SIMULATION OF OSMOTIC AND REACTIVE EFFECTS IN MEMBRANES WITH RESOLVED MICROSTRUCTURE

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ABSTRACT

Mathematical modeling and computer simulation are useful approaches, supporting membrane researchers and manufacturers in their work on designing better membranes and on selecting appropriate membranes for a particular application. In this work we examine two processes where the membrane morphology plays a crucial role, the first being osmosis (both forward and reverse), and the second micro/ultra/nano-filtration.

We first discuss the mathematical modeling and simulation of solute transport through membranes used for forward and reverse osmosis. 3D simulations on virtual membranes generated using the software tool GeoDict based on SEM images, with two separate membrane morphology types, both finger-like and sponge-like membranes, are performed. By resolving the microstructure of the support layer, we investigate the influence of the support layer structure on the separation process. Numerical simulation also allows us to test the theoretical membrane performance under various operating conditions, such as varying flow rate and particulate concentration.

Another process where the morphology of the membrane is highly influential is the micro/ultra/nano-filtration. The functionalization of these membranes is a recent approach enabling efficient removal of impurities, such as bacteria and viruses, using a lower pressure. This is achieved by using membranes with larger pores than in reverse osmosis, while the functionalization of the pore walls results in the increased adsorption of the selected contaminants. Computer simulation is performed at the pore-scale on resolved membrane microstructures with absorptive walls and results are presented. Such numerical modeling will aid manufactures in designing efficient membranes requiring lower flow rates, thus reducing the operational energy requirements.

KEYWORDS

Membrane, Microstructure, Osmotic Pressure, Pore-scale reactive transport

1 Introduction

One of the important factors influencing membrane performance is the membrane microstructure, due to the significant effect it has on the local flow rate, the pressure drop, and the filtration/separation efficiency. A common practice is to select or to develop membranes based on their experimental evaluation. This is an expensive procedure requiring a prototype. Mathematical modeling and computer simulation can lead to a significant reduction in the number of required experiments and can aid membrane researchers and manufacturers in designing better membranes, tailored to specific applications. The decision about the characteristics of a membrane, for example the material used, pore size, pore configuration or tortuosity, can be significantly supported by the simulation results.

Our aim is to understand and quantify the influence of the membrane microstructure on the water (or other fluid) treatment efficiency, by describing the processes of interest at the pore–scale. A pore–scale resolution yields a more detailed and more accurate picture of the processes under consideration, but at the same time implies a high computational cost. In this paper, we describe the procedure and present results for pore–scale simulation of the processes in membranes for two important applications, in order to illustrate the power of this approach. The first application area under consideration is forward and reverse osmosis (FO and RO, respectively) [4, 12], and the second one is micro/ultra/nano-filtration [5, 9]. Although, from technical point of view, these two applications are rather different, the underlying mathematical models are similar and the computational simulation shares common steps, enabling us to present them together.

Ideally, the computational procedure would be as follows. 3D computerized tomography (CT) or scanning electron microscopy (SEM) images are taken of membrane samples, and through image analysis, a 3D pore–scale geometry of a portion of the membrane is extracted directly. The fluid flow and transport of the species under consideration (solute or contaminants) at the pore–scale of the geometry is then computed in a customized software tool, an extension of FiltEST [1]. In a separate step, the software tool GeoDict [2] is used to measure characteristics of 3D membrane geometry, such as porosity, pore size distribution, tortuosity, of the different layers comprising the membrane, from which a virtual membrane is generated. Validation of the virtual membrane generation process can then be performed by evaluating the fluid flow and species transport and comparison of the results to those obtained from the 3D geometry obtained directly from the images. An iterative procedure may then be undertaken, whereby the results obtained from the pore–scale simulation are used as a guide with which to manipulate the membrane geometry, for which the fluid flow and species transport can then be recomputed and the results fed back into the virtual membrane geometry design. For this

process to work, it is is important that the software tool used can generate the virtual membrane microstructures by varying different characteristics (e.g., the same porosity, but different pore size distribution, etc.). In this manner, the performance of the virtual membranes can be evaluated, and membrane scientists and engineers can be provided with information which modifications of the membrane can improve the performance. In many cases, however, a 3D geometry of the real membrane can not be directly obtained, either because the resolution of the imaging technique is not high enough or because the equipment required is not available. In these cases a virtual membrane matching the statistical characteristics of the real membrane microstructure, which may be evaluated experimentally, must be generated. This is the method used in this paper.

