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ORIGINAL ARTICLE

New ceramic microfiltration membranes from mineral coal fly ash

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Ceramic microfiltration membrane;
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Abstract This work aims to develop a new mineral porous tubular membrane based on mineral coal fly ash. Finely ground mineral coal powder was calcinated at 700 °C for about 3 h. The elaboration of the mesoporous layer was performed by the slip casting method using a suspension made of the mixture of fly ash powder, water and PVA. The obtained membrane was submitted to a thermal treatment which consists in drying at room temperature for 24 h then a sintering at 800 °C. SEM photographs indicated that the membrane surface was homogeneous and did not present any macro defects (cracks, etc.). The average pore diameter of the active layer was 0.25 μm and the thickness was around 20 μm. The membrane permeability was 475 l/h m^2 bar.

This membrane was applied to the treatment of the dying effluents generated by the washing baths in the textile industry. The performances in term of permeate flux and efficiency were determined and compared to those obtained using a commercial alumina microfiltration membrane. Almost the same stabilised permeate flux was obtained (about 100 l/h m^2). The quality of permeate was almost the same with the two membranes: the COD and color removal was 75% and 90%, respectively.

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1. Introduction

Ceramic membranes are used in the crossflow filtration mode, which allows maintaining a high filtration rate compared with the direct-flow filtration mode used in conventional filtration process.

Thermal, chemical and mechanical properties of ceramic membranes give them significant advantages over polymeric ones (Chan and Brownstein, 1991). Conventionally, alumina,

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Nomenclature

P_{inlet}	inlet pressure (bar)	J_{f}	permeate flux (l/h m^2)
P_{outlet}	outlet pressure (bar)	J_{w}	water flux (l/h m^2)
P_{f}	filtrate pressure (bar)	TMP	trans-membrane pressure (bar)
J_{w}	water permeate flux (l/h m^2)	τ	shear stress (mPa)
L_{p}	water permeability (l/h m^2 bar)	D	shear rate (s^{-1})
COD	chemical oxygen demand (mg/l)		

zirconia, titania and silica are considered as the main materials of commercialized ceramic membranes (Tsuru, 2001). Unfortunately, these membranes are too expensive for a technico-economic point of view. For example, in the environmental field, great volumes of wastewater are generally treated. So, the use of membrane separation techniques requires a great membrane area. Recently, the development of low cost ceramic membranes based on natural materials such as clays and apatite appeared as an efficient solution to treat waste water at a low cost (Weir et al., 2001; Masmoudi et al., 2005; Bentama et al., 2002, 2004; Khemakhem et al., 2007).

Mineral coal fly ash obtained from coal-fired power stations could be also a good material to make low cost membranes. Indeed, this way allows a good management of this subproduct which represents a major problem in many parts of the world due to the resulting pollution. It is noticed, by the same way, that significant quantities are being used in some range of applications like in construction and other civil engineering applications (Mulder, 1996) where fly ash is used as a substitute for cement in concrete (Asserman and Bentur, 1997). During the past years, some researches have been performed concerning the integration of fly ash in the manufacture of bricks and tiles which use a large volume of silicate-based raw materials (Carty and Senapati, 1998; Palmonari and Nassetti, 1994). Conventional porous ceramic products prepared using only fly ash have been also investigated (Ilic et al., 2003; Barbieri et al., 1999). Little research work has focused on upgrading this material in the membrane preparation field like the preparation of stainless-steel/fly ash membrane suitable for hot gas cleaning (Jo et al., 1996).

This work describes the elaboration worth on ceramic fly ash microfiltration membrane applied to the clarification and the decolouration of the effluents coming from the dying industry.

2. Experimental

2.1. Materials and methods

2.1.1. Characterisation of the fly ash powder

The fly ash powder used was obtained by calcination at 700 °C of a finely ground mineral coal. The particle size analysis of the powder was determined using the Particle Sizing System AccuSizer Model 770 (Inc. Santa Barbara, CA, USA). The grinding of the mineral coal was performed using a planetary crusher at 300 revolutions/min.

