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DIRECT FILTRATION OF MARBLE WASTEWATER BY GLASSY CERAMIC MEMBRANE FILTERS

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ABSTRACT

Marble factories use plenty of liquid in the processes of cutting, washing and polishing. Conventionally, pretreatment techniques such as coagulation and flocculation have been applied and the sediment has been dewatered by pressing. This study indicated the possibility of direct filtration of the wastewater by glassy ceramic membrane filters. The marble wastewater obtained from Afyon region has varied in sizes of particles in which 5% solids wt. are sub-micron in size and the maximum size of the particles is about 100 μm. Two different pore sizes of filters (the mean pore sizes being 1.15 μm and 0.4 μm) were tested for the filterability of marble wastewater stream through the periodic filtrate back-flushing process. The coarse pore size filter indicated filtration with seriously pore clogging phenomena, thus the filter recovery required ultrasonic application. The performance of the finer pore size filter is superior in which non-clogging phenomena could be obtained. The filtration capacity of the fine pore size filter was of 9 tons of filtrate per m^2 of the filter area through filtration conducted for one hour operation. Besides the high filterability, the filter proved highly clear filtrate (0.2 NTU turbidity).

Key Words: *Ceramic filter, filtration, wastewater*

MERMER FABRİKASI ATIK SUYUNUN CAM YAPILI MEMBRANE FİLTRELER İLE DOĞRUDAN SÜZÜLMESİNİN ARAŞTIRILMASI

ÖZET

Mermer fabrikaları kesme, yıkama ve parlatma gibi süreçlerde büyük miktarda su kullanmaktadırlar. Genel uygulama atık suyun ön hazırlama teknikleri, örneğin koagulasyon ve flokülasyon ile çöktürülmesi ve çöken kısmın filtre presler yardımıyla susuzlaştırılması şeklindedir. Bu çalışma atık suyun cam esaslı seramik membran filtreler ile doğrudan süzülerek kazanılmasının mümkün olduğunu göstermektedir. Afyon bölgesinden temin edilen atık suyun katı içeriği %5, buradaki katı 100 μm ile mikron altı boyutlara kadar değişen partiküllerden oluşmaktadır. Ortalama gözenek boyutu 1.15 ve 0.4 μm olan iki farklı cam yapılı membran filtre hazırlanmış olup, atık su periyodik geri yıkamalı filtrasyon sistemi ile süzülmüştür. İri gözenekli filtre süzme işlemi süresince tıkanmış ve filtrenin tam olarak temizlenebilmesi için ultrasonik yıkamaya ihtiyaç duyulmuştur. Buna karşılık ince gözenekli filtre tıkanmayıp yüksek filtrasyon performansı sağlamıştır. Filtrenin süzme kapasitesi her bir metrekare yüzey alanından bir saat süre içersinde 9 ton temiz su sağlanması şeklinde olmuştur. Filtrenin yüksek süzme kapasitesi yanı sıra sağladığı suyun berraklığı da yüksektir (0.2 NTU bulanıklılık).

Anahtar Kelimeler: *Seramik filtre, filtrasyon, atıksu*

1. INTRODUCTION

Marble factories use plenty of liquid in the processes of cutting, washing and polishing. These require a large volume of fresh water and the resulting wastewater leads to environmental problems. The high water consumption increases the plant cost. Recovering the water from wastewater treatment is not convenient for the water use in working machines and it is not environmentally friendly to discharge the water. Wastewater treatment, such as thickening by flocculation, is a commonly applied process, but the obtained water has high turbidity containing fine particles with polymeric species. Furthermore, purification of the recovered water is possible by membrane filtration but its cost is still high and the polymeric species adversely affect the filter performance; membrane clogging and blocking occurs and the cleaning and recovery of the filters can only be possible by chemical treatment, which also increases the cost of water processing. This study focused on to the filtration possibility of the marble wastewater stream with filtrate back-flush cleaning to enhance long-term filtration with high separation capacities.

Recently, glass-based ceramic membrane filters have been fabricated 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 wt.%, 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. Such composition 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 resultant 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 is 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 were sub-micron 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 compatibilities. The filtration processing of the sub-micron clay particles using relatively coarse pore size membrane filters has been a new approach. Significant success was achieved by the filtration operated in periodic mode through the filter material cleaned with filtrate back-flushing and flowing air-blowing processes.

Filtration is a major solid–liquid separation process in mineral, chemical and ceramic production industries and their wastewater treatments. The wastewater commonly has dilute slurries and contains varying sizes of solid particles without and with polymeric species due to the water used in the processes. Filtration of the dilute slurries is easy if the particles are only the solid types and are similar in sizes as well as being relatively large in size. If the water contains varying sizes of solid particles with sub-micron particles, then the structural properties of the used filter have great importance, such as the pore sizes, pore shape, smoothness of pore surface and hydrophilic nature. The finer-sized particles within the wastewater produce filtration with high migrating phenomena and lead to cake and filter medium clogging. Particles with different sizes and shapes lead to high compaction within the filter pores. The compaction phenomenon has a high significance for filtration operated during the periodic cycles in which the cleaning and recovery performance of the filter determines the fouling resistance of the filter media as either reversible or irreversible.

In cake filtration, the medium resistance itself (R_m) could be obtained directly by measuring the pressure drop across the filter medium (P_m):

$$R_m = P_m / \mu q \tag{1}$$

where q is the instantaneous superficial filtrate rate $\left(m^3 / m^2 s\right)$ and μ is the filtrate viscosity $\left(Ns / m^2\right)$. The pressure drop on the filter medium is measured by a sensor located at the cake–filter medium interface. The approach of the sensing probe located on the filter medium surface has limitations: the distance was given at about 0.4 mm above the filter medium [5]. Thus, the measured pressure drop is a composite value comprising the pressure drop of the filter medium itself and a cake layer adjacent to the filter medium.

