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Fabrication of highly hydrophilic tubular type perlite membrane support

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We fabricated and characterized a highly hydrophilic membrane support using only perlite as an ore without altering its chemical and physical properties. Tubular-type microfiltration supports were fabricated by an extrusion technique. Plastic perlite paste was obtained by adding organic additives and water. The extruded samples were carefully dried to prevent cracks during the drying period of 6 days with a controlled drying temperature and humidity. Green bodies were sintered at temperatures of 1000 °C, 1025 °C, and 1050 °C for 1, 3, and 6 hours. Tubular membrane supports were characterized in terms of microstructure, porosity, pore size distribution and crystalline phases. Additionally, the hydrophilicity of the samples was determined by a thin layer wicking (TLW) approach. The water contact angles of the samples sintered at 1025 °C for 3 hours were determined to be 20 °, and the porosity and mean pore size of the sample were 23.54% and 13 μm, respectively. The clean water permeability of the sample was 10.677 L/h.m^{2}bar. According to the results, the obtained sample functions well as a highly hydrophilic membrane support, and it is also a good candidate for a filter used in macro- and microfiltration processes. Filtration tests indicated that the median particle size of the solids in waste water is 500 nm, with a turbidity of 100 NTU, and the waste water can be cleaned by the newly fabricated perlite tubular ceramics up to a turbidity level of 0.35 NTU, which is acceptable in various industries.

Key words: Perlite, Membrane, Cross-flow, Support.

Introduction

Membrane-based technologies for waste water treatment have emerged in recent years as important separation and purification methods in various process industries to prevent the pollution of water resources caused by different sources. Inorganic membranes (oxide-based) such as Al_2O_3, ZrO_2, and TiO_2 have attracted more attention due to their high mechanical, chemical, and thermal resistance properties that can potentially be applied in water treatment. However, these oxide-based membranes are expensive, and researchers are seeking cheaper materials to make the membranes cost effective. Membrane supports fabricated from natural raw materials and some organic additives are cheaper, and they have been used successfully in many studies [1-12]. Majouli *et al*. [13, 14] prepared flat and tubular ceramic membrane supports from local Moroccan perlite for microfiltration. These membrane supports were composed of an average pore diameter of 6.64 μm and a porosity percentage of 42% at a sintering temperature of 1000 °C. The membrane supports also have better chemical resistance in acidic medium than in basic medium.

The main aim of this work was to develop new and cheaper highly hydrophilic membrane supports based on local natural perlite which is abundant in western Saudi Arabia. Perlite is an amorphous volcanic glass that is normally gray in color, and it is mainly composed of > 70% silica ground mass and 12% Al_2O_3.

Materials and Methods

The perlite used in this study was obtained from the western region of Saudi Arabia, where large deposits are exposed and mined (Saudi Perlite Factory). Crystalline phases of the raw material were determined by X-ray diffraction (XRD) (MiniFlex, Rigaku, Japan) analysis. XRD analyses were performed at a speed of 2 °/min with 0.01 ° steps using CuK irradiation between 4 ° and 70 °. The chemical analysis of the represented raw materials was carried out at the ALS Lab in Canada.

Perlite powder with a diameter < 180 μm and organic materials were used in the batch calculations to prepare single channel tubular ceramic supports. The batch was mixed in a Winkworth MA 10 Z-blade mixer for 3 hours. Then, water containing CMC as a binder was added into the powder in the mixer and processed for 2 hours to obtain homogenous plastic mud. The plasticity of the mud was determined using a Pfefferkorn Clay Plasticity Tester.

Tubular membrane tubes were obtained by an extrusion method using the prepared mud. First, green bodies were dried at room temperature for 3 days. Then, they were placed in a dryer where the temperature was

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increased to 105 °C with steps of 15 °C beginning at 30 °C.

