

Controlling Pore Size and its Distribution of γ -Al₂O₃ Nanofiltration Membranes

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Abstract: The preparation process of γ -Al₂O₃ nanofiltration membranes were studied by N₂ absorption and desorption test and retention rate vs thickness gradient curve method. It was found that template and thermal treatment were key factors for controlling pore size and its distribution. Under the optimized experimental conditions, the BJH (Barret-Joyner-Halenda) desorption average pore diameter, BJH desorption cumulative volume of pores and BET (Brunauer-Emmett-Teller) surface area of obtained membranes were about 3.9 nm, 0.33 cm³/g and 245 m²/g respectively, the pore size distribution was very narrow. Pore size decreased with the increasing of thickness and no evident change after the dense top layer was formed. The optimum thickness can be controlled by retention rate vs thickness gradient curve method.

Keywords: Nanofiltration, γ -Al₂O₃ membrane, membrane pore size, N₂ absorption-desorption test.

Ceramic nanofiltration membrane is the latest outcome of membrane science. Presently, the preparation, especially the controlling pore size and its distribution of membrane is one of the knotty problems in membrane study^{1,2}. J. Lugten *et al.*¹ tried to control pore size by film process. J. Schaep *et al.*³ studied the effect of the calcining temperature on γ -Al₂O₃ membrane pore size. They found that the γ -Al₂O₃ membrane calcined at 600°C, its average pore diameter was more than 5 nm, the average pore diameter was 3.4 nm at 400°C. These methods all have good function for controlling pore size, but the film process is too complicated. The membranes calcined at 600°C have a little big pore size. Those calcined at 400°C have an ideal pore size, but there are some organic residue. In this work, pore size and its distribution were controlled effectively by template and temperature programming, the thickness was controlled effectively by retention rate vs thickness gradient curve method.

The membranes were produced by sol-gel technique. First, some aluminium iso-propoxide was added into HNO₃ solution of a certain concentration. After being stirred for 5 to 10 minutes, the solution was heated to 80°C to 95°C rapidly and kept for 4 to 6 hours at constant temperature and reflux conditions. Subsequently, a certain quantity PVA was added into the solution. The mixture was stirred until PVA was resolved totally. Then, the solution was cooled and aged to obtain a subtransparent

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AlOOH colloidal sol. The colloidal sol was coated on a side of substrates that were biscuit ceramic plates having a thickness of 3 mm, an average pore diameter of 1 to 10 μm . The substrates were polishing by metallographic polisher used 320[#] abrasive papers and cleaned, dried before they were coated on. The coating technique was dipping or pouring. The coated plates were natural dried at room temperature. Then, the plates were heated at a certain rate to a certain temperature and calcined 2 to 5 hours in muffle furnace. At last, the $\gamma\text{-Al}_2\text{O}_3$ nanofiltration membranes were obtained.

N_2 absorption and desorption test was used to characterize the obtained membranes by ASAP2010 rapid surface area & pore size tester (Micromeritics Co., USA). The $\gamma\text{-Al}_2\text{O}_3$ membranes average pore diameter and cumulative volume of pores were calculated by BJH desorption method, which are very accurate for measuring mesoporous size and volume. And the surface area was determined by multi-molecular adsorption theory BET formula⁴. The retention rate (R) and the water volume flux (Jv) of these membranes were measured by a static pressure flat sheet membrane device, in which the effective area was 10.17 cm^2 by treating 0.01 mol/L CaCl_2 solution (pH 4). N_2 was added into the device to pressurize. The penetrate solution was collected continuously, its volume was determined and the Ca^{2+} concentrations of treated solution and penetrated solution were measured. Then, the R and Jv of these membranes were obtained by formulae as the follows:

$$J_v = V/S \cdot t$$

$$R = (1 - C_p/C_b) \cdot 100\%$$

Where V is the volume of penetrated solution (L), S is effective membrane area, t is treating time (h), C_p is the Ca^{2+} concentration of penetrated solution (mol/L) and C_b is the Ca^{2+} concentration of treated solution (mol/L).