Instead of direct measurement, the medium fouling resistance for constant pressure filtration could be obtained from the conventional cake filtration theory, which is based on a two-resistance-in-series (the filter medium resistance and the cake resistance) model [6]:

$$R_m = R - R_c \qquad (2)$$

where R_c is the cake resistance $(1/m)$ and R is the filtration resistance $(1/m)$. The filtration resistance can be expressed as:

$$R = P/\mu < q > \qquad (3)$$

where P is the applied pressure of the filtration (N/m^2) and $< q >$ is the average filtrate rate. The conventional cake filtration theory has been derived by assuming that the medium resistance (R_m) is constant and the cake resistance (R_c) depends primarily on the particle size of the material and the pressure drop across the filter cake. The analysis of the filtration data using the classical approach provides good fitting for the non-clogging filter medium or slightly medium clogging phenomena [5, 7–8]. If the medium clogging is serious and continues throughout the course of filtration, then this theory indicates an erroneous implication in which the predicted medium fouling resistance is unrealistic (negatively).

An alternative filtration theory, namely multiphase continuum theory, dictates that the least permeable part of the filtration system occurs at the cake–filter medium interface and controls the filtration system [9–10]. The permeability at the cake–filter medium interface is determined by keeping the cake pressure drop at a constant value. In that case, the sensor is located at the cake–filter medium interface and it measures the cake pressure drop. A constant cake pressure can only be achieved after a thin layer of powder has formed on the filter medium. Thus, the measured permeability at the cake–filter medium interface is again the indication of a composite value comprising the permeability of the filter medium itself and a cake layer adjacent to the medium.

In the filtration of dilute slurry, the filtration is controlled mainly by the filter medium resistance itself and its resistance after clogging by the migrated fine particles. The resistance of the skin layer occurring on the filter surface has also high significance. The porosity of the skin layer decreases by the migrated fine particles and thus its permeability significantly decreases through the longer filtration produced. The periodic filtration with high frequency back-flush cleaning is advantageous and thus such a filtration is an important part of the water treatment process, particularly in dilute slurries [11]. The second consequence of the fine particle migration is the occurrence of pore clogging, either with high compaction or loosely. In this study, these phenomena will be discussed for different pore sizes of glassy membrane filters.

In this study, the filtration of a marble wastewater stream without any pretreatment was studied using the recently fabricated glassy ceramic membrane filters with different pore sizes. The filtration was operated periodically with filtrate back-flush cleaning without and with ultrasonication. The cleaning and recovery performance of the filters is discussed with respect to their pore sizes.

2. Experimental

2.1. Filter preparation

Two different pore sizes of glassy filters, the mean pore sizes of 1.15 µm and 0.4 µm, were used for the filtration of a wastewater stream from the marble industry. The filters are cylindrical in shape and the external surface areas are about 100 cm^2. The fabrication procedure for the coarse pore size filter has been given in a previous study [12]. The filter was compacted by slip casting with a special casting routine to achieve gradient porosities.

The fine pore size glass filter was obtained by surface coating of the above glassy filter with the lead-borosilicate glass particles. The glass particles were prepared by attrition milling and sedimentation: after 2 hrs of milling, the slurry was settled and the fine-sized fraction was recovered and used as a coating material. The slurry was adjusted to a solid content of about 2 wt.%. The particle coating on the filter surface was achieved by stirred vacuum filtration under 0.1 bar of constant pressure differential. The filtration technique for the deposition of the particulate sol was preferred because of its advantage of yielding a uniform coating of the desired thickness onto a porous support [4]. The coating 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 hours. The filter was then sintered at 600°C at a rate of 5°C/min. for 40 minutes. The low sintering temperature was determined from the study of hot stage microscopy.

The microstructure of the filters was investigated by scanning electron microscope (LEO 1430VP). The pore size range of the filtering layers was determined by the mercury porosimetry technique (Quantachrome PoreMaster). The heat treatment of the glass components of the filters was determined by hot stage microscope (Misura ODHT–HSM 1600/80). The surface charge of the wastewater solid particles was measured by Zeta-meter (Malvern Zeta-Sizer Nano ZS) at about the natural pH. The surface charges of the filters were also investigated; for this purpose, the glassy components of the filters were prepared as follows: (i) lead-borosilicate particles were sintered in powder form at 600°C for 40 minutes and deagglomerated by gentle crushing in an agate mortar, (ii) a lead-borosilicate and zeolite mixture was shaped and sintered at 1000°C for 20 minutes and later ground into finer sizes. Then, the powders in an aqueous medium were used separately for surface charge measurement.

2.2. Filtration experiments

The wastewater stream was obtained from a marble company located in Afyon, Turkey. The water was filtered with glassy ceramic membrane filters using pressure filtration in 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 a previous study [4]. During the periodic filtration, the filter was removed each time from the filter chamber and compressed air was supplied through the filtrate discharge point without and with ultrasonic application. The back-flushing in the ultrasonic bath (Transsonic T 780/H) was operated with ultrasonic frequency at 35 kHz. The periodic filtration cycle was of 5-minute intervals. The applied trans-membrane pressure was of 5 bar. The filtrate back-flush pressure was studied through 1 and 3 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 [4]. In this study, the cleaning of filters was achieved only by the 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. The time for back-flushing was selected as a short time, such as 10 seconds, and thus no air flow was obtained from the filter pores.

