The preparation and characterizations of pyrophyllite-diatomite composite support layers

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Recently, porous ceramic membranes have become a subject of significant interest because of their outstanding thermal and chemical stability. To reduce the high manufacturing costs of these porous ceramic membranes, recent research has investigated the utilization of low-cost natural materials. Therefore, in this paper, we report the results of our efforts to determine whether we could utilize sodium borate as a bonding phase, and we also report the results of an attempt to prepare a pyrophyllite-diatomite composite support layer that could effectively filter the ISO 12103-1 A3 test dust while exhibiting acceptable water permeability. The pore characteristics of the specimens were studied by scanning electron micrography, mercury porosimetry, capillary flow porosimetry, and a dead-end microfiltration system with particle counters.

Key-words : Pyrophyllite, Diatomite, Sodium borate, Ceramic membrane, Microstructure

1. Introduction

Porous ceramics have recently been the subject of great interest,1–3 as researchers have endeavored to exploit their unique properties.4–6 In particular, ceramic membranes4–8 are among the most promising application of porous ceramics. Therefore, the precise control of the average pore size, the largest pore size, the flexural strength, and the water permeability of the porous ceramic membranes while minimizing the processing cost is important.

However, there are limitations on the reduction of the processing cost simply by altering the process conditions while utilizing commonly used, expensive high-purity ceramic materials, such as alumina, zirconia, and silicon carbide. Therefore, in this study, we employed porous ceramic membranes prepared from pyrophyllite as the matrix and diatomite as a pore former, because both of these materials are inexpensive, natural, and abundant.

Pyrophyllite is an environmentally friendly clay material that is abundant especially in the Jeollanam-do Province of Korea. Pyrophyllite is a hydrated aluminosilicate with a composition of Al₂O₃ · 4SiO₂ · H₂O. The crystals of the pyrophyllite possess a plate-like form and are close to talc in structure. As the Al-OH bonds in the pyrophyllite might also possess the capacity for fluoride adsorption,9 pyrophyllite was recently considered to be one of the promising new candidate materials for utilization in porous ceramic membranes.10,11

Diatomite is a sedimentary rock resulting from the siliceous fossilized skeletons of diatoms, which are composed of rigid cell walls called frustules.12–15 Previously, we reported possible approaches for the fabrication of a diatomite-based support layer that allowed for control over the pore characteristics, such as the largest pore size and the flexural strength, while an acceptable level of air permeability was retained. These approaches enabled the control of the pore characteristics of the diatomite-based support layer beyond what was previously achieved by only controlling the sintering temperature.16–22

Recently, we reported that the air permeability and the largest pore size of the pyrophyllite support layer could be controlled through the addition of diatomite while suppressing the overall processing cost.22) Therefore, we subsequently collected further data regarding the pore characteristics of pyrophyllite-diatomite composite support layers and wish to report on the detail of our investigation.

Notwithstanding the outstanding properties of a pyrophyllite-diatomite composite support layer for potential microfiltration applications, the flexural strength of a pyrophyllite-diatomite composite support layer should also be considered with regard to its use as a free-standing membrane. Although there are many complicated parameters affecting the overall flexural strength of a pyrophyllite-diatomite composite support layer, it can be expected logically that if the amount of diatomite (as a pore former) addition is increased to enhance the air permeability, the flexural strength would be decreased sharply as a trade-off.

Therefore, in this study, to improve the feasibility of the pyrophyllite-diatomite composite support layer as a porous ceramic membrane for microfiltration, we introduced the sodium borate as a strength enhancer. Because sodium borate (Na₂B₄O₇ · 10H₂O) melts at a temperature below 750°C, it can be used as a bonding phase for the pyrophyllite-diatomite composite support layer. Studies using sodium borate as a bonding phase for the pyrophyllite-based support layer have not yet been reported.