Membranes for Forward and Reverse Osmosis. In this work we first examine membranes for forward and reverse osmosis. These membranes usually consist of at least two separate layers, namely a selective layer and a support layer. The main function of the thin selective layer is to reject the solute, while the supporting layer acts as a base and provides mechanical support for the selective layer. The characteristics of both the layers significantly influence the performance of the membrane and quantitatively predicting their effect will help to improve the performance of the membrane. The most influential characteristics include the following: the water permeability of the selective and support layers as well as the solute rejection of the selective layer [13]; the concentration polarization (CP) [4, 10], namely external and internal concentration polarization, ECP and ICP, respectively; membrane fouling. In this work we focus on studying the concentration polarization and in particular how it is influenced by the morphology of the supporting layer.

Membranes for Micro/Ultra/Nano Filtration. The second application considered in this work is functionalized membranes, typically used for the filtration of water. Clean water is essential for human health, and the supplies of water free from contaminants are not sufficient in many areas of the world [7]. Consequently, the purification of water and the removal of contaminants from waste water to prevent pollution of groundwater supplies or allow reuse of the water, is an active area of research [11]. One method of achieving this is through the use of functionalization of membranes. This process involves chemically altering the internal surfaces of the membrane so that the rate of absorption of particular pollutants is increased. The functionalization may be achieved by processing the membrane, for example by plasma treatment, or by the addition of specific functional groups [9]. Among the membranes currently used in water filtration and purification, functionalized membranes are characterized by a larger pore-size [3], allowing a lower operating pressure and hence reducing energy consumption.

The remainder of the paper is structured as follows. The mathematical model, describing the conservation of mass and momentum, is presented in Section 2. Section 3 then contains

an illustrative and instructive example how a microstructure for a sponge type membrane can be generated. In Section 4 we present the numerical experiments performed for the both applications. Finally, we draw some conclusions in Section 5.

2 Mathematical model

In this work we examine two flow configurations, namely dead–end and cross–flow setups (see Figure 1). For the forward and reverse osmosis modeling we consider a cross–flow setup, where the membrane separates two channels (see Figure 1 on the left), and the fluid flows tangentially to the membrane along the channels in co-current or counter-current directions. In contrast, a dead–end setup is considered for the functionalized membranes, a schematic of which is illustrated on the right hand side of Figure 1. In this configuration, all of the feed is forced through the membrane, which can result in a filtration–cake developing. We note that, although we here consider the functionalized membranes in a dead–end setup, they are often also used in a cross–flow configuration.

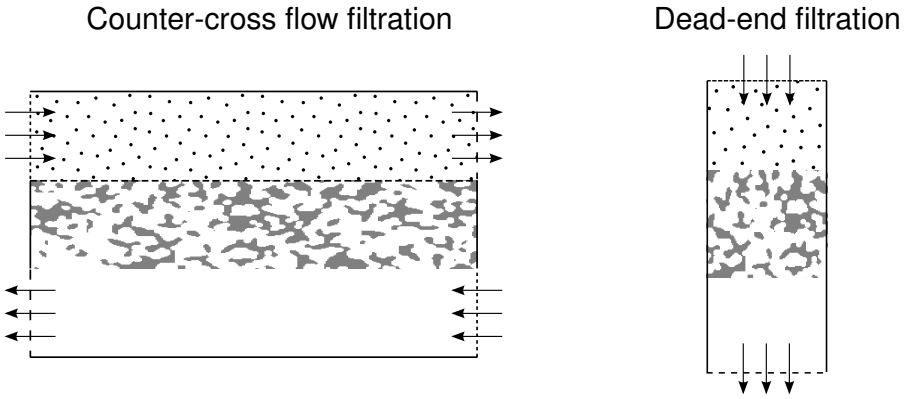

Figure 1: Counter-current cross flow setup (on the left) and dead-end setup (on the right); both with support layer resolved at pore scale.

