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An investigation on manufacturing of alumina microfiltration membranes

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ABSTRACT

In this research, disk-type alumina microfiltration membranes with an approximate diameter of 21 mm were synthesized via isostatic pressing method. Many samples were made and characterized based on the Taguchi experimental design to optimize the manufacturing procedure. The effect of alumina powder size, binder type and amount, sintering temperature, and pressing pressures was investigated. Porosity and water permeability of samples were measured, and SEM images were taken. The results showed that using different binders amounts can alter porosity from 25 to 49%, while type of binder has few effects on MF characteristics. Furthermore, water permeability of the samples varies from 170 to 3700 ($kg/m^2.h.bar$) depending on pressing pressure, alumina powder size, and sintering temperature. Using finer alumina powders and higher sintering temperatures can provide fewer porous and permeable membranes. SEM images confirmed formation of defect-free membranes. Confirmation of homogenized MF membrane approved by filtration of an industrial mineral oil. The results showed as follows: 100% rejection for particle size greater than 2 micron and more than 95% rejection for particle size bigger than 250 nm.

Keywords: Microfiltration membranes; Alumina; Sintering; Water permeability; Porosity

1. Introduction

The use of ceramic microfiltration (MF) membranes for treatment of water or oily feeds has been performed by many researchers [1–12]. Isostatic pressing is one of the most effective methods for manufacturing of MF ceramic membranes. De Colle et al. manufactured MF membranes via isostatic pressing method using mixed alumina and zirconia. They used milling techniques for blending the powders and binder, which led to finding optimum milling time and powder composition [13]. Using different powder size, binder type, binder amount, pressing pressure, sintering temperature, and other conformation parameter potentially affect pore size, porosity, and water permeability of membranes significantly. Mohammadi et al. investigated some of the effective parameters on mullite tubular MF membranes [14]. Bernard-Granger et al. studied densification mechanism and investigated the effect of grain

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size using pure α-alumina [15]. K. Prabhakaran et al. used a gelling agent to prepare microporous alumina with porosity higher than 70% via gel casting. They found sintering temperature effects on porosity and shrinkage percentage [16]. Centrifugal deposition of a colloidal suspension is more expensive than extrusion or isostatic pressing [17]. Abbasi et al. prepared mullite and mullite–alumina ceramic MF membranes and could achieve acceptable performance [3].

In this research, some effective parameters in manufacturing of disk-shaped MF α-alumina membrane via isostatic pressing using Taguchi experimental designs were successfully investigated. Water permeability and porosity of the manufactured membranes were measured, and SEM analysis was also performed. Using the results of this study could be useful in manufacturing of the MF alumina membranes with the desired characteristics (porosity and water permeability). Rejection of suspended fine particles in a pre-treated industrial hydraulic oil was measured for evaluation of membrane's performance using PSA analyzer.

2. Experimental

For manufacturing of considered MF alumina membranes, the mineral powders mixed with binder solution and put specified amount of that in molding systems and altogether put in pressing machine for making of non-sintered raw membranes. The planned sintering temperature exerted, and the final membranes characterized by different methods.

In this study, two kinds of industrial grade α-alumina (1 and 4 microns) and three different polymeric materials as a binder (CMC, PVA, and xanthan gum) were used. A hydraulic press and specific casting were used for molding the non-sintered of alumina granules. Concentration of the binders was 1.2 wt.% in distilled water. In design of experiments, Taguchi (L27) pattern was used in order to reduce cost and time. So, five more important parameters were considered as below:

- *Mean size of powder*: Two types of Fibrona company α-alumina powders were applied in this study. WDR4 and SRM-30 are more commercially available types.
- *Binder type*: Three polymeric binders were used. Carboxymethyl cellulose (CMC), poly vinyl alcohol (PVA), and xanthan gum. Specification of these materials is presented in Table 1.
- *Amount of binder*: Three different amounts of binder solution were used as follows: 1, 2, and 3 cm^3 binder solution per 30 g of α-alumina powder.
- *Pressing pressure*: Applied pressure in pressing implies on aggregation of granules. Therefore, to observe compression effectiveness, three different amounts of pressure were applied as follows: 300, 400, and 500 bar.
- *Sintering temperature*: One of the most important parameters is sintering temperature that is very effective on mechanical strength, total porosity, etc. Three different temperatures (1,350, 1,425, and 1,500˚C) were applied in sintering process. The Taguchi experimental design (L27) is presented in Table 2.