A Hitashi Scanning Electron Microscope (SEM) was used to study the powder morphology as well as the microstructure formed in the sintered material. The chemical composition of the powder was determined by spectroscopic techniques: X-ray fluorescence for metals and atomic absorption for alkaline earth metals. Phases present in the powder composition were analysed using an X-ray diffractometer (Siemens, Germany) with Cu K_α radiation ($\lambda = 0.154$ nm).

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the fly ash powder were carried out at temperature ranging between 0 and 1000 °C at a rate of 5 °C/min under air.

2.2. Membrane elaboration

The slip casting process was applied to form a microfiltration layer based on mineral coal fly ash, coated on a macroporous support, previously elaborated in our laboratory from the same material with the following characteristics: a mean pore diameter of 4.5 μm and a porosity of 51%.

2.3. Slip casting process

The active microfiltration layer from fly ash was prepared by a slip casting process on fly ash support (closed-end tubes of 150 mm in length, with an inner diameter of 5 mm) in dip solution containing the powder and an aqueous solution of polyvinyl alcohol (PVA) (Rhodoviol 25/140 (Prolabo)), used as a binder. Fig. 1 describes the slip casting process. It consists of:

- Putting in suspension the mineral powder in water.
- Adding a binder (12-wt% aqueous solution of PVA) and homogenisation by a magnetic stirring.
- Coating the support for a few minutes at room temperature. In the case of the tubular membranes, the tube was closed at one end and filled with the solution.
- Drying is carried out for 24 h at room temperature.

2.3.1. Composition and characterisation of the slip

In order to make a slurry solution suitable for the slip casting, empirical study was performed to select the optimum composition. The optimised slip composition was based on a rheological study using a viscosimeter LAMY model TVe-05 (five shear speeds were used) and the SEM observation of the sintered layer obtained according to a fixed temperature–time schedule previously determined using clay material (Khemakhem et al., 2007).

The investigation was focused on the uniformity of the coating deposited on the inner surface of the macroporous support. The optimum composition was shown in Table 1.

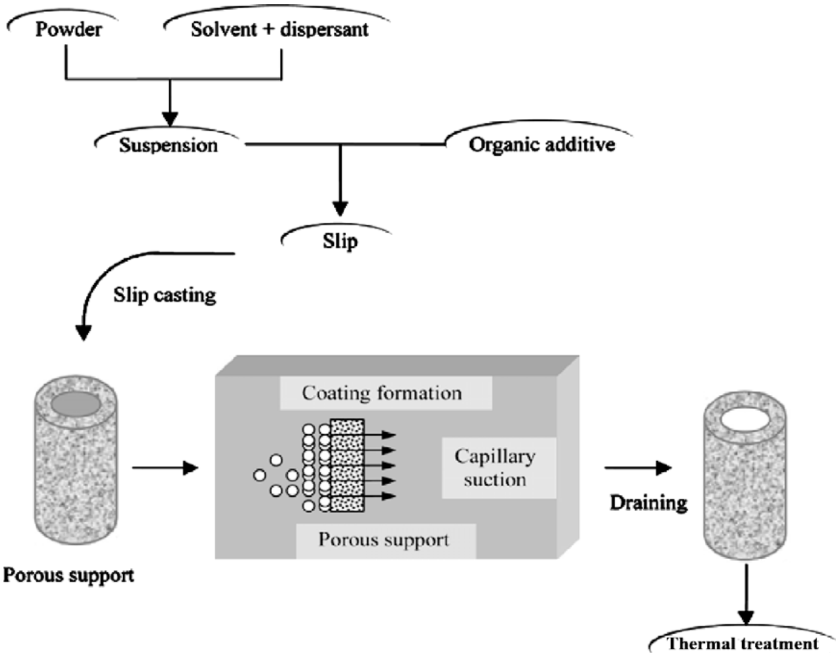

Figure 1 Showing scheme of a slip casting process.

Table 1 Composition of the slurry solution.

Component	Conditions	Proportion (wt%)
Water	Deionised	66
Polyvinyl alcohol (aqueous solution)	12% aqueous solution	33
Fly ash	Particle size < 5 μm	4

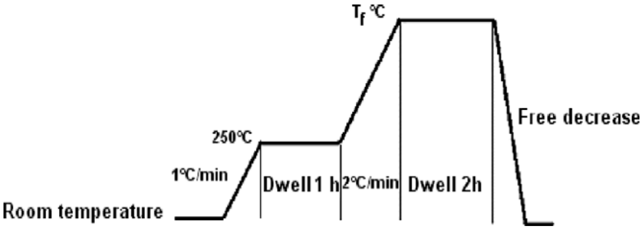

Figure 2 Shown the temperature–time schedule used in the active layer sintering.

