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Single-nanoparticle tracking reveals mechanisms of membrane fouling

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ABSTRACT

While membrane fouling has been studied for decades, it remains challenging to obtain direct information about the dominant mechanism of fouling in a specific scenario. Here, we employed a high-throughput particle-tracking approach, which enabled the visualization of particle transport in actual microfiltration membranes under flow conditions and provided direct evidence for distinct fouling mechanisms under different operating conditions. Our results suggest that the "stickiness" of particles can qualitatively change the dominant fouling mechanism. In particular, the evolutions of effective flux, particle velocity and pathway tortuosity were found to be systematically different under "sticking" vs "reduced-sticking" conditions in two different microfiltration membranes, composed of PVDF and PTFE, respectively. Under "sticking" conditions, fouling was rapid, and individual pathways were observed to disappear with the reduction of flux. However, the average particle velocity and the tortuosity of particle trajectories were unchanged throughout the fouling process, consistent with the complete blocking of random pathways. Conversely, under "reduced-sticking" conditions, the average particle velocity decreased and the tortuosity of particle pathways increased systematically with fouling, consistent with the gradual narrowing of pathways causing increased resistance. The comprehensive information about particle dynamics in membranes achieved with this approach will assist design and optimization of reduced-fouling separation processes as well as advance the understanding of complex mass transport.

1. Introduction

Microfiltration is a type of separation process used to remove undesired contaminants in liquid formulations, and is commonly applied in bio-processing [1–3], water treatment [4,5], dairy processing [6,7] and pharmaceutical purification [8–10]. Despite intensive efforts and significant improvements, membrane fouling remains an impediment for filtration technology since it can cause rapid declines in permeate flux and reduce the efficiency of separations [11,12], resulting in higher costs related to energy, operation time, and membrane maintenance/replacement in order to maintain productivity [13]. In recent decades, researchers have conducted extensive studies on membrane fouling and developed mathematical models to describe different fouling processes, including complete blocking, intermediate blocking, standard blocking and cake filtration [11,14,15]. The most common way to study fouling mechanism is to measure the permeate flux as a function of time, and then determine the most likely mechanism(s) by comparing experimental flux curves to mathematical models [14,16–18]. However, this approach provides indirect and model-dependent information about fouling processes. Here we developed a complementary approach based on direct visualization of particle transport within filtration membranes under flow conditions, providing explicit evidence for distinct fouling mechanisms [19].

It has been previously reported that the decrease of membrane permeability can be related to the binding of solutes to the membrane [15,16]. Here, we applied a particle tracking approach to study the effects of particle sticking on fouling mechanisms systematically. Specifically, we used fluorescent nanoparticles as foulants and traced the fouling processes in two model polymer microfiltration membranes. Conditions representing "sticking" and "reduced-sticking" environments were formulated in both membranes, and the behaviors of fluorescent tracer particles were directly imaged using epifluorescence microscopy under the two types of condition, respectively. Compared to conventional methods that measure ensemble-average information of permeate flux through membranes, the particle-tracking technique applied here enables the observation of individual particle motions during fouling processes and provides direct evidence for fouling mechanisms [19,20]. For example, decreased flux may be due to a reduction of open pathways, slower flow velocities, or a combination of the two. In typical macroscopic measurements, these effects cannot be distinguished, but particle tracking provides this information directly. Moreover, we explored the evolution of the functional membrane tortuosity as a function of fouling. The detailed information provided by this approach affords new insights into membrane fouling mechanisms

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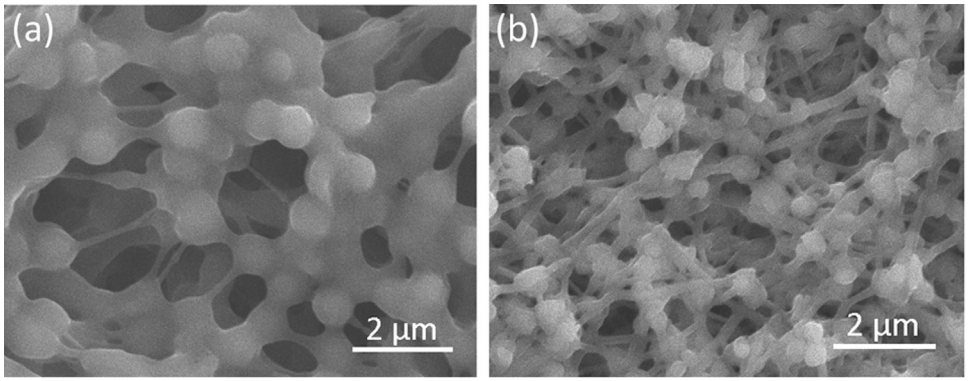

Fig. 1. Scanning electron microscope (SEM) images of a (a) Durapore (PVDF) filtration membrane with nominal pore size of 0.65 μm and an (b) LCR (PTFE) filtration membrane with nominal pore size of 0.45 μm.

as well as valuable reference data for the rational design of reduced-fouling separation processes.

