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Wastewater filtration performance of multilayer glassy microporous filters

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Abstract

The glassy composition (quartz, clinoptilolite and frit glass mixture) provides a filter having glassy pore wall microstructure and thus enables easily cleaning through the filter recovery by back flushing. The filter was obtained as multilayer compaction by one step slip cast-processing where a cylindrical filter, consisting of filtration layer on granular assemblies with specific interlayer was shaped by a fine particle migration phenomenon. The multilayer compaction has low resistance to liquid flow and thus the filter great potential to use for wastewater filtration. It is known that high capacity filtration also requires correct pore size/interval with respect to filtered particles. In this study, a wastewater overflow from marble factory (0.035 wt.% of solid with a size distribution of 0.58–1.46 μm) was filtered by different pore sizes of the glassy filters (pore size intervals: 0.4–10 μm, 0.2–4 μm, 0.1–1.5 μm and 0.04–2 μm) and significantly different filtering capacities was obtained; the irreversible fouling capacities were determined between 2.9 and 8.5 m^3 of filtrate per m^2 of the filter area through the filtration produced 5 min intervals. The filtration pressure was 5 bar and backflushing was achieved at 1 bar. The high filterability (8.1 m^3/m^2 in 5 min) with high filtrate clarity (∼0.5 nephelometric turbidity units) could be obtained using finer pore sized filters. The large size filter was seriously clogged during the filtration.

Keywords: A. Slip casting; Ceramic filter; Wastewater; Filtration

1. Introduction

In addition to a variety of other industrial fields, microporous ceramics have become increasingly popular in manufacturing filters for large-volume solid/liquid separation purposes. Such bulk applications, however, require low-cost mass production of microporous ceramics having desired properties. Ceramic filter media must have low resistance for liquid flow (multilayer filters), narrow pore size distribution (specially fabricated filtering layer), and high bend strength for filtration and backflush cleaning (required an interlayer). Additionally, the filter must be produced from low cost materials (natural ceramic powders) and the fabrication should be simple with a low cost process (i.e., produced by conventional ceramic processing, low temperature sintering).

Recently, glass-based ceramic membrane filters have been fabricated by the authors using low-cost ceramic powders and with simple fabrication processing [1–4]. Crystalline silica particles are ground into finer sizes and mixed with lead-borosilicate glass particles at about 15% by weight, and sintering is applied above the fusion temperature of the glass component. The spreading of the glass well through the microstructure, which is due to the capillary pressure between the grains and the wetting of the grains by the glass, leads to the fabrication of a porous microstructure in which the silica particles are coated by glass phase and thus glass-based porosities are obtained. The material has the potential for use in water filtration as the pore surfaces have high smoothness with a highly hydrophilic nature and thus the cleaning and recovery performance of the filters are significantly higher. The membrane filters have been tested for spring water filtration for more than eight months and obtained about the same irreversible fouling resistance and it was found that the filters did not require any chemical cleaning processing during this period [4]. The spring water contained clay particles of the montmorillonite type and those are finer than 1 μm in size; however, the pore sizes of the glass filter used in this study were finer than 4.5 μm. Thus, medium clogging phenomena occurred; besides, the clay material has a sticky nature and high compatibility. The filtration processing of the sub-micron clay particles using relatively coarse pore size membrane filters

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is a new approach. Significant success is achieved by the filtration operated in periodic mode through the filter material cleaned with filtrate back-flushing and flowing air-blowing processes.

