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Ceramics International 39 (2013) 4355–4361
CERAMICS INTERNATIONAL
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# Fabrication of ceramic membranes with controllable surface roughness and their applications in oil/water separation

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Received 9 September 2012; received in revised form 3 November 2012; accepted 8 November 2012
Available online 14 November 2012

**Abstract**

Knowledge of the surface roughness of ceramic membrane is useful for the understanding and improvement of their filtration performance. In this study, ceramic membranes with controllable roughness were fabricated with a template formed by PMMA particles uniformly deposited on the filter paper. Scanning electron microscopy (SEM) and vertical scanning interferometry (VSI) characterizations demonstrated that size distribution of template particles had an important effect on the morphology of membrane surface. The surface morphology formed by templating method was more homogeneous than that by the polishing method. The influence of surface roughness on the vegetable oily wastewater treatment was investigated. It was found that surface roughness had little effect on the pure water flux of membrane and oil rejection, but it played an important role in the filtration flux of oily wastewater. A high and stable flux was observed through the smooth membrane; its steady flux was obtained more quickly than that of the rough membrane. The results indicated that the smooth membrane is the control of membrane fouling during filtration of oily emulsion wastewater.


*Keywords:* Ceramic membrane; Roughness control; Oily wastewater

## 1. Introduction

The surface morphology of the filtration membranes plays an important role in determining the characteristics of membrane fouling [1]. Rough surfaces have been reported to be fouled more easily because of large surface area and also, they affect other properties of membranes such as hydrophobicity, zeta potential and hydrodynamics and influence fouling rate [2]. A great number of studies have been carried out to gain better understanding of the influence of surface roughness on the performances of organic membrane. Vrijenhoek et al. [3] reported that colloidal fouling of RO and NF membranes was correlated with the surface roughness of the membrane, regardless of physical and chemical operating conditions. Particles preferentially accumulate in the "valleys" of rough membranes, resulting in "valley clogging" which causes more severe flux decline than in smooth membranes [4–6]. This type of fouling could be minimized by using membranes with roughness value where adhesion happened only at peaks [7]. The greater the surface area of the membrane (due to the roughness), the stronger the interaction between membrane materials, foulants and cleaning agents [8]. However, other studies showed that fluxes through rough membranes are less affected by fouling formation compared with the smooth membranes. For example, Riedl et al. [9] suggested that a loose fouling layer was produced at the rough membranes resulting in a lower flow resistance rather than the dense fouling layers observed on the smooth surfaced membranes. In our previous studies, highest flux was obtained when carrying out filtration of nano-sized particles using the membrane with a certain roughness [10].

Therefore, methods to control the surface roughness of membrane will be of importance to the filtration process. The roughness of solid surfaces can be modified by lithographic methods, template-based techniques, plasma

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0272-8842/$ - see front matter 
http://dx.doi.org/10.1016/j.ceramint.2012.11.019

treatment, self-assembly and self-organization, chemical deposition, layer-by-layer (LBL) deposition, colloidal assembly, phase separation, and electrospinning [11,12]. Polishing was an easy method to change the surface roughness of the ceramic membrane, but the homogeneity of morphology was found to be difficult to control [10]. Templating of surfaces is often fast, has a very low cost and reproducible and so is a widely used method for the preparation of rough surfaces. Any surface can be used as a template, such as colloidal, lithographic and woven material surfaces, some of these masters maybe reused and some may be intentionally destroyed to reveal the replica surface [13]. For example, Sun et al. created a rough superhydrophobic surface using a lotus leaf as template and replicated it by nanoscale casting instead of conventional microfabrication or chemical synthesis [14]. Electrochemically prepared textured aluminum sheet could be successfully used as a replication master for the generation of large-area-nanostructured metallic films [15]. However, there are few reports addressing the membrane surface roughness control with a template method.