The membrane is considered to have microstructure resolved at pore scale. To simulate the fluid flow in the channels and through the membrane we use the Navier-Stokes system of equations, given by

$$\rho\frac{\partial \mathbf{u}}{\partial t} + (\rho\mathbf{u}, \nabla)\,\mathbf{u} - \nabla\cdot(\mu\nabla\mathbf{u}) = -\nabla p, \tag{1}$$

$$\nabla\cdot\mathbf{u} = 0. \tag{2}$$

Here $\mathbf{u}$ and p denote the fluid velocity vector and the fluid pressure respectively, ρ and μ are the fluid density and dynamic viscosity respectively, and t represents time. The solute transport is modeled using the following reaction-diffusion-convection equation

$$\frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) + \nabla \cdot (\mathbf{u} c) = 0, \tag{3}$$

where c denotes the solute concentration, D is the diffusion coefficient. The system of equations (1) – (3) is supplemented by appropriate boundary and initial conditions.

Forward and reverse osmosis application. The membranes used in forward and reverse osmosis applications consist of two layers; a support layer and a selective layer. The selective layer is thin and is therefore approximated by a zero-thickness layer, namely this layer is modeled as an interface condition between the free fluid region and the supporting layer, which reads

$$\mathbf{u} \cdot \mathbf{n} = -\frac{A}{\mu} (\nabla p - \phi \nabla \pi) \cdot \mathbf{n}, \tag{4}$$

$$\mathbf{J}_s \cdot \mathbf{n} = -B \nabla c \cdot \mathbf{n}. \tag{5}$$

Here $\mathbf{J}_s$ is the solute flux, A and B are the water and solute permeability values of the selective layer, respectively; ϕ is the reflection coefficient; π is the osmotic pressure; $\mathbf{n}$ is the unit normal vector.

Functionalized membranes. In order to account for a reaction occurring at the fluid-solid interface, we assume that the change in adsorbed surface concentration is equal to flux across the surface [8]. Hence, the following condition is satisfied at the fluid-solid interface

$$\mathbf{J}_s \cdot \mathbf{n} = \frac{\partial M}{\partial t} = k_{ads} c - k_{des} M. \tag{6}$$

where M is the surface concentration of adsorbed pollutant, k_{ads} is the rate of adsorption and k_{des} is the rate of desorption. These rates may be measured via molecular dynamics, for example, as performed in [6].

3 Generation of virtual microstructures

Before proceeding to generate a virtual membrane, the real membrane first needs to be characterized. The porosity and the permeability of the real membrane are determined in laboratory experiments, and the thickness of the membrane, pore size, pore shape and pore distribution are estimated from SEM images. Using this information, virtual 3D membranes