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 on a turbidimeter (Merck Turbiquant 1500−T).

3. Results and Discussion

3.1. Microstructure of the membrane filters

Besides the glass-based microstructure, the recently fabricated ceramic membrane filters have multilayer compaction (Fig. 1). A filtering layer with a median pore size of 1.15 μm to a granular assembly up to 1 mm in size could be obtained. It is believed that this type of material used as a membrane filter for water filtration reduces the liquid flow resistance. The detailed fabrication procedure of the membrane filter has already discussed [12]. In this study, the filter was tested in filtration both in dead-end and periodic modes using the marble wastewater stream as a filtering material. This experimental study focused on the cleaning and recovery performance of the filter by filtrate back-flushing.

Fine pore size glassy filter has been obtained by coating the lead-borosilicate glass particles onto the silica-based substrate [13]. The sub-micron particles significantly narrowed in size (1.0 to 0.4 μm, as shown in Fig. 2). After the sintering processes, a porous coating was obtained (Fig. 3). Similar coating was also achieved onto the above multilayer glassy filter. The mean pore size of the coating was measured by Hg- porosimetry and found to be 0.4 μm.

3.2. Filtration testing

The wastewater stream obtained from the marble factory contained varying sizes of solid particles (Fig. 4). They consist of relatively large sizes (d_{50} = 15 μm) with smaller amounts of sub-micron particles (d_5 = 1.0 μm). The solid concentration is at about 0.69 wt.%. The crystalline phase detected by X-ray analysis is calcite (Fig. 5). A high migrating phenomenon is expected with the filtration of such material because of the lower solid content with the particles of varying sizes.

Figure 6 shows the clarities of the filtrates with respect to filtering times through the used filters with coarse and fine porosities. At the initial stage of filtration, the filters provided different filtrate clarities. At the later stages of filtration (i.e. three minutes later), those filters supplied filtrate at about similar clarities, such as 0.9 NTU turbidity. After a long filtration time (i.e. eight minutes later), the filtrate clarities for the two filters were the same and the filtrate clarities were superior (less than 0.2 NTU turbidities). 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 the coarse pore size filter may be an indication of the occurrence of medium clogging.

Figure 7 presents the filtration resistance versus the cumulative filtrate volume plots for the dead-end filtration of the wastewater stream. The filtration resistance is calculated from Darcy's resistance model (see Equation 2). The dashed lines indicate the resistances of the two filters for clear liquid flow. The fine pore size filter has high filter medium resistance; more than twice compared with the coarse pore size filter. It is obvious that the filtration rate is initially determined by the filter medium resistance itself and later by the occurrence of clogging phenomena as well as the resistance from the formed skin layer on the filter surface. The total filtration resistances, occurring during the filtration of the wastewater, are also given in the same figure. The coarse pore size filter indicates linear plotting except in the first initial stage, but the linearity with the fine pore size filter could be obtained after a longer time of the filtration procedure. The result with the fine pore size filter is attributed to the filter clogging phenomena.

The attribution of clogging phenomena with the fine pore size filter is questionable: (i) the filtered material contained smaller amounts of fine-sized particles, (ii) the wastewater did not contain particles finer than 0.3 μm in size, and (iii) the filtrate had low turbidity even at the initial stage of the filtration operation. Because of these results, it is necessary to discuss the occurrence of the types of filter medium clogging phenomena for the fine porosity filter. The initially observed different turbidity with the fine pore size filter is attributed to the occurrence of some pore clogging but the actual medium clogging occurred through the surface clogging of the pores; the fine particles migration occurred during the filtration operation and produced a skin layer at the cake–filter medium interface and adversely affected the filtration rates. With a high filter cake thickness, the migration does not occur sufficiently, so the filtration resistance increases only by the amount of cake deposition. The observed linear part of the resistance plot with the fine pore size filter is attributed to the insignificant migrating phenomena during the later stage of the filtration.

The periodic mode of filtration is advantageous during the solid–liquid separation process, providing high separating capacities [1, 4]. Figure 8 presents the plots of the filtrate volume per cycle as a function of the number of cycles. The back-flushing pressure applied as one bar is used successively for the filter cleaning and recovery through the filter having fine pore sizes in which almost the same filtrate could be obtained for each cycle. The coarse pore size filter used for the experiments was different: the obtained filtrate amounts decreased through the operation conducted as the following cycles, meaning that the back-flush cleaning of the filter was not sufficient. Then, the pressure for back-flushing was increased up to 3 bar. The process was again insufficient: only the amount of filtrate was increased. The success of the filter cleaning and recovery could be obtained through the back-flushing applied within the ultrasonic batch. At this time, the pressure achieved for back-flushing, such as one bar, is good enough for the filter cleaning and recovery.

The filtrate amounts obtained from periodic filtration were different for the two glassy filters. The coarse pore size filter provided significantly higher filtrate collection (see Fig. 8). It was mentioned previously that the high performance periodic filtration was obtained with an additional process for filter cleaning, such as ultrasonic application. The filtration capacity was, of course, low with the fine pore size filter but it did not require the ultrasonication during the filtrate back-flushing and the obtained cleaning and recovery was the best: almost the same filtrate amount was obtained for each periodic cycle. It should also be stated that the filtrate collection within each cycle was compared with the filtrate collection of the filter used for filtration for the first time, thus the obtained similar filtrate amount indicated that the cleaning and recovery performance of the filters is the best.