In recent years, large quantity of effluents was produced from the refinery processes during the growth of vegetable oil industry. In addition, catering trade discharges considerable amount of oily wastewater containing vegetable oil. If the discharged effluent is untreated, it can certainly cause serious environmental problems due to its high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [16]. Therefore, removing oil from wastewater is an important aspect of pollution control in many industry fields.

In this work, ceramic membranes with different roughnesses were prepared using a template formed by ultrafine particles uniformly deposited on a filter paper, and the influence of surface roughness on the vegetable oily wastewater treatment was investigated. We try to make a contribution to the membrane surface design in the membrane preparation.

## 2. Material and methods

### 2.1. Membrane roughness control

Three symmetric plane $Al_2O_3$ microfiltration membranes were prepared by the dry pressing method [17]. Fig. 1 shows the process of membrane preparation and surface morphology control. The main experimental procedures are as follows: first, the suspension of poly(methyl methacrylate) (PMMA) particles (5 g/L) were prepared by adding them to deionized water at room temperature. Then the suspension was filtered through a filter paper with mean pore size of 0.45 μm (Whatman, Millipore, USA). A template was obtained after PMMA deposition on the filter paper surface uniformly. Second, appropriate amount of $Al_2O_3$ powder (average size of 2 μm) was blended with polyvinyl alcohol (PVA) and glycerin to enhance the shaping property of the green discs. The template was placed in the stainless mold and $Al_2O_3$ mixtures were poured into the stainless mold and pressed at a pressure of 10 MPa to flatten the surface and

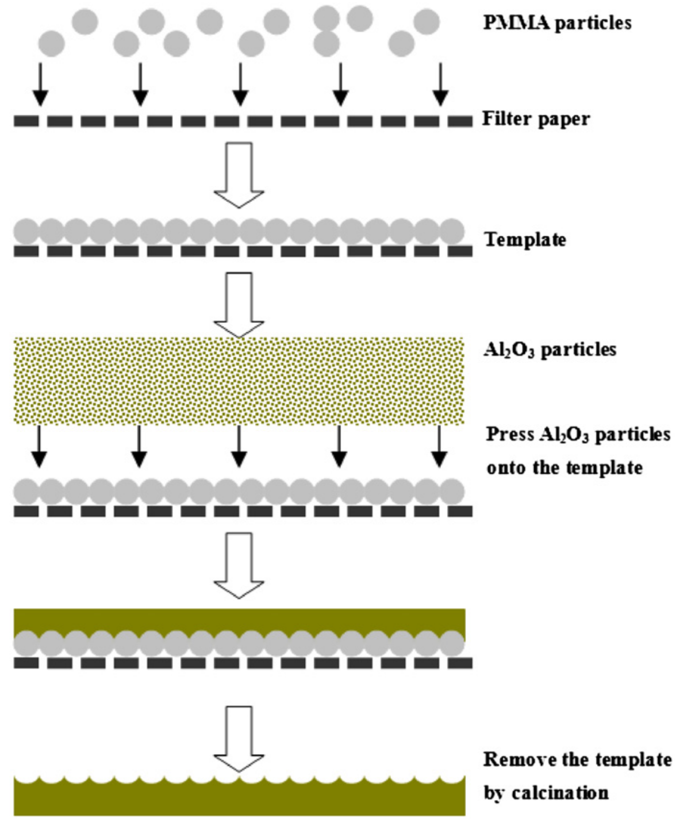

Fig. 1. Schematic illustration of membrane preparation and surface control.

increase its mechanical strength. The green disc was formed with a diameter of 30 mm and thickness of 3 mm. And third, the $Al_2O_3$ membranes were obtained after the green discs were sintered in air at 1300 °C for 2 h with the heating and cooling rates of 2 °C/min$^{-1}$. The template was removed by calcination, leaving the inverse of its pattern on the membrane surface. The average pore size of the membranes was $0.35 \pm 0.04$ μm and the porosity was about $0.30 \pm 0.03$.

