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ScienceDirect
Ceramics International 37 (2011) 73–78
CERAMICS INTERNATIONAL
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Preparation and filtration testing of diatomite filtering layer by acid leaching

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Received 22 February 2010; received in revised form 26 May 2010; accepted 20 July 2010
Available online 22 August 2010

Abstract

Ceramic membrane filter consisting of the filtration layer obtained from natural diatomite particles (finer than 50 μm) by coating onto a large porosity support made of quartz-based materials was fabricated. The coating was achieved by pressure filtration at 5 bar and later sintering applied at 600 °C. The sintered product was leached by the hot acid solution (5 M HCl; 75 °C) for 1 h. The characteristic skeletal structure of diatomite (fine microscopic pores) could be obtained without deforming the structural integrity of coating. Filtration response of the filter was tested in dead-end and periodic pressure filtration modes. The filtered particles were of calcite (finer than 1.5 μm) obtained from a marble factory wastewater stream. The diatomite leaching increased the filtration capacity of the filter media more than two times. The filtrate has high clarity (0.1 NTU turbidity). The coating maintained structural stability during a filtration process performed at 5 bar and backflushing of 4 bar.

Keywords: Membrane; Diatomite; Leaching; Filtration; Wastewater

1. Introduction

Generally, the custom-made ceramic filters have two layers: a filter body (substrate), and its surface coating. The surface coating performs the separating function and the substrate beneath it serves as a support. Great attention has been continued on the coating layer where the layer must have high porosity, narrow pore size distribution and high structural integrity. Besides some other structural properties, the available pore area of the coating layer has great importance which determined the filtration capacities as well as the filterability of solid particles. Notably, the coating layer having more available and well-dissipate pores provide a parallel stream during filtration applications and thus high performance during solid/liquid separation could be obtained [1].

Fabrication of such a high permeable coating is possibly using the coating material being finer size of particles, otherwise the coated particles has opened porosities itself. It should be remembered that the fine size particles using as coating material required fine porosity substrate or more than one layer produced for obtaining low pore size in the external filtering layer. It is the fact that each additional stage of membrane fabrication increased the cost. On the other hand, a good coating with the finer particles initially requires preparing of a homogeneous mixture of particles, liquid, and additives, and the complementary stage is the forming process where the selected type of compaction and its process variables predominantly determine the characteristics of product densification. The suspension consisting of a dispersed phase can only permit particle rearrangement or compactions that result in the formation of a dense uniform green microstructure. Instead of the conventional application, the present approach shows the possibility of obtaining highly permeable coating with relatively coarse sizes of particles. In here diatomite particles are used as the coating material which contains numerous fine microscopic pores, cavities and channels, and therefore the material leads to production of highly permeable coating layers.

It is not easy to use diatomite particles as a coating material where the high-grade diatomaceous earth containing a minimum of about 95% diatomite ($SiO_2 \cdot nH_2O$) is less abundant in nature and mostly the diatomite materials contains alumina with the other impurities. The natural material has impurities such as

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0272-8842/$36.00 © 2010 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2010.08.030

calcium which directly coats the surface of diatomite particles and limits the use of this material for filtration application [2]. In some cases, the impurities are less but their effect on sintering is great. Recently, some porous ceramics obtained from diatomite powders contained minor amounts of impurities such as smectite and kaolinite, but the material led to products of highly variable porosities after sintering [3]. It is clearly reveals that the impurities cause fusion during high temperature sintering and closes the microporosities.

Normally, calcination (at about 600 °C) of the diatomite particles increased the powder qualities [4,5] but this process did not open the fine microscopic pores in being the diatomite particles. At this point, different application is proposed that the diatomite coating was achieved using raw powder and sintering applied at the calcination temperature and later, leaching performed through the porous mass product. This type of processing will provide the high permeable coating, but the structural integrity of the coating is adversely affected by the leaching process as well. Normally, the leaching damages the coating integrity so badly.