2.4. Sintering program

The firing temperature, fixed at 800 °C, is reached following the program shown in Fig. 2. A temperature plate at 250 °C for 1 h is necessary in order to completely eliminate the PVA, which is in great quantities in the slip. A relatively slow temperature increasing rate (2 °C/min) was needed in order to avoid the formation of cracks on the layer.

2.5. Membrane characterisation

The average pore diameter of the active layer was determined by mercury porosimetry on a Micrometrics Autopore II9220 V3.05. The membrane texture was characterised by scanning electron microscopy (SEM).

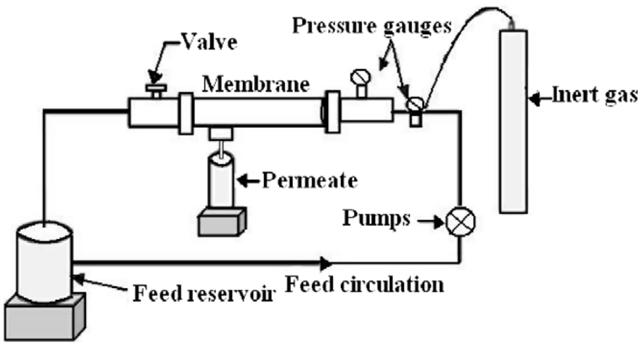

Figure 3 Shown the scheme of the pilot plant.

2.6. Filtration tests

Crossflow microfiltration tests were performed using a home-made pilot plant (Fig. 3) at a temperature of 25 °C and transmembrane pressure (TMP) range between 1 and 4 bars. The transmembrane pressure was controlled by an adjustable valve at the concentrate side. The flow rate was fixed at 1.76 m s^{-1}. Before the tests, the membrane had been conditioned by immersion in pure deionised water for at least 24 h. The duration of each test ranged from 1 to 3 h.

2.7. Effluents characterisation

The microfiltration membranes have been applied to wastewater treatment coming from the dying industry. Conductivity, absorption (using an “OPTIMA SP-3000” UV–VIS spectrophotometer at a λ = 600 nm, since the raw effluent color is blue) and pH measurements were performed.

3. Results

3.1. Fly ash characterisation

3.1.1. Chemical composition and particle size distribution

The chemical composition of the fly ash is given in Table 2. The majority of the used fly ash (82.4%) consists of SiO_2, Al_2O_3 and Fe_2O_3. The other percentage is a mixture of different alkali metals.

The fly ash powder obtained by calcination of the finely ground mineral coal at 800 °C showed a particle size diameter less than 2 μm (Fig. 4). Fig. 5 shows that the particles size distribution of the powder used for the elaboration of the microfiltration layer is homogeneous within the interval 0–5 μm. However, it appears that a majority of the particles are sized between 0 and 1 μm which is in accordance with the particle size distribution diagram of Fig. 4.

3.1.2. Thermal analysis

The DSC–TGA data shows that the mass loss is around 1.5% (Fig. 6) which is due to some impurities and the small percentage of unburned mineral coal powder, since the phenomenon started at 250 °C and lasted until it reached 800 °C.

3.1.3. Phase identification

XRD data for a sample sintered at 800 °C are shown in Fig. 7. The major crystalline phases identified were quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), hematite (Fe_2O_3) and mullite ($3Al_2O_3{\cdot}2SiO_2$). A minority of anhydrite ($CaSO_4$) can be seen on the spectrum.

Table 2 Chemical composition of the used fly ash.

Elements	Proportion (wt%)
SiO_2	49.09
Al_2O_3	24.34
Fe_2O_3	8.93
CaO	4.88
MgO	3.15
K_2O	1.74
SO_3	2.15
LOI[a]	1.07

[a] Loss on ignition.