Membrane pore size was determined by mercury porosimetry (Poremaster GT-60, Quantachrome, USA). PMMA particles with different size were used. Size distribution of the PMMA suspension was performed on a particle size analyzer (MasterSizer 2000, Malvern, UK). Fig. 2 shows SEM micrographs of PMMA particles with average size of $0.64 \pm 0.03$, $89.09 \pm 4.50$ and $176.10 \pm 8.80$ μm respectively.

### 2.2. Roughness determination

The membrane roughness was determined using a surface roughness tester (SRT) with a resolution of 0.001 μm (JB-4C, Shanghai Taiming Optical Instrument Co., Ltd., PR China). While measuring the roughness of a surface, the sensor was placed on the surface and slid uniformly along the surface. The surface roughness was obtained by the sharp built-in probe on the sensor. Measurements were performed on at least 5 different locations on the membrane surface of each sample. The average values of the

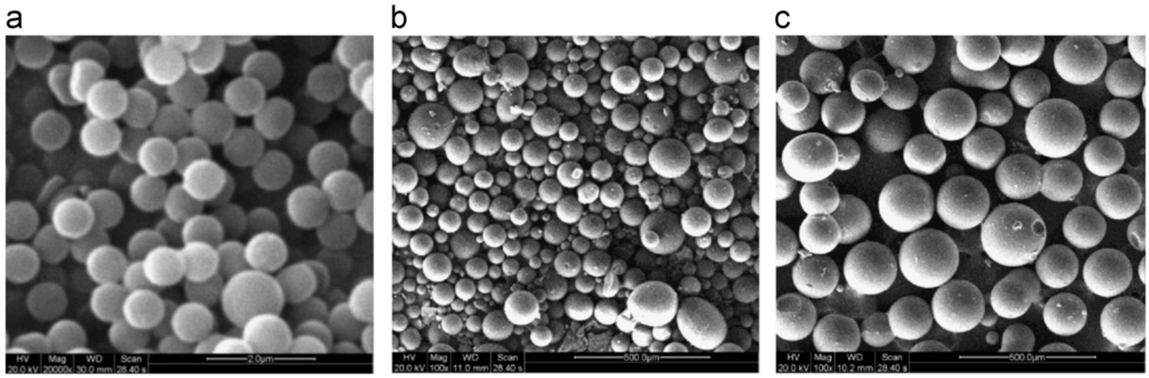


Fig. 2. SEM micrographs of PMMA particles with different diameters: (a) 0.64 ± 0.03 μm; (b)89.09 ± 4.50 μm; (c) 176.10 ± 8.80 μm.

roughness of each sample were provided in terms of Ra (arithmetical mean deviation of the profile).

### 2.3. Surface morphology characterization

Various techniques were used to characterize the surface topology of ceramic membranes. Samples were examined with a scanning electron microscope (SEM, Quanta200). Optical interferometry measurements were carried out using a MicroXam vertical scanning interferometer (VSI, ADE-phase Shift Technology, Tucson, AZ). The basic operating principles of the interferometer are presented in references [18,19]. The interferograms are digitized with a CCD camera and converted into a topographic map with softwares. All interferometric measurements were carried out on dry membrane samples.

### 2.4. Filtration experiments

The crossflow filtration was run at a crossflow velocity of 3 m/s with a constant temperature of 60 °C and a transmembrane pressure of 0.15 MPa. The feed was maintained at a constant volume by recycling the permeation back into the feed tank [20].The vegetable oil wastewater used in this study was prepared by mixing edible oil with tap water and sodium dodecylbenzene sulfonate for 30 min at different speeds (1000, 2000, and 4000 rpm) using a disperse mill, and the volume ratio of oil and surfactant was 8:1. The oil concentration in water was about 5 g/L. Size distribution of the oil droplet was performed on a size analyzer (S3500, microtrac). Size measurement showed that the oil droplet diameter was approximately 1.427 ± 0.070, 1.115 ± 0.050 and 0.801 ± 0.040 μm. The oil concentration was measured by an infrared photometric oil analyzer (ET1200, Euro, Shanghai).