Besides the above problem, this study is aimed to fabricate a highly permeable coating layer using natural diatomite particles. For this purpose some specific processes are considered: (i) coating material partially filled the substrate pores, (ii) coating produced by filtration technique and (ii) a glassy nature of substrate is used. It is the fact that the coating is not necessarily on the substrate-surface, it may be produced within the substrate pores and the coating on the substrate-surface is so thinner. The production of a thinner coating is advantageous, in which low filtration resistance could be obtained during filtration operations and the filter could easily be cleaned by backflushing. Another advantage of the thinner coating is the sintering processing; high integrity could be obtained between the substrate and the coating material. The mechanism of thick coating is differently which required approximately the same thermal expansion between the substrate and coating materials, however the thin coating tolerated some diverge expansions.

The filtration technique is selectively applied for the fabrication of diatomite filtering layer. It is a preferred technique because of its advantage of yielding a uniform coating of the desired thickness onto thin, porous supports [6–9]. The particulate packing is profoundly controlled by the applied external force, suspension rheology and the micro-structure of substrate material (pore size, shape, distribution and available pore area). High compaction could be obtained with well-dispersed particles and with a high pressure application. The high compaction is necessary for complete and uniformly densification.

This study used a glassy nature of substrate material where the glassy component strongly binds the coating particles by melting at relatively low temperatures. On the other hand, the raw diatomite has contained some impurities and thus those helped the sintering. In light of these, the calcination temperature may be good enough for the diatomite coating. If the above-mentioned diatomite coating is successful, a high performance ceramic filter has been obtained by a low cost ceramic powder and with less capital investment and also being simple process. This makes the filter wide used in liquid/solid separation. The filtration performance of filter also tested in dead-end (conventional cake filtration) and periodic (thin-cake formation followed by backflushing) filtration modes, with the use of submicron size of calcite particles carried from wastewater stream.

2. Materials and methods

The composition of substrate material was designed as 93.50% SiO_2, 1.53% Al_2O_3, 0.57% MgO, 0.17% Fe_2O_3, 3.27% CaO, 0.52% K_2O, 1.1% Na_2O and 0.35% CaO. It was prepared using powder mixtures of quartz, natural zeolite (clinoptilolite), soda silica glass and calcium carbonate. The substrate was formed as a tubular form using relatively coarse particles (finer than 75 μm). The particles were wetted with water for agglomeration and sieved through the aperture size of 45 μm, and the agglomerates were shaped by uniaxially pressing at 650 kg/cm^2, and sintered at 1100 °C for 1 h to provide sufficient mechanical strength. The external surface area of this tubular porous support was of 190.8 cm^2.

The coating material was a raw diatomite obtained from the Kütahya region of Turkey. The main chemical composition was as follows (wt.%): 68.08 SiO_2, 17.99 Al_2O_3, 4.22 MgO, 3.36 Fe_2O_3, 1.32 K_2O, 0.98 CaO, 0.67 Na_2O and 0.29 TiO_2. The sample was ground in an attrition mill for more than 1 h using alumina balls. The slurry was dried in 105 i°C for 24 h, and then stored. The coating was of a colloidal suspension (0.1% solids by weight) and achieved by pressure filtration (see Fig. 1). The coating was achieved at 5 bar of filtration pressure. The thickness of coating was varied; the first coating was operated for the filtration time that the collection of filtrate was measured as 400 ml (thin film coating), the second coating was produced for 800 ml filtrate collection (moderate thickness). The thick coating was performed for the filtrate amount gained 1000 ml. The coated substrates were first air-dried overnight in a room at 60% humidity, and then kept in ambient conditions for a day and finally oven-dried at 105 °C for 12 h. The coatings were

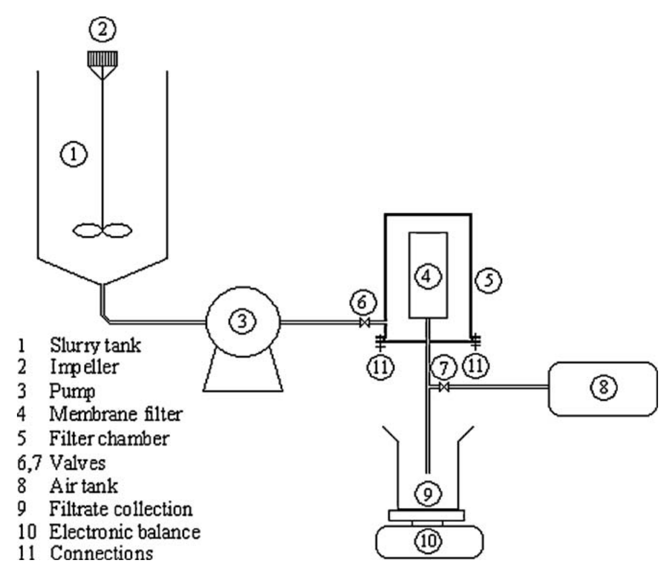

Fig. 1. A schematic drawing of the filtration setup.

then sintered at 600 °C at a rate of 3 °C/min and 20 min of densification time.