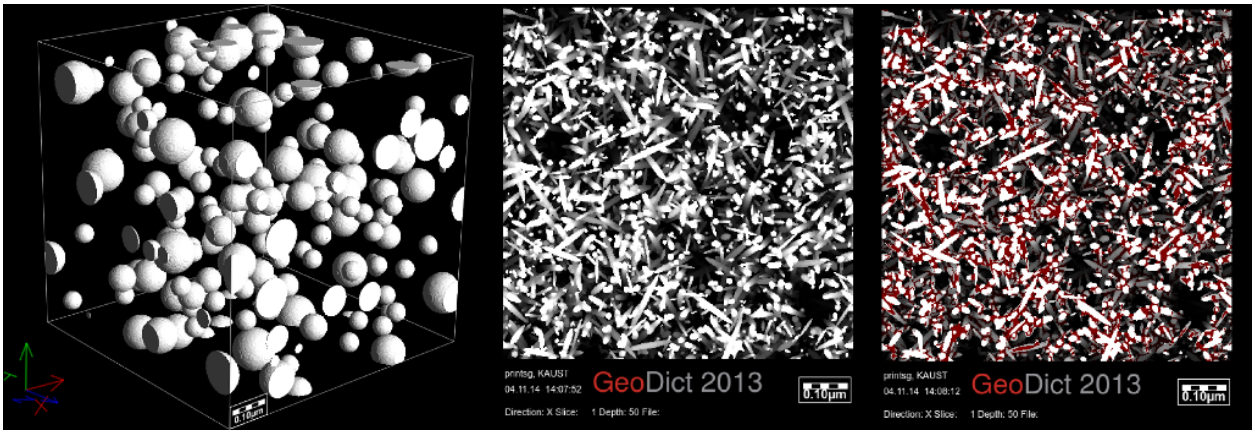

Figure 2: Generation steps of the virtual sponge

with resolved morphology are generated using the software tool GeoDict [2]. In order to illustrate how this is performed, we now discuss the generation of a virtual sponge membrane in detail, which consists of three main steps.

First we generated large pores represented by spheres as shown in Figure 2 on the left. Then, small ellipsoids with centers uniformly distributed everywhere, except for in the spheres, are generated as shown in the middle Figure 2. This way, the spheres representing the pores become an empty space. The last step is to put a binder between the ellipsoids, which is shown as red substance in Figure 2 on the right. The resultant virtual geometry in comparison with the original SEM image of the real membrane is shown in Figure 3.

4 Numerical experiments

The simulations are performed using the finite volume method on a 3D Cartesian grid. The mathematical model was implemented as an extension of the simulation tool FiltEST (*Filter Element Simulation Toolbox*) [1].

Forward osmosis experiment. Based on the data from the media characterization, we virtually generate 3D morphology of different support layers. We use such data as SEM images and laboratory measurements of porosity and water permeability. In this work we use sponge-like and finger-like support structures, produced at the Water Desalination and Reuse Center at the King Abdullah University of Science and Technology (KAUST). The software tool GeoDict [2] is used to generate the virtual structures. In Figures 3 and 4 we present results for the virtual support layers. Then, we run simulations for the fluid flow and the spices transport

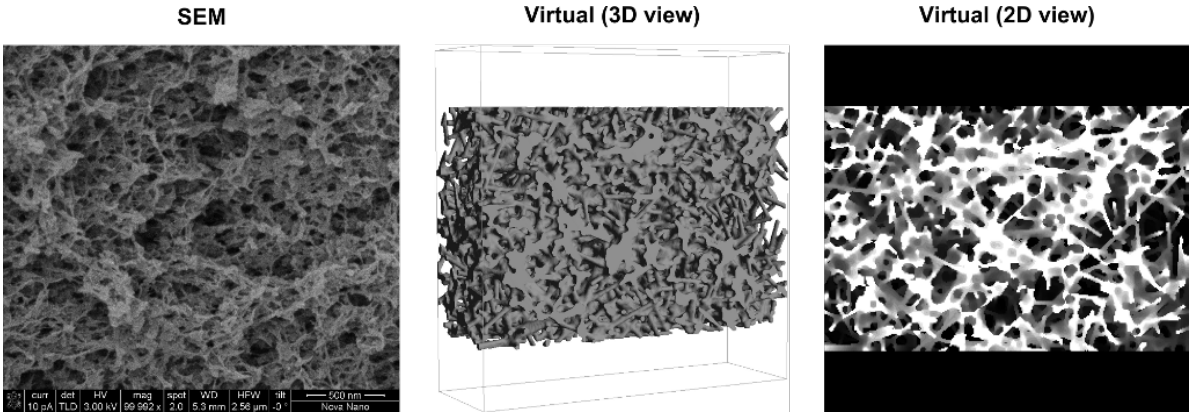

Figure 3: SEM image (left) and virtually generated structures of sponge-like support layer