Dried green bodies were sintered at temperatures of 1000 °C, 1025 °C, and 1050 °C for 1, 3 and 6 hours. The sintering processes was conducted in two steps: 1) the organics were slowly burned out from the membrane support by heating at 0 °C to 400 °C at a rate of 1 °C/min, and 2) the density of the ceramic network was increased by sintering at temperatures ranging from 400 °C to the final temperature at a rate of 2 °C/min. The selected sintering temperatures were slightly higher than the softening point of the perlite, which was determined by DTA/TG (Perkin Elmer-Diamond).

The microstructure of the obtained samples was recorded by scanning electron microscopy (Mini-SEM; Micro Optic), and the pore size distributions of the membranes were determined by Hg-porosimetry (Quantachrome, Poremaster 60000). The mechanical properties of the samples were characterized by the three-point bending principle (Shimadzu) with a crosshead speed of 0.5 mm/min. The porosities of the samples were determined by Archimedes' principle.

The hydrophilicity of the membrane was determined by the thin layer wicking method. The thin layer wicking method is an approach based on the migration of a liquid on a specific material. Thus, it is very important to determine the true migration rate. In general, a hydrophilic support carries the liquid from the bottom to the top at a rapid rate, and it is not possible to determine the rate of liquid migration on the filtration layer. To overcome this phenomenon, a tube sample with a length of 6 cm was divided vertically into four pieces, and the all samples were characterized.

The prepared samples were cleaned in an ultrasonic bath for 2 minutes and dried in an oven at 105 °C for 24 hours to remove any residual pore water before the samples were stored in desiccators. Wicking experiments were performed by immersing the samples in the vertical position to a depth of approximately 5 mm in a test liquid using a container. Before actual immersion, the plate was stored inside the closed desiccator for approximately 1 hour to allow the material to reach equilibrium with the vapor of the wicking liquid. This procedure was carried out to equalize the spreading pressure which can disturb the measurements. The plate was then immersed in the liquid, and the vertical movement of the liquid through the slide was observed. After the liquid traveled to the required distance (e.g., between 1 and 3 cm, but short enough to avoid gravity effect), the experiment was stopped by removing the filter plate from the glass container. The effective pore radius of the membranes was investigated using the following apolar liquids: heptane (J.T. Baker, 99%), octane (J.T. Baker, 99%), decane (Sigma, 99%) and dodecane (Sigma, 99%). Later, the contact angle of the membrane surface with water was investigated by the wicking experiments using distilled water. The tests were conducted at least four times using the same samples. All experiments were performed in the same conditions.

The filtration performance of the prepared perlite tubes was determined by the principle of tangential filtration. The length of the tubes used was 10 cm, and the filtration area was approximately 20 cm^2. Pure water was used for the permeability test. Recovery performances of the tubes were determined using dirty water (turbidity 100 NTU) in which the mean particle size of the powder in the water was 500 nm. The turbidity of the feed water and filtrate was characterized by a turbidity meter (HACH 2100P).

Results and Discussion

The use of raw materials for the fabrication of functional engineering ceramics is cost effective. It is clear that the materials fabricated from raw materials are cheaper than the materials fabricated from advanced materials. However, it is more important to characterize the raw material that will be used based on its chemical composition, crystalline phases and thermal behavior.

The perlite used in this study is composed mainly of 72.5 wt % SiO_2 and 12.96 wt % Al_2O_3. Perlite also contains 0.88 wt% Fe_2O_3, 0.7 wt% CaO, 0.35 wt% MgO, 2.9 wt % Na_2O, 4.64 wt% K_2O, 0.1 wt % TiO_2, 0.22 wt % P_2O_5, and 3.94 wt % loss of ignition as secondary components.

The crystalline phases of the perlite tubular supports were characterized by XRD, and its pattern is shown in Fig. 1. Perlite is an amorphous material with a low amount of crystalline phases such as quartz, cristabolite and feldspar. It is advantageous that the amounts of alkaline- and alkaline earth-based metal oxides are relatively low. Perlite also includes some crystalline phases. Thus, it has a wide working temperature range without vitrification.