2.1. Leaching of the filtering layer

The above filter is potential to use in water filtration. On the other hand, it is also potential material for production of much more permeable during filtration. The diatomite particles after leaching indicated highly porous microstructure [10,11]. The leaching applied for the diatomite particles those were in acid solution and continuously stirring was proceeds. By this way, some impurities covering the fine microscopic pores of the diatomite particles were removed. The present study is differently where the leaching will be applied to the mass product; the particles coated onto a silica-based substrate and later applied the leaching processing.

The mass product leaching has great difference than the freely particles where the hot-acid solution was recycled through the filter mass. A schematic layout of the leaching experimental setup is shown in Fig. 2. The filter chamber was made of a glass tube of 12 cm diameter and 18 cm height, which was placed on a magnetic stirrer plate. The chamber was initially filled with the acid solution and heated to the desired temperature. The prepared filter material was placed into the acid solution, and first time the acid flowing through filter pores was achieved with vacuum pump (65 kPa) while the slurry was being continuously stirring. Later the acid flowing maintained without the pumping because of the difference of the filter chamber and discharging point of the acid solution which was settled at about 100 cm below.

2.2. Filtration experiments

The marble wastewater was obtained from the Afyon region of Turkey. The wastewater was settled and the fine particles obtained from overflow stream were filtered through the diatomite filters produced with and without leaching. The filtration was in conventional cake filtration and periodic filtration modes. The conventional filtration experiments were conducted on the same setup which was previously prepared for the filter coating studies (see Fig. 1). 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 cycle was 5-min intervals and applied pressure for filtration mode was of 5 bar and the backflushing being 4 bar. The filtrate within the connected pipe was removed from the system by backflushing through the filter; after that the compressed air flow completely cleaned the filter pores.

2.3. Evaluation and characterization

The study of the samples included: (i) chemical composition measurement by X-ray fluorescence (Spectro X-LAB 200), (ii) crystalline phase identification by X-ray analysis (Rigaku Miniflex powder diffractometer employing Cu Kα radiation in $2\theta = 10–65°$ at a ganiometer rate of $2\theta = 2°$/min), (iii) particle size determination by laser particle size analyzer (Malvern Mastersizer 2000), (iv) microstructural analysis using a SEM (Zeiss Suprat 50), (v) measurement of porosities by immersion technique according to Archimedes' principle, and (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 on a turbidimeter (Merck Turbiquant 1500 T), (vii) acid resistance of the substrate material was determined in which the hot acid solution (75 °C; 5 M HCl) recycled through the substrate pores under 0.1 bar pressure difference for 1 h and later the weigh of substrate before and after leaching was weight.

3. Results and discussion

The substrate pictures and pore size of the materials were given in Figs. 3 and 4, respectively. The substrates were shaped as tubular by pressing. The pore size has varied between 5 and

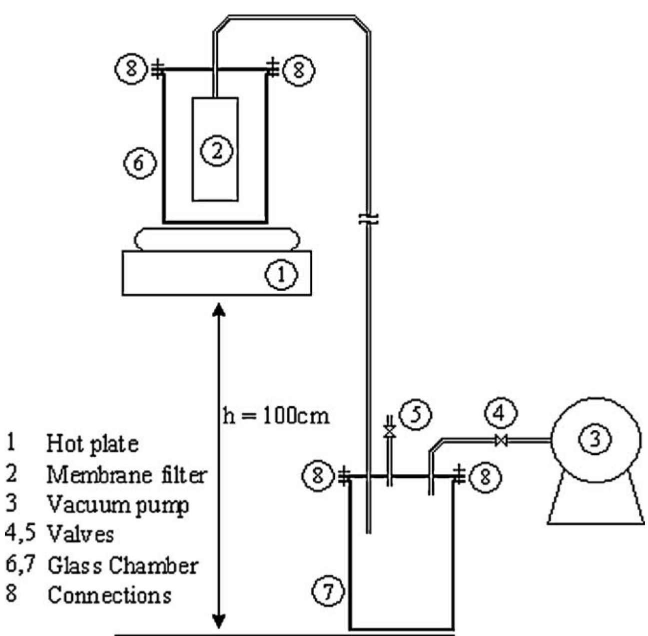

Fig. 2. A schematic drawing of the leaching setup.