The above conclusions indicate the potential of glassy filters for large volume water filtration. For industrial applications, the filter should be developed such that the liquid flow resistance should be lowered and a simple fabrication processing should be applied. It is known that a high porosity substrate coated with fine porosity filtering layer produces high filtration capacity with high selectively particle separation. It is obvious that coating a microporous filtering layer on a substrate having large pores is very difficult. Usually, more than one layer are required for obtaining low pore size in external filtering layer and each additional stage increases the cost of filters. Instead of the conventional application, Özgür and Şan, 2008 [5] proposed a new approach in which the production of an apparent density gradient was possible by a simple and one stage cast−proces-processing. The process has a high migration phenomenon, obtained by using a mixture of cast slurry designed as powder slurry and granules. The granules were deposited, and the fine particles were carried by the liquid that was flowing through the pores and those deposits were close to the surface of the mould surface and thus formed the gradient compaction. This is the first time the technique has been applied to the fabrication of glassy pore wall filters and then tested with relatively coarse particles [5]; the average size of the particles (δ_{50}) was 1.82 μm and the size of the granules was between 500 μm to 1000 μm. The investigation had focused on determining the influence of slurry concentration on particle migrating phenomena; the results led to the conclusion that the best concentration was 10% solids in weight. The same experiment was also used for fine sizes of powder particles and with fine size of granules [6]. Table 1 indicate that there are limitations due to the possibility of no surface cracking of the dry product and using finer sized particles cause without problems through the mould remove of the sample. The following are the benefits to using certain combinations of powder particles and granules: (i) fine size particles (d_{50} = 0.65 μm) with fine size granules (125–250 mm); (ii) moderate size particles (d_{50} = 0.98 μm) with moderate size granules (250–500 mm) and (iii) coarse size particles (d_{50} = 1.82 μm) with coarse size granules (500–1000 mm). The finer size particles (d_{50} = 0.22 μm) did not lead to the production of filter material; both used the granules as coarser to finer sizes. Low casting rate was observed with the fine size particles and thus the migrating phenomena could not be obtained.

In this study, the above new casting procedures were used for fabrication of varied pore sizes of filter materials. At this time, the only difference was of the size of coarse particles; the size was increased to δ_{50} = 2.05 μm and thus planned to fabrication of relatively large size of filter material. Another new application was production of finer size of capillary filter which was not possible by one stage casting. Such a filter was produced by coating of finely ground frit glass particles onto the coarse size of filter material. The coating was achieved by filtration technique. In light of these, the study was focused on the filtration testing of the fabricated glassy ceramic membrane filters with coarser to finer pore sizes. Filtration was conducted on the marble wastewater stream obtained from a factory where the water was of the overflow of the thickening. The settling was achieved without any pretreatment (coagulation/flocculation). The filtration was operated periodically with filtrate back-flush cleaning. The high performance ceramic membrane filters produced from inexpensive natural ceramic powders with simple casting route enhances wider use of the filter materials in the large volume liquid/solid separation.

2. Experimental

2.1. Ceramic filter preparation procedure

The composition for ceramic filter was designed as 86.86% SiO_2, 3.47% Al_2O_3, 5.28% PbO, 1.54% B_2O_3, 0.28% Na_2O, 0.71% MgO, 1.11% CaO and 0.11% K_2O, and prepared by using powder mixtures of quartz, lead borosilicate frit glass and natural zeolite (clinoptilolite). The powder mixture was ground for different times using alumina balls in water. The shorten time milled sample (δ_{50} = 6 μm) was used for the granule production. The ground material was dried at 105 °C for 24 h, and wetted with water (5 wt.%) for agglomeration and was sintered at 900 °C for 20 min with a heating rate of 5 °C/min. The agglomerates were sized for different intervals ($500 < \delta < 1000$; $250 < \delta < 500$ and $125 < \delta < 250$). The long time milled particles were of the size δ_{50} = 2.05 μm, δ_{50} = 0.985 μm and δ_{50} = 0.65 μm, those were used for preparation of slurries for casting of the filter materials. The details of the powder and granule preparation were given in previous studies [5,6].

The casting unit used was unique and was presented for the first time in the published paper [5]; it consisted of a hollow, cylindrical mould and a funnel (see Fig. 1). The funnel is tightly attached to the casting mould using rubbers. The mould was made of plaster-of-paris in which gypsum was added to water as

Table 1
The influence of powder and granule sizes on the production of the multilayer membrane filter (6(.

Powder sizes ($(_{50}$) ((m)	Size interval of granules, (m $500 < \delta < 1000$ (coarse)	$250 < \delta < 500$ (moderate)	$125 < \delta < 250$ (fine)	$75 < \delta < 125$ (finer)
0.22 (finer)	Surface cracking after drying	Surface cracking after drying	Surface cracking	Crack observed after casting
0.65 (fine)	Surface cracking after drying	Surface cracking after drying	Well production	–
0.98 (moderate)	Surface cracking after drying	Well production	–	–
1.82 (coarse)	Well production	–	–	–