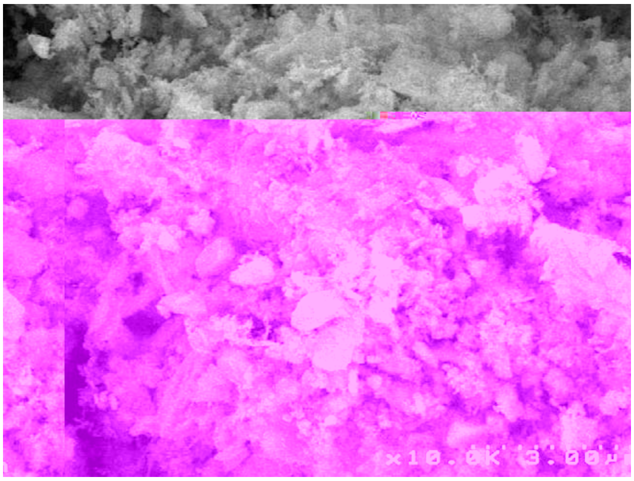

Figure 5 SEM picture of fly ash powder after calcination of a finely ground mineral coal at 700 °C.

3.2. Membrane characterisation

3.2.1. Slip characterisation

Three slips with a percentage of 4% of fly ash and three different rates of PVA (30%, 39% and 45%) were prepared. The rheological data of the three compositions are given in Fig. 8 which represents the curve of shear stress (τ) versus shear rate (D). Fly ash slip was found to exhibit a rheo-thickener behaviour, controlled by the presence of PVA. The decrease of PVA percentage leads to the maintenance of particles in a stable suspension.

3.2.2. Scanning electron microscopy

Slips S1 and S2 were used to prepare an active layer on the macroporous support. The same casting time was used during the slip casting operation. The sintering conditions, previously mentioned, were respected. Figs. 9 and 10, which show SEM pictures for surface and cross-section of respectively S1 and S2 elaborated layers, give information about the thickness

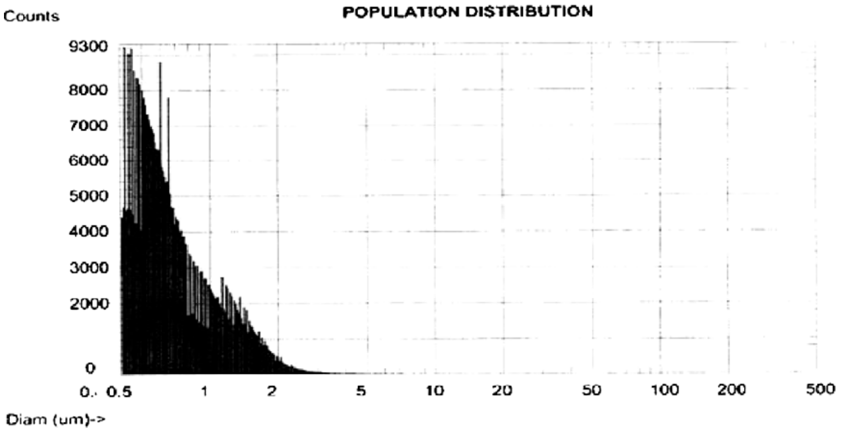

Figure 4 Fly ash particle size distribution.

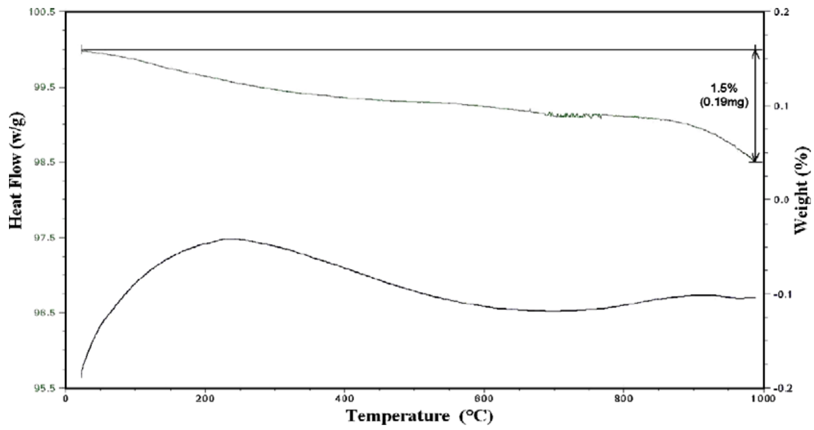

Figure 6 DSC-TGA data of the fly ash powder.