## 3. Results and discussion

### 3.1. Surface morphology characterization

Two surface analysis techniques including scanning electron microscopy (SEM) and vertical scanning interferometry (VSI) were used to characterize the membranes. As shown in Fig. 3, it is found from the SEM results that membrane A was smoother than membrane B and C. Some circular valleys on the surface of membrane B and C were clearly observed. They were inverse patterns of PMMA particles after being removed by calcinations. As for membrane A, template particles in Fig. 2(a) were smaller than $Al_2O_3$ particles of membrane, so their inverse patterns could not be formed or be observed at the studied magnification. On membrane B, circular valleys with varied size were observed corresponding to the non-uniform distribution of the template particles, as shown in Fig. 2(b). Template particles in Fig. 2(c) had a relatively uniform distribution, so circular valleys on membrane C seemed more uniform than that on membrane B. Therefore, size distribution of template particles had an important effect on the morphology of membrane surface.

In our previous study, polishing was found to be an easy method to change the surface roughness of the ceramic membrane, but the homogeneity of morphology was found to be difficult to control [10]. Comparison between Fig. 3(c) and Fig. 3(d) showed that the morphologies of two membranes were significantly different. The membrane surface prepared by the template method was more homogeneous than that prepared by the polishing method.

VSI is a type of microscopy that can determine nanoscale characteristics of a sample surface through the interpretation of light reflected from a surface. As shown in Fig. 4, VSI images had similar scan area with SEM images but provided three-dimensional information. Peak-to-peak distance or valley-to-valley distance of rough membrane B and C was larger than that of the smooth membrane A. Dark color of circular valleys indicated a high depth on the surface of the membrane. Depth differences of circular valleys were the results of different-sized template particles and their aggregates embedded into membrane under pressure.

### 3.2. Roughness determination

Three typical 1-D linear profiles taken from membranes prepared with PMMA-particle templates are shown in Fig. 5. It indicates that membranes had different profiles