Table 1
Specifications of binder raw materials

No	Binder name	Specification	Origin
1	CMC	Viscosity: (2%, H_2O, 25˚C): 25–75 mPa.s	Merck Co: 217,277
2	PVA	Granule-density: 1.3 g/cm^3 (20˚C) Viscosity: (0.5–1% H_2O, 25˚C): 0.1–0.5 Pa.s	Merck Co: 141,360
3	Xanthan gum	Food grade-Mesh powder: 200 Viscosity: (0.5–1% H_2O, 25˚C): 1–3 Pa.s	Food grade

Porosity of manufactured membranes was measured by water adsorption method and using differences between dry and wet weight membranes. All water permeability of membranes was measured in specific module, using water flow under 3 bar pressure. And mechanical resistance was measured by the impressive method (measuring of required force on the surface of membrane to compress it for 1.5 mm).

3. Results and discussion

Three samples were prepared for each designed experiment. The results showed less than 1% difference in porosity and to the smaller extent than 1.5% difference in water permeability. The results of porosity, water permeability, and mechanical resistance are presented in Table 2 on average. Table 3 presents the response table of Taguchi analysis for porosity of MF membranes when CMC binder is used. Response parameters for water permeability and other binder are explained below.

Table 2
Experimental design, porosity, and water permeability of the membranes

Sample No.	Alumina 1μ (%)	Binder type	Volume of binder in 30 g powder (cm^3)	Pressing pressure (bar)	Sintering temperature (°C)	Porosity (%)	Water Permeability ($kg/m^2.h.bar$)	Mechanical resistance (bar)	Notes
S01	0	CMC	1	300	1,350	47.4	–	–	Sample crushed in water flux test because of low mechanical resistance
S02	0	CMC	2	400	1,425	45.7	3793.5	5,132	
S03	0	CMC	3	500	1,500	46.3	4034.0	5,572	
S04	50	CMC	1	400	1,500	39.1	887.1	6,012	
S05	50	CMC	2	500	1,350	48.4	374.0	5,001	
S06	50	CMC	3	300	1,425	42.9	1135.3	4,809	
S07	100	CMC	1	500	1,425	43.1	165.6	5,910	
S08	100	CMC	2	300	1,500	26.1	251.2	5,449	
S09	100	CMC	3	400	1,350	49.6	173.4	4,809	
S10	0	Xanthan	1	300	1,350	47.6	–	–	Sample crushed in water flux test because of low mechanical resistance
S11	0	Xanthan	2	400	1,425	41.1	2925.2	–	
S12	0	Xanthan	3	500	1,500	41.7	2467.6	–	
S13	50	Xanthan	1	400	1,500	35.4	231.1	–	
S14	50	Xanthan	2	500	1,350	44.1	336.2	–	
S15	50	Xanthan	3	300	1,425	42.4	614.3	–	
S16	100	Xanthan	1	500	1,425	40.7	155.7	–	
S17	100	Xanthan	2	300	1,500	31.9	208.8	–	
S18	100	Xanthan	3	400	1,350	49.7	180.5	–	
S19	0	PVA	1	300	1,350	46.7	–	–	Sample crushed in water flux test because of low mechanical resistance
S20	0	PVA	2	400	1,425	46.7	3328.9	–	
S21	0	PVA	3	500	1,500	40.9	2851.8	–	
S22	50	PVA	1	400	1,500	35.7	489.1	–	
S23	50	PVA	2	500	1,350	45.9	327.3	–	
S24	50	PVA	3	300	1,425	41.4	801.1	–	
S25	100	PVA	1	500	1,425	41.6	139.4	–	
S26	100	PVA	2	300	1,500	33.0	201.0	–	
S27	100	PVA	3	400	1,350	47.8	178.3	–	