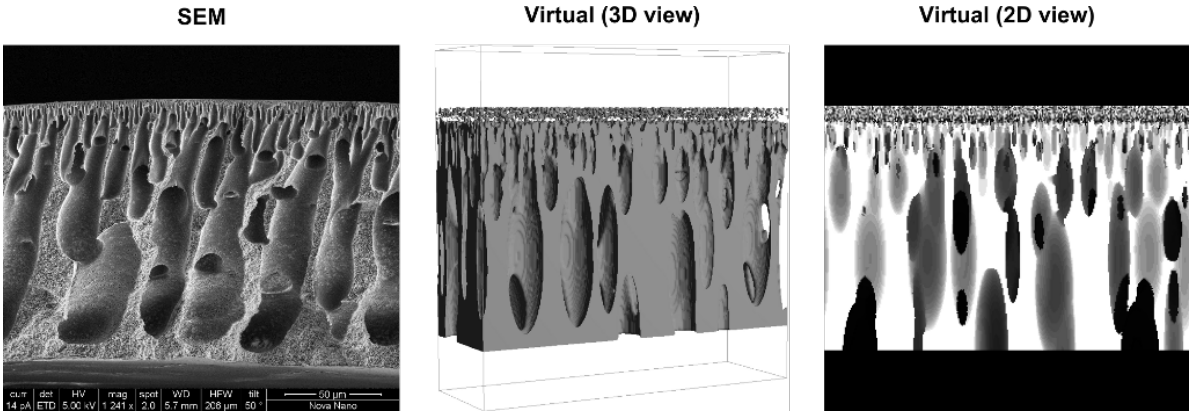

Figure 4: SEM image (left) and virtually generated structures of finger-like support layer

with the same input parameters but different support layers. The distributions of concentration, pressure, and velocity are presented in Figures 5–6.

Reactive transport experiment. Experimental measurements of the porosity and permeability of a commercially available microfiltration Polyvinylidene fluoride (PVDF) membrane with a nominal pore size of 0.2 microns, of which an SEM image of a section is shown on the left hand side of Figure 7, were performed. We use this information, assuming the membrane is isotropic and symmetric, to generate two separate 3D virtual membrane geometries with the aim of representing the membrane morphology. This is performed using software tool GeoDict [2] in a similar manner to the osmosis experiment. These virtual membranes are labeled membranes A and B, and are illustrated in the middle and on the right hand side of Figure 7. Flow and efficiency experiments are then performed on the virtual membrane geometry, and the pressure, velocity and fluid concentration results are presented in Figures 8 and 9. In addition, Figure 10 illustrates the mass of the pollutant adsorbed into the membrane over the numerical

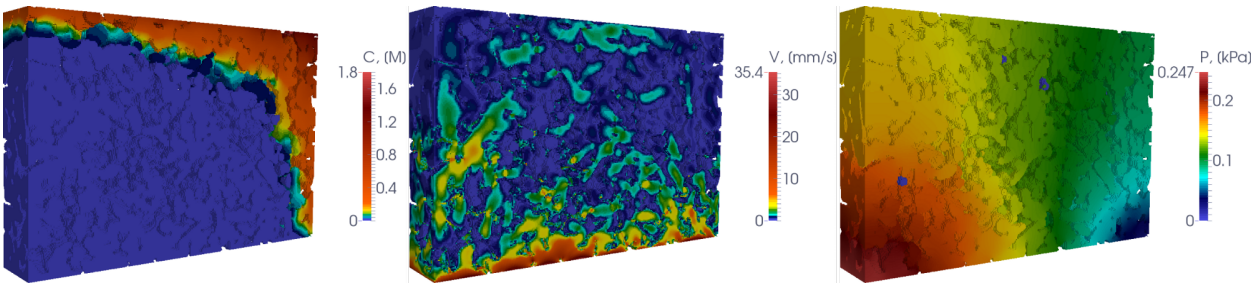

Figure 5: Distributions of concentration, velocity, and pressure from top to the bottom, respectively, for the sponge-like support layer

