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Fabrication of superhydrophilic membrane filters using spherical glass particles obtained by ultrasonic spray pyrolysis

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Abstract

Fabrication of high performance membrane filters requires that both the substrate and the filtering layer have low resistance to liquid flow. The thickness, uniform porosity and hydrophilic nature are the main responsible parameters. Due to the antimicrobial property of the material it is widely used in solid/liquid separation. In this study, the substrate was of quartz type and the additives (frit glass and zeolite) made the filters with glassy pore walls as the sintering temperature applied was above their fusion temperature. The coating layer produced by antimicrobial and superhydrophilic (contact angel 8°) borosilicate glass particles has spherical shapes and their size intervals are narrow (0.65–2.4 μm). A thin layer coating without any cracks on the surface pores of the substrate has been obtained successfully. The coating was achieved by filtration and used for different amounts of feed material through dead-end pressure filtration modes. Sintering temperature and duration times determine the structural integrity of the coating as well as the pore evaluation.

Key words : Superhydrophilic; Glass membrane; Antimicrobial; Spherical particle; Contact angel

1. Introduction

Microporous ceramics have become increasingly popular in the manufacturing of filters for large-volume solid/liquid separation purposes, such as drinking, agricultural and waste water treatments which require low-cost mass production of microporous ceramic filters having the desirable properties. The ceramic filter medium must have high porosity, narrow pore size distribution and high bend strength as well as high performance for the chemical nature of the filtered water. Moreover, the filters have to be hydrophilic in order to serve the intended function during the operation process [1–10].

Custom-made ceramic membrane filters have two layers: a filter body (substrate) and its surface coating (filtering layer); the surface coating performs the separating function whereas the substrate beneath it serves as a support [11]. The substrates of high performance membrane filters should have large porosities with uniform pore sizes [12] so that less resistance to flow could be obtained with large porosities. The uniform pore size is important during the coating process in which a sufficiently thin coating could be obtained with the substrate having a narrow pore size distribution.

Highly hydrophilic filters which are advantageous for filtration and dewatering processes can be produced by using ceramic powders having special compositions [13,14], coating of glass particles onto a substrate [15] or coating of pore walls with a polymeric substance [16,17]. The hydrophilic nature provides two advantages: (i) results in low friction during liquid flow and (ii) is less dirty since the particles remain within the filtrate. Hydrophilic filters produced by coating of polymeric substances may have some disadvantages during industrial applications where high chemical resistance to acids or bases and high temperature are required.

Glassy pore wall membrane filters with high chemical and temperature resistances have been produced by using a mixture of quartz and a glassy phase consisting of glass frit and zeolite [13,14]. Sintering temperature was selected above the melting temperature of the glassy phase which homogeneously spread through the microstructure and covered the quartz matrix phase, thus leading to a glassy pore wall of a hydrophilic nature. The success of the hydrophilic nature for this type of

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filters depends on the spreading degree of the glassy phase through the microstructure [14,18,19]. But, it is difficult to fabricate high hydrophilic membrane filters with submicron pore size by the technique where the spreading degree is not enough.

Glassy membrane filters with submicron pore sizes have been prepared by coating of glass powders (ground) onto a substrate and sintering at the softening temperature of the glass particles [15]. Porous microstructure occurs when the particles contact on some points and form the neck. The prepared microstructure has a high hydrophilic nature. However, local vitrifications have occurred depending on the morphology of the glass particles which have flat edges and non spherical morphologies [15].

It is clear that the submicron pore sizes and glassy pore wall membrane filters with high hydrophilic nature without any local vitrifications could be fabricated by using spherical glass particles. This study focused on the fabrication of super-hydrophilic ceramic membrane filters with narrow pore size distribution by using spherical glass particles. The evaluation of the coating layer is also investigated.

2. Materials and methods

Superhydrophilic membrane filters were fabricated by coating of spherical glass particles onto a substrate by filtration and filtration characteristics of the prepared membranes were investigated.

