydrogel traps water creating a hydrated layer that hampers permeation of the oil phase due to differences in surface energy. However, this modification involves lengthy steps such as production of nanofibrillated cellulose with nanometric size (10–40 nm) and careful crosslinking of the hydrogel to avoid possible coating fractures [51].

The above mentioned examples were all carried out with model solvent mixtures or emulsions, with very few dealing with use of composite materials, or modified surfaces, to separate real w/o emulsions. These emulsions in oil processing (stabilized by asphaltenes and by naphthenic acids) exhibit high viscosity and are extremely stable [27,44,59]. It is widely known in the petroleum industry that asphaltenes comprise a huge number of molecules interfacially active which form a thick layer around the water droplets impeding the coalescence and separation of w/o emulsions [25,45]. In this contribution, we fabricated a hydrophobic cellulose membrane by changing surface roughness and reducing surface energy via attachment of SiO_2 to the surface by a sol-gel method, for the former, and grafting hexadecyltrimethoxysilane groups, for the latter. The morphological modifications were monitored by scanning electron microscopy whereas the chemical changes in the membrane were confirmed by infrared spectroscopy and contact angle measurements. This composite material enables oil/water mixtures separation by gravity and more importantly breaking of tight water in oil emulsions stabilized by asphaltenes with efficiencies between 75 and 95%.

2. Experimental section

2.1. Materials and reagents

Tetraethyl orthosilicate (TEOS-$SiC_8H_{20}O_4$) and hexadecyltrimethoxysilane (HDTMS-$H_3C\ ((CH_2)_{15}Si(OCH_3)_3)$) were purchased from Sigma Aldrich (St. Louis, MO, USA). HPLC grade ammonium hydroxide (32% ammonia in water), ethanol (EtOH), dichloromethane (DCM), n-heptane, potasium chloride (KCl), dihydrate calcium chloride