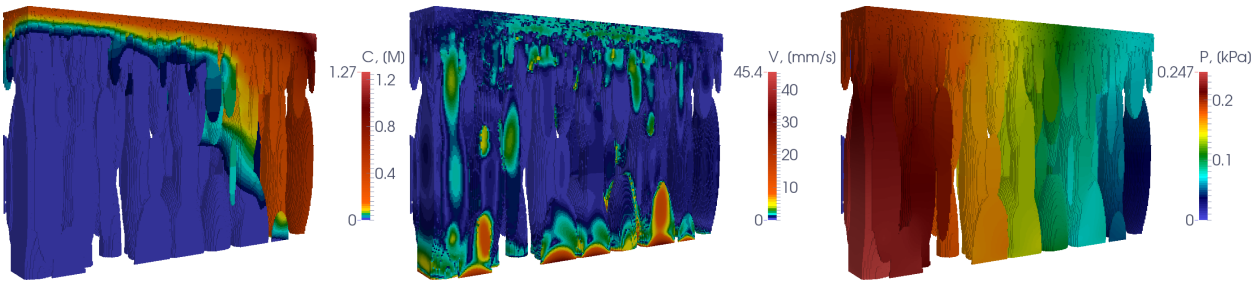

Figure 6: Distributions of concentration, velocity, and pressure from top to the bottom, respectively, for the finger-like support layer with impermeable pore walls

experimental time frame.

5 Conclusions

The focus of this work was on two separate applications of membranes, from one side for forward and reverse osmosis, and from another side for functionalized micro/nano/ultra–filtration membranes. In particular we have concentrated on the effect of the membrane morphology on the predicted membrane efficiency. For both applications, we presented numerical results for the performance of virtual generated membranes with resolved microstructures at the pore–scale.

For forward and reverse osmosis, the mathematical model accounts for the osmotic effect, which is main driving factor for this kind of processes. Two separate types of support layer, sponge–like and finger–like, were generated virtually based on images of real membranes which were produced in Water Desalination and Reuse Center in KAUST. Using these, numerical simulation results were presented which illustrated the influence of different support layers