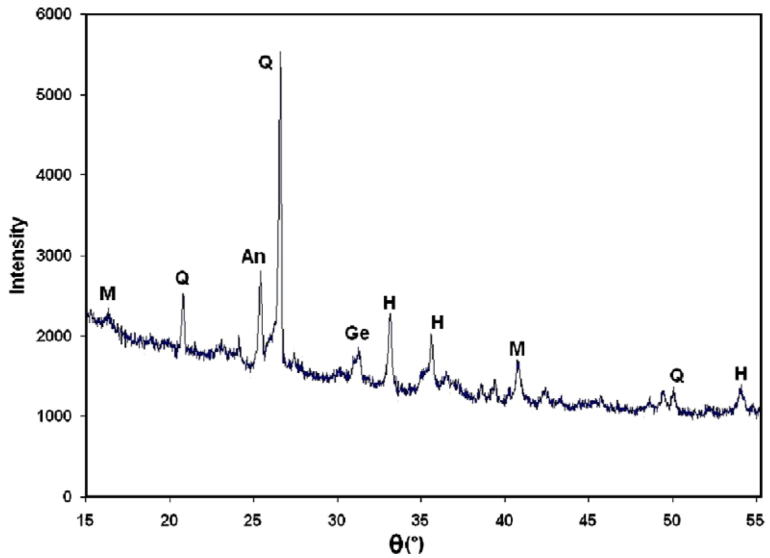

Figure 7 XRD pattern of fly ash powder fired at 800 °C (Q = quartz, M = mullite, An = anhydrite, Ge = Gehlenite, H = Hematite).

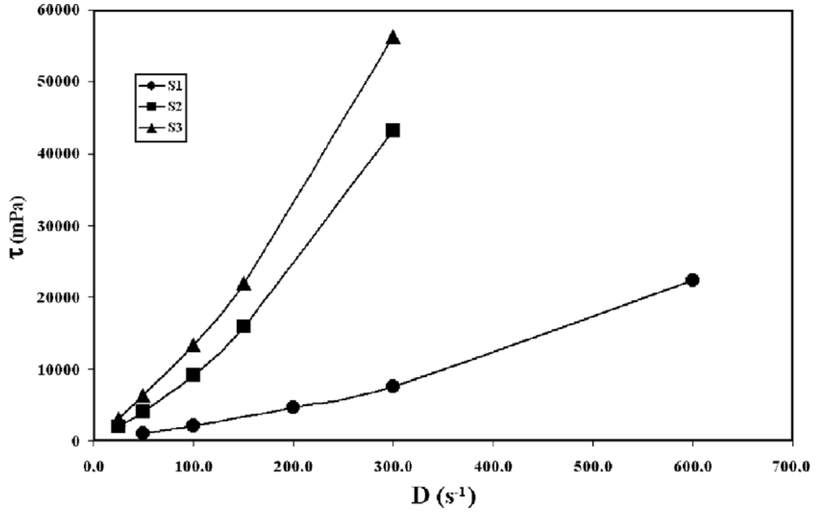

Figure 8 Evolution of the shear stress (tau, τ) versus shear rate (D) for different PVA percentages in fly ash slip: –●– (S1: 4% fly ash/66% water/30% PVA), –■– (S2: 4% fly ash/57% water/39% PVA), –▲– (S3: 4% fly ash/51% water/45% PVA).

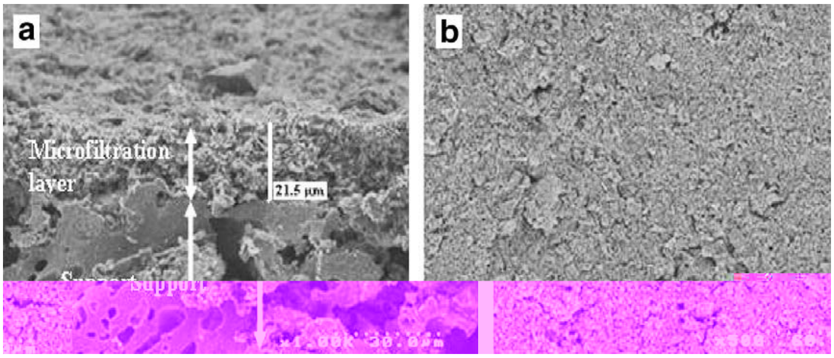

Figure 9 SEM micrographs of the optimised active layer obtained with the slip composition S1 (4% fly ash/66% water/30% PVA) and sintered at 800 °C. (a) Cross-section and (b) surface.