2.1. Preparation of spherical glass particles

Spherical glass particles with a chemical composition of 59.69% SiO_2, 17.10% B_2O_3, 16.80% Na_2O, 3.9% Al_2O_3 and 2.5% Ag_2O in wt were prepared by ultrasonic spray pyrolysis technique at a reactor temperature of 1200 °C. Ultrasonic spray pyrolysis system used for the fabrication of spherical glass particles is given elsewhere in detail [18]. A quartz tube with a diameter of 5 cm and a height of 120 cm was used within the reactor and the prepared powders were obtained by filtration where 0.2 μm membrane filters (Schliecher and Schuell-NL 16) were used. The frequency of the ultrasonic nebulizer and the feed rate of the carrier gas were 1.63 MHz and 2 lt/min, respectively.

Tetraethylorthosilicate, TEOS (Fluka 98%), boric acid, H_3BO_3 (Merck extra pure) and sodium nitrate, $NaNO_3$ (Merck extra pure), aluminum nitrate nanohydrate, $Al(NO_3)_3{\cdot}9H_2O$ (Merck extra pure) and silver nitrate, $AgNO_3$ (Merck extra pure) were used as a precursor and solutions were prepared by adding 2.5 M. TEOS was added to the water and mixed with a magnetic mixer at 500 rpm during which 0.2 M HNO_3 was added as well in order to obtain a clear solution. After a clear solution was obtained, other precursors (boric acid and sodium nitrate) were added and mixing with a magnetic mixer was continued in order to obtain a clear solution. The clarity of the solutions was measured by a turbidimeter, and solutions were accepted to be clear when the turbidity value was below 0.1 NTU.

The phase analyses of the prepared powders were determined by X-ray (Rigaku-miniflex) at a speed of 2°/min and 0.01° steps, by using CuKα radiation, between 10° and 60°. Particle size distributions were measured by a Zetameter (Malvern-Nano ZS) and the morphologies of the powders were investigated by microscopic studies using a scanning electron microscope (Zeiss Supra 50 VP). The hydrophilic properties of the powders were determined using thin layer wicking technique which was described further in detail [15].

2.2. Preparation of the substrate

The substrate was prepared using 76% Quartz, 10% zeolite and 14% frit glass. For the preparation of the substrate with a narrow pore size distribution, particles with a narrow size distribution are required. So quartz particles with narrow size distribution were obtained by serial sedimentation processes. Quartz particles finer than 75 μm were poured into the water and mixed at a rate of 500 rpm for 10 min after which the sediment was taken prior to a 1 min sedimentation. Then water was added to the sediment and they were mixed at 500 rpm for another 10 min thus preventing sedimentation. By this method, fine particles (first sedimentation process) and coarse particles (second sedimentation process) were removed leaving behind quartz particles with narrow particle size distributions.

Zeolite and frit glass were separately agitated via attrition milling for 1 h where alumina ball mills were used. The amount of water and powder was equal during the milling process. Milled powders were dried at a temperature of 105 °C for 24 h. Zeolite and frit glass were mixed according to the composition and were homogenized using ball mill at a low rate of 80 rpm for 30 min. Afterwards, quartz particles were added and homogenized again using a ball mill at a slow rate of 20 rpm for 10 min. Second homogenization should be carried out at low speed to prevent the breaking of the quartz particles. The mixture was moisturized (6–10 wt% water) and sieved to obtain granules of sizes under 1 mm. The obtained granules were shaped by pressing at a pressure of 100 bars using a metal mold with a diameter of 3 cm. The obtained green samples (diameter = 3 cm and height = 0.4 cm) were sintered at a temperature of 1100 °C for 1 h where the heating and cooling rate of the furnace was 5 °C/min.