Porous materials can be obtained using glassy material via the principle of viscous flow. In general,

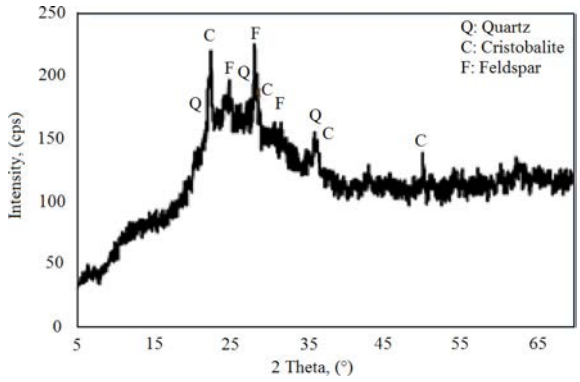

Fig. 1. XRD pattern of the Saudi perlite.

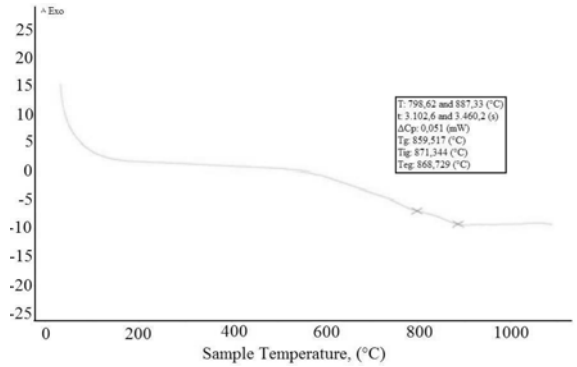

Fig. 2. Differential thermal analysis of perlite.

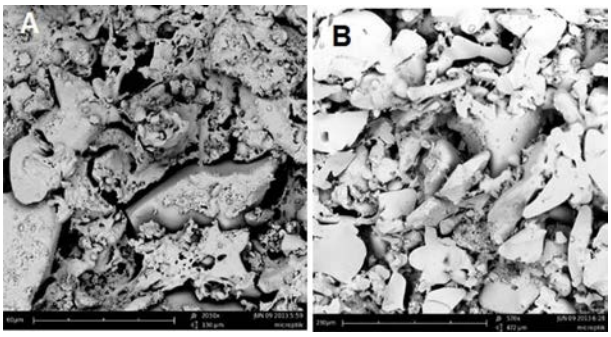

Fig. 3. Microstructure of the membrane sintered at 1000 ºC for 1 hour (A) and 6 hours (B).

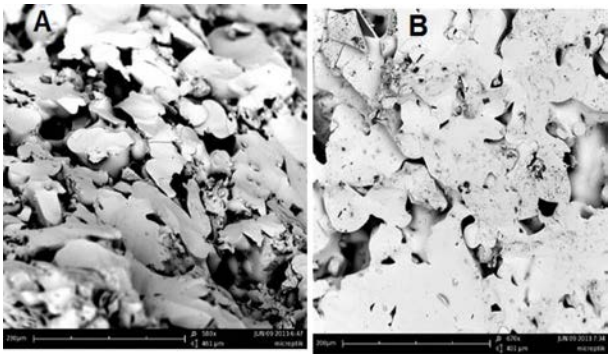

Fig. 4. Microstructure of the membrane sintered at 1025 ºC for 3 hour (A) and 6 hours (B).

control of the microstructure, especially the pore structure, is difficult in viscous flow processes depending on the narrow sintering temperatures where the viscosity of the amorphous phase rapidly decreases with increasing temperature. Consequently, the sintering of glassy structures to form porous structures needs to be carefully controlled by the driving forces of sintering temperature and soaking duration. The potential sintering temperature should be slightly higher than the glass transition temperature of the material. The glass transition temperature of perlite was determined to be 859 ºC using DTA analysis (Fig. 2). The DTA curve also has an endothermic reaction at a temperature of approximately 100 ºC, which is related to the loss of absorbed water in perlite.

