Effects of Membrane Pore Morphology on Fouling Behavior of Polymeric Micro-fabricated Membrane During Crossflow Micro-filtration

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ABSTRACT

The effects of the membrane pore geometry on the fouling mechanism of high-flux polymeric micro-fabricated membranes were studied using latex particles with different sizes and concentrations. The micro-fabricated membranes are made of a thin layer SU-8 photoresist with smooth surface and well defined slotted (or circular) pores using dissolving mold technique. For particles larger than the membrane pore size, the fouling mechanism was pore blockage followed by cake filtration while pore narrowing was the dominant mechanism when the particles were smaller than the membrane pore size. Filtration with slotted membrane offers some interesting advantages over conventional filtration with circular pores. The initial rate of flux decline was slower for the membrane with slotted pores compared to the membrane with circular pores since the initial particle deposition only covered a small fraction of the slits. The flow resistance is also much lower for the slotted membrane compare to the circular membrane.

Keywords: micro-fabricated membrane, high-flux, fouling, crossflow, microfiltration

1 INTRODUCTION

Crossflow microfiltration is a widely used technique for processing particulate suspensions in different areas such as wastewater treatment and mineral processing. In crossflow microfiltration, a deposit cake layer tends to form on the membrane which usually controls the performance of the filtration process [1]. Recent studies demonstrated that the membrane pore morphology can have a significant effect on the rate of flux decline (i.e. initial stages of filtration) where the dominant fouling mechanism is pore blockage. For instance, membranes with slit shape openings, having a high porosity would be very difficult to block during filtration of typical cell or particle suspensions [2,3]. Such membranes can provide the adequate selectivity needed for sterile filtration and microorganism removal, while minimizing the rate of flux decline. Recent developments in micro/nanotechnology have provided novel techniques for controlling the detailed microstructure of membrane materials, allowing the fabrication of membranes with perfectly controlled pore structures [4]. Recently, we have reported a novel dissolving mold technique for fabrication of polymeric microfilters with perfectly array of pores using UV-curable resins like SU-8 [5]. This method is low-cost and high-yield and can thoroughly overcome the existing difficulties in current microfabrication techniques.

In this study, we employed two high-flux micro-fabricated membranes with two different pore geometry (i.e. circular and slotted) to determine the flux decline rate as a function of the particle concentration and also study the fouling mechanism by post-SEM analysis. Surface treatment of SU-8 membranes was performed using oxygen plasma in order to increase the surface wettability and make a stable hydrophilization during microfiltration tests. The results clearly show the importance of the membrane pore morphology on both the initial flux decline, flow resistance and on the transition to cake filtration at larger degrees of fouling on the surface of high-flux micro-fabricated membranes.

2 MATERIAL AND METHODS

2.1. Micro-fabricated membrane

Polymeric membranes with circular and slotted openings were prepared using dissolving mold technique [5]. The obtained membranes have a pore dimension (diameter or slit width) of 3 μm and thickness of 10 μm. The slotted pore membrane had a pore length of 8 μm and a porosity of approximately 36% while this value is around 20% for the circular membrane. Figure 1(a) and (b) shows SEM images of the polymeric micro-fabricated membranes with circular and slotted openings, respectively.

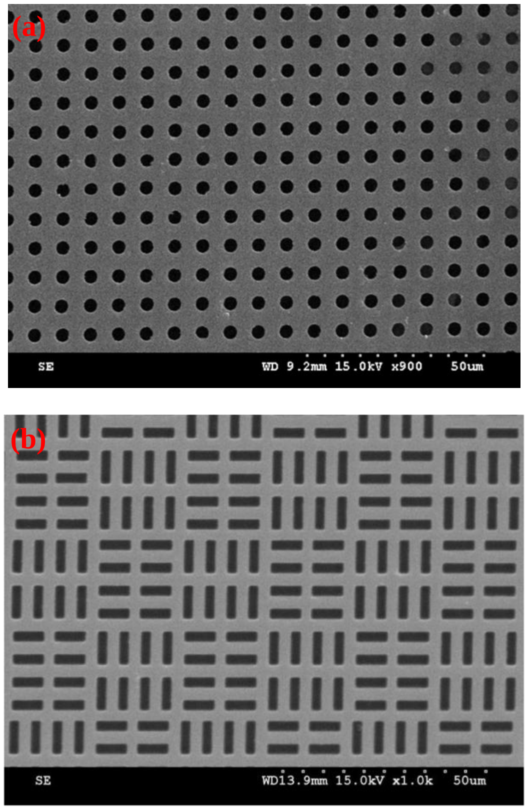

Figure 1: SEM images of the micro-fabricated membranes with a pore dimension (diameter or slit width) of 3 μm, (a) circular and (b) slotted.