2. Experimental methodology

2.1. Materials and sample preparation

Durapore (PVDF) membrane filters and LCR (PTFE) membrane filters were purchased from MilliporeSigma. The Durapore (PVDF) membrane filters had a nominal pore size of 0.65 μm, a thickness of 125 μm and a porosity of 70% (Fig. 1**a**). The LCR (PTFE) membrane filters had a nominal pore size of 0.45 μm, a thickness of 140 μm (maximum) and a porosity of 80% (Fig. 1**b**). Both membranes were modified to be hydrophilic by the manufacturer. Membrane filters were cut into annuli and sealed in a flow cell for imaging as described previously [19]. A schematic diagram describing the experimental setup is shown in Fig. 2. Tracer particle solutions were introduced from the inlet and flowed radially outward through the annulus of the membrane being imaged. The mean direction of flow was nominally parallel to the focal plane within the flow cell. As discussed in previous work, with the depth of focus being relatively shallow (~3 μm), this approach emphasized trajectories that were extensive in the *x*-*y* plane but barely meandered in the *z*-direction [19]. For experimental consistency, the focal plane was set to be 20 μm from the external surface of membrane in each experiment. FluoSpheres carboxylate-modified microspheres (Invitrogen) with nominal sizes of 0.04 μm (dark red fluorescent, 660/680) and 0.2 μm (orange fluorescent, 540/560) were used as tracer particles. The tracer particle concentration in solution was $\sim 3 \times 10^8$ particles/mL for single particle tracking experiments in PVDF membranes and $\sim 10^{10}$ particles/mL for experiments in PTFE membranes. These concentrations were low enough to minimize particle-particle interactions and enable localization of individual particles in membrane. Hydrostatic pressure was used to drive flows through membranes and the pressure drop (~0.2 psi for experiments in PVDF membranes and ~0.3 psi for experiments in PTFE membranes) for each experiment was constant. The corresponding initial flux values were estimated using the initial velocity and membrane porosity, which was $\sim 10 \pm 1$ L/(h m^2) in PVDF membranes and $\sim 15 \pm 3$ L/(h m^2) in PTFE membranes. Due to limitations of our current imaging capabilities, these flow rates were substantially lower than those employed in actual industrial filtration processes. While the initial velocity as well as initial flux values were similar under the same pressure drop, no systematic effects of initial flux on fouling behavior were observed in those experiments.

In order to minimize light scattering from the interior surfaces of membranes, index-matching liquids were formulated with alcohols and Triton X-100 for the two materials. Triton X-100 also functioned as a surfactant to reduce the immobilization of tracer particles. Index-matching liquids with different concentrations of surfactant were used to create conditions with desired particle "stickiness" as indicated in Table 1.

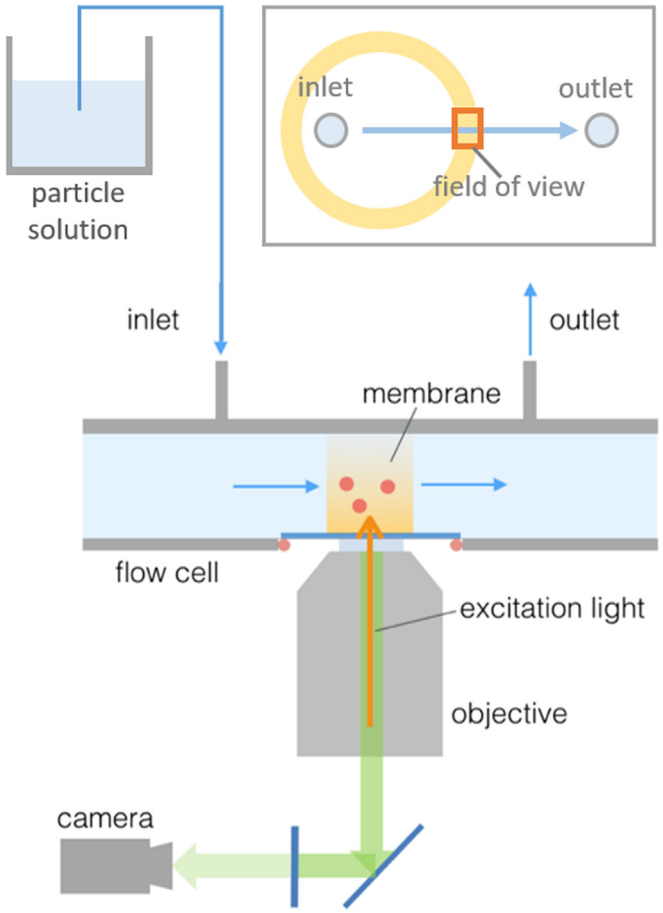

Fig. 2. Schematic diagram showing the flow cell construction (with flow driven by hydrostatic pressure) and the imaging system (only the part of membrane being imaged is shown). Top right inset demonstrates the shape of membrane sample and the field of view being imaged.

2.2. Fluorescence microscopy and single-particle tracking

All experiments were performed at 21 °C on a Nikon Ti-E epi-fluorescence microscope with a CFI Plan Apo Lambda 100 × oil immersion objective and a 532/638C-TIRF filter cube (Chroma). A CMOS camera (Hamamatsu) was used to capture images with a pixel size of