The above experimental results indicate that the high performance glassy membrane filter also requires the correct selection of the pore size for the used filter media with respect to the sizes of the filtered material. This indication is previously stated about the filtration of spring water using large pore sizes of glassy filters [4]. The large pores are filled by particles which vary in size and shape. The orientation and/or rearrangement of the particles within the pores leads to high compaction and the particles from the filter pores can only be removed by ultrasonication. The particles within the fine pore size filter will be of a relatively narrow size interval and their concentration is significantly lower. Besides, the smooth glassy surface with the negative charging of the filter surface and the waste particles leads to easy cleaning and recovery. At a natural pH, the measured zeta potential for glass surfaces and the marble waste solid particles is -25 and -8.9 mV, respectively.

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. Filtration of the wastewater stream without pretreatment is the most convenient technique 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 have the potential for the filtration of a large volume of wastewater. These are low-cost ceramic filter media which have been fabricated from inexpensive natural ceramic powders and have the desirable structural properties, such as a highly hydrophilic nature and a smooth pore wall surface. This study indicated that the cleaning and recovery performance of the glassy filters are significant, but the used pore size of the filter again has the main parameter for controlling the filter cleaning and recovery. The glassy pore wall filters have high performance if the pore clogging is poor. The serious medium clogging requires ultrasonication during the back-flushing.

The present study indicates that the periodic filtration of marble wastewater with glassy filters is superior through the correctly selected pore size of the filter in which high filtration performance could be obtained with the fine pore size filter. The significant conclusions are: (i) the cleaning and recovery of the filter are possible with only the filtrate back-flushing applied, (ii) it is possible to produce high clarity filtrate at about 0.2 NTU turbidity and (iii) the filtration capacities are of 9 tons of filtrate per m^2 of the filter area through filtration conducted for one hour in which the turbidity of the wastewater stream is of 800 nephelometric turbidity units (NTU).

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REFERENCES

[1] Şan, O and Hoşten, Ç., “Filtration testing of a ceramic capillary filter produced from a high-silica glaze”, Miner. Eng,, 15, 553–556 (2002).

[2] Şan, O., “Microstructural characterization of capillary filter produced from a high silica-containing glaze”, Mater. Lett., 57, 2189–2192 (2003).

[3] Şan, O and Yener, S., “Capillary filters produced from a quartz-natural zeolite-lead borosilicate frit”, Ind. Ceram., 25, 183–186 (2005).

[4] Şan, O and Özgür, C., “Fabrication of glassy ceramic membrane filters for filtration of spring water with clogging phenomena”, J. Membrane Sci., 305, 169–175 (2007).

[5] Hosten, C and San, O., “Role of clogging phenomena in erroneous implications of conventional data analysis for constant pressure cake filtration”, Sep. Sci. Technol., 34. 1759–1772 (1999).

[6] Tiller, F. M. and Crump, J. R., “Solid–liquid separation: An overview”, Chem. Eng. Prog., 65-75 (1977).

[7] Lee, D. J., “Filter medium clogging during cake filtration”, Am. Ins. of Chem. Eng. Journal, 41, 273–276 (1997).

[8] Şan, O., “Some filtration parameters of diluted TiO_2/water suspensions and the cake microstructure after sintering”, Ceram. Int, 32, 779–784 (2006).

[9] Willis M. S. and Tosun, I., “A rigorous cake filtration theory”, *Chem. Eng. Sci.*, 35, 2427–2438 (1980).

[10] Willis, M. S., “The interpretation of nonparabolic filtration data, in Encyclopedia of Fluid Mechanics”, (N. P. Cheremisinoff, Ed.), Gulf Publishing Co., Houston, TX, 839–864 (1986).

[11] Caroine, S. and Fitzpatrick, B., “Instrumentation for investigating and optimising filter backwashing”, *Filtr. & Sep.*, 69–72 (1998).

[12] Özgür, C. and Şan, O., “Slip cast forming of multilayer ceramic filter by fine particles migration”, *Ceram. Int.,* 34 1935–1939 (2008).

[13] C. Özgür, C., Şan, O. and Karagüzel, C., “Preparation of high performance capillary ceramic filter using frit glass powder”, J.G. Heinrich and C. Aneziric, Proc. 10 th ECerS Conf., Goller Verlag, Baden-Baden, 2116-2121, ISBN: 3-87264-022-4 (2007).

Figure Captions

Figure 1. SEM micrograph of the fracture surface of the high apparent density gradient glassy ceramic membrane filter.

Figure 2. Size distribution of the lead-borosilicate particles.

Figure 3. Microstructure of lead-borosilicate coating after sintering at 600 °C for 40 minutes.