It is known that there is a narrow range of the sintering temperatures for glassy-type materials. The microstructure

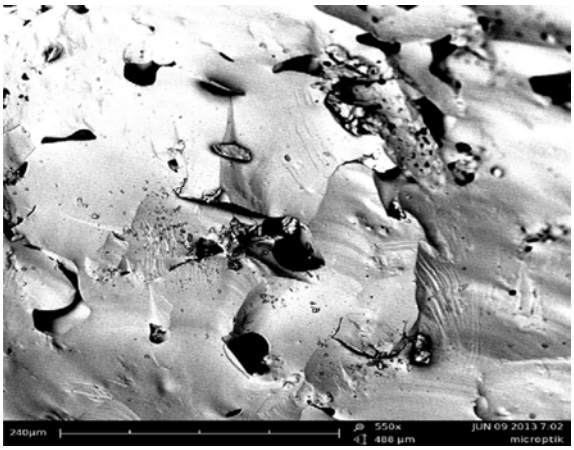

Fig. 5. Microstructure of the membrane sintered at 1050 ºC for 3 hours.

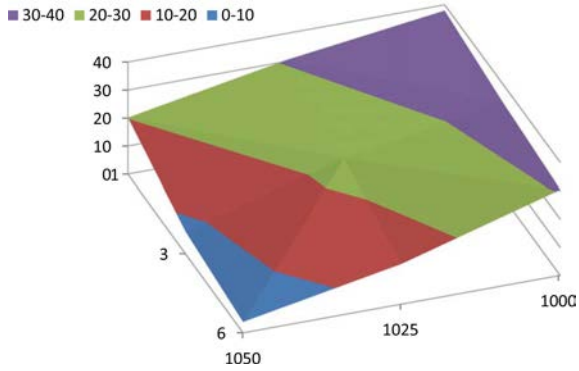

Fig. 6. Apparent porosity of the membrane supports.

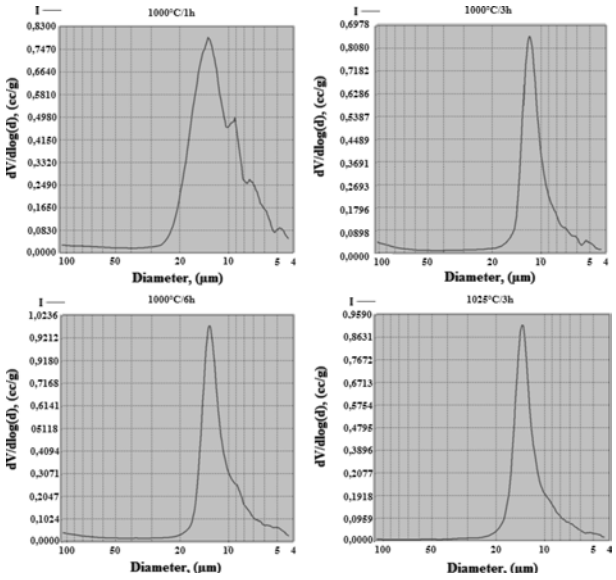

Fig. 7. Pore size distributions of the selected membrane supports.

of the sample changes rapidly when the sintering conditions are changed. Accordingly, the initial sintering temperature of the samples was selected as 1000 ºC, which is slightly higher than the glassy transition temperature of the perlite. To observe the microstructure change according to the sintering temperature, additional

sintering processes were carried out by increasing the sintering temperature in steps of 25 °C up to 1050 °C. Sintering times of 1, 3, and 6 hours were also used.

The microstructure of the samples after sintering is shown in Fig. 3-5. During sintering, the temperature is low (1000 °C) and the samples are highly porous (Fig. 6), but the perlite particles still have sharp edges after soaking periods of 1 hour (Fig. 3A) and 6 hours (Fig. 3B). Additionally, there is no detectable neck formation between the particles. The samples are not strong enough to be used as substrates for cross flow filtration experiments where filtration pressure is applied from the inside to the outside. The mechanical strength of the membrane support sintered at 1000 °C for 1 hour was determined to be 14.94 MPa. Increasing the sintering temperature to 1025 °C (soaking time of 3 hours) leads to the formation of necks between the perlite particles and the sharp edges become round (Fig. 4A). The mechanical strength of the membrane support is approximately 28.9 MPa, which is adequate for the majority of the cross flow filtration applications where the applied pressure is within 6 bar. Additionally, the porosity of the sample is calculated to be 23.54%. Increasing the soaking time to 6 hours leads to an increase in the size of the necks formed between two perlite particles (Fig. 4B). The total porosity decreased to 14.39%.