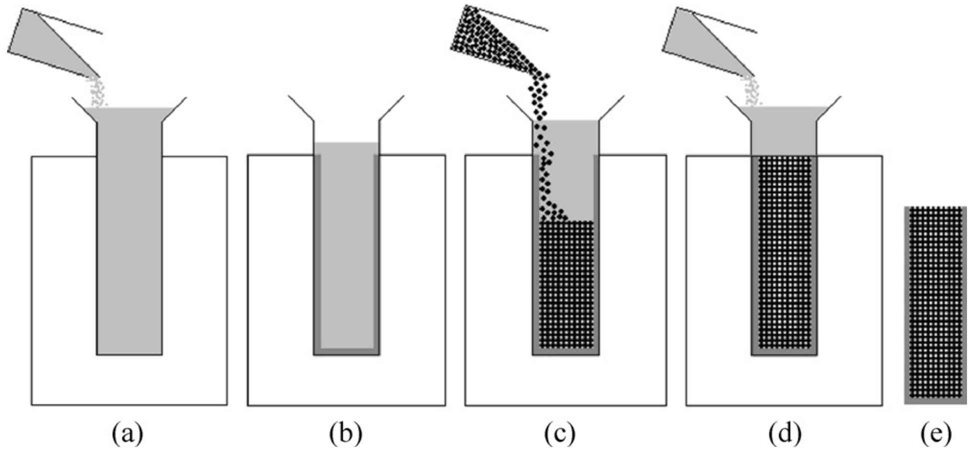

Fig. 1. (a–e) Schematic description of slip casting process: the slurry poured into the mould (a), the thin filtering layer formed on the inner surface (b), the granular particles placed into this same mould (c), the excess slurry supplied into the granular medium produced a secondary compaction (d), the compacted sample removed from the plaster mould (e).

70 wt.% of the water content, and the gypsum slurry was stirred for 1 min, and then degassed under vacuum. The gypsum slurry was poured into a resin mould and a hollow cylinder (Ø 20–100 mm) was obtained. The mould was dried at 40 °C before slip casting.

The slurry for casting of the filter material was poured into the mould where some part of the slurry remained in the funnel which was a reservoir during the one-stage casting operation (Fig. 1a). The water of the cast slurry was absorbed into the walls of the mould whereupon a thin filtering layer formed on the inner surface (Fig. 1b). The thickness of filtering layer was controlled by the casting time which was previously investigated from the conventional plot: the cake thickness (L) versus square root of casting time ($t^{1/2}$) [6]. A cast thickness of about 500 mm was selected for the fabrication of the present filters. After that the granular particles were placed into the same mould over laying the powdered slurry (Fig. 1c). At this stage, the slurry within the mould was rise through the funnel. Because of the casting produced, the amount of slurry within the funnel becomes less and it was needed to use additional slurry for produce of a constant head. The level of cast-slurry was easily monitored from the transparent funnel and thus a non-stop casting was achieved. The additional slurry supplied into the granular medium was produced a secondary compaction due to the fine particle migration (Fig. 1d). After a given casting time, the process is stopped and the shaped sample was removed from the plaster mould and dried (Fig. 1e). In here it should be stated that the compacted sample is a cylindrical shape. The casting of present filter as tubular configuration will be further studies to enhance wider use of the filter material in industrial needs.

These are the experimental invariables: (i) a fresh mould was used for the each casting experiments, by this way the applied capillary pressure was the same. The mould preparation procedure of our work was the same as the previous study conducted by Hotta et al. [7], this study indicated the capillary pressure of the gypsum mould as 1.5–105 Pa, (ii) the slurries have a pH 7 and the same temperatures (∼20 °C), (iii) the same solid concentration (10% solids in weight) and the agitation time (30 min) before the cast operation.

The shaped filters were dried overnight in a room with 60% humidity, and then kept in ambient conditions for a day, and finally oven dried at 105 °C for 12 h. The bodies were sintered at 1000 °C for 20 min with a heating rate of 5 °C/min. The frit glass was coated onto the coarse pore size filter under the same coating conditions as with previous studies [8], then the coated filter was first air-dried overnight in a room at 60% humidity, then kept in ambient conditions for a day, and finally oven-dried at 105 °C for 12 h. The filter was then sintered at 600 °C at a rate of 5 °C/min for 40 min.

2.2. Filtration experiments

The filtered wastewater was obtained from the marble company (located in Afyon-Türkiye). The water contained fine particles in which large particles were removed by gravitational thickening without use of any chemicals. The overflow waste was filtered using glassy filters in which filtration was of both dead-end and periodic modes. The experimental set-up consisted of a slurry tank, a pump, a stainless steel filter unit, a compressed air tank, an electronic balance, pressure gauges and other accessories. The detail of the experimental set-up was given in our previous study [4]. During the periodic filtration, the filter was removed each time from the filter chamber and compressed air was applied through the filtrate discharge point. The periodic filtration cycle was of 5 min intervals. The applied trans-membrane pressure was 5 bar. The filtrate back-flush pressure was applied at 1 bar and the pressure for back-flushing was operated from compressed air.