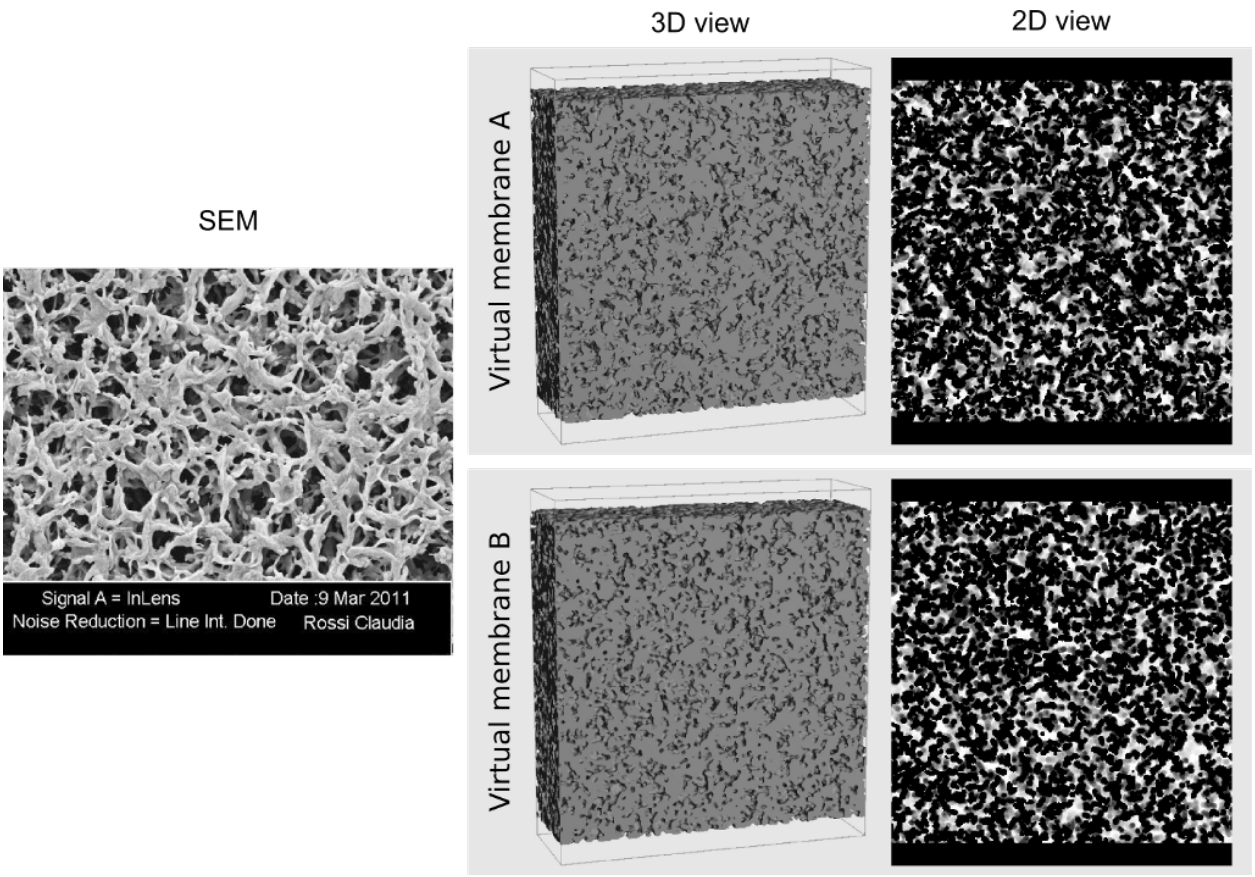

Figure 7: SEM image of the top surface of a section of a commercially available PVDF microfiltration membrane with a nominal pore size of 0.2 microns (left–hand side), and two virtually generated membranes with similar properties. We note that the SEM image and the virtual membranes are shown at different magnifications.

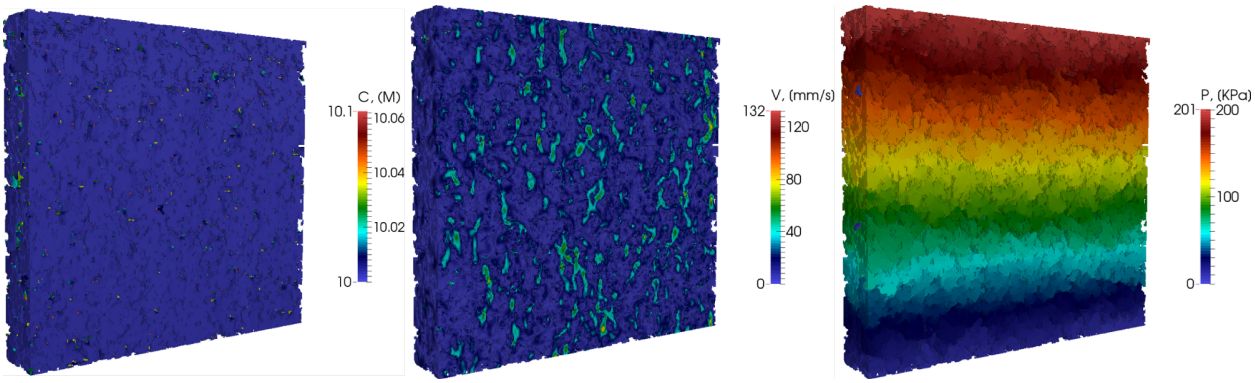

Figure 8: Distributions of concentration, velocity, and pressure from left to the right, respectively, for the virtually generated membrane A