2.3. Coating of substrate

The obtained spherical glass particles were coated on a substrate by filtration at an applied pressure of 0.5 bar and the solid concentration of the solution used for the coating was 0.1% in wt. The thickness of the coating layer was controlled by controlling the amount of glass powder (7, 14, 28, 56, 112 and 224 g) for the unit area of the substrate. The coated samples were dried at room temperature and at 105 °C for 24 h, respectively. The dried samples were sintered at different temperatures (590, 610 and 630 °C) for different soaking times (10, 30 and 60 min) where heating and cooling rates of the furnace were 5 °C/min.

The pore size distributions of the substrate and coating layers were determined using Hg-porosimetry (Quantachrome-Poremaster) and, porosities were determined by Archimedes principles. Also, the microstructures of the prepared membranes were investigated by scanning electron microscopy (SEM) (Zeiss Supra 50 VP).

3. Results and discussion

3.1. Preparation of uniformly porous glassy substrate

The substrate was of quartz type and the additives used were frit glass and zeolite. Since the sintering temperature applied was above the fusion temperature of the additives, pore walls of the filters became glassy. The substrate material was designed to be obtained by using large particle size quartz (with no crystals of small size) and finer sized additives. Hence, larger quartz particles with easily fusible additives will produce a uniformly porous substrate. The size distribution of the powder samples is given in Fig. 1. Besides these large sizes, quartz particles have a relatively narrow size distribution (8–100 μm).

Fig. 2 shows the SEM micrograph of the fracture surface of substrate. It is obvious that the porosities were uniform and interconnected to each other. The amount of the apparent porosity was measured by Archimedes' technique and was

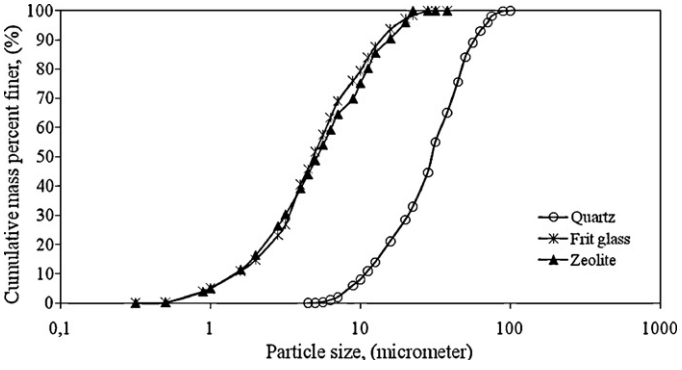

Fig. 1. Size distribution of substrate powders.

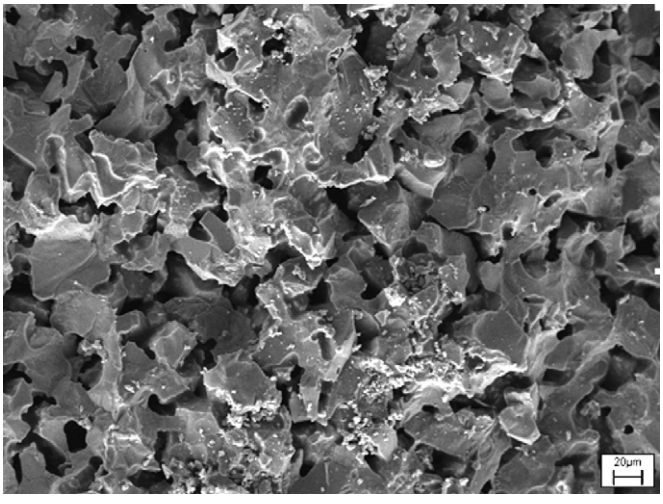

Fig. 2. The SEM photograph of the typical edge of substrate material.