It must also be noted that one of the major obstacles hindering more widespread applications of microfiltration is that water permeability declines over time. This phenomenon is commonly termed 'membrane fouling'.23) Membrane fouling significantly reduces the operation efficiency because the microfiltration system has to be stopped frequently to restore the water permeability through a physical and/or chemical cleaning process.24)
However, while the membrane fouling of conventional ceramic membranes, such as α-alumina\textsuperscript{(26–30)} and zirconia,\textsuperscript{11)} has been reported, there are only a small number of studies on the membrane fouling of low-cost natural material-based ceramic membranes.\textsuperscript{(35,36)}

Therefore, the present study investigates several important aspects. First, we determined whether the flexural strength of a pyrophyllite-diatomite composite support layer with the addition of diatomite could be enhanced to a level that can be handled and the microfiltration test can be performed by employing sodium borate as a bonding phase. Secondly, we determined whether the water permeability of the pyrophyllite-diatomite composite support layer would decline sharply by pore blockage and cake formation due to the complexity of its pore structure or remain at a certain level. Third, we investigated whether the decline in water permeability of the pyrophyllite-diatomite composite support layers resulting from the foulants could be recovered by back-washing without chemical cleaning.

2. Material and methods

Pyrophyllite (Korea Powder Co. Ltd., Korea), diatomite (Celite 499, Celite Korea Co. Ltd., Korea), and sodium borate (Shinyo Pure Chemical Co. Ltd., Korea) were prepared for the preparation of the pyrophyllite-diatomite composite support layers. To supplement sodium borate, calcium carbonate (Sigma-Aldrich, U.S.A.) and barium carbonate (Sigma-Aldrich, U.S.A.) were also selectively used. Distilled water was used as a solvent, and the slurry was ball-milled for 24 h with an alumina ball-to-powder volume ratio of 2:1. After ball-milling, the slurry was dried at room temperature for 24 h. With the use of 2 wt.% of polyethylene glycol as a binder, the pyrophyllite-diatomite composite support layers were dry-pressed to the coin-shaped specimens (diameter 4 cm and thickness 0.4 cm) at 18.7 MPa and sintered between 1200–1400°C for 1 h.

The flexural strengths of the pyrophyllite-diatomite composite support layers were measured by a four-point bending test (Instron 4206, Instron, U.S.A.). The pore characteristics of the pyrophyllite-diatomite composite support layers were investigated by scanning electron micrographs (JSM-5800, JEOL, Japan) and mercury porosimetry (Autopore IV 9510, Micromeritics, U.S.A.). The air permeability and the largest pore size were measured by capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., U.S.A.). A pyrophyllite-diatomite composite specimen (diameter 4 cm and thickness 0.4 cm) was fitted between the O-rings in the bottom of the chamber and the bottom of the chamber insert in the capillary flow porosimetry. Next, the flux was measured automatically by sensors while the diameter of the motorized valve and the pressure of the regulator were incrementally changed.

To extrude the pyrophyllite-diatomite composite support layers for a microfiltration test, 15 wt.% of methyl cellulose (Sigma-Aldrich, U.S.A.) as a binder, and 15 wt.% of distilled water as a solvent were added. The mixed slurry was aged for 48 h at room temperature, and extruded by a double screw extruder (KTE-50S, Kosentech, Korea). An extruded pyrophyllite-diatomite composite support layer has flat tube-type dimensions (width 50 mm, height 4 mm, and length 200 mm), and it has 16 inner holes (width 2 mm and height 2 mm). The water permeability and membrane fouling of the pyrophyllite-diatomite composite support layer were measured using a dead-end microfiltration system (MTS2000, Sam Bo Scientific, Korea) equipped with particle counters (PAMAS-4132, PAMAS, Germany). The schematic diagram of the dead-end microfiltration system with particle counters and an image of the installed system in the laboratory were already described in previous report.\textsuperscript{37)}

The particle separation characteristics were tested at room temperature via a rejection experiment using ISO 12103-1 A3 test dust (ISO 12103-1, A3 Medium Test Dust, Powder Technology Inc., U.S.A.) with an average particle diameter of approximately 1.0 μm. The concentration of the ISO 12103-1 A3 test dust in-feed was a constant 0.02 g/L, and the operating trans-membrane pressure was maintained at 2.4 bar. After the filtration of the ISO 12103-1 A3 solution for 0.5 h, the pyrophyllite-diatomite composite support layer was backwashed with air at 3 bar for 10 s before being filtered again. An extruded pyrophyllite-diatomite composite support layer has flat tube-type dimensions (width 50 mm, height 4 mm, and length 200 mm), and it has 16 inner holes (width 2 mm and height 2 mm). Figure 1 show a fixture assembled in the membrane module for use in the water permeability and dead-end microfiltration tests. The water permeates the flat membrane and flows out up and down through the inner holes in the membrane.\textsuperscript{37)}

A typical SEM image of the ISO 12103-1 A3 test dust is shown in Fig. 2. The average particle size (number distribution) and the average particle size (volume distribution) of the ISO 12103-1 A3 test dust were 0.97 and 25.13 μm, respectively.

