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Effect of ammonium nitrate on microstructure and permeability characteristics of tubular alumina support using slip casting fabrication method

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Tubular porous alumina supports were manufactured by slip casting process for microstructure and permeability study. In this regard, effect of ammonium nitrate addition in presence of Tiron dispersant on slurry stability and microstructure of samples was specifically studied. Furthermore, rejection of ions dissolved in water as well as permeation flux of water was evaluated considering ionic conductivity, total dissolved solids (TDS) and flow rate analyses. Results showed that the addition of ammonium nitrate and Tiron led to more stable initial slurries before slip casting and more porous tubular supports. In this case, the water flux and permeability through the supports were increased considerably. However, as expected, the ions rejection was not affected comparatively for the supports with and without ammonium nitrate.

Key words: Alumina, Slip casting, Tubular, Porous, Permeability, Slurry, Dispersant.

Introduction

Because of the advantages of ceramic membranes, synthesis and application of these materials has been the subject of numerous studies in the last two decades. In recent years, ceramic membrane supports made of metal oxides such as alumina, mullite, cordierite, zirconia, silica, titania and non-oxides such as silicon carbide, silicon nitride, etc. have gained ground replacing the conventional membranes [1, 2]. Proper support should have good mechanical strength, narrow pore distribution, high permeability and high surface area. Alumina supports have high advantages such as: good mechanical strength and chemical resistance, tolerance to high temperature and low sedimentation rates. The manufacturing methods of membrane supports include pressing, extrusions, gel casting and slip casting. Various factors should be considered in order to optimize the performance of support. Most researchers have focused their studies on the optimization of layers while not enough researches have been done about making membrane supports [3-5]. In addition, ceramic supports reported in open literatures are often flat formed with pressing or cylindrical made by extrusion method. There are a few reports about porous supports made by slip casting method [6, 7]. In this study, slip casting process with lower operation cost and easier forming technique, was selected for manufacturing of supports. The effect of ammonium nitrate addition in presence of Tiron dispersant on slurry stability, permeability and microstructure of supports was investigated.

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Experimental

The alumina powder (WDR4, Indal chemical, $d_{50} = 1$ μm, BET surface area 1.5 m^2/g and 99.4% pure) and SiO_2 powder (SYLOID AL-1 FP pharmaceutical Excipient, $d_{50} = 6.8\text{-}8.1$ μm, 99.4% pure) were used as starting materials. PVA (MW = 72000, Merck) and Tiron dispersant ($C_6H_4O_8S_2Na_2 \cdot H_2O$, Flukachemie), were employed as binder and dispersant, respectively. Ammonium nitrate powder (Merck) was used as additive in the study.

Slurries with 50 wt.% of solid content, containing 95 wt.% alumina and 5 wt.% silica, were prepared in a planetary mill with rotational speed of 180 rpm for 15 min. A predetermined Tiron dispersant was gradually added where its amount depended on the alumina value in the slurry [8]. Moreover, 0.5 to 2 wt.% of solids content ammonium nitrate (AN) and 4 wt.% PVA (2 wt.% aqueous solution) were added to the slurry. The resulting slurry was finally poured into the homemade plaster mold as shown in Fig. 1. After 5 to 8 min, a solid cake with proper thickness was formed on the internal surface of the mold. The remaining slurry was outpoured and after 24 h, the plaster mold was opened and the raw support body was brought out having the external diameter 45 mm and thickness of 5 mm. The samples were placed for 24 h at room temperature and for 12 h in a cabinet drier at 100 °C. At last, they were sintered at 1400 °C for 3h in an electric furnace (Carbolite RHF15). Heating rates increasing from room

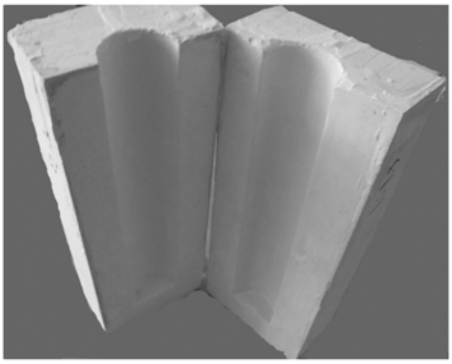

Fig. 1. The photograph of plaster mold.

Fig. 2. Module with sealed support.

temperature to 1000 °C and from 1000 °C to 1400 °C were set as 20 °C min^{-1} and 5 °C min^{-1}, respectively.