The compressed air in filtration systems has two functions: (i) as a pressure source for filtrate back-flushing and (ii) cleaning of the filter pores by additional air flowing. In this study, the cleaning of filters was achieved only by water back-flushing using compressed air as a source of pressure. During the operation, the filtrate within the connected pipe was removed from the system for a short back-flushing time of 10 s was selected and thus no air flow was obtained from the filter pores.

2.3. Evaluation and characterization

The study of the samples included: (i) crystalline phase identification by X-ray analysis (Rigaku Miniflex powder diffractometer employing CuKα radiation in $2\theta = 10–65^\circ$ at a goniometer rate of $2\theta = 2^\circ$/min.), (ii) the particles sizes of the powders were measured by Zeta-meter (Malvern Zeta-Sizer Nano ZS), (iii) the pore size range of the filtering layers was determined by the mercury porosimetry technique (Quantachrome Poremaster), (iv) the heat treatment of the frit glass particles was determined by hot stage microscope (Misura ODHT–HSM 1600/80), (v) the surface charge of the wastewater solid particles was measured by Zeta-meter (Malvern Zeta-Sizer Nano ZS), (vi) the data acquired from the filtration experiments as a function of time were the cumulative filtrate volume and the turbidity of the filtrate. The amount of filtrate was determined by an electronic balance and the turbidity measurements were conducted via a turbidimeter (Merck Turbiquant 1500 T),

3. Results and discussion

3.1. Microstructure of the membrane filters

Fig. 2 shows a typical picture of the fracture surface of filter which indicates the thickness of the filtering layer and the granular substrate. The granular substrate has two layers; granular core and an interlayer. The interlayer indicated that the space between the granules, along the filtering layer, was filled by fine particles. It is clearly shown that the core of filters is a granular assembly where weak interconnections occur at neck points. The core being poor with respect to fine particles are observed. But the migration phenomenon of fine particles can be improved into the granular medium by favoring the liquid-flow between the granules and the settlement onto the filtering layer. By this way, the porosity of the granules assembly close to the filtering layer is low and the porosity of the core is very high. Besides, the sintering of fine particles between the granules increases the mechanical strength of the whole material [6].

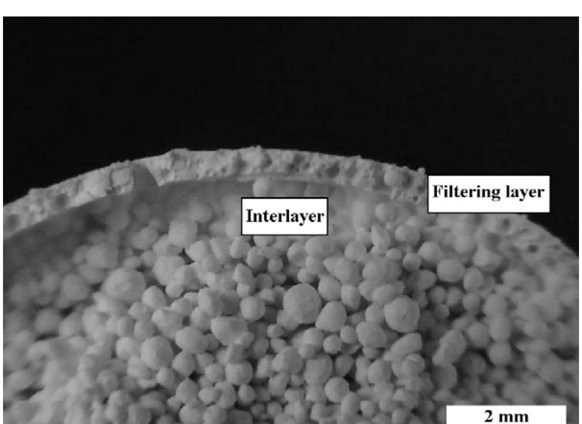

Fig. 2. Photos of the fracture surface of the cast sample prepared from the coarse sizes of powder ($(_{50}$ = 1.82 mm) and granules (500 < δ < 1000 mm) [6].

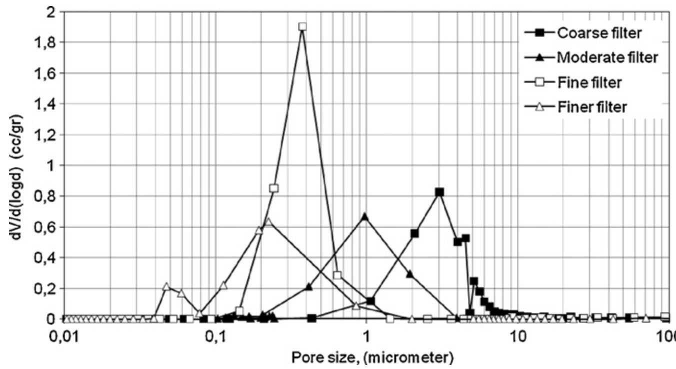

Fig. 3. The pore sizes of filtering layers of the fabricated multilayer glassy ceramic filters.