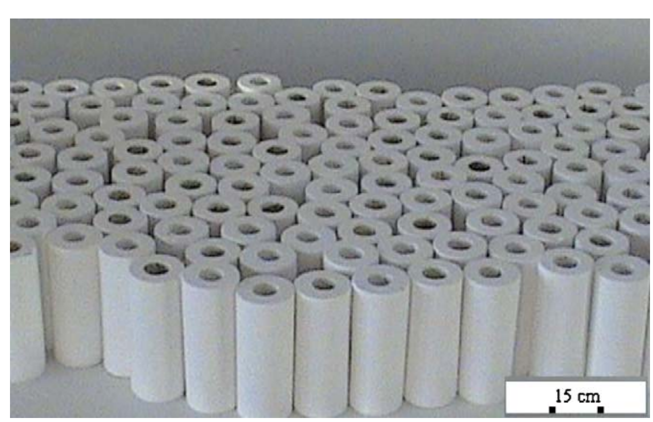

Fig. 3. Photos of the tubular porous substrates.

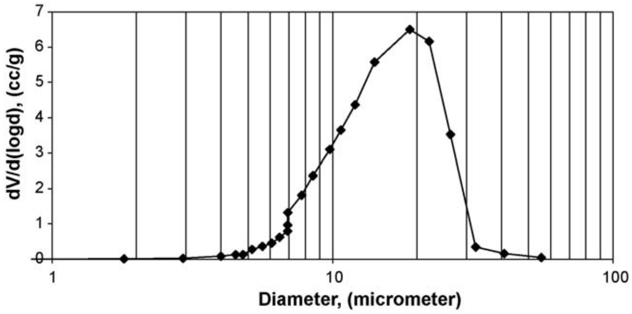

Fig. 4. Pore size distribution of the substrate.

30 μm with some coarse and fine pores. The amount of apparent porosity was measured by Archimedes technique and found as 42%. The dimensions (5 cm of diameter and 12 cm of high), pore size and their porosities are good enough for the materials used as membrane substrates. Consequently, the substrate was high silica-containing (93.50 wt.% SiO_2) and thus sintered material attained a glassy nature. Similar compositions were studied previously and obtained that the microstructure was of grains coated by glass [8,9,12]. The glassy pore microstructure should have high acid resistance. In here such testing was produced on the present substrate and obtained that the substrate has the same weight before and after the leaching operation where the experiment was conducted with the same leaching condition for the substrate without coating.

The diatomite particles used as coating material was ground through the attention that the particle size being close value with the maximum pore size of the substrate material (see Figs. 4 and 5). By this way, the particles filled the substrate pores could be obtained. In here, a clogging phenomenon of filtration coating was designed because of the partially filling of the diatomite particles within the substrate pores which produced denser layer at the surface could be obtained. Fig. 6 shows fracture surface of the diatomite coated membrane filter. The coating produced with less time coating (thin layer). It is clearly shown that the substrate pores filled by the diatomite particles during the filtration coating to yield narrower pore entrances at the surface. The coating is shown significantly thin (see Fig. 6) but the diatomite particles completely covered the substrate-surface (see Fig. 7). The

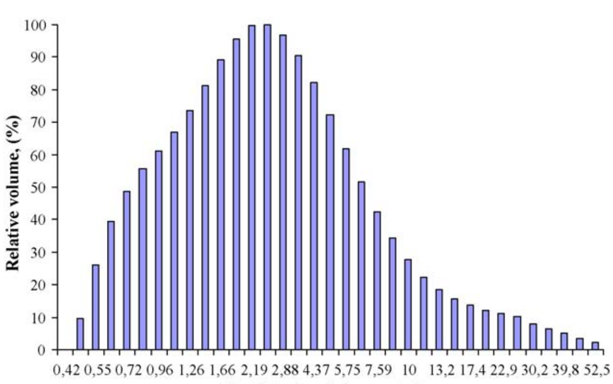

Fig. 5. Size distributions of the diatomite particles for coating.