Table 3
Response table of Taguchi analysis for porosity of MF membranes when CMC binder is used

Level	1μ alumina powder %	Binder solution volume	Pressing pressure	Sintering temperature
1	46.47	43.20	38.80	48.47
2	43.47	40.07	44.80	43.90
3	39.60	46.27	45.93	37.17
Delta	6.87	6.20	7.13	11.30
Rank	3	4	2	1

3.1. Effect of parameters on porosity

The results show, sintering temperature is the most effective parameter on porosity through Taguchi responses, followed by, the pressing pressure, concentration of binder, and alumina powder size, which have less effectiveness, respectively.

As illustrated in Fig. 1, when CMC binder is applied, using finer powder causes to porosity decrease drastically. By reduction in particle diameters and increasing of surface area of bulk powder, void fraction will be decreased and porosity will decline rationally, too. When high pressure applied, compression of membranes will increase and high mechanical strength will be achieved. The effect of pressing pressure on porosity is negligible. Amount of binder concentration had not considerable effect on porosity in our usage percentage. Sintering temperature is the most effective parameter on bulk porosity. It is shown in Fig. 1(A). By increasing of sintering temperature up to 1,500 bulk porosity will decrease drastically. Using other types of considered binders had no effect on the variation manner. It just effects on the amount of porosity. Variation manner of xanthan and PVA binder is shown in Fig. 1(B) and (C). The highest porosity belongs to CMC binder, and lowest ones belong to xanthan.

3.2. Effect of parameters on water permeability and mechanical resistance

The results show, powder size of alumina powder is the most effective parameter on water permeability through Taguchi responses, followed by, the sintering temperature and binder concentration, which have less effectiveness, respectively.

As the results show, when CMC binder is applied, like porosity, using finer powder causes water permeability to decrease drastically. The effect of pressing pressure on permeability and porosity is the same. Amount of binder concentration has a considerable