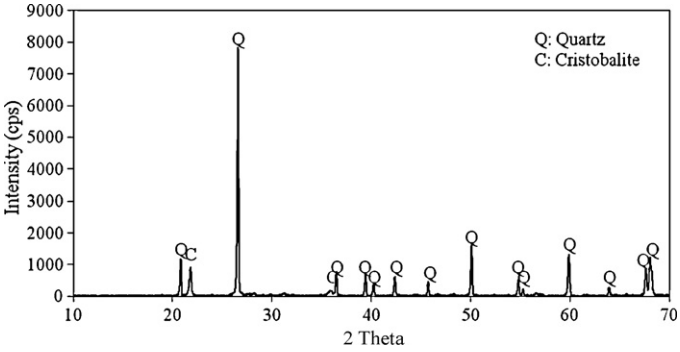

Fig. 3. Phase composition of the substrate.

determined to be 38%. The pore size was determined using Hg-porosimetry. Results indicate narrow pore size intervals (4–12 μm). It is believed that the substrate has good enough porosity for filtration applications and the narrow pore size distribution makes the material advantageous for thin layer coating as a filtering layer.

Fig. 3 shows XRD patterns of the substrate where the material indicates quartz phase and a small amount of cristobalite crystallization is observed. Previously, the same composition has been studied for membrane fabrication [13,14] and the appearance of cristobalite crystallization has been attributed to the glassy dispersion through the filter matrix and later crystallization. The glassy phase has proven the filter matrix as a glassy pore wall microstructure. Sintering temperature has great influence on the crystallization in which higher temperatures or longer soaking times lead to α-cristobalite crystallization. Low temperature sintering may be advantageous for the production of high hydrophilic substrates but at this time the sintering is poor. In such cases the uniformity of the substrate porosities has a greater importance than the hydrophilic nature. Thus the substrate has been sintered at 1100 °C and a uniformly porous material was obtained.

3.2. Spherical glass powder for filtering layer

Spherical glass powder was obtained by ultrasonic spray pyrolysis in which the particles had high sphericity and narrow size distribution (see Fig. 4). The sizes of particles varied between 0.65 and 2.4 μm.

Sizes of the glass powders are relatively finer when compared to the pore sizes of the substrate. The maximum pore size of the substrate was 12 μm, thus the glass powder initially filled the substrate pores. The coating produced by filtration and the pressure applied was significantly low (0.5 bar). Thus, less amount of particle migration through the substrate pores is expected and the deposition of particles at the substrate surface is believed to be necessary for the integrity of the coating.

Contrary to the substrate material, the hydrophilic nature of the coating has great importance on the engineering property of the produced membrane filter. Filters with high hydrophilic coating are capillary type membranes which provide high

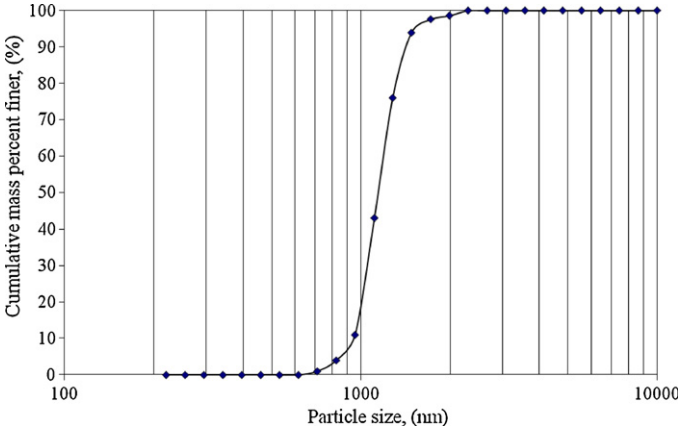

Fig. 4. Size distribution of the glass powders.

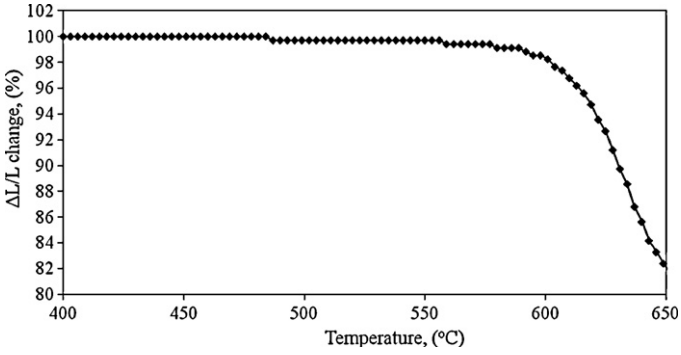

Fig. 5. The effect of heating on the glass particles by hot-stage microscopy.