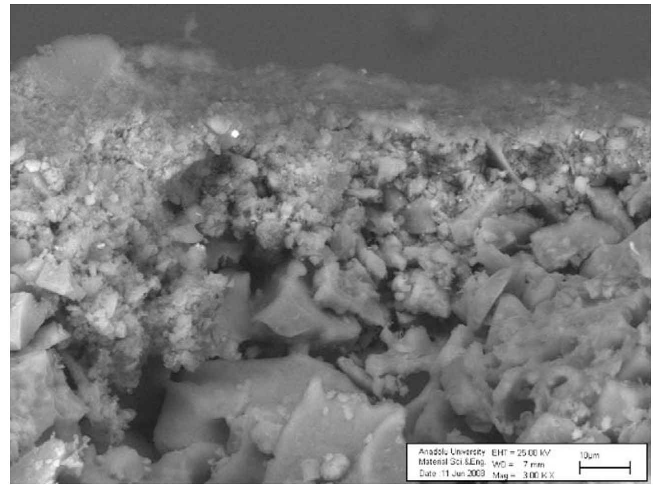

Fig. 6. The SEM photograph of the typical edge of the ceramic membrane filter for thinner coating.

thickness of coating was increased (moderate thickness), at this time, some crack was observed which can be detected by scanning electron microscopy. The thick coating produced large cracking and can be seen by eyes. These results indicated that the only thin coating is successful for the membrane fabrication.

Fig. 8 shows the surface picture of the diatomite coated filter. This picture focused on the investigation of grains microstructures where we are looking the characteristic skeletal structure of the diatomite particles after sintering where the sintering applied at 600 °C produced either the microscopic pores opened or not. The diatomite particles are shown to be densely; some impurities have been deposited on the particles. It is obviously that the impurities covered the diotamite particles and those were not melted during the sintering. Thus, the application of 1 h of leaching is good enough for remove of the impurities where the skeletal structure of diatomite could be obtained after the leaching for 1 h (see Fig. 9). It is clear that such a microstructure has high permeability during water

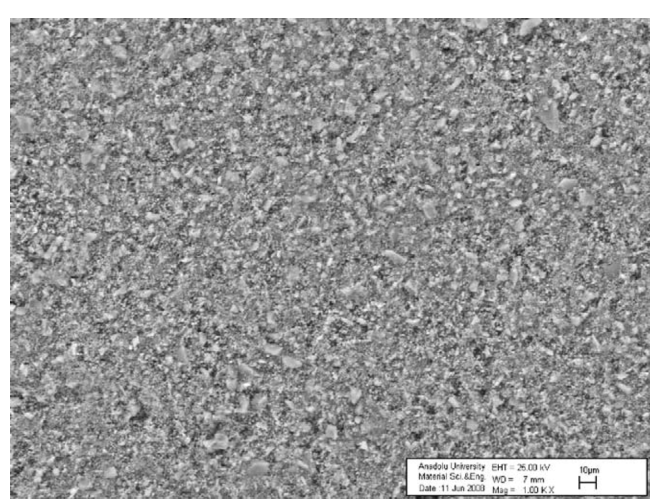

Fig. 7. The SEM photograph of the surface of the ceramic membrane filter after coating.

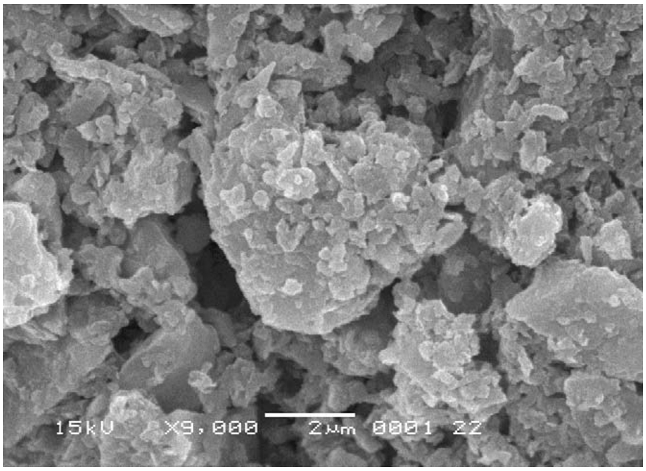

Fig. 8. The SEM photograph of the diatomite particles from surface of the coating before leaching.

filtration studies where the number of pores at the filtering layer was increased.

