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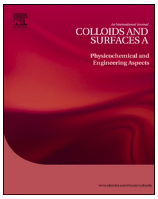
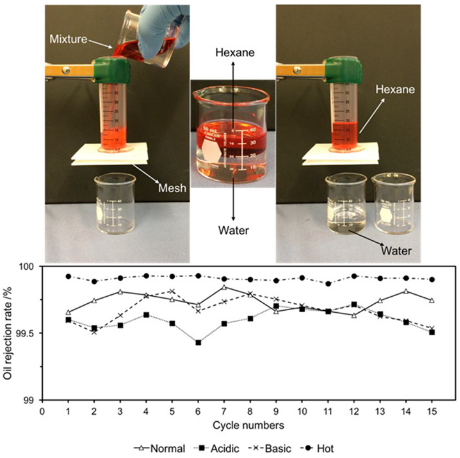


Boron substituted MFI-type zeolite-coated mesh for oil-water separation

Ruochen Liu[a], Seth Young[a], Shailesh Dangwal[a], Imran Shaik[a], Elena Echeverria[b], David McIlroy[b], Clint Aichele[a], Seok-Jhin Kim[a,*]

[a] School of Chemical Engineering, Oklahoma State University, 420 Engineering North, Stillwater, OK, 74078, United States
[b] Department of Physics, Oklahoma State University, 145 Physical Sciences Bldg., Stillwater, OK, 74078, United States

GRAPHICAL ABSTRACT



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ABSTRACT

A boron substituted zeolite-coated mesh was synthesized by a secondary growth method. The inclusion of boron ions significantly increased the hydrophilicity of the resultant mesh. Using gravity as the driving force and upon exposure to a water/oil mixture, water permeated into and through the zeolite mesh, while oil was rejected. With increasing boron content in the zeolite-coated mesh, the hydrophilicity of the mesh was enhanced, while the oil droplet contact angle increased from 136.8° to 162.0°. For a B/Si ratio of 0.04, the zeolite-coated mesh showed super-hydrophilicity. At this ratio, the oil rejection rate of the zeolite-coated mesh reached > 99% for a water flux of $> 14{,}000\,\mathrm{L\,m^{-2}\,h^{-1}}$. The zeolite-coated mesh showed high chemical stability and the aforementioned oil rejection rate whether treated with acidic, basic or hot media. The mesh were successfully reproduced by a simple re-calcination method due to their thermal stability. Slight degradation of the oil rejection performance less than 1% was observed after the third re-calcination. Various organic solvents, such as n-hexane, cyclohexane, mineral oil, and vegetable oil were also separated via boron substituted zeolite-coated mesh, in conjunction with oil rejection rates of > 96.5%.

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* Corresponding author.
E-mail address: seokjhin.kim@okstate.edu (S.-J. Kim).

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1. Introduction

Because of the ever-increasing demand for clean water, combined with the increasing generation of industrial oily water discharge, there is a worldwide water crisis. The presence of oil in water is immediately detrimental to the environment, but also has the long term effect of damaging the self-cleaning circulatory processes of the ecological system [1]. Thus, considerable efforts are underway to obtain energy-efficient and environmentally-friendly methods for the remediation of oily contaminants. Over the past few decades, polymeric membranes have dominated the R&D landscape because of their good performance and oil rejection rates of more than 95% [2–10]. However, due to their extremely small pore sizes, large pressure gradients across these membranes are required, which translates into power consumption and a rising cost of operation. In addition, at these pressures, polymeric membranes are prone to fouling [4–11], where the flux through the membrane rapidly declines [12,13]. Despite efforts to develop novel self-cleaning polymeric membranes, the ratio of oil droplets adsorbed onto the surfaces of such membrane is 70–90% and the ratio of oil droplets cleaned away from membrane surface is as low as 30–40% [9–11].

In an effort to resolve the fouling problem, super-hydrophilic polymeric materials have been coated on stainless-steel wire mesh, which allow water to pass through the mesh and reject oil [14–18]. These super-hydrophilic membranes exploit the differences in density between water and oil and the formation of a water layer on the membrane surface that acts as barrier to oil [19]. Xue et al. [14] successfully fabricated hydrogel-coated mesh to realize a 99% oil rejection rate within only a few seconds of operation, while Xiao et al. [17] synthesized super-hydrophilic polymeric materials and with oil rejection rates of 99% or better. Chen et al. [18] prepared inorganic-organic thiol-ene coated mesh with almost 100% oil rejection. The downside of polymeric coated membranes is their intolerance to corrosive solutions, such as acids and bases, organic solvents and high temperatures [12,20,21]. They are also susceptible to swelling, which detrimentally impacts molecular diffusion and the convection of water in the pores [22]. This can produce a swelling ratio in hydrogels upwards of 2.0–3.7 [23,24], thereby limiting their use in challenging environments.