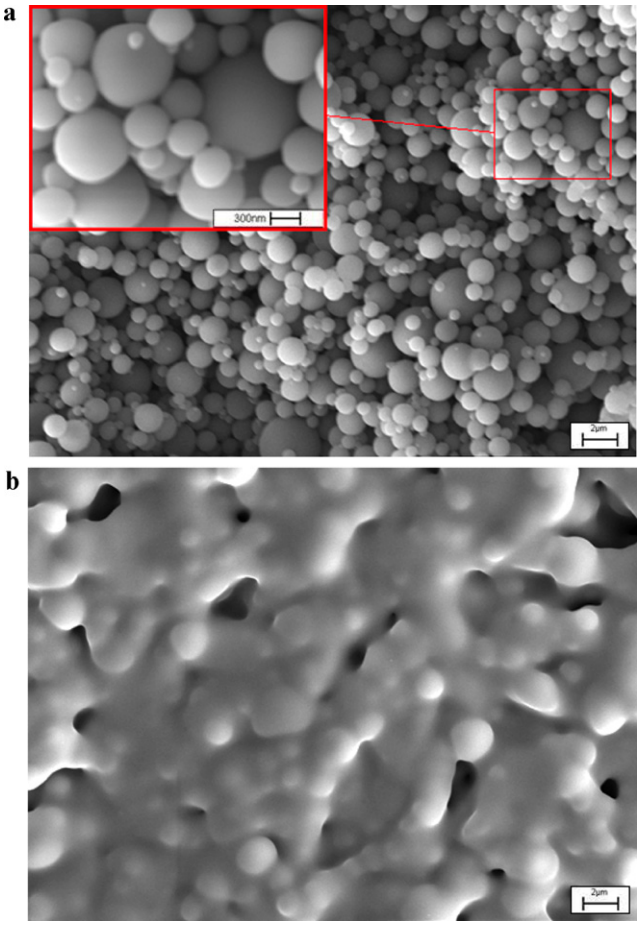

Fig. 6. The SEM photograph of the glass powder after heat treatment: 610 °C for 30 min (a) and 610 °C for 60 min (b).

filtration capacities during water filtration. The hydrophilic property of the glass powder was investigated by thin layer wicking method. The measured water contact angle was 8°, meaning that the particles are of super hydrophilic nature. Thus the powders are potential materials that can be used in the production of a capillary type membrane filter. The antimicrobial properties of the powder against the microorganisms of gram-positive bacteria (*Bacillus cereus*, *Stapylococcus aureus*), gram-negative bacteria (*Escherichia coli*) and yeast (*Candida albicans*) were determined by two different test methods, agar-disc diffusion and modified agar well, and it was determined that the powder has strong antimicrobial effects against all the above microorganisms where these effects were discussed in further detail [20].

Sintering behavior of the glass powder has been investigated by hot stage microscopy and the results are given in Fig. 5. The results indicate that the temperature at about 600 °C is critical temperature for sintering. This temperature will produce neck forming between the compacted particles. But the microstructure should be investigated with respect to the high performance membrane surface where pore evaluation has great importance. Thus this study is focused on the applied temperature and soaking time. The results of heat study are given in Table 1 and Fig. 6. Results have indicated that the sintering of glass particles at 590 °C for long time soaking (60 min) do not cause neck formation. Sintering at 610 °C is shown to be good enough for the connection of particles through the neck points (see Fig. 6a). Long time soaking (Fig. 6b) and high temperature with less soaking times did not produce the sufficient particle connection. The particle connection was either poor or excessive.

Table 1
The heat treatment shell on the glass powder observed by hot stage microscopy.