Some factors affecting membrane structure were studied, which were the preparation process of sol (including the concentration and pH of reactants, temperature and time of reaction, kinds and quantity of template agents and cooling and aging process), sol coating technique, drying of coated membranes and thermal treating process. It was found that the transparent sol that meet the requirement has been obtained under many conditions, and the sol coating technique and drying process of coated membrane can be changed in wide range. However, the key factors that effected on the pore size and its distribution are template and thermal treating process. The optimized experimental condition is as follows: the concentration of template agent PVA is 0.5%, the rate of warm-up temperature process is 1°C / min, and the coated membranes are kept for 3 hours at 600°C after the temperature was up to 600°C. Under this experimental condition, the result of N_2 absorption and desorption test for $\gamma\text{-Al}_2\text{O}_3$ membrane is showed as **Figure 1** and **Figure 2**. Obviously, it can be viewed that there is very apparent hysteresis loop in N_2 absorption and desorption isotherm plot, which suggest that the pore size of obtained membranes are in mesoporous range. From the curve of BJH desorption cumulative volume vs pore size plot, it can be seen apparently that the pore diameters concentrated in the range of 3 to 5 nm, the range is very narrow. The pores whose diameters were more than 6 nm are very few. The BJH desorption average pore diameter, BJH desorption cumulative volume of pores and BET surface area of obtained membranes were about 3.9 nm, 0.33 cm^3/g and 245 m^2/g respectively,

which showed that the obtained membranes are high quality γ -Al₂O₃ nanofiltration membranes.

Figure 1 N₂ adsorption and desorption isotherm plot

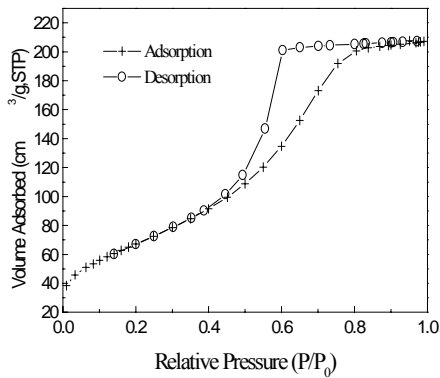


Figure 2 BJH desorption dV/dD pore volume

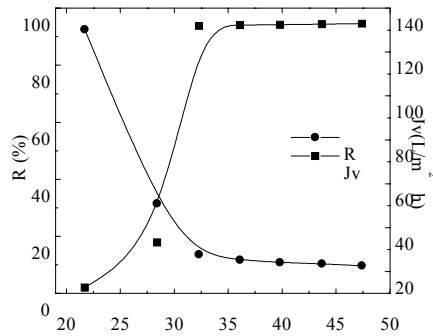
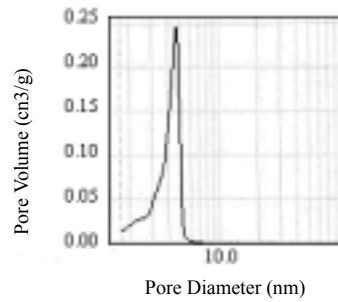


Figure 3 Retention (R) and volume flux (Jv) as functions of the thickness of membrane for 10⁻² mol/L Ca²⁺ solution (pH=4, $\Delta P=0.5$ MPa)

In this experiment, the R vs thickness gradient curve method was used to measure the pore size changing with membrane thickness. Compared with usual microscope observing methods of membrane cross section, this method characterizing the practical texture of membrane surface is entire, but microscope observing methods can only reflect the texture of cross section locally. **Figure 3** showed the R and Jv changing with

thickness of membranes. It is indicated that pore size decreases with the increasing of membrane thickness and is no evident change after the thickness is up to a certain value. Obviously, the pore structure transiting from intermediate layer to dense top layer is reflected visibly by this experimental phenomenon. Anyway, the control point of optimum thickness can be decided from this curve.

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