3.1. Filtration testing of the membrane filters

The filters produced with and without leaching were tested for fine particles supplied from marble wastewater stream. The wastewater obtained from the marble factory contained varying sizes of solid particles. They consist of relatively large sizes ($\delta_{50} = 15$ μm) with smaller amounts of submicron particles ($\delta_5 = 1.0$ μm). The solid concentration is at about 0.69% by weight. The crystalline phase detected by X-ray analysis was calcite. The wastewater was settled in a thickener without pretreatment (coagulation or flocculation) and obtained that the oversize waste containing fine size of particles (see Fig. 10) with the solid content having the turbidity at about 187 NTU. The settling time of the wastewater was not too much; it was applied for 7 min and obtained effectively settling.

The waste contained submicron calcite particles were filtered using the presently fabricated filters. Fig. 11 shows

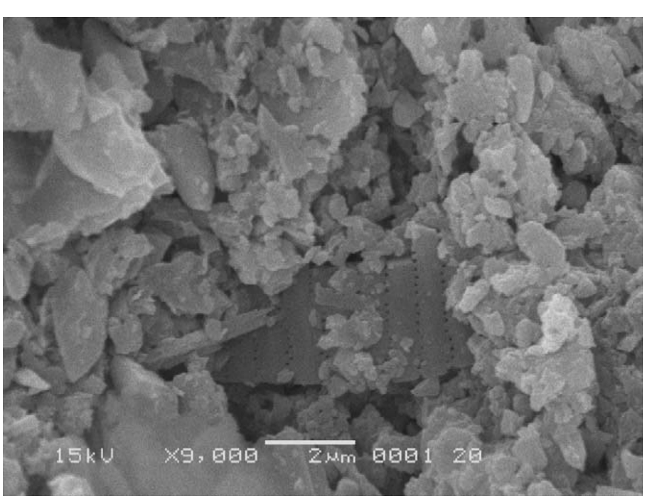

Fig. 9. The SEM photograph of the diatomite particles from surface of the coating after leaching.

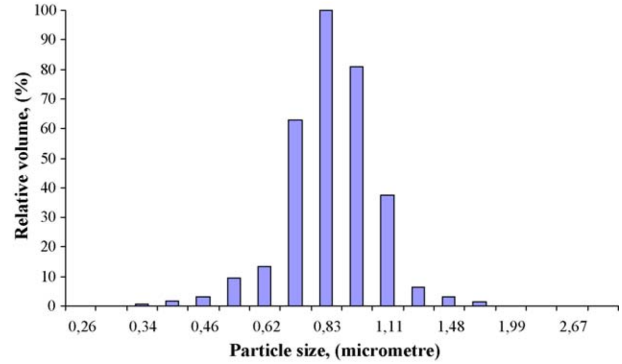

Fig. 10. Size distributions of the marble wastewater stream (overflow from thickening by gravity).

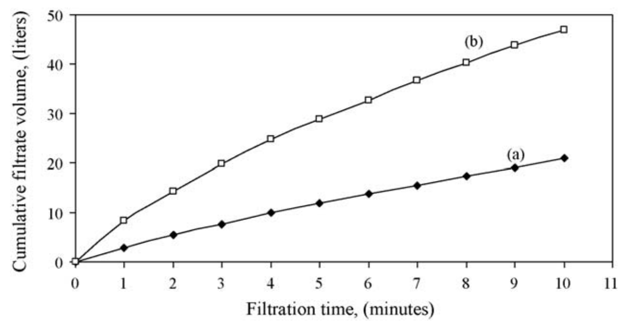

Fig. 11. Filtrate collection versus filtration time for the diatomite coated filter without (a) and with (b) leaching.

the total filtrate collection versus filtration times. Significant difference was observed between the diatomite filters with and without leaching; the diatomite purification by leaching increased the filtration capacity more than two times. The filtrate turbidities were also taken and observed that the leaching increased the turbidity but not significantly (see Fig. 12). It is pleasantly that the fine microscopic pores of the diatomite particles proved non-clogging filtration and thus advantageously to use of this material for filtration of fine size particles.