Instead of the particle sizes such as δ_{50} = 1.82 μm, the new approach achieved the filter with the coarser size of particles (δ_{50} = 2.05 μm). Similar microstructure was expected where the surface of the filter was examined by the naked eye and no cracking or dent was observed. A further study was made where the filter surface was coated using finely ground frit glass particles. The same success was obtained with frit glass coating. The sintering of frit glass was carried out at a low temperature (at 600 °C) and also the sintering time is important for the production of high porosity coating [8]. The sintering time was 40 min. Fabrication of the filter at fine and moderate pore sizes was carried out as described in the previous study [6].

Fig. 3 shows the pore size of filtering layer for the fabricated materials using different size of powders. The filtering layer obtained using coarse size (δ_{50} = 2.05 μm), moderate (δ_{50} = 0.98 μm), fine (δ_{50} = 0.65 μm) and finer (δ_{50} = 0.22 μm) powders indicates the pore sizes intervals such as 0.4–10 μm, 0.2–4 μm, 0.1–1.5 μm and 0.04–2 μm, respectively. Irrespective of the finer pore sizes of filter, the pore size distributions were mono modal with relatively narrow pore sizes. In the case of finer sizes, the coating of glassy particles to produce uniform porosity filtering layer is not easy where the finer size of glass particles melts leading to clustering [8]. The study of the microstructure by scanning electron microscopy (SEM) indicates the locally melting glass particles, but some finer pores were determined. Such a microstructure is not desirable where the porosities of filtering layer decreased. But finer pores were significant. According to Laplace equation (see Eq. (1)), the finer pores increased the capillary pressure and thus the detrimental effect of melting may be decreased to some extent.

$$\Delta P_{\text{cap}} = \frac{2\sigma Cos\theta}{r} \quad (1)$$

where σ is the surface tension, r is the capillary radius and θ is the contact angle between the liquid and the solid.

3.2. The properties of wastewater from a marble company

The wastewater stream obtained from the marble factory contained fine sizes of solid particles (see Fig. 4). The particles were finer than 1.5 μm and 85% weight being less than 1 μm in size. The pH of the slurry was measured and observed close to

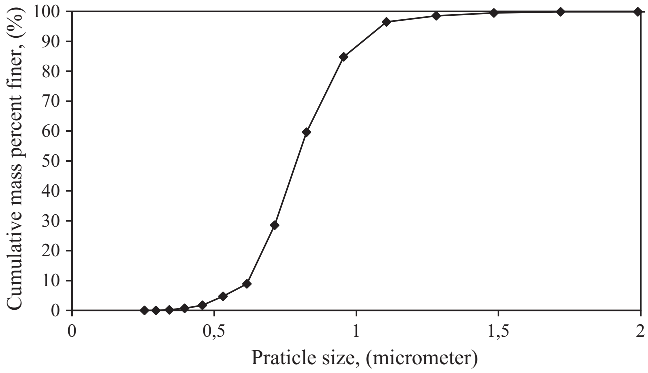

Fig. 4. Size distributions of filtered particles (overflow of the marble wastewater stream).

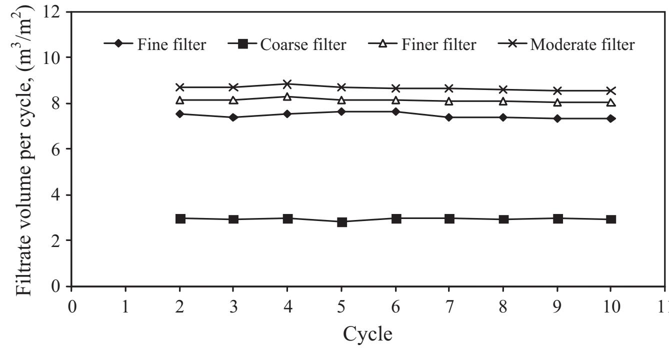

Fig. 6. Periodic filtration plots for the filter having different pore sizes of coating layer.

natural (pH 7.98). The solid concentration is about 0.035% by weight. The crystalline phase of particles was detected by X-ray analysis as completely calcite.