3. Results and discussion

3.1 The pore characteristics of a pyrophyllite support layer

A typical scanning electron microscope (SEM) image of the pyrophyllite support layer sintered at 1200°C for 1 h is shown in Fig. 3(a). In Fig. 3(a), the plate-like pyrophyllite phase in the microstructure was easily identified. Because the inter-connected pore channels are not observed in the microstructure due to the plate-like pyrophyllite particles, the air and water permeability of the pyrophyllite support layer cannot be high enough to be used as a microfiltration membrane, unless employing diatomite as a pore former, as we already reported.\textsuperscript{37)}
The flexural strengths of conventional clay materials such as mullite,\textsuperscript{38} kaolin,\textsuperscript{39} and diatomite\textsuperscript{40} are usually below 30 MPa. In this study, a flexural strength of 8.01 MPa was measured for the pyrophyllite support layer sintered at 1200°C for 1 h, and a flexural strength of 58.90 MPa was measured for the pyrophyllite support layer sintered at 1400°C for 1 h, as shown in Fig. 3(b). However, by increasing the sintering temperature, the flexural strength of a pyrophyllite support layer could be enhanced. The air permeability of a pyrophyllite support layer is not acceptable for microfiltration applications, regardless of the enhanced flexural strength.

3.2 The effects of diatomite addition on the pore characteristics of a pyrophyllite support layer

Therefore, the air permeability of the pyrophyllite support layer needs to be enhanced further by introducing diatomite as a pore former, despite the inevitable decrease in the flexural strength. A typical SEM image of the pyrophyllite-diatomite composite support layer sintered at 1200°C for 1 h with the addition of 25 wt.% diatomite is shown in Fig. 3(c). With the addition of the 25 wt.% diatomite, the microstructure of the pyrophyllite-diatomite composite support layer possessed intermediate microscopic features between the irregular and porous diatomite matrix and the plate-like pyrophyllite matrix. With an addition of 25 wt.% diatomite, the pore size distribution of the pyrophyllite-diatomite composite support layers significantly shifted towards

![Fig. 2. A typical SEM image of the ISO 12103-1 A3 test dust.](image)

![Fig. 3. (a) A typical SEM image of the pyrophyllite support layer sintered at 1200°C for 1 h; (b) flexural strengths and air permeabilities of the pyrophyllite support layers sintered at 1200, 1300, and 1400°C for 1 h; (c) a typical SEM image of the pyrophyllite-diatomite composite support layers sintered at 1200°C for 1 h with 25 wt.% diatomite; (d) pore size distributions of the pyrophyllite-diatomite composite support layers with the addition of 0 wt.% diatomite, 25 wt.% diatomite, and 50 wt.% diatomite, sintered at 1200°C for 1 h.](image)
the diatomite support layer, as shown in Fig. 3(d). This result implied that the minimum amount of addition of diatomite could affect the pore structure of the pyrophyllite-diatomite composite support layer, unlike the case of the kaolin-diatomite composite support layer.19)

The air permeability of the pyrophyllite-diatomite composite support layer was enhanced significantly when more than 25 wt. % diatomite was added, and the flexural strength of the pyrophyllite-diatomite composite support layer decreased at a level that cannot be used as a free-standing membrane, as will be discussed again in Fig. 6(a). In general, increasing the sintering temperature could be used to increase the flexural strength of a ceramic membrane.

3.3 The effects of sodium borate addition on the pore characteristics of a pyrophyllite-diatomite composite support layer

However, Fig. 4 shows that though the sintering temperature of the pyrophyllite-diatomite composite support increased from 1200 to 1300°C, the flexural strength of the pyrophyllite-diatomite composite support layer still remained under 10 MPa.