The above good result alone is not enough for the filter used industrial applications. The filter should be cleanable with a simple technique such as backflushing. Actually, the high filtration capacity could not be continued through the longer

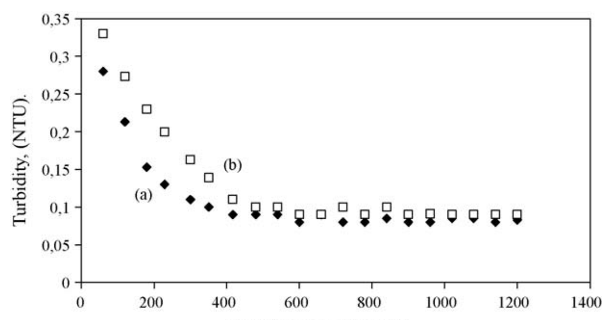

Fig. 12. The turbidity of filtrate obtained from the diatomite filter without (a) and with (b) leaching.

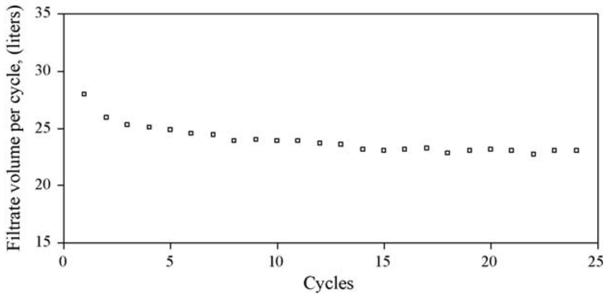

Fig. 13. Periodic filtration plots for the leached diatomite filtering layer.

time of filtration in which the surface pores of filter media filled with fine particles and formed a skin layer. The less permeable part of the system decreased the permeability. Thus, the formed cake on the filter surface should be removed periodically. In this study, cleaning of the filter media was applied by combined filtrate backflushing and air blowing outside the filter unit. The backflush pressure was applied at 4 bar and the cleaning performance of filter was examined. Fig. 13 presents plots of the filtrate volume per cycle as a function of number of cycles. It is clear from the plots that the membrane provided is at about the same filtrate amounts, meaning that the present membrane filter could be cleaned effectively.

It should be noted that the diatomite coating after leach proceeds has high integrity where the backflush cleaning of filter serviced was of 4 bar. The high integrity may due to followings: (i) coating was greatly produced within the substrate pores, (ii) diatomite impurities with the glassy pore produced good wetting during the sintering (at 600 °C) and (iii) filtration coating produced dense compaction and thus high efficiency could be obtained during the sintering.

4. Conclusions

Highly porous coating onto a ceramic substrate can be successfully prepared from raw diatomite particles where sintering applied at 600 °C and later hot-acid (75 °C and 5 M HCl) leaching produced for 1 h using the acid solution which recycled through the mass product by low pressure (0.1 bar) filtration. The success can be explained by the structural integrity of the diatomite coating after leaching operation where the coating maintained the structural stability for 4 bar of backflushing. These following salient conclusions related to the substrate, coating and leaching operations can be advanced: (i) the substrate prepared from a high silica-containing glaze where the obtained pores were of interconnected to each other and grains were coated by glass. This type of microstructure sufficiently for coating and provided high sinterability with low temperature, (ii) the substrate pores were relatively large for filling the diatomite particles into the pores where the high structural integrity could be obtained after sintering, (iii) filtration technique was advantageously during the coating where the diatomite particles migrated through the substrate pores and produced a dense compaction at the surface pores and thus obtained high integrity, (iv) the hot-acid solution recycled through the filter pores and thus obtained high performance leaching, thus less time leaching produced high permeable filter material.

The filtration performance of the present filter was examined using submicron size of calcite particles from a marble wastewater stream. The filter media was produced more than two times higher filtration capacities than the coating without leaching. Additionally, the obtained filtrate has high clarities (~0.1 NTU). The filter is also cleanable with backflushing and air blowing. The periodic filtration experiment of the marble wastewater showed that the filter (5 cm of diameter and 12 cm of high) provided ~23 l of filtrate through the filtration conducted at 5-min intervals at 5 bar pressure.

Acknowledgement

The authors acknowledge with sincere gratitude the financial support provided by the Turkish State Planning Organization (DPT) project 2003K120380.

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