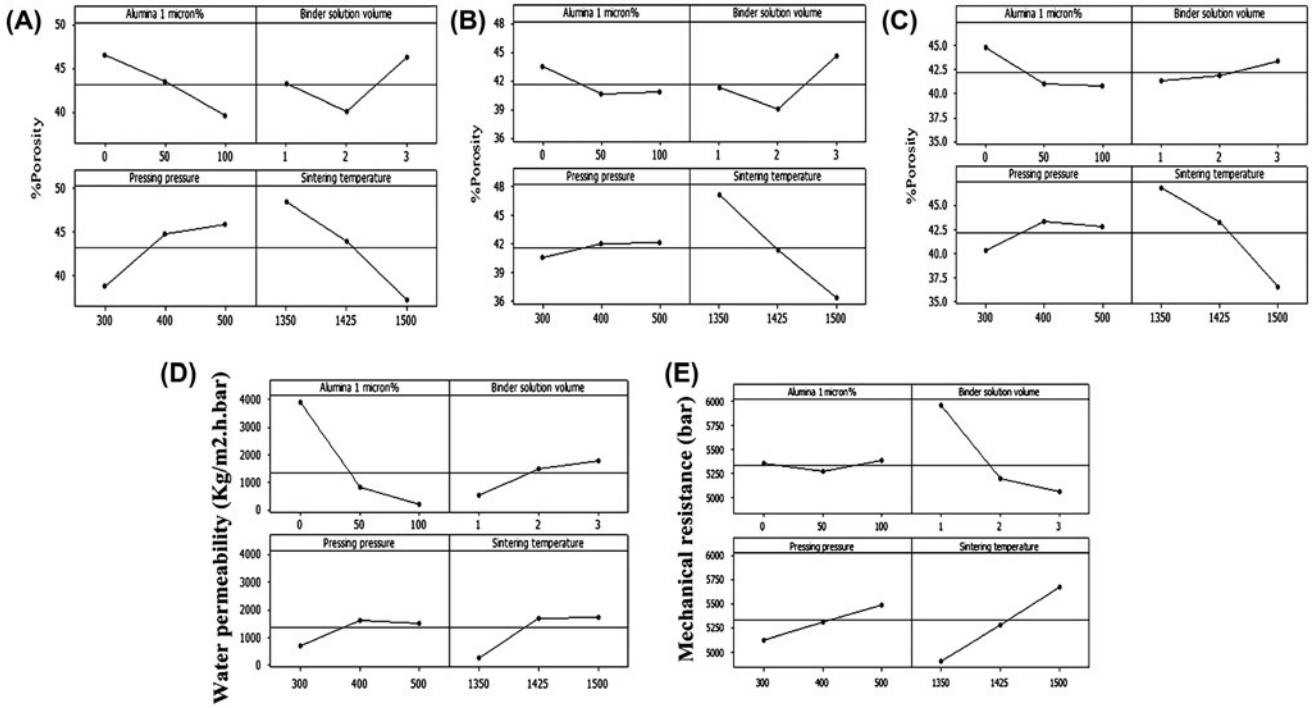

Fig. 1. Effect of parameters on porosity and permeability (A) porosity-CMC binder, (B) porosity-xanthan binder, (C) porosity-PVA binder, (D) permeability-CMC binder, and (E) mechanical resistance (bar).

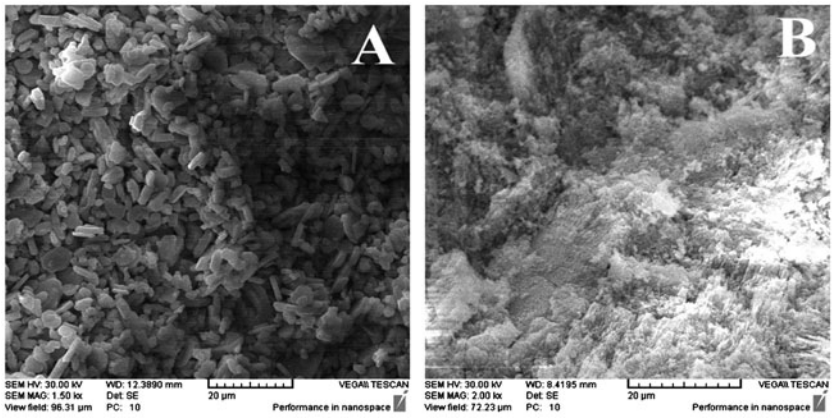

Fig. 2. Cross-section SEM photos of sample (A) S01 and (B) S07.

effect on water permeability value. Applying of more binder solutions led the permeability to increase. Sintering temperature was not wide effects on water permeability value, as like as porosity, and there is no significant difference between 1,425˚C and 1,500˚C. Applying low sintering temperature like 1,350˚C let some alumina particles inside of created backbones of membrane to be unsintered. These particles are free bodies and have not come into the sintering reaction. So, they had no influence on membrane porosity. On the other hand, these bodies involve on sticking reaction by increasing of sintering temperature, and this process led membrane to form larger pores and have higher permeability (Fig. 1). Using another binder type had no significant influence on the variation manner. It just effects on the total amount of water permeability value. The highest permeability belongs to CMC binder. PVA and xanthan had the same results less than CMC solution as a binder.

As shown in Fig. 1(E), addition of more binder solutions led the membrane to be fragile and have low mechanical resistance. Increasing of porosity and water permeability confirms the results. Approaching of alumina particles to each other by exerting more pressing pressure and using higher sintering temperature led the particle to stick each other more and more and raising of mechanical resistance logically.