2.2. Preparation of latex solution

White polystyrene latex particles with diameters of 1, 3 and 6 μm were obtained from Sigma Aldrich (Sigma-Aldrich®). Feed solutions were prepared by diluting the stock solution with ultra-pure water (18.2 MΩ cm) from a Millipore purification unit (MilliQ plus). The latex stock suspension was sonicated for 2 minutes in an ultrasonic bath before each test, and the suspension was kept homogenous by stirring the solution with a magnetic stirrer during experiments.

2.3. Surface modification of the membrane

SU-8 is a hydrophobic material [6], which is used in this study to fabricate polymeric membranes. We employed oxygen plasma surface treatment [7] to change the wettability of the surface and enhance the throughput while reducing fouling. Plasma treatment of the samples was performed under 0.4 mbar pressure at low frequency (40 kHz) for 8 minutes with a power of 50 W prior to each microfiltration test. Figure 2 shows the AFM images of a sample before and after plasma treatment. The contact angle of the samples was also measured with a goniometer after each surface treatment. It can be seen that wettability increased significantly with this method. It should be noted that treated surfaces can remain hydrophilic for several months showing a moderate hydrophobic recovery.

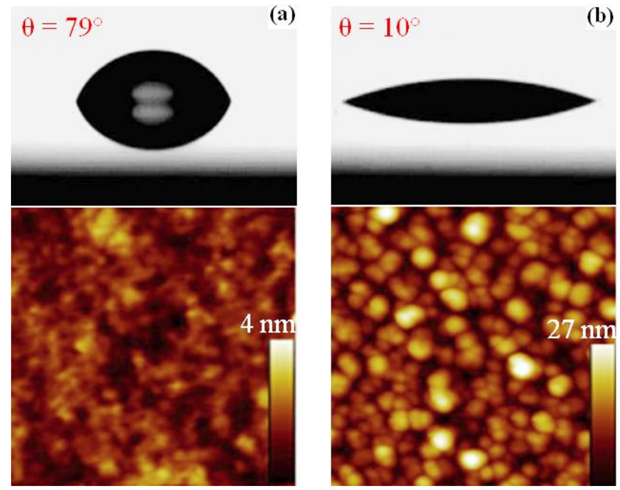

Figure 2: Contact angle and topographic AFM images of SU-8, (a) untreated surface, (b) treated surface with O_2 plasma for 8 min. The scale was set to the maximum peak to valley distance in each image as shown.

2.4. Experimental setup

The microfiltration experiments performed in both crossflow and dead-end modes. The effective membrane area and height of the crossflow channel were 6.25×10^{-4} m^2 and 0.0015 m, respectively. The clean water permeability of the membranes was measured in the pressure range of 5–20 kPa at 20 °C. The average clean water permeability value of the circular membrane was around 0.38×10^{6} l/m^2hbar while this value was around 2×10^{6} l/m^2hbar for slotted membrane.

3 RESULTS AND DISCUSSION

3.1. Fouling studies with a model particle smaller than the pore size

Microfiltration with latex particles with different sizes can reveal how a pore is blocked and how the performance of a micro-fabricated membrane will be with feeds with different particle loads. In order to calculate the performance of the micro-fabricated membranes, latex solutions with two different concentrations of particles with a diameter of 1 μm were tested. The goal was to determine the flux decline rate as a function of the particle concentration and study of the blockage by SEM analysis. Therefore, two solutions with concentration of 0.1 gr/l and 1 gr/l were prepared. The filtrations were performed in dead-end mode at constant pressure for both circular and slotted membranes, and the permeate volume was measured over time. As shown in figure 4, reletavie permeability (i.e. P_{latex}/P_w) was calculated versus time for circular pore membrane. P_{latex} is the recorded permeability from the experiments and P_w is the maximum water permeability obtained from the tests with ultra-pure water.