For the highest sintering temperatures, the porosity of the samples rapidly decreases, and the pores of the samples become closed, which is not acceptable in the case of porous materials for filtration applications. The porosity of the sample sintered at 1050 °C for 6 hours is approximately 8%, and 70% of the total porosity is closed. The typical shape of the closed pores in a glassy structure is spherical, and this type of structure is shown in Fig. 5. The sintering temperature is more effective than the sintering time for the purpose of structural evaluation.

Table 1. Water contact angels of samples calculated by TLW principle.

Sintering temperature	Sintering time		
	1 hour	2 hours	3 hours
1000 °C	69	56	54
1025 °C	39	20	21
1050 °C	33	–	–

The pore size distributions of the samples were determined using Hg-porosimetry. The membrane support was sintered at 1000 °C for 1 hour, and it contained pores with a wide range of sizes. The maximum and minimum pore sizes are approximately 25 and 4 μm, respectively (Fig. 7). Small pores disappear and the maximum pore size decreases to < 20 μm when the soaking time is increased to 3 hours. The pore size distribution curve of the sample follows a mono-model, and it is relatively narrow. The curve shifts to a higher pore size when the sintering time is increased to 6 hours. This pore evaluation is a good example of sintering where the small pores first disappear and then the pore size increases depending on the pore growth mechanism during sintering.

The water contact angles of the samples are shown in Table 1. The contact angles change with sintering

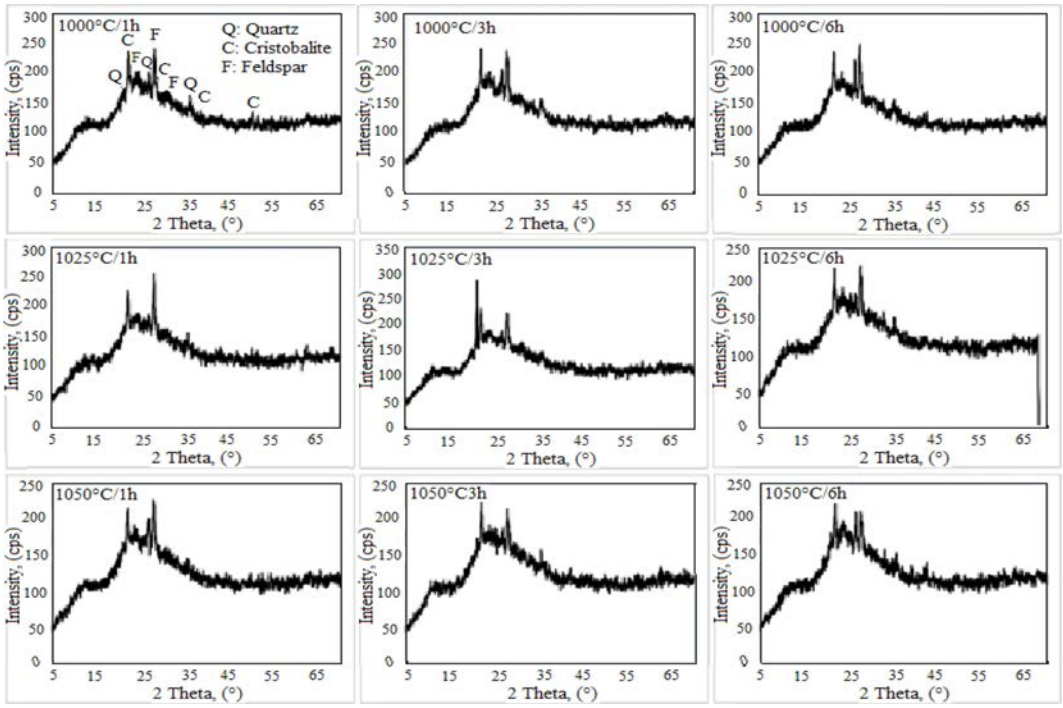

Fig. 8. XRD pattern of samples sintered at different temperatures with varying soaking times.