Recently, researches have turned their attention to ceramic materials as an alternative to polymers. Li et al. [23] coated SiO_2 on stainless steel mesh, which separated 98% kerosene from corrosive and hot water. Li's group utilized a spray coating process for the development of ZnO-coated mesh and TiO_2-coated mesh to obtain kerosene/water separation rates of 97.3% and 97.5%, respectively, over 40–50 separation cycles [25,26]. More recently, the separation efficiencies of a variety of materials coated on stainless steel mesh coating, such as zeolite [19,27], ZnO [25,28,29], TiO_2 [26], Cu_2S [30], CuC_2O_4 [31], and SiO_2 [23,32] have been examined. Among these, pure-silica or high-silica zeolite are the most promising due in part to their corrosion-resistance and their chemical, mechanical, and thermal stability [33–35], which enables their operation under severe conditions. The IIIA ion (e.g. B^{3+}, Al^{3+}) can be introduced into zeolite structure in order to make use of their empty orbitals so that more hydroxyl groups can be connected, which will form more hydrogen bonds and thereby increase the hydrophilicity [36].

Herein, we demonstrate for the first time the novel fabrication of boron substituted zeolite-coated meshes that resist fouling, highly recyclable, and efficiently separate water from oil. With the substitution of B^{3+} ions, the zeolite mesh becomes more hydrophilic and a higher water flux. In order to evaluate the stability of the zeolite-coated mesh when operating in corrosive aqueous solutions, oil/water separation was conducted under acidic, basic, and hot-media conditions, respectively. The rejuvenation and reusability of the zeolite-coated mesh by re-calcination was also investigated. We also report on the separation efficiency as a function of oil type.

2. Method

2.1. MFI seed synthesis

The detailed MFI seed synthesis steps have been described elsewhere by Kim et al. [37]. First, NaOH (99.99%, Sigma-Aldrich) was dissolved in a mixture solution of H_2O and tetrapropylammonium hydroxide (TPAOH) solution (1 M, Sigma-Aldrich), followed with gradually adding SiO_2 (0.2–0.3 μm powder, Sigma-Aldrich) in water bath at 80 °C to obtain clear suspension with stirring. The molar ratio of the above suspension was NaOH: H_2O: TPAOH: SiO_2 = 1: 131.5: 2.86: 9.42, respectively. The suspension was aged at room temperature for 4 h before being transferred into a hydrothermal vessel and synthesized at 120 °C for 6 h. The synthesized powder was washed with deionized water several times until a milky colloid was obtained.

2.2. Zeolite-coated mesh synthesis

One inch × one inch pieces of the pristine stainless steel mesh (100 scale, MSC) were washed with ethanol, acetone, and deionized water, respectively, and dried overnight at 50 °C. To prepare a seeded mesh, clean mesh was immersed in the seed suspension for 1 min. The secondary growth solution was prepared by dissolving sodium metaborate tetrahydrate ($NaBO_2 \cdot 4H_2O$, Sigma-Aldrich) into the mixture of water and TPAOH and stirred for 30 min. The tetraethyl orthosilicate (TEOS) (98%, Sigma-Aldrich) was added into the transparent solution dropwise while stirring for 3 h. The molar ratio of the suspension was TEOS: TPAOH: H_2O: $NaBO_2 \cdot 4H_2O$ = 1: 0.095: 35.42: X, respectively [37]. The value of X varied from 0 to 0.04. The dried seeded mesh was placed vertically into the secondary growth solution and synthesized at 150 °C for 17 h. After hydrothermal synthesis, the zeolite-coated mesh was calcined at 550 °C for 6 h at the temperature increasing and decreasing rate of 30 °C/h [38].

2.3. Oil/water separation experiments

The synthesized zeolite-coated mesh was fixed between two 10 cm × 10 cm Teflon sheets and sealed with an epoxy resin. In this study, the oils (cyclohexane, hexane, crude oil and vegetable oil) were selected to study the separation performance of the zeolite mesh. Just prior to beginning the oil/water separation tests, the zeolite mesh was pre-wet by pouring 20 mL of deionized water onto its top surface. A typical test consists of pouring a 40 mL, 50% v/v, water/hexane mixture, for example, on top of the pre-wet mesh and the gravity-driven separation process to take place, where filter product was collected in a beaker placed directly beneath the mesh (Fig. 1). The oils were colored with Sudan Red to aid in distinguishing it from water. The oil rejection rate η was calculated using the following equation:

$$\eta = 1 - m_i/m_0 \quad (1)$$

where m_i is the weight of hexane passing through the zeolite-coated mesh and m_0 is the initial weight of hexane in the solution. The permeation flux J was obtained with:

$$J = V/(A \times t) \quad (2)$$

where A (m^2) is the zeolite-coated mesh area, V (L) is the volume of permeate, and t (h) is the permeant time.

Displayed in Fig. 1 are images of the gravity-driven separation experimental setup and before and after pictures of the separation process. Surface tension measurements of dyed hexane showed no surface activity of Sudan Red. Upon introduction of the mixture, water quickly passed through the mesh while hexane was excluded by the mesh (Video S1). Depending on the B/Si ratio of zeolite mesh, separation of a 40 mL of oil/water mixture takes ~10 s.

The intrusion pressure (P) was determined by measuring the maximum height (h_{max}) of the oil column that the mesh can support and