Sintering temperature (°C)	Soaking time (min)	Observation by microscopy (SEM)
590	60	No neck formation
610	30	Sufficiently neck formation (see Fig. 6a)
610	60	Excess neck formation (see Fig. 6a)
630	10	Excess neck formation
630	30	Nonporous structure

3.3. Preparation of filtering layer

The production of a thinner coating is advantageous, in which low filtration resistance could be obtained during filtration and the filter could easily be cleaned by backflushing. On the other hand, the coating should be sufficiently thick for production of clear filtrate. The required thickness strongly depends on the clogging and non clogging phenomena occurred during the filtration proceeds. Besides the necessity, the

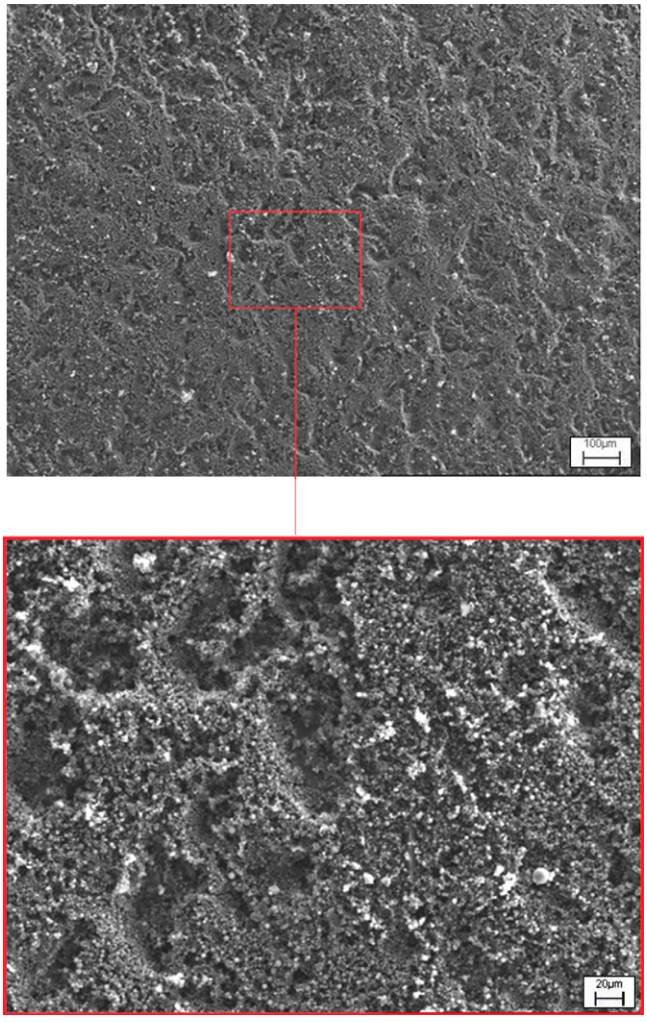

Fig. 7. The SEM photograph of the surface of substrate after coating using 28 g/m^2 powder.

thickness of coating should provide smooth surface without defect. Where the large pores at the surface of substrate initially filled by the coating materials and later produced the sufficiently coating.

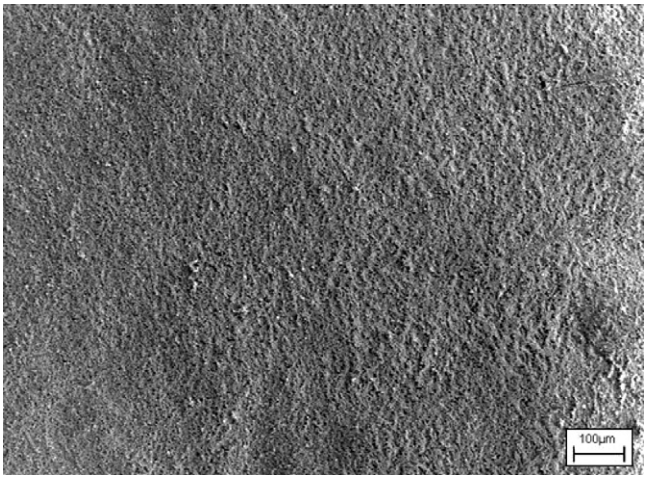

Fig. 8. The SEM photograph of the surface of substrate after coating using 112 g/m^2 powder.