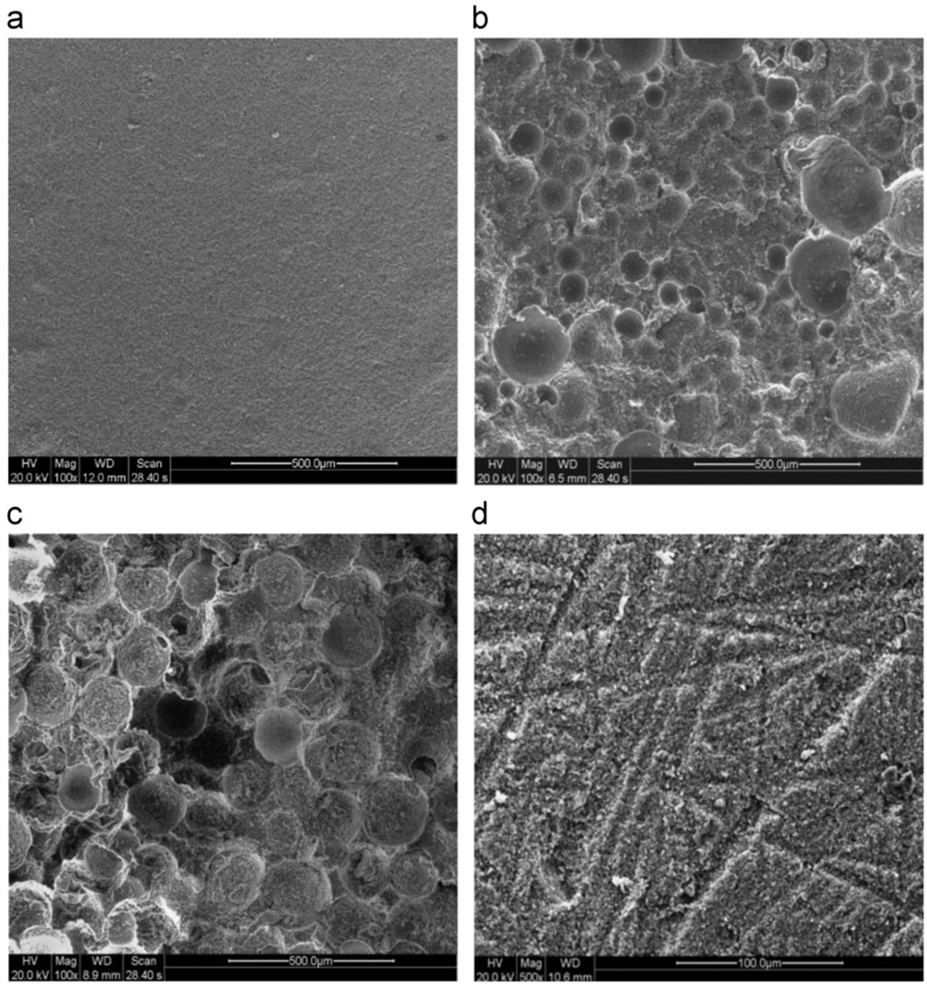


Fig. 3. SEM images of membrane surfaces formed by templating: (a) membrane A; (b) membrane B; (c) membrane C, and by polishing: (d) membrane D [10].

when different-sized PMMA particles were used. Height variation appears to be much wider for membrane B and C as compared to membrane A, but all three profiles showed a clear random character of the peaks and valleys. The roughness value (Ra) of the membrane A, B and C were $0.543 \pm 0.270$, $9.103 \pm 0.450$ and $16.507 \pm 0.820$ μm respectively, corresponding to PMMA particle size of $0.64 \pm 0.03$, $89.09 \pm 4.50$ and $176.10 \pm 8.80$ μm. It is also found from Fig. 6 that the average roughness increased almost linearly with PMMA particle size. Therefore, surface roughness could be controlled by selecting templates with proper sized PMMA particles.

### 3.3. Effect of roughness on membrane performance

#### 3.3.1. Effect of roughness on pure water flux

Fig. 7 shows the effect of surface roughness on pure water flux. The pure water flux of different membranes increased slightly with roughness. It was reported that surface roughness increased the surface area of asymmetric membrane [8]. The increase of flux with roughness was consistent with the increase in surface area with roughness [21–23]. However, it indicated that roughness had little effect on the pure water flux of membrane in this study. This was expected because the membrane used was symmetric and thick, and the morphology modification of the membrane surface only changed the pore structure and thickness of membrane slightly. The pore size characterization showed that pore size distribution of membranes was nearly the same and not affected by surface modification. Therefore, the total membrane resistance was not significantly affected.

#### 3.3.2. Effect of roughness on oily wastewater filtration

Cross-flow filtration of oily wastewater (oil droplet diameter is around $1.427 \pm 0.070$ μm) using the ceramic membranes with the same average pore size but different surface roughness were investigated. Variations in permeate flux for the different membranes are illustrated in Fig. 8. The initial permeate flux decreased significantly for three membranes. This was because that the $Al_2O_3$ membrane had a positive charge, which is opposite to the charge of the oil droplet in neutral pH solution [24]. The electrostatic affinity between the membrane surface and oil

