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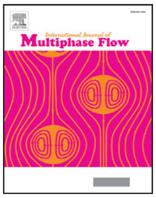

A numerical model for the performance assessment of hydrophobic meshes used for oil spill recovery

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A R T I C L E I N F O

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A B S T R A C T

Accidental oil spills in the ocean have a big impact on aquatic environments and human activities, and one of the most promising clean-up techniques is the use of hydrophobic and oleophilic meshes. It is important to understand the underlying physics of these meshes and their behavior under different conditions. Here, a mesh is conceptualized as an equivalent porous medium where the oil recovery and water breakthrough depend on the fluid column height and material properties. A model of two-phase flow through the mesh was implemented in COMSOL Multiphysics®. Hydrophobicity, contact angles and surface tension effects are considered through a capillary retention curve, while flow properties are represented by permeability functions. The model was verified and tested with existing experimental data. It constitutes a powerful tool for future research and optimization of environmental solutions based on hydrophobic and oleophilic meshes.

1. Introduction

Oil spills are complex events: crude oil consists on hundreds of thousands of different compounds and there are several processes affecting the oil after a spill, such as weathering, dissolution or volatilization (Prendergast and Gschwend, 2014). Because of this complexity, it is very difficult to predict what the immediate effects of an oil spill are. The slick also emulsifies with the water, reducing the efficiency of treatment methods with time. Therefore, oil spills must be treated as early as possible.

The proper choice of cleanup technique depends on oil type, spill location and size, weather conditions, and local regulations and standards (Prendergast and Gschwend, 2014). There are two types of oil cleanup technologies: destructive and recovery methods. The destructive methods, which comprise for example in-situ burning, the use of dispersants and bioremediation, transform the oil instead of removing it. Recovery methods, on the other hand, include skimmers, sorbents and hydrophobic meshes, among others (Prendergast, 2013).

Sorbents and hydrophobic meshes are the only two methods that can retrieve relatively water-free oil. Depending on the conditions of the recovered oil, it could be feasible to recycle and use it without additional conditioning. This is an important economic advantage with respect to the other available methods. The sorbents, however, have a limited capacity and require mechanical handling to extract the oil from the sorbent (Song et al., 2014).

In the last years, there has been an increase in the study of hydrophobic meshes and their application for oil spill recovery. They are prepared by coating a stainless-steel mesh with a material that provides the desired hydrophobic and oleophilic properties (Feng et al., 2004; Deng et al., 2013; Song et al., 2014; Ge et al., 2014). Hydrophobic meshes separate oil from water in-situ, continuously and without energy input except for pumping away the recovered oil. They act much like a filter, allowing oil to pass through the mesh while preventing water breakthrough. This process is passive and driven by interfacial tension but oil must be collected and removed from the space enclosed by the mesh to maintain the continuity of the operation. The operation depth of the meshes is limited by the water breakthrough pressure: if the meshes are operated below their breakthrough depth, the hydrostatic pressure becomes too high and causes water to enter into the mesh (Deng et al., 2013). This kind of filter can also be used for other oil/water separation applications such as industrial emulsified wastewater treatment or fuel purification (Prendergast and Gschwend, 2014; Song et al., 2014).

The advances in the development of hydrophobic meshes have focused mainly on the material properties conferring the

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[1] Software availability: Name of the Software: COMSOL Multiphysics® Developers: COMSOL Contact Address: COMSOL, Inc. 100 District Avenue, Burlington, MA 01803, USA. Telephone: +1-781-273-3322 Fax : +1-781-273-6603 E-mail : info@comsol.com Year first available: 1998 Hardware required: 1GB RAM memory, 1–5 GB of disk space. Operating systems: Windows, Mac OS X, Linux. Availability: Licenses available for purchase at https://www.comsol.com/contact User interface: Graphical user interface

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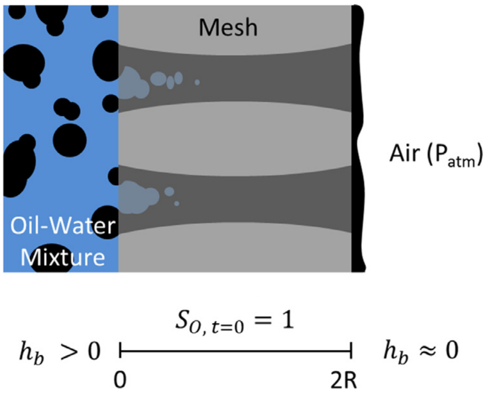

Fig. 1. Conceptual model of a hydrophobic mesh and the initial and boundary conditions assumed in the COMSOL model.

hydrophobic-oleophilic ability to the mesh. Feng et al. (2004) developed a hydrophobic and oleophilic mesh by spraying a stainless-steel structure with a polytetrafluoroethylene (PTFE) emulsion. The mesh was found to effectively separate oil and water. Deng et al. (2013) dip-coated steel meshes in low-density polyethylene (LDPE) and tested them, finding that the rate of oil recovery was faster than its spreading rate on the water surface. Thus, field-scale devices incorporating hydrophobic meshes would need a way to store the recovered oil, as well as continuously moving the mesh towards unrecovered oil. Song et al. (2014) tested and analyzed a Cu-coated, super-hydrophobic steel mesh, showing good oil collection efficiencies and high filtrate purities. The prototype device also showed high stability and good performance over repeated use. Crick et al. (2015) showed that zeolitic silica membranes can be used to perform complete oil-water separation. Bong et al. (2015) found that treated graphene foams can be used for gas-oil-water separation. There are also more sophisticated systems, like the one proposed by Ge et al. (2014), which combines pipes and a pump with a porous hydrophobic/oleophilic membrane in order to collect oil continuously. All the above experimental studies have been performed considering thermodynamics fundamentals, at most. To our knowledge, there is no model providing a thorough description of the dynamics of the different mechanisms causing the phase separation by a hydrophobic mesh.