Water permeability could be influenced by fouling resistance (FR). FR in ceramic membranes for oil or water treatment could be controlled by hydrophilicity or hydrophobicity of the membrane materials. Fouling of the alumina and/or mullite–alumina membranes was investigated in our previous works [3]. As mentioned there, permeation flux decreases when fouling layer (cake) forms. Regularly, after a specific time, permeation flux and FR remain constant with filtration time.

3.3. SEM results

The manufactured membranes at 300 bar pressure and 1,350˚C sintering temperature like S01 were crushed in water permeability test as mentioned in Table 2 because of low mechanical strength. On the other hand, by applying temperature at 1,500˚C or upper, a dense and low porous ceramic membrane with a low permeability would be resulted. As shown in Fig. 2(A), sample S01 has not been enough cohesion of particles and rupture of alumina powders cause low mechanical strength of the membrane.

SEM image results of surface and/or cross-section of other membranes are presented in Figs. 3 and 4. The achieved high or low permeability/porosity of them can be observed here visually. The effect of interfering of particle size and pressing pressure can easily observe in comparison with SEM images of S01–S08, S11, S15, S17, and S20–S26.

3.4. PSA results

S07 membrane (Fig. 2(B)) was used for fine particle rejection of pre-treated hydraulic oil performances. Table 4 shows results of PSA analysis for the origin and treated hydraulic oil. As the PSA results show, there is no pore in the membrane larger than 2 microns and is rarely bigger than 1 micron. The most pore sizes belong to less than 0.5 micron.

Pore size distribution of the S07 membrane is presented in Fig. 5 for better comparison. Mercury intrusion porosimetry technique reveals that S07 membrane has no open pore bigger than 1 micron, and the most active pores belong to 200 up to 600 nm. As observed, the results of PSA analysis are confirmed by the mercury porosimetry analysis.