Therefore, we introduced sodium borate as a bonding phase for the pyrophyllite-diatomite composite support layer to increase the flexural strength. To determine the microstructure, a typical SEM image of the pyrophyllite support layers with the additions of 50 wt. % diatomite and 1.5 wt. % sodium borate sintered at 1200°C for 1 h will be shown in Fig. 7(a). Although there are many inherent pores in the diatomite matrix, because of the addition of 50 wt. % diatomite, the presence of sodium borate, which covers or blocks the inherent pores, was not easily identified.

A typical SEM image of the pyrophyllite-diatomite composite support layer with the additions of 25 wt. % diatomite and 1.5 wt. % sodium borate sintered at 1300°C for 1 h is shown in Fig. 7(a). Although there are many inherent pores in the diatomite matrix, because of the addition of 50 wt. % diatomite, the presence of sodium borate, which covers or blocks the inherent pores, was not easily identified.

Fig. 4. Flexural strengths and the air permeabilities of the pyrophyllite-diatomite composite support layers sintered at 1300°C for 1 h, with the addition of 0 wt. % diatomite, 25 wt. % diatomite, and 50 wt. % diatomite.

In the preliminary experiments, we added calcium carbonate and barium carbonate to supplement the sodium borate as the bonding phase, and we found that the presence of calcium carbonate and barium carbonate induced too much of the glassy phase. Figure 5(b) shows a typical SEM image of the pyrophyllite-diatomite composite support layer with the additions of 25 wt. % diatomite, 1.5 wt. % sodium borate, 1 wt. % calcium carbonate, and 2 wt. % barium carbonate sintered at 1300°C for 1 h. It was observed that the pores of the pyrophyllite-diatomite composite support layer were mostly covered with the glassy phase.

Therefore, hereafter, we limited the sintering temperature of the pyrophyllite-diatomite composite support layer to 1200°C because of the addition of diatomite, and we focused on only sodium borate as a bonding phase of the pyrophyllite-diatomite composite support layer.

Figure 6(a) presents the air permeability and the flexural strengths of the pyrophyllite-diatomite composite support layers with the additions of 25 and 50 wt. % diatomite, sintered at 1200°C for 1 h, with/without the addition 1.5 wt. % sodium borate. Although the air permeabilities decreased slightly because of the addition of sodium borate, the flexural strengths of the pyrophyllite-diatomite composite support layers increased significantly (approximately four times).

The increase of the flexural strength of the pyrophyllite-diatomite composite support layers with the addition of sodium

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Fig. 5. Typical SEM images of the pyrophyllite-diatomite composite support layer (a) sintered at 1300°C for 1 h with the additions of 25 wt. % diatomite and 1.5 wt. % sodium borate, and (b) sintered at 1300°C for 1 h with the additions of 25 wt. % diatomite and 1.5 wt. % sodium borate, 1 wt. % calcium carbonate, and 2 wt. % barium carbonate.

Na₂B₄O₇·10H₂O (sodium borate). These impurities and additives favor low-temperature eutectics and thus the formation of a melt phase in the silica-rich grains.14)
borate was explained by the decrease of the largest pore size, as shown in Fig. 6(b). Because the sodium borate was soluble in water, it could be uniformly dispersed in water, and then be coated to pyrophyllite and diatomite particles through the ball-milling process. Therefore, after the sintering process of the pyrophyllite-diatomite composite support layer, the sodium borate could act as a bonding phase. This strengthening effect was well-matched with the cases of silicon carbide\(^{41}\) and kaolin\(^{42}\) in the literature. Furthermore, the largest pore sizes of the pyrophyllite-diatomite composite support layers could still be controlled in the sub-micron size range regardless of the addition of sodium borate. These results demonstrated the feasibility of using a pyrophyllite-diatomite composite support layer without a separation layer as a porous ceramic membrane for microfiltration.