The permeability tests of supports were carried out using a lab scale reverse osmosis/ultrafiltration set up (Armfield FT18), and a custom made at the university of Sistan and Bluchestan, as shown in Fig. 2.

Slurries' pH was measured by pH-meter (Metrohm 780). Sedimentations tests were performed using 20 ml slips inside of 20 mm I.D. test tubes. Height of sediment (%) was measured after 24 h. Open porosity of the supports was measured using Archimedes method according to ASTM C373-88. Microstructure analyses of samples were performed using field emission scanning electron microscopy (FESEM, MIRA\\ TESCAN) technique. The pores size distribution of supports surface were determined using ImageJ2X software.

Results and discussion

Results showed that alumina slurries having no dispersant were quickly settled producing thick sediments, while the sediment height for the slurry containing Tiron (as dispersant) was only 5 mm after 24 h. The slurries containing AN also were relatively stable. Therefore, sedimentation experiments were performed on two slurries. The first slurry was contained Tiron and the other, Tiron and AN. The results showed that height of sediment for slurries containing Tiron (without AN) was 4.28% after 24 h, but for slurries with AN and Tiron no sediment was observed in this period. Therefore, AN addition led to more stability. Table 1 lists pH values of slurries. It can be seen that pH of slurries decreases with increasing AN.

Table 1. pH values of slurries.

Ammonium nitrate (AN) [wt.%]	0.0	1.0	1.5	2.0
pH	8.8	7.79	7.6	7.4

In fact the alumina suspensions containing Tiron and AN were more stable in lower pH values. These results are in contrast with the work of Gulicovski et al. reported that the alumina suspensions containing Tiron were stable in the basic region [8]. The dispersant adsorption onto the oxide ceramic powders is a function of slip pH [9]. On the other hand, the dissociation of the chemical functional groups of the adsorbed dispersant is also a function of pH. Hence, the sedimentation behavior is a result of competition of these two phenomena.

Fig. 3 shows dependence of open porosity on initial AN content. It can be seen that open porosity of the samples increases from 40.65% to 63.65% with increasing AN content. This is due to two reasons: first nitrate decomposition and gas release during sintering process of alumina, which leaves the porous volume instead, and second the better stability of slurry that causes less aggregation of the particles and therefore uniform dispersion of particles in the slurry. As shown in Fig. 3 sample without and with 2 wt.% of initial AN had two extremes of lower and higher porosity, as compared to each other. Therefore, these two types of supports were chosen for further experiments.

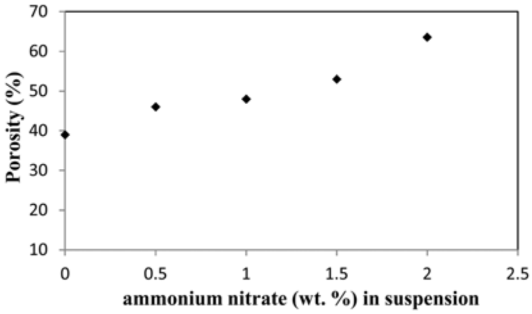

Fig. 3. Dependence of open porosity on initial ammonium nitrate content (wt.%).

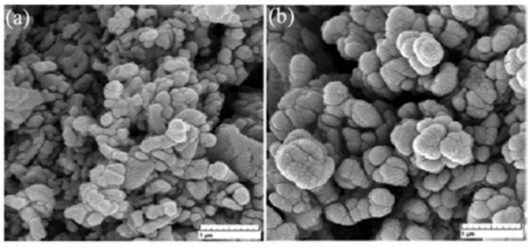

Fig. 4. SEM micrographs of supports' cross section (a) without and (b) with initial AN (2 wt.%).

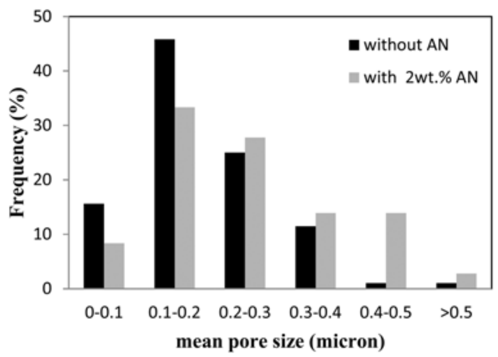

Fig. 5. Pore size distribution of supports surface (a) without and (b) with initial AN (2 wt.%).