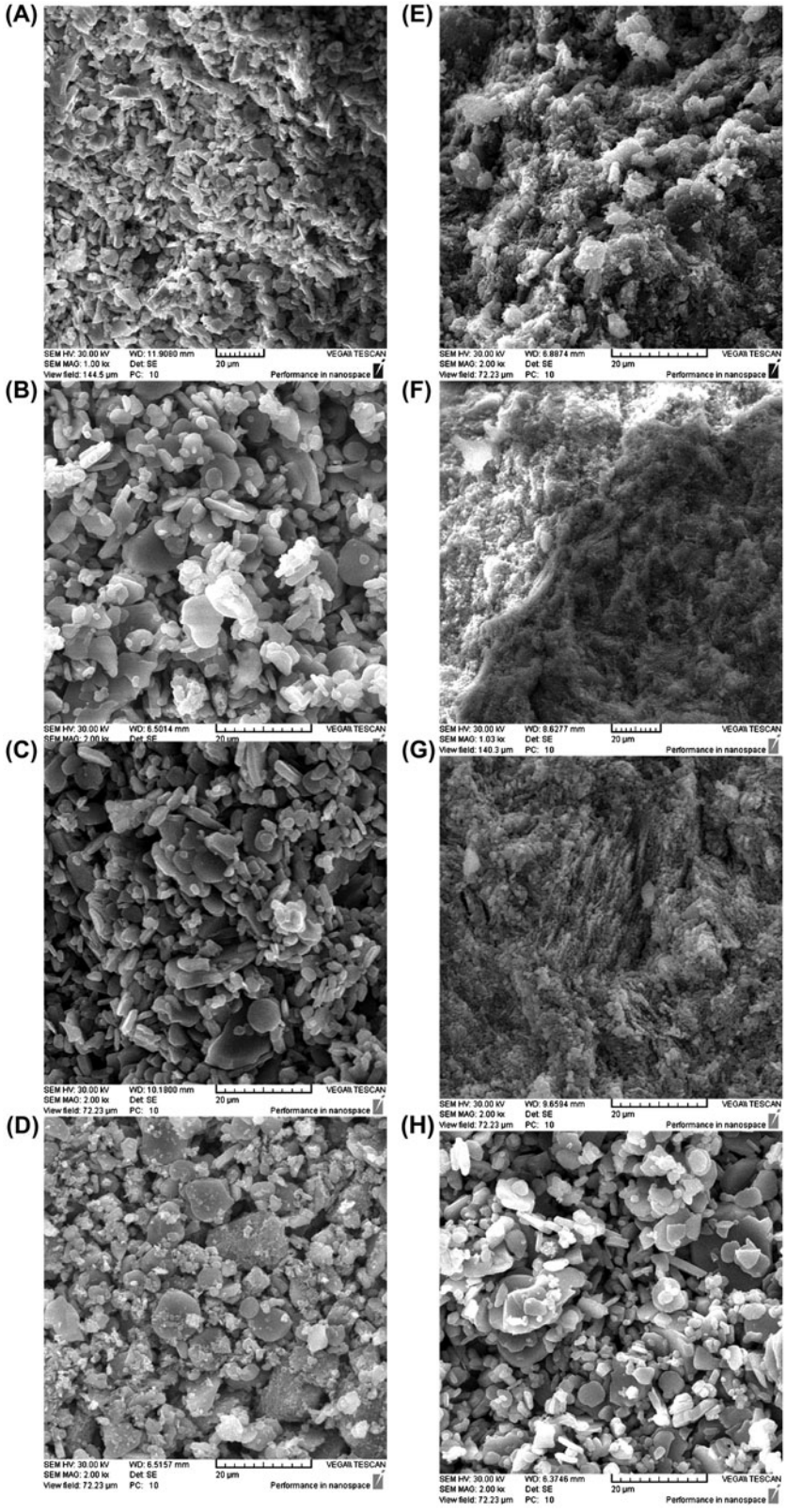

Fig. 3. SEM images of other membrane samples (A) S01 Cross, (B) S02 Cross, (C) S03 Cross, (D) S06 Surface, (E) S06 Cross, (F) S07 Cross, (G) S08 Cross, and (H) S11 Surface.