3.3. Filtration testing

Fig. 5 shows the clarities of the filtrates with respect to filtering times through the filtration achieved with the varied pore sizes of filters. At the initial stage of filtration, the filters provided significantly different clarities. After long times of filtration (i.e., 800 s later), those filters supplied filtrate at about similar clarities, such as 0.2 NTU turbidity. Moderate and coarse size filters indicate similar turbidities, and at the initial stages, the turbidities are significantly higher than the fine size filters. Fine pore size filters indicate similar turbidities through the filtration proceeds; after a short filtration time (i.e., 200 s) the turbidity was observed at about 0.2 NTU turbidity and later stayed the same. The observed different turbidities through the filtration operation are attributed to the occurrence of medium clogging phenomena. At the initial stage of the filtration, the high turbidity filtrate produced with coarse pore size filter may be an indication of the occurrence of serious medium clogging.

The periodic mode of filtration is advantageous during the solid–liquid separation process, providing high separating capacities [1,4]. Fig. 6 presents the plots of the filtrate volume per cycle as a function of the number of cycles. It is obviously that the filter used for first time in filtration has high filtration

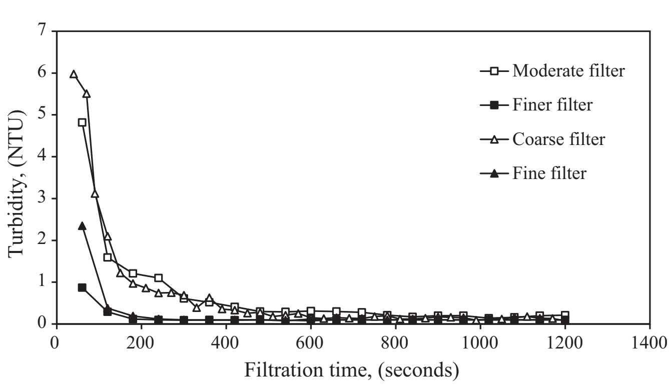

Fig. 5. The turbidity of filtrate obtained from different pore size of coating.

rates, thus the amount of filtrate for the first time cycle was not considered. After than the back-flushing pressure applied at about 1 bar is used successively for the filter cleaning and recovery where a constant fouling could be obtained in each of the filters. But, the filtration capacities are different. The coarse pore size filter is not economical and high capacity could be obtained with a moderate filter. It should be remembered that the filter does not produce clear filtrate as much as a finer pore size filter (see Fig. 5). If the clarity of the filtrate is important, a finer size filter should be used for the filtration studies.

The current results showed the following factors are thought to be responsible to obtain high filtration capacity with the new glassy ceramic filters: (i) the filters have low resistance to liquid flow where the substrate was formed by granules, (ii) for the conventional filters, the fine size pores increased the filtration resistance but the capillary filters did not display the same phenomena where the finer pores increased the capillarity and thus high filtration capacity was obtained, and (iii) the smooth pore walls (glassy nature) of the filter and its negatively charging (−25 mV) makes advantage for filter cleaning and recovery during backflushing where the marble waste solid particles is also being negative surface charge (−8.9 mV). At this point, the proposed mechanism was the compaction of particles within the filter pores being loose.

4. Conclusions

Some industries, such as marble fabrication, use a high volume of water and have great problems with the cost of fresh water or poor quality of the recycled water from thickening by flocculation. After gravity thickening, the filtration of overflow wastewater stream is necessary for producing high quality water. However, this technique requires a filter medium providing a high flux, easy cleaning and recovery, and, of course, a long lifetime in filtration. The recently fabricated glass-based ceramic membrane filters with multilayer compaction have potential materials; this is the significant conclusions: (i) the one stage new casting approach is a superior technique for fabrication of gradient compaction but it is limiting in terms of the production of finer pore size capillary filter. The problem is not great where the finely ground frit glass particles coated onto the filter and thus sufficient accomplishment is obtained (ii) high filtration capacity (8.1 m^3/m^2 in 5 min) with high clarity (~0.5 nephelometric turbidity units) could be obtained with a finer pore size of glassy filter (the pore size interval: 0.1–1.5 μm) where the filtration achieved at 5 bar pressure and filter recovery by backflushing produced at 1 bar, and (iii) it is possible to obtain a higher filtration capacity (8.5 m^3/m^2 in 5 min) with moderate pore size of glassy filter (the pore size interval: 0.2–4 μm), but at this time, the filtered water has slightly high turbidity; the average turbidity was measured as ~2.5 NTU).

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