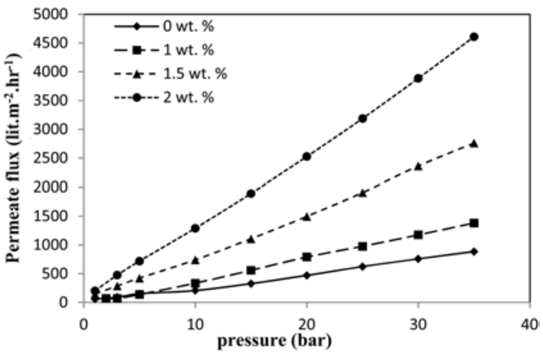

Fig. 6. Permeate flux versus pressure for supports fabricated with different AN contents.

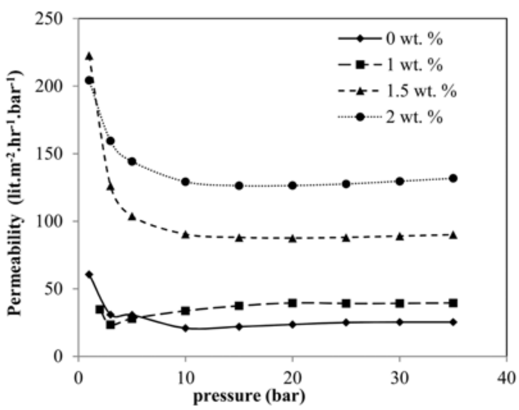

Fig. 7. Permeability of supports versus initial ammonium nitrate content (wt. %).

Figs. 4a and 4b show SEM micrographs of cross section of these samples, respectively. It can be seen that initial AN addition leads to formation of more porous microstructures with less interconnections (open' structures). Pore size distributions of the supports, surface are shown in Fig. 5. As shown, initial AN addition shifts quasi-normal pore size distribution of samples to broader pore size distributions with larger mean pore size, confirming formation of 'open' structure.

The permeate flux and permeability of the supports as a function of pressure were estimated using distilled water and as shown in Figs. 6 and 7, respectively. As it is seen in the Figs. 6 and 7, with increasing initial AN content, permeate flux and permeability of samples were strongly increased (more than five-fold at a pressure of 35bar). As shown in Fig. 3 addition of initial AN led to more open porosity, about 50%, in the supports, mainly due to slurry stabilization. But this porosity increase is not the cause of considerable permeate flux and permeability. It seems that formation of 'open' structure with more through pores and larger mean pore size results a dramatic increase of the permeate flux and permeability. Similar behavior was reported for pressed reaction bonded alumina supports [3]. It should be noted that the permeability is initially (1-10bar) decreased with increasing the pressure, and then at the pressures higher than 10bar, permeability of supports was reached to constant values. It seems that in this pressure range, increasing of pressure resulted filling of small pore and so no increase of the permeability was observed, accordingly. By increasing applied pressures (more than 10bar), almost all small pores were filled and then the water flux was increased proportionally. In fact, rapid filling of small pores, the real permeability can be estimated.

Table 2. TDS and ion conductivity measured before and after filtration.

	Without initial AN	With 2 wt% initial AN
Input TDS (ppm)	960	770
Output TDS (ppm)	770	698
Input ion conductivity (is/cm)	1064	1182
Output ion conductivity (is/cm)	955	1110

The total dissolved solids (TDS) and ion conductivity were measured before and after filtration process. The results are listed in Table 2. It can be seen TDS of samples without and with initial AN (2 wt.%), were reduced up to 19.8% and 9.35%, respectively. Also, for these samples, ion conductivities were reduced to 10.24% and 6.1%, respectively. Therefore, although porosity increase (due to AN addition) led to increase of the flux and permeability, but the rejection of the ions was not affected accordingly. This is due to forming of open structure with large mean pore radius, which is much larger than the sizes preventing ions permeation.

Conclusions

An ammonium nitrate addition in presence of Tiron as a dispersant to alumina slurries leads to formation of more stable suspensions. Slip casting of such slurries results more porous alumina supports with higher flux and permeability. But initial AN addition decreases ability of water treatment as microfilter supports due to formation through pores with higher radius. So samples with initial 2 wt.% AN addition can serve as an appropriate supports for fabrication of multilayer nanofilters.

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