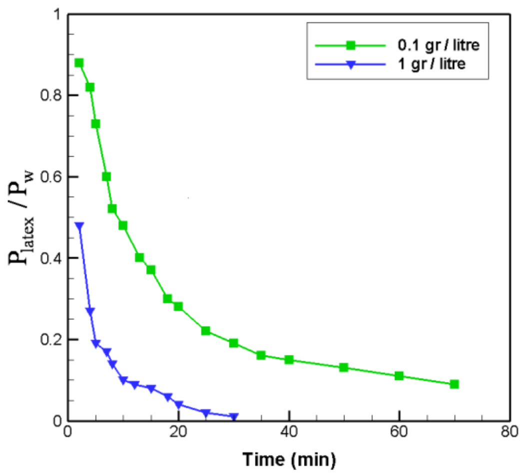

Figure 4: Relative permeability of two latex solutions as a function of time.

It can be seen that severe flux decline occurred with the most concentrated solution, producing a permeated volume of only 70 ml during 30 min filtration. Post-filtration SEM analysis of the samples revealed that how the blocking mechanism have been occurred within the pores (see Fig. 5).

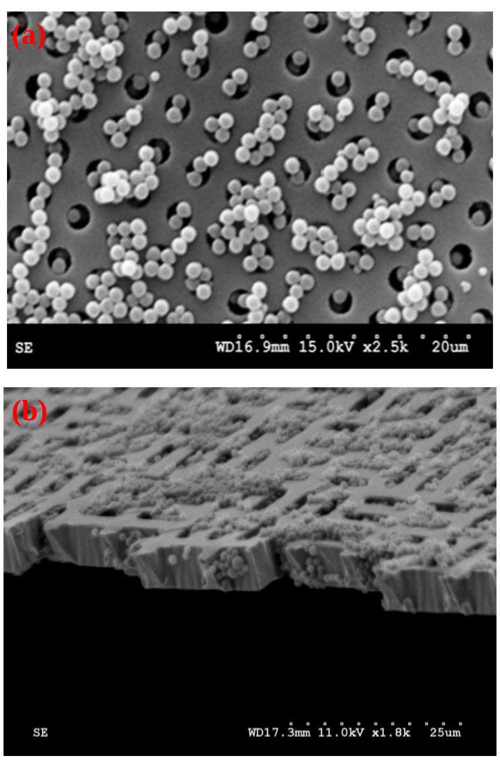

Figure 5: SEM images of two polymeric micro-fabricated filters with deposited latex particles with a diameter of 1 µm, (a) circular pore and (b) slotted pore.

3.2. Fouling studies with a model particle equal to and bigger than the pore size

Filtration test with 3 µm diameter particles was also performed to examine how particles with diameter equal to the pore size would deposit on the membrane surface. Experiments were performed with both crossflow and dead-end mode with identical particle concentrations. Microscopic observation during microfiltration shown that very rapid flux decline took place within a couple of minutes, until a steady state condition was achieved resulting in a very low residual water flux. Figure 6(a) shows the flux comparison of the circular and slotted shape micro-fabricated membrane. The flux decline data were consistent with initial fouling by intermediate blockage followed by cake filtration. The initial rate of flux decline was slower for the membrane with slotted pores compared to the membrane with circular pores since the initial particle deposition only covered a small fraction of the slotted holes.