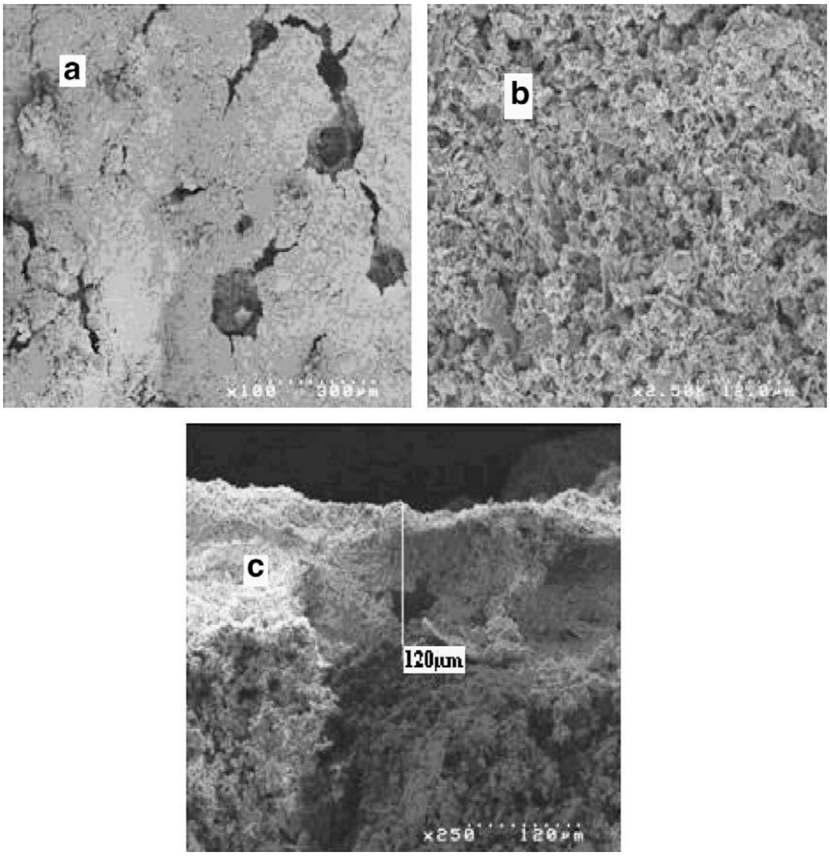

Figure 10 SEM micrographs of the multi-defects active layer obtained with the slip composition S2 (4% fly ash/57% water/39% PVA) and sintered at 800 °C. (a) and (b) surface views with different magnitudes and (c) cross-section.

and texture. For S1 slip, a defect-free microfiltration membrane was obtained with a layer thickness of around 20 µm. However, as regards to S2 slip, a multi-defect layer was noticed (a thick layer with many cracks).

3.2.3. Determination of the porosity

Porosity and pore size distribution were measured by mercury porosimetry. This technique is based on the penetration of mercury into a membrane's pores under pressure. The intrusion volume is recorded as a function of the applied pressure and then the pore size was determined. The pore diameters measured were centred near 0.25 µm for the deposited microfiltration layer (Fig. 11).

3.2.4. Determination of membrane permeability

The membrane permeability (L_p) can be determined using the variation of the water flux (J_w) with the transmembrane pressure (ΔP) following the Darcy's law:

$$J_w = L_p \cdot \Delta P,$$

where $\Delta P = [(P_{\text{inlet}} + P_{\text{outlet}})/2 - P_f]$; P_{inlet} = inlet pressure; P_{outlet} = outlet pressure; P_f = filtrate pressure.