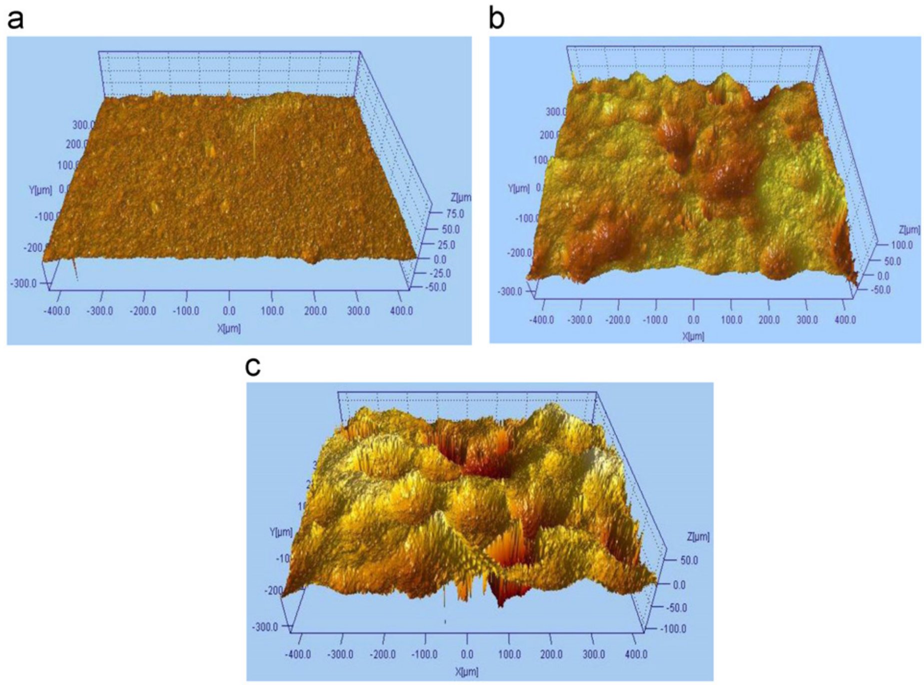


Fig. 4. VSI images of membranes: (a) membrane A; (b) membrane B and (c) membrane C.

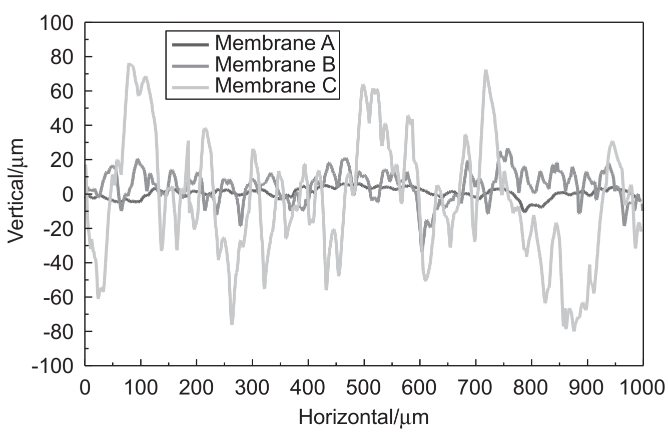


Fig. 5. Typical 1-D profiles of membranes polished to different degrees (black, gray, light gray represent Ra = 0.543 ± 0.270, 9.103 ± 0.450, 16.507 ± 0.820 μm, respectively).

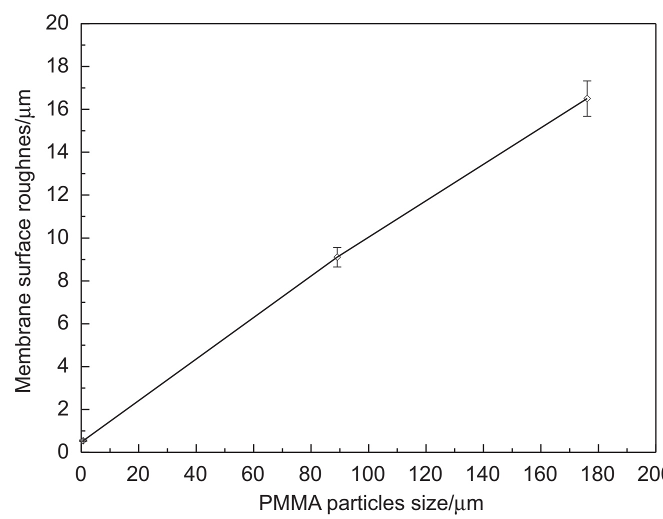


Fig. 6. Average roughness (Ra) as a function of PMMA particle size.