Fig. 9. The SEM photograph of the surface of substrate after coating using 224 g/m^2 powder.

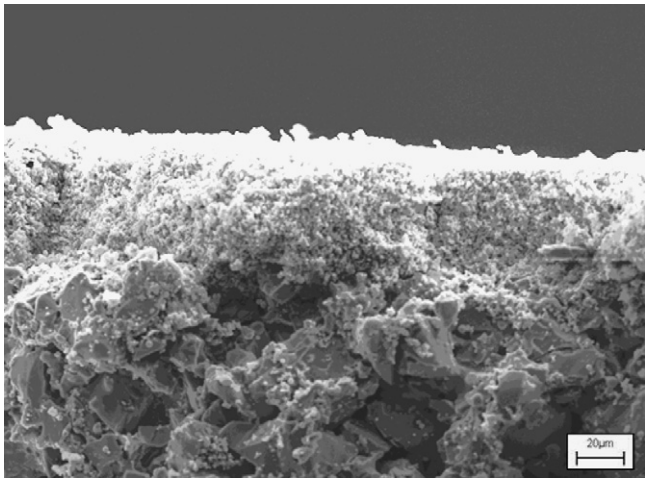

Fig. 10. The SEM photograph of the typical edge of the membrane filter through produced using 112 g/m^2 powder for coating.

In our system, the substrate has large pores up to 12 μm and thus requires more powder. The amount of coating material was examined. The powder used for the coating operation was 28 g/m^2, some large pores were not completely covered by the particles (see Fig. 7). The coating material increased 112 g/m^2, the substrate surface pores are completely filled by the coating material and a smooth surface is obtained (see Fig. 8). When the coating material is increased to 224 g/m^2; surface cracking is observed (see Fig. 9), meaning that the integrity of coating also depends on the thickness.

Fig. 10 shows the fracture surface of the membrane filter produced using 112 g/m^2 of powder sample which has a smooth surface without cracking. The thickness of coating layer is determined from the picture to be about 35 μm. It is obviously seen that some particles migrate through the substrate pores and are deposited: the spherical shape provides easy observation of the particles. The pore sizes of the filtering layer and substrate were determined using Hg-porosimetry and results are given in

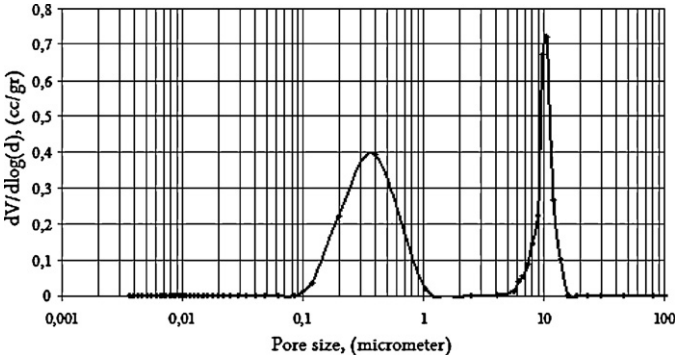

Fig. 11. Pore size distribution of the filtering layer and substrate for the membrane produced using 112 g/m^2 powder for coating.

Fig. 11. The coating layer showed pores finer than ∼1 μm and the substrate has relatively larger pores.

4. Conclusion

High performance ceramic membrane has been fabricated where the following properties are determined: (i) the substrate has glassy pore wall microstructure with uniform porosities, (ii) filtering layer made of spherical particles with similar sizes thus the produced coating is uniformly porous, (iii) the coating material is glass and the water contact angle is 8° and thus the obtained coating is of super hydrophilic nature, (iv) the selectivity of membrane filter is high where the maximum pore size of filtering layer is 1 μm. Results indicate that the prepared membrane has great potential to be used in industrial applications.

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