3.4 The microfiltration test of a pyrophyllite-diatomite composite support layer

In a previous report,\(^{17}\) we measured only the air permeability of the pyrophyllite-based support layers to compare our results with the air permeability and/or water permeability of typical ceramic microfiltration membranes reported in the literature. However, at low flow rates, the air permeability of the specimens may be higher than the water permeability of the same specimens, because gas does not adhere to the pore walls the way liquid does and because the slippage of gases along the pore walls causes an apparent dependence of the permeability on the pressure (this is known as the Klinkenberg effect).\(^{39}\) Therefore, in this study, we have extended our investigation to include the water permeability of the pyrophyllite-diatomite composite support layer.

Figures 7(a) and 7(b) present a typical SEM image, and the pore size distribution of the as-prepared pyrophyllite-diatomite composite support layer with the additions of 25 wt.% diatomite and 1.5 wt.% sodium borate, sintered at 1200°C for 1 h, respectively. The average pore size of the pyrophyllite-diatomite composite support layer which was measured by mercury porosimetry was 0.90 μm.

The largest pore size of pyrophyllite-diatomite composite support layer with the additions of 25 wt.% diatomite and 1.5 wt.% sodium borate, sintered at 1200°C for 1 h was 0.9 μm in Fig. 6(b). However, in Fig. 7(a), there seemed to exist that the pores which were larger than 0.9 μm. This discrepancy usually occurs when the pore structure is complex and partly interconnected, as is the case of the pyrophyllite-diatomite composite support layer. In principle, the largest pore size measured by capillary flow porosimetry ensures that the pores are fully interconnected and act as pore channels. Therefore, the pores which were larger than 1 μm which we could identify in the SEM image really existed but not inter-connected. So, the (inter-connected) largest pore size was 0.9 μm.

Generally, if the particle size of the foulants is similar to the pore size of the membrane, blocked pores can occur during a microfiltration test. Furthermore, when the particle size of the foulants is much larger than the pore size of the membrane, cake formation, which is more easily removed may occur.\(^{24,44}\) Because the average particle size (number distribution) was approximately the same as the average pore size and the largest pore size of the pyrophyllite-diatomite composite support layer, it was expected that the ISO 12103-1 A3 test dust would be an appropriate foulant to determine the effects of foulants on the water permeability of the pyrophyllite-diatomite composite support layer. Furthermore, because the average particle size (volume distribution) of the ISO 12103-1 A3 test dust was 25.13 μm, backwashing was performed to determine whether the decline in water permeability of the pyrophyllite-diatomite composite support layers due to cake formation could be recovered without chemical cleaning.

Figure 8(a) shows the water permeability (pure water) of the pyrophyllite-diatomite composite support layer with the additions of 25 wt.% diatomite and 1.5 wt.% sodium borate, sintered at 1200°C for 1 h, which was measured by the microfiltration system already described in Figs. 1(a) and 1(b).

The water permeability (pure water) of the pyrophyllite-diatomite composite support layer was maintained at approx-
on materials such as the pure water or 1.6 are shown in Figs. 8(b) and 8(c). A decrease in the composite support layers using the ISO 12103-1 A3 test dust above 99.9 fouling from direct observed in Fig. 8(b) because of reversible and irreversible applications. The micro-

alumina, zirconia or silicon carbide), the pyrophyllite-diatomite low cost of the raw material (unlike the costs of high-purity fl sintering temperature, the acceptable for 1 h with the additions of 25 wt. of the pyrophyllite-diatomite composite support layer sintered at 1200°C borate.

Fig. 7. (a) A typical SEM image and (b) the pore size distribution of the pyrophyllite-diatomite composite support layer sintered at 1200°C for 1 h with the additions of 25 wt.% diatomite and 1.5 wt.% sodium borate.

imately 1.0 \times 10^3 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} for 5 h. In the literature, the pure water flux of ceramic microfiltration membranes based on materials such as \( \alpha \)-alumina,\(^{20}\) \( \gamma \)-alumina,\(^{9}\) or zirconia\(^{43}\) were 1.5 \times 10^3 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}, \sim 1.0 \times 10^3 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}, \) or 1.6 \times 10^3 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}, respectively. Considering the low sintering temperature, the acceptable flexural strength, and the low cost of the raw material (unlike the costs of high-purity alumina, zirconia or silicon carbide), the pyrophyllite-diatomite composite support layer is a feasible candidate for microfiltration applications.