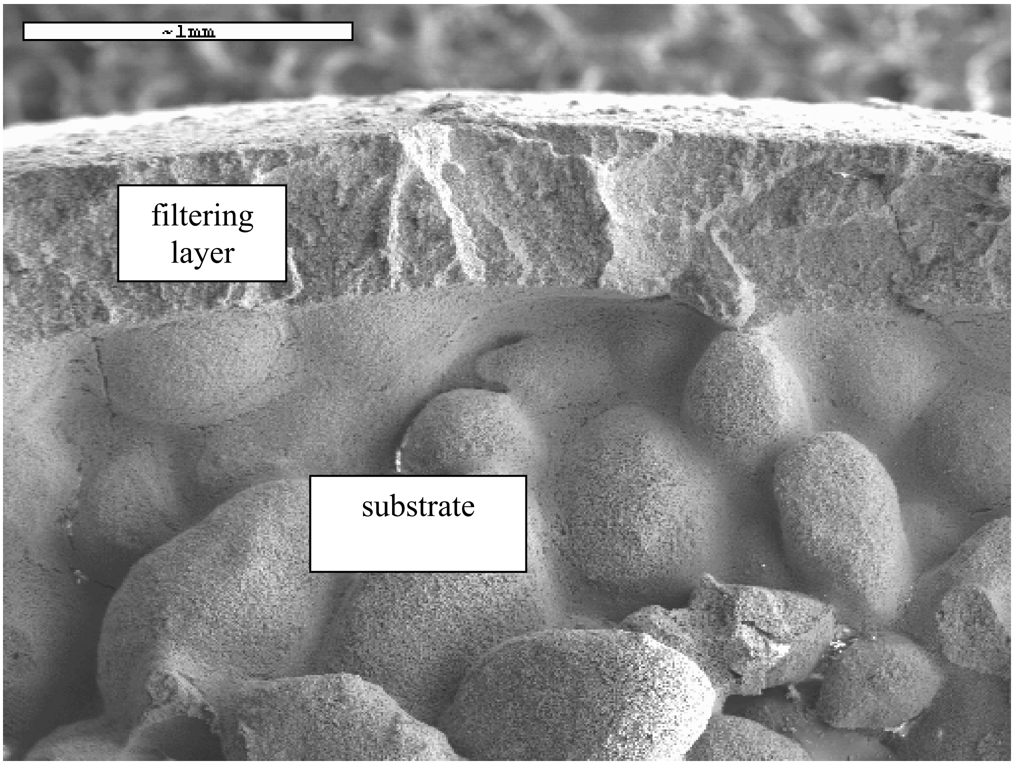
Figure 4. Size distribution of the solid particles in the marble wastewater stream.

Figure 5. Phase compositions of the particles in marble wastewater.

Figure 6. The turbidity of filtrates obtained from the filters with two different pore sizes.

Figure 7. Plots of filtration resistance versus filtrate for the filters with two different pore sizes.

Figure 8. Periodic filtration plots for the filters with two different pore sizes.



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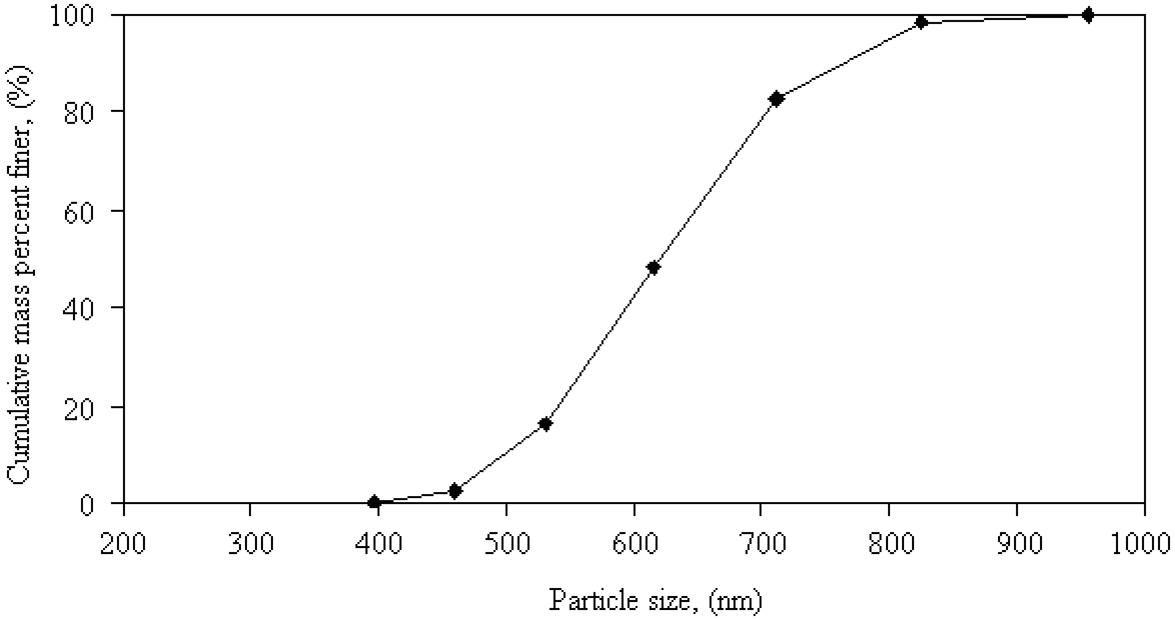


Figure 2.