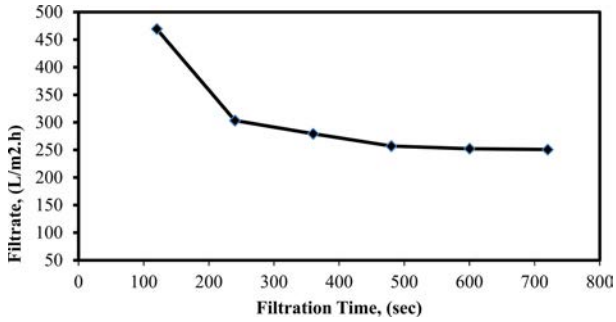

Fig. 9. Permeability of the perlite membrane support.

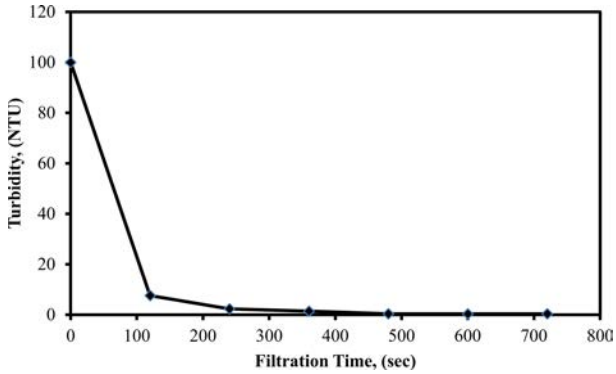

Fig. 10. Filtration of the perlite membrane support.

conditions. It is not possible to obtain a low water contact angle when the sintering temperature is 1000 ºC. An increase in the sintering temperature to 1025 ºC leads to an immediate decrease in the water contact angle of the samples. The best results are obtained when the soaking time is 3 hours at a temperature of 1025 ºC. These results are explained by the surface roughness. It is known that the surface of the pores should be smooth to obtain low water contact angles. Evaluation of the pore microstructure as discussed above proves the formation of low water contact angles. However, in general, smooth glassy surfaces result in a water contact angle < 10 º, where the best result is twice this value. The water contact angle is also related to surface energy. The surface energy of glassy materials is generally high; thus, water tends to spread on these types of surfaces, which decreases the total energy of the system when the energy of the solid-liquid interlayer is less than the energy of the solid-gas interlayer. The crystalline phases embedded in the glassy surfaces may decrease the surface energy. Consequently, the water contact angle of these composite surfaces may be slightly higher than those of the pure glassy surfaces.

It is clearly seen from Fig. 8 that the membrane supports after sintering have similar crystalline structures. The crystalline phases were indicated for the sample sintered at 1000 ºC for 1 hour as an example. The materials are not fully glassy. They contain small amounts of crystalline phases such as quartz, cristobalite and feldspar, which are similar to the raw perlite. These remaining crystalline phases can explain why we could not obtain lower water contact angles.

The filtration performance of the fabricated perlite tube, which is sintered at 1000 ºC for 3 hours, is characterized by permeability and solid recovery tests. The clean water permeability of the perlite tube varies between 3670 L/m^2.h and 10.677 L/m^2.h for 0.2 bar and 1 bar, respectively (Fig. 9). The obtained permeability is adequate for a wide range of filtration applications. Additionally, the solid recovery test is performed for the same tube using a wastewater whose solid recovery is different depending on the mean particle size (near 500 nm) of the solids present in the waste water. It is well known that the finer particles, especially submicron solid particles, penetrate into the pore and immediately block the filters. Fig. 10 shows the clarity of the filtrate and the amount of the filtrate with respect to the filtering times. The cleaning efficiency of the filtrate obtained in the first few minutes is approximately 93%, whereas clean water with a turbidity close to 0.3 is obtained with 250 L/m^2.h of filtrate.

Acknowledgments

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