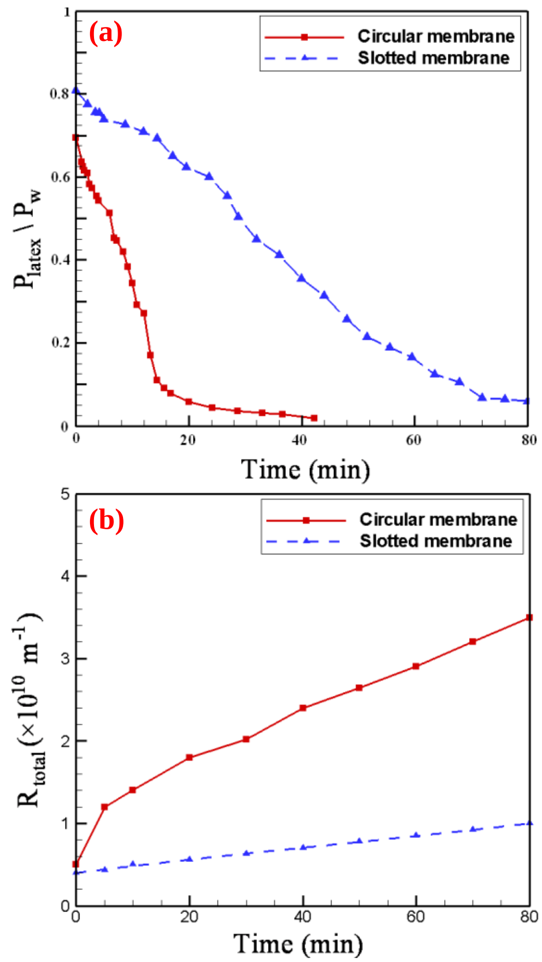

Figure 6: (a) Relative permeability, and (b) total resistance vs.time for the circular and slotted pore membrane. The concentration of the solution was 1gr/liter for the experiment.

For the slotted membrane, the flow resistance is much smaller than circular one because the slit has a smaller perimeter than several pores with the same total surface area. This fact has been also reported by other researchers elsewhere [8]. SEM images of the membrane surface shown in figure 7 also corroborate this matter clearly.

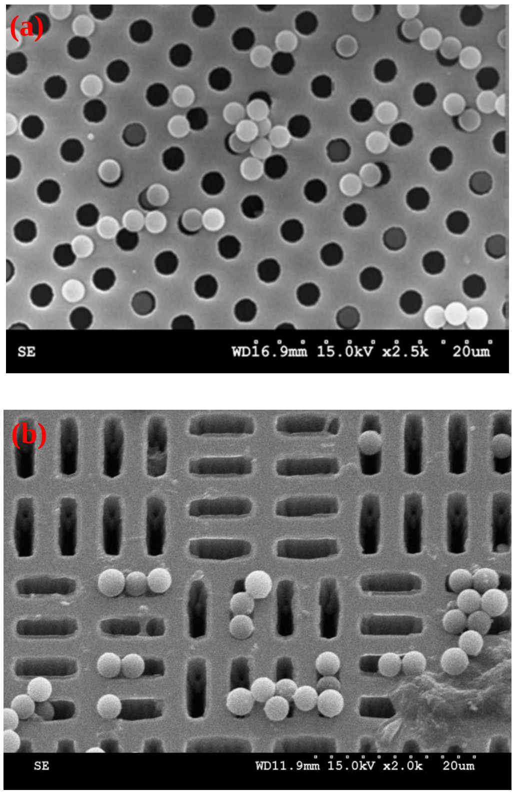

Figure 7: SEM images of two polymeric micro-fabricated filters with deposited latex particles with a diameter of 3 μm, (a) circular pore and (b) slotted pore.

For comparison to the previous cases, we also examined how particles with a diameter larger (i.e. 6 μm) than the pore size would deposit and cause the fouling on the membrane surface. The experiments performed under crossflow mode with low concentration slurry to visualize the mechanism of cake formation on the surface of micro-fabricated membranes. In-line inspection of the membrane surface during filtration confirmed that all the latex particles rejected and caused external fouling and cake formation. SEM analysis of the samples revealed that a single 6 μm particles can block a circular membrane completely, while slotted pore membrane with 8 μm length has still some open area for water penetration.

4 CONCLUSIONS

In this research the performance of two polymeric micro-fabricated membranes were investigated. The obtained results in this study provide significant insight into the effects of pore morphology on the membrane fouling and also demonstrate a further application of transparent micro-fabricated membranes as an excellent tool for studying the fouling phenomenon. Experimental data for latex particles filtration smaller than the pore size shows that pore narrowing and cake formation are the dominate mechanisms during filtration. For the particles equal to or larger than the pore size, the flux decline data were consistent with initial fouling by intermediate blockage followed by cake filtration. The initial rate of flux decline was slower for the membrane with slotted pores compared to the membrane with circular pores since the initial particle deposition only covered a small fraction of the slotted holes. In addition, from the obtained results we can conclude that by proper selection of the membrane pore geometry, the flux decline can be hindered while maintaining a high selectivity during microfiltration.

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