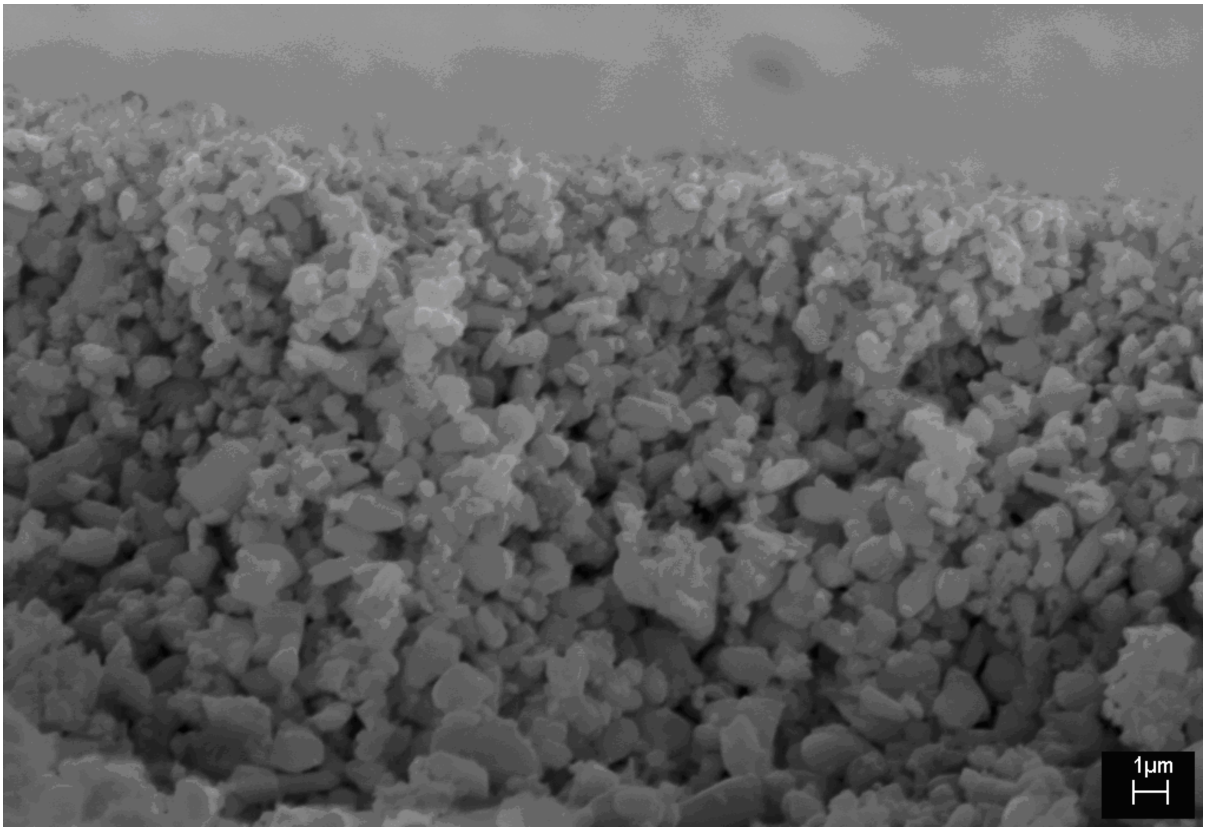
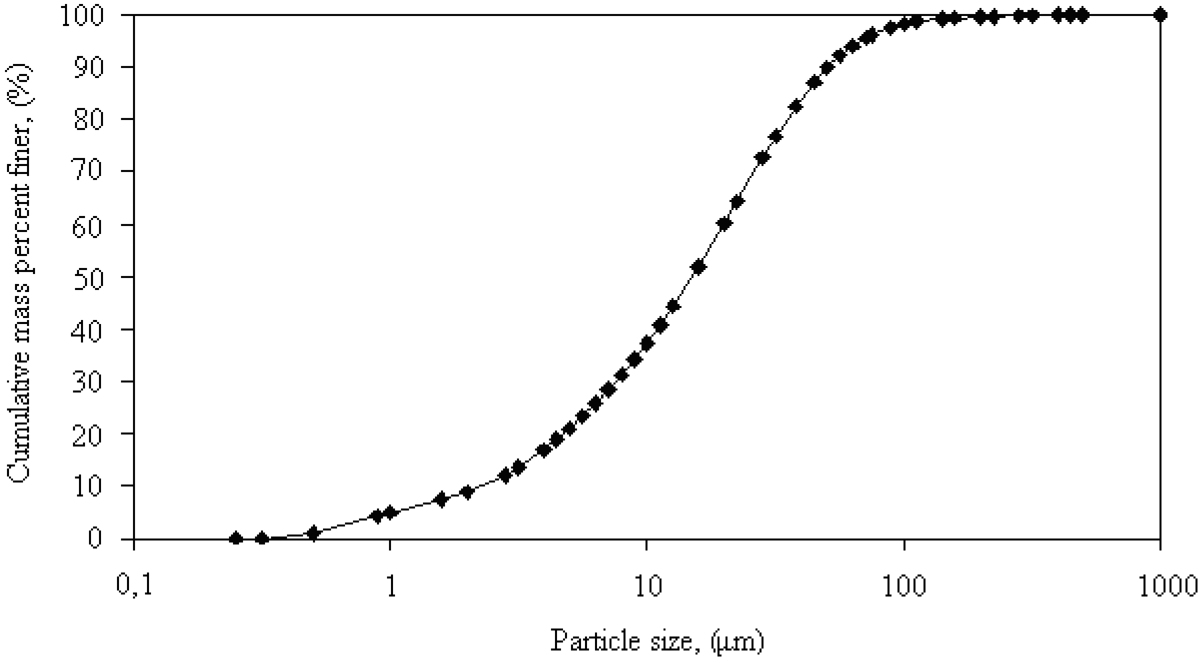


Figure 3.