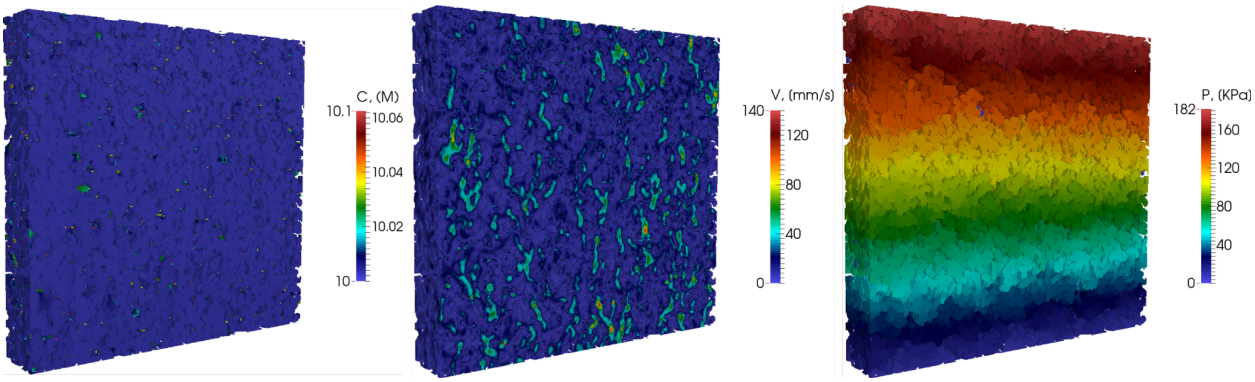

Figure 9: Distributions of concentration, velocity, and pressure from left to the right, respectively, for the virtually generated membrane B

on the water flux through the selective layer under same operational conditions.

We then presented illustrative results for reactive transport in functionalized virtual membranes, constructed to be similar to a commercially available microfiltration membrane. The two virtually generated membranes, although sharing similar characteristics, demonstrate different pressure and velocity distributions. This results in the quantity of pollutant being captured over the time period of the experiment being higher under membrane A than membrane B. In particular, we note that, as the velocity and pressure distributions influence the capturing kinetics, the imposed flow rate will have a large influence on the efficiency of the membrane. The mathematical model and numerical methods presented could be used to optimize the flow rate, module design, and calculate when is best to replace or chemically clean the membrane, so as to provide optimal removal of containments.

The numerical experiments presented in this paper illustrate the influence of the membrane

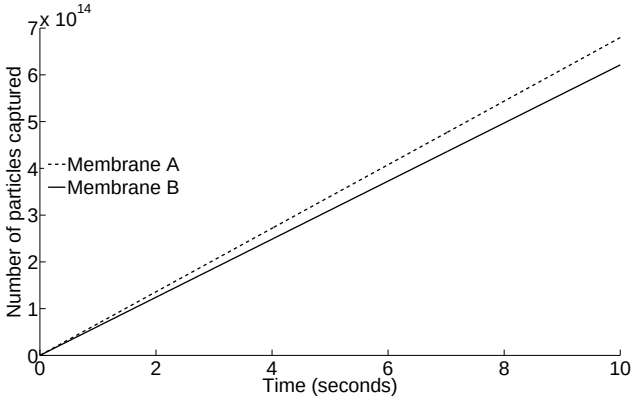

Figure 10: Number of particles of the pollutant captured over the numerical experiment time horizon, for the two virtually generated membranes under consideration.

microstructure on the predicted efficiency of the membrane. Using mathematical modeling and numerical simulation of the processes within the membrane microstructure at the pore–scale can lead to significant improvements in membrane design and technology.

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