In the present work, a conceptual and mathematical model of a hydrophobic and oleophilic mesh is developed and implemented in the numerical platform COMSOL Multiphysics® (hereafter referred to as COMSOL). A sensitivity analysis is carried out to assess the performance and effectiveness of a generic mesh and to show the models usefulness for design purposes. Finally, the model is verified with experimental data.

2. Methods

Hydrophobic meshes can be conceptualized as an equivalent porous medium with a selective wettability, where the porosity, specific surface area and permeability are a function of the wire and opening radii. There are, in fact, systems based on using a granular material like a beach sand and limestone to trap oil floating on seawater (Boglaienko and Tansel, 2015).

Fig. 1 shows the conceptual model considered in this work to describe a hydrophobic mesh. The proposed model is inspired by the works of Díaz-Viera et al. (2008), Prendergast (2013), and Deng et al. (2013) and considers isothermal two-phase flow in porous media. The model considers only the mesh itself, while the water-oil mix at the left and the air at the right are implemented as boundary conditions. The governing equations are derived from the mass conservation equations for each of the phases and the Darcy's equations of motion. There are several possible numerical formulations for isothermal two-phase flow, which can be found in Chen et al. (2006) and Kolditz et al. (2012). In short, the present model allows calculating the oil flux through the mesh thickness and the water column pressure (h) necessary for water to break through it.

2.1. Governing equations

Here, the *water pressure - capillary pressure* scheme of isothermal two-phase flow in porous media is adopted (Kolditz et al., 2012). The system is assumed to be composed of the mesh (solid phase) and two fluid phases: oil and water. Given the hydrophobic and oleophilic properties of the mesh, oil and water are the wetting and non-wetting phases, respectively. In addition, the fluids are considered to be incompressible. Under isothermal conditions, the mass balance equations for both fluids are given by

$$\phi \frac{\partial}{\partial t} S_i + \nabla \cdot \mathbf{v}_i = q_i \tag{1}$$

where t [T] is time, ϕ [L^3L^{-3}] is the porosity of the mesh, S_i [-] is the saturation of phase i ($i = w$ for water and $i = o$ for oil), $\mathbf{v}_i$ [LT^{-1}] is the Darcy's velocity vector of phase i, and q_i [T^{-1}] represents an external source. The fluid saturation S_i is defined as the ratio of volume occupied by that fluid to the total free volume available.

Two state variables are required to solve the system of equations (1). In the present work, water pressure P_w [$MT^{-2}L^{-1}$] and oil-water capillary pressure $P_{c,\,ow}$ [$MT^{-2}L^{-1}$] are adopted as the state variables of the system.

The total velocity vector $\mathbf{v}$ [LT^{-1}] is defined as

$$\nabla \cdot \mathbf{v} = \nabla \cdot \sum_i \mathbf{v}_i = q_o + q_w \tag{2}$$

given that $S_o + S_w = 1$. Darcy's law describes the flow rate of a phase through a porous medium as

$$\mathbf{v}_i = -\frac{k_{ri}}{\mu_i} \mathbf{k} (\nabla P_i - \rho_i g \nabla z) \tag{3}$$

where P_i [$MT^{-2}L^{-1}$] is the pressure of phase i, μ_i [$MT^{-1}L^{-1}$] is the dynamic viscosity of that phase, ρ_i [ML^{-3}] its density, and g [LT^{-2}] the gravitational acceleration. The intrinsic permeability tensor $\mathbf{k}$ [L^2] is a property of the porous medium that measures its capacity to transmit fluids. When two or more fluids flow at the same time, the relative permeability (k_{ri} [-]) of each phase is the ratio of its effective permeability to the intrinsic permeability. For practical purposes, it is convenient to introduce the phase mobility (λ_i [$M^{-1}TL$]) and total phase mobility (λ [$M^{-1}TL$]), variables that are defined as

$$\lambda_i = \frac{k_{ri}}{\mu_i} \tag{4}$$

$$\lambda = \sum_i \lambda_i \tag{5}$$

Also, the fractional flow function (f_i [-]) is defined as

$$f_i = \frac{\lambda_i}{\lambda} \tag{6}$$

In porous media, the disequilibrium of forces at the interface of two phases is accounted for through the difference of their pressures or potentials. The capillary pressure is defined as the pressure difference between the non-wetting phase and the wetting phase, i.e.

$$P_{c,\ ow} = P_w - P_o \tag{7}$$

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