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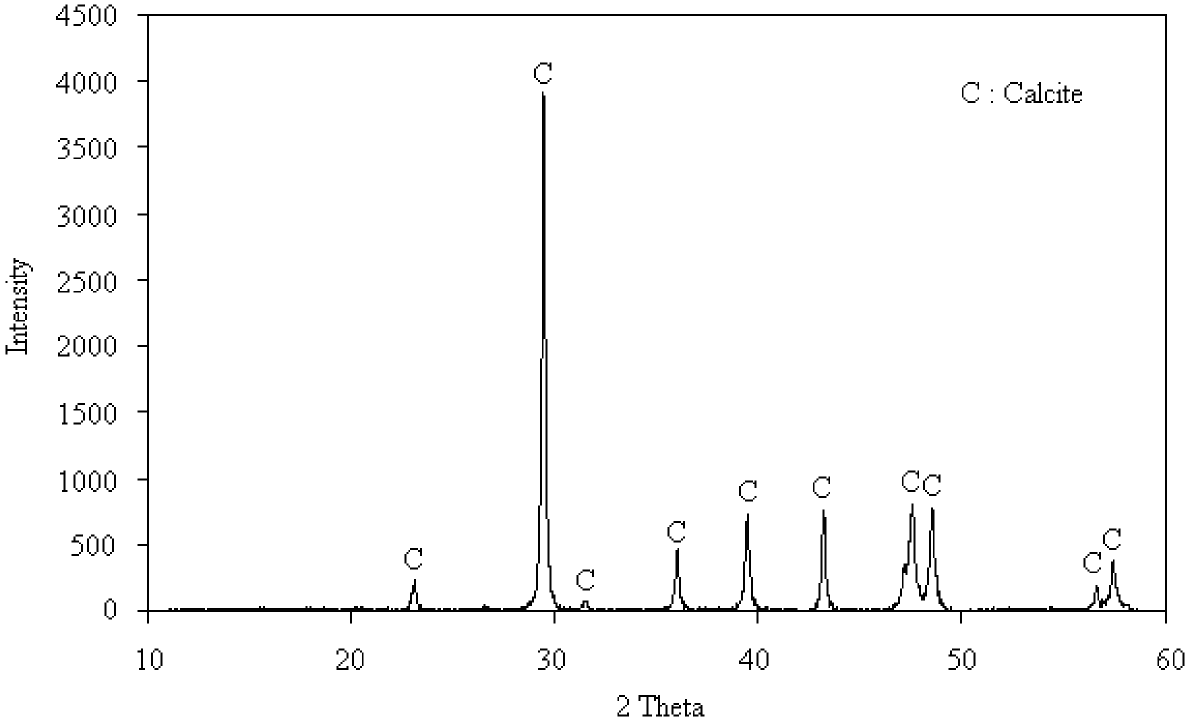

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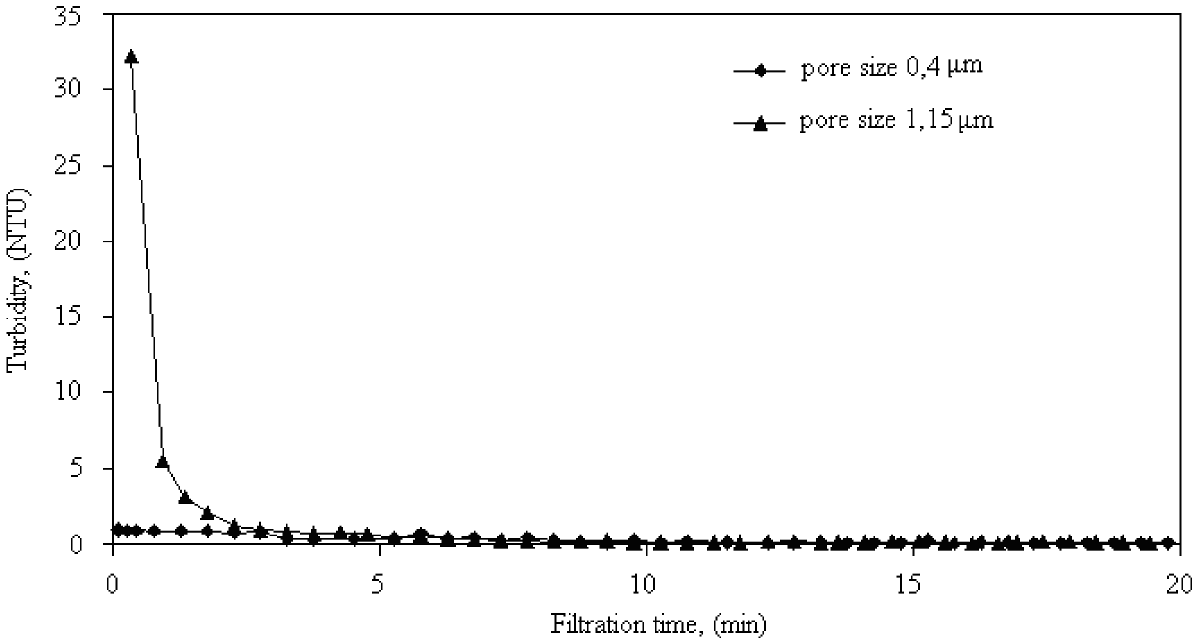