droplets accelerated the deposition of oil droplets and the formation of a fouling layer on the membrane surface, leading to a decrease of permeate flux. Then a higher and more stable flux was observed through the smooth membrane A. Its steady flux was obtained more quickly than that of the rough membrane B and C. In the test time, flux of membrane B and C declined continuously and their steady states were not reached. This can be explained by Fig. 9, the aforementioned membranes showed greater surface area or roughness, which strengthened the interaction between membrane surface and oil droplets, resulting in more oil adsorption on the membrane surface. The authors suggested that oil droplets were preferentially accumulated in the deep valleys of the rough membranes, and resulted the formation of a fouling layer on the membrane surface, causing more severe flux decline than smooth membrane A. In contrast, membrane A had a surface with small amount of shallow valleys. There were less oil droplets accumulating on the surface, so a high steady flux was obtained. The results indicated that the smooth membrane improved the control of membrane fouling during filtration of oily emulsion wastewater.

### 3.3.3. *Effect of roughness on oil rejection*

Effect of membrane surface roughness on oil rejection (oil droplet diameter is around 1.427 ± 0.070 μm) is shown in Table 1. It can be seen that the oil rejections were all

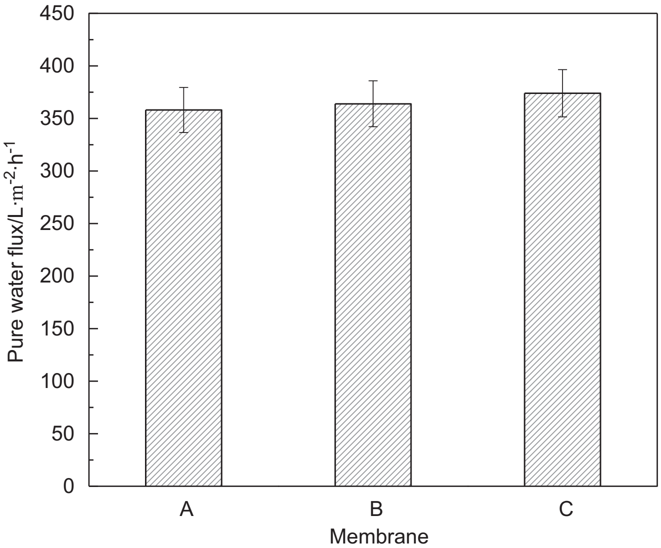


Fig. 7. Pure water flux of membranes.

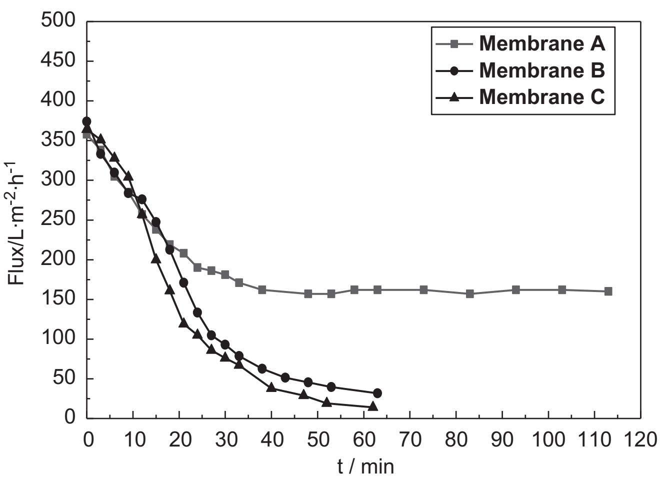


Fig. 8. Effect of surface roughness on the decline of flux.