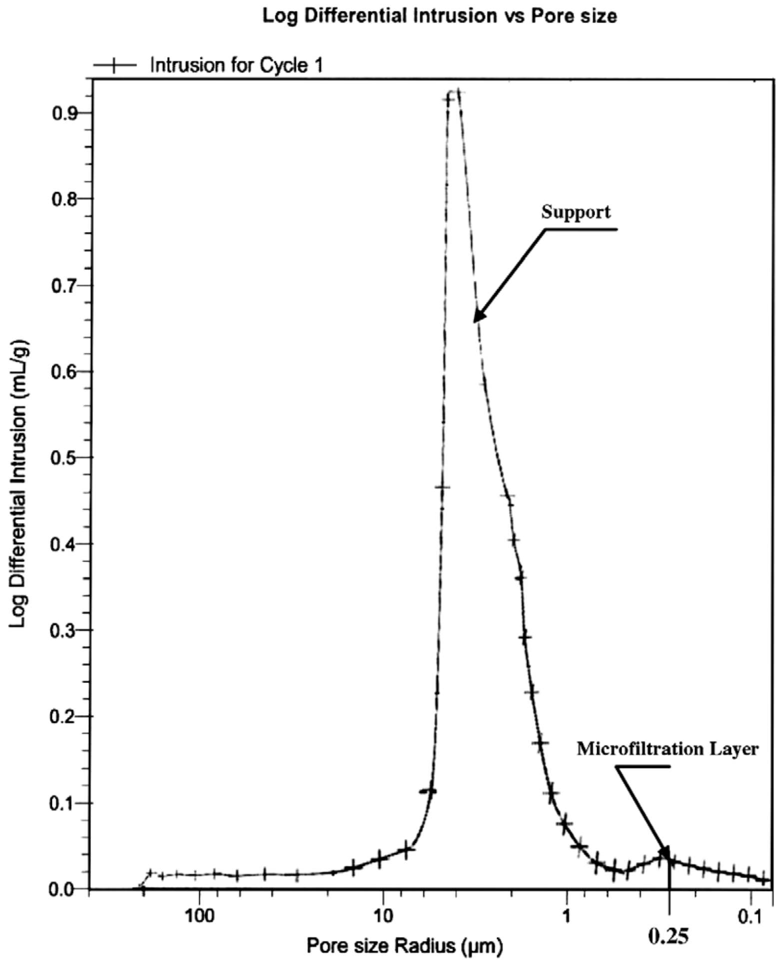

Figure 11 Pore diameters of the fly ash membrane.

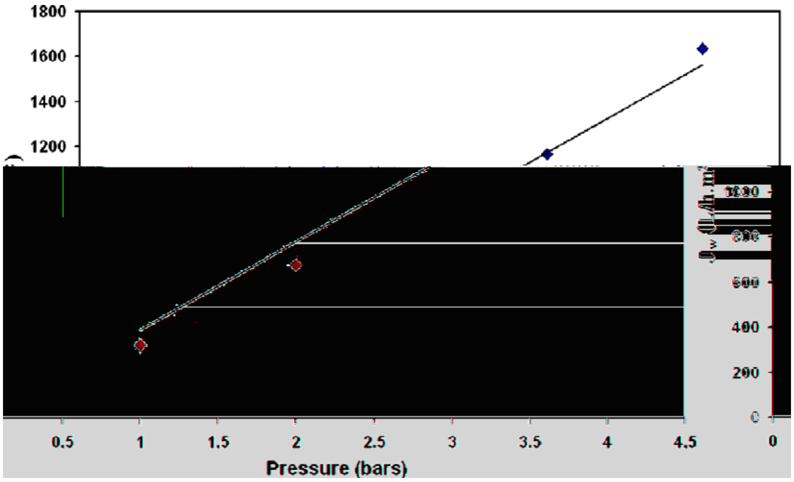

Figure 12 Water fluxes versus working pressure.

It can be seen that the water flux increases linearly with increasing applied pressure (Fig. 12). The membrane permeability (L_p) was found to be equal to 475 l/h m^2 bar.