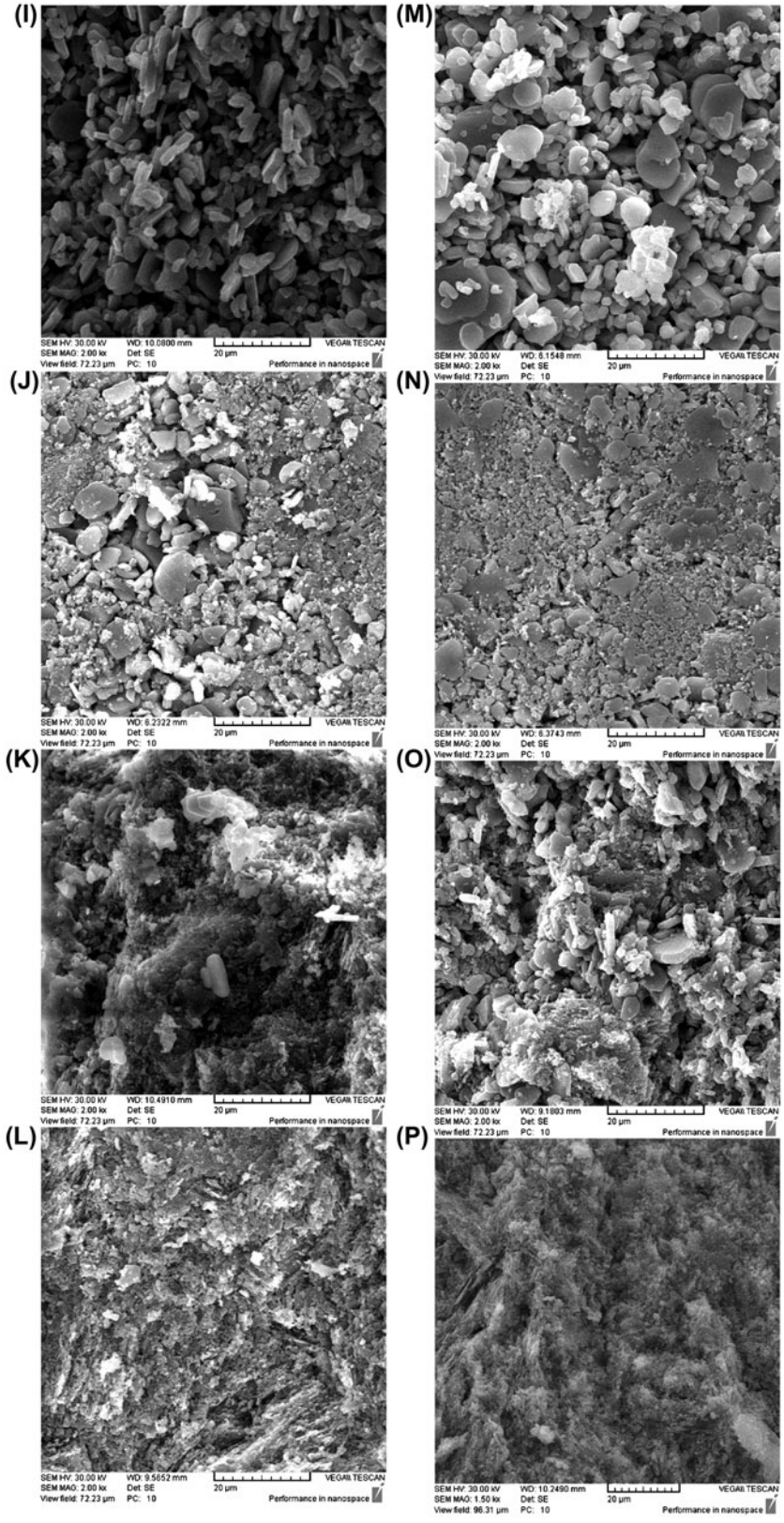

Fig. 4. SEM images of other membrane samples (I) S11 Cross, (J) S15 Surface, (K) S15 Cross, (L) S17 Cross, (M) S20 Surface, (N) S24 Surface, (O) S24 Cross, and (P) S26 Cross.

Table 4
PSA analyzer results for hydraulic oil

Particle size range (nm)	Original oil (particle number in 10 ml)	Treated oil (particle number in 10 ml)
Under 100	102,000	65,000
101–250	18,000	7,450
251–500	3,200	150
501–1,000	570	11
1,001–2000	102	2
>2001	20	0

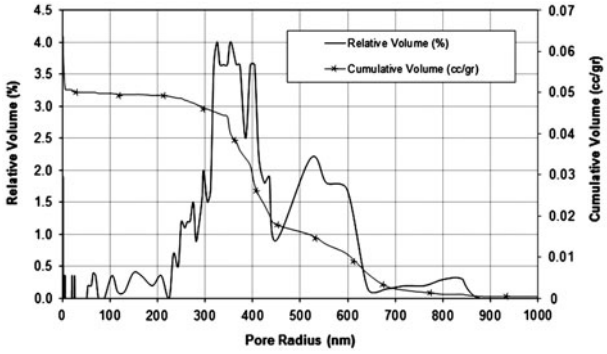

Fig. 5. Pore size distribution of sample S07 membrane.

4. Conclusions

α-alumina membrane manufacturing and optimization successfully performed. The effect of powder size, pressing pressure, binder type (CMC, xanthan, and PVA), binder solution, and sintering temperature were investigated. Porosity and water permeability measurements were performed, and SEM images and PSA analyzing of a treated oil were used for characterization of membranes. The results showed that the most important parameters on membrane porosity are sintering temperature and alumina powder size, respectively. To achieve higher porosity, the minimum sintering temperature and maximum alumina powder size should be employed. Powder size and sintering temperature were also the most important parameter on membrane water permeability. Using different binders has no substantial effects on the membrane quality. Amount of binder solution, sintering temperature, and pressing pressure has significant influences on mechanical resistance of membranes, respectively. There must be a balance between these parameters.

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