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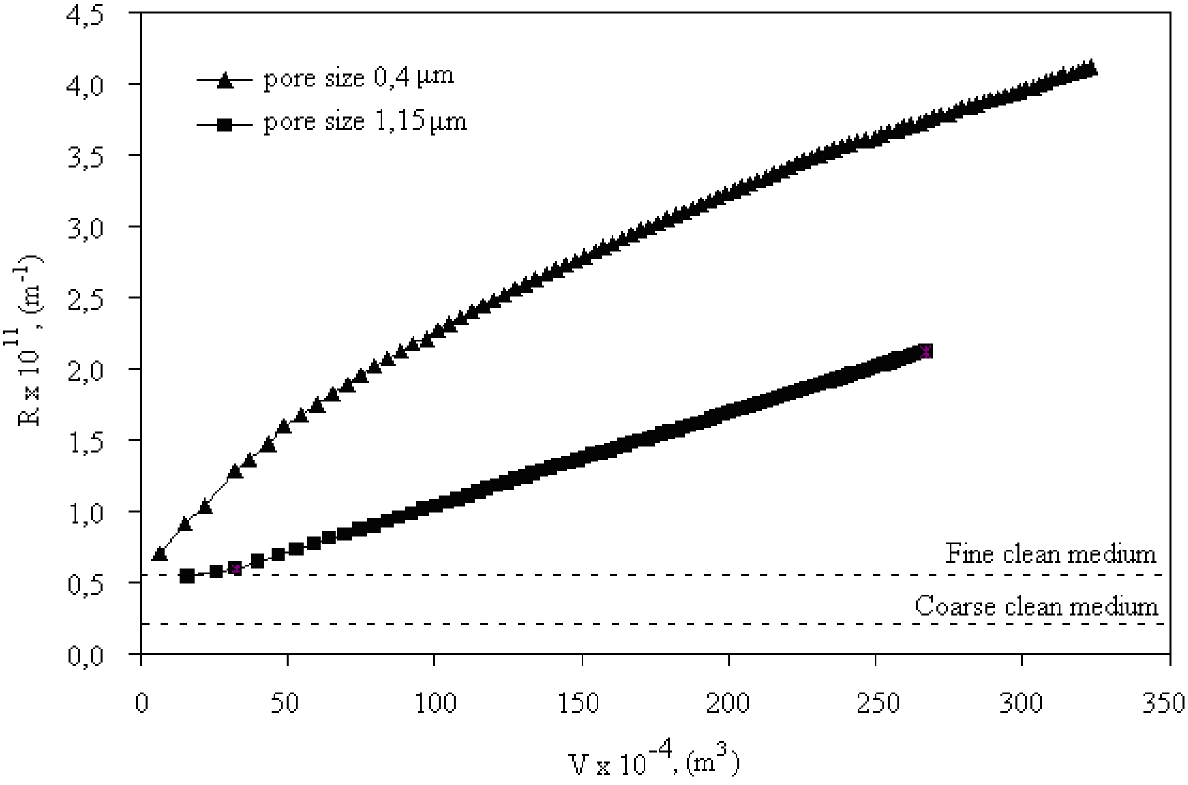

Figure 7.

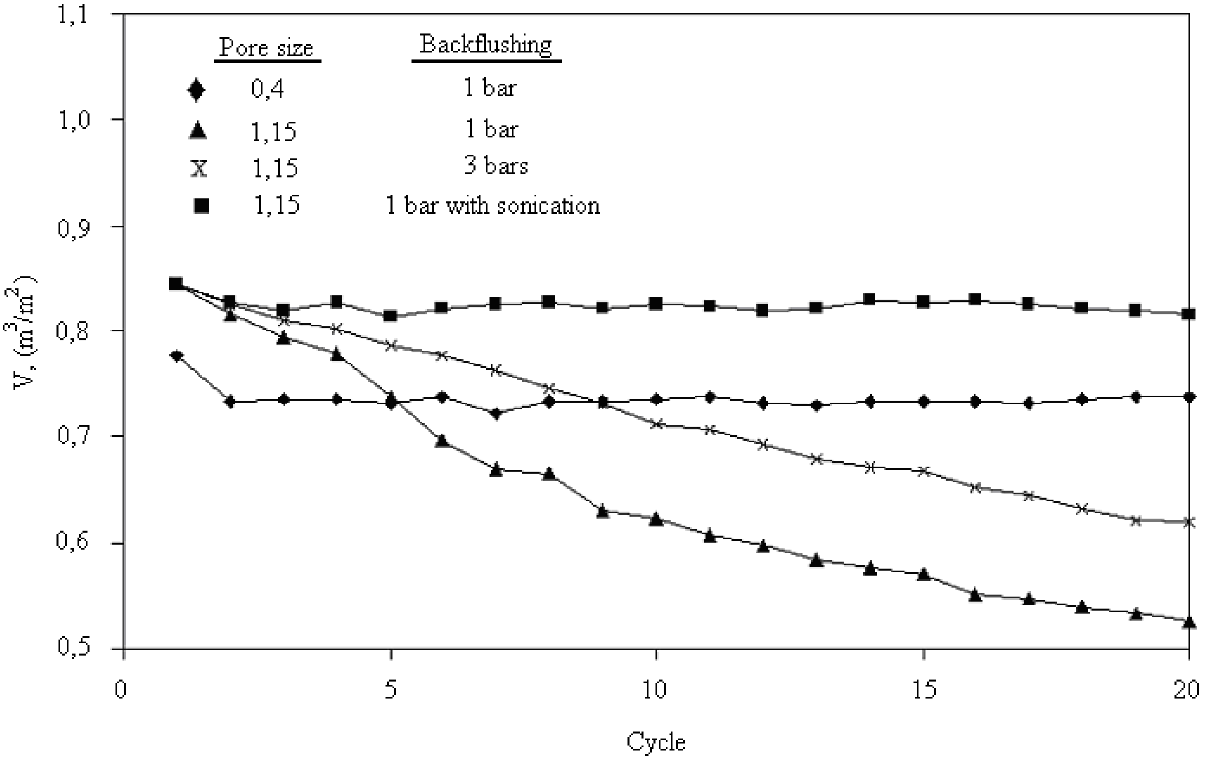
Pore size
Backflushing
♦ 0,4 1 bar
▲ 1,15 1 bar
x 1,15 3 bars
■ 1,15 1 bar with sonication
V, (m3/m2)
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0
5
10
15
20
Cycle

Figure 8.