The microfiltration test results of the pyrophyllite-diatomite composite support layers using the ISO 12103-1 A3 test dust are shown in Figs. 8(b) and 8(c). A decrease in the flux was observed in Fig. 8(b) because of reversible and irreversible fouling from direct filtration using the ISO 12103-1 A3 test dust. Figure 8(c) shows that the rejection rate of the A3 test dust is above 99.9% regardless of the particle size after the microfiltration test of the pyrophyllite-diatomite composite support layer. It should be noted that the number of particles (y-axis) is shown in a logarithmic scale. As shown in Fig. 8(d), the ISO 12103-1 A3 test dust partially or totally blocked the pores of the pyrophyllite-

diatomite composite support layer after the microfiltration test. Therefore, the water permeability of the pyrophyllite-diatomite composite support layer decreased gradually during the microfiltration test.

After the pores of the pyrophyllite-diatomite composite support layer were blocked, further deposition of the ISO 12103-1 A3 test dust on the surface formed a cake layer. Cake formation creates an additional resistance layer to the permeate flow. Hence, the water permeability decreases as the thickness of the cake layer increases with time, as observed in Fig. 8(b). In practice, a dead-end microfiltration system is prone to the build-up of cake because of the absence of high-speed cross flow.\(^{44,45}\) For instance, after 30 min of dead-end microfiltration of beer, the membrane was completely plugged, and cake layers are assumed to be formed on top of the membrane.\(^{46}\) It is worth noting that, despite the complex pore structure of the pyrophyllite-diatomite composite support layer, the pores were not clogged instantly by the ISO 12103-1 A3 test dust, despite the dead-end microfiltration test, and the water permeability was partially recovered through each back-washing step.

The water permeability of the pyrophyllite-diatomite composite support layer remained above 5.0 \times 10^{-3} \text{m} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1} (2.0 \times 10^2 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}) without any chemical cleaning for 5 h. In previous paper,\(^{37}\) the flux of the diatomite-kaolin composite support layer was relatively high. Therefore, it maintained over the detectable flux level for 12 h. However, the flux of the pyrophyllite-diatomite composite support layer was lower than that of the diatomite-kaolin composite support layer. 6–7 h later, the flux partially reached undetectable lower. However, it would be possible that the water permeability of the pyrophyllite-diatomite composite support layer could be increased further. This increase may be possible if a cross-flow microfiltration set-up and optimized cleaning process parameters have been applied, including the selection of suitable cleaning agents, cleaning agent concentrations, the order and duration of cleaning steps, operating pH, and operating temperature.

4. Conclusion

In summary, first, we determined that the flexural strength of a pyrophyllite-diatomite composite support layer with the addition of 25 wt.% diatomite could be enhanced to a level (16.3 MPa) that can be handled and the microfiltration test be performed by employing 1.5 wt.% sodium borate as a bonding phase. The addition of sodium borate provided an effective means of tailoring the pore characteristics of the pyrophyllite-diatomite composite matrix.

Secondly, we determined that the water permeability of the pyrophyllite-diatomite composite support layer declined gradually by pore blockage and cake formation, remained at above 2.0 \times 10^2 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} without any type of chemical cleaning for 5 h during the dead-end microfiltration test using the ISO 12103-1 A3 test dust. After the dead-end microfiltration, the rejection rate of the ISO 12103-1 A3 test dust was above 99.9% regardless of particle size.

In this study, as we examined on the feasibility of a pyrophyllite-diatomite composite support layer as a free-standing microfiltration membrane, any type of physical and chemical cleaning on the surface of the pyrophyllite-diatomite composite support layer, except a back-washing step was not employed. Therefore, the effect of the operation types, and the effect of operation parameters on the membrane performance of the pyrophyllite-diatomite composite support layer remain important issues for further research.
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Fig. 8. (a) The water permeability (pure water) of the pyrophyllite-diatomite composite support layer sintered at 1200°C for 1 h with the additions of 25 wt.% diatomite and 1.5 wt.% sodium borate; (b) the water permeability and (c) the particle separation characteristics of the pyrophyllite-diatomite composite support layer using the ISO 12103-1 A3 test dust; and (d) a typical SEM image of the surface of the pyrophyllite-diatomite composite support layer, after the dead-end microfiltration test.
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