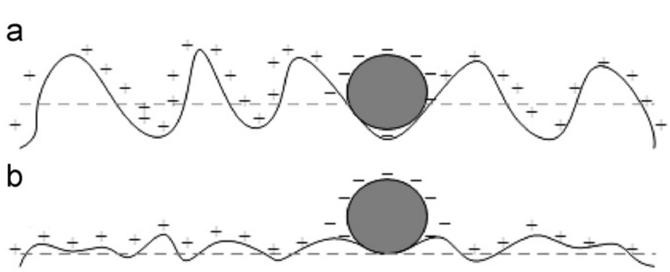


Fig. 9. The principle of membrane fouling under different surface roughnesses: (a) rough membrane; (b) smooth membrane.

higher than 99%. The reason was that the membranes used in this work have an average pore size of $0.35 \pm 0.04$ μm, which was smaller than the oil diameter. In addition, we found that oil rejections were all nearly equal for three

Table 1
Effect of membrane surface roughness on oil rejection.

| | Membrane A | Membrane B | Membrane C |
|---|---|---|---|
| Roughness/μm | $0.543 \pm 0.270$ | $9.103 \pm 0.450$ | $16.507 \pm 0.820$ |
| Oil rejection/% | $99.59 \pm 0.10$ | $99.57 \pm 0.10$ | $99.54 \pm 0.10$ |

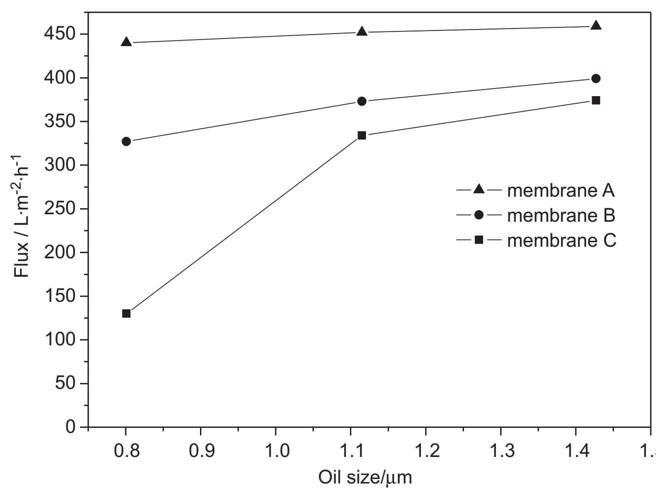


Fig. 10. Effect of average oil diameter on the steady flux of membranes.

membranes. It seemed that the difference in roughness did not affect the rejection of membrane.

### *3.3.4. Effect of oil diameter on the filtration performance*

Fig. 10 shows the effect of average oil size on the steady flux of membranes. For smooth membrane, steady flux increased very slowly with oil size. It was reported that the adhesion of particles with size similar to those of asperities depended mainly on the size and shape of the asperities and slightly depended on particle sizes [25]. For rough membrane, especially for membrane C, oil size played an important role in filtration process, and a low steady flux was obtained during the filtration of the smallest oil droplets. As shown in Fig. 9, when the particles were smaller than the size of the asperities on the membranes, there was a greater probability for the particles to be deposited in the circular valleys of the rough membranes. The decrease of oil size contributed to the oil accumulation on the valleys surface and formed a dense fouling layer. The results indicated that smooth membrane was more applicable in treatment of oily wastewater from complicated sources which often had different oil size.

## 4. Conclusion

Ceramic membranes with controllable roughness were fabricated with a template formed by PMMA particles uniformly deposited on the filter paper. It indicated that size distribution of PMMA particles had an important effect on the roughness value. Therefore, surface roughness could be controlled by selecting templates with proper sized particles. Based on the membrane characterization and crossflow filtration, the results showed that roughness had an important effect on the performance of the membrane. A high and more stable flux was observed through the smooth membrane and its steady flux was obtained more quickly than that of the rough membranes. Therefore, membrane roughness is one important factor that needs to be considered when selecting a membrane to treat oily emulsion wastewater.

## Acknowledgments

Financial supports from the National Natural Science Foundation of China (Nos. 21125629, 21276124), Key Projects in the National Science & Technology Pillar Program (No. 2011BAE07B09-3), the Research Project of Natural Science for Universities Affiliated to Jiangsu Province (10KJB530002), Jiangsu Province Industrial Supporting Project (No. BE2011831).

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