3.3. Application to the treatment of textile dye waste water

The treatment of industrial waste water can be achieved by membrane process. Thus, microfiltration was used in this study

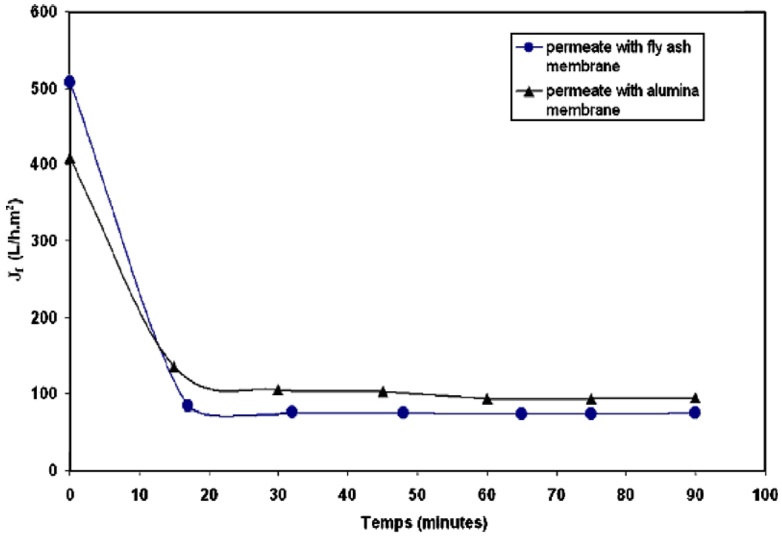

Figure 13 Variation of permeate flux with time (T = 25 °C, TMP = 1 bar).

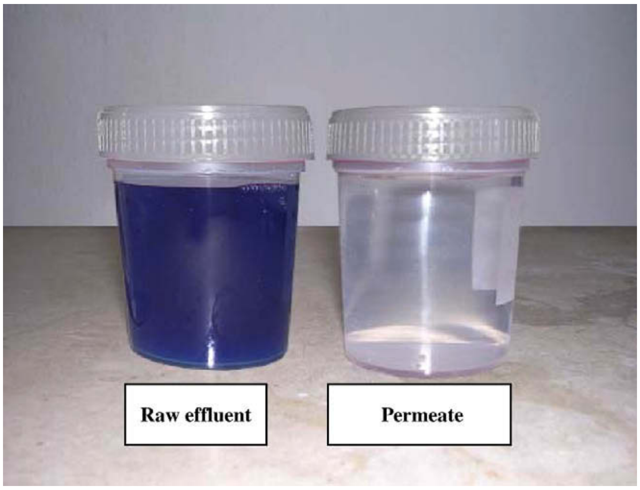

Figure 14 A photograph of the dying effluent before and after MF treatment (T = 25 °C, TMP = 1 bar).

to the clarification of textile dye waste water. Two ceramic membranes are used: on 0.2 μm alumina membrane and the fly ash elaborated membrane. Fig. 13 shows typical microfiltration experiments for the two membranes. For fly ash membrane, the flux drops fast in the first 15 min from 410 l/h m^2 to 135 l/h m^2 then stabilises at a permeate flux (J_f) of about 90 l/h m^2. The same behaviour was obtained with alumina membrane which then was made to be stabilised at a permeate flux of 110 l/h m^2 (see Fig. 14).

The average effluent quality (before and after microfiltration treatment) is illustrated in Table 3. Microfiltration using fly ash membrane proved to be effective in removing the COD, turbidity and color with almost the same efficiencies as that obtained with alumina membrane: 75% for COD, 90% for color. A very low turbidity value of the two permeates was also obtained (0.5 NTU).

4. Conclusion

New ceramic microfiltration membranes made of mineral coal fly ash have been prepared and characterised. The fly ash powder characterisation was performed. It was found that the crystalline phases composition is changing with the increase of the calcinations temperature and that the weight loss is very slight. The optimised composition of the slip was determined: 30% PVA, 66% water and 4% fly ash powder. The obtained membrane was defect free and has the following characteristic: thickness of about 20 μm, mean pore diameter of 0.25 μm and porosity of 51%.

The performances of the fly ash microfiltration membrane for the treatment of the textile dye waste water was determined and compared with those obtained using commercial 0.2 μm alumina membrane. Almost the same stabilised permeate flux was obtained (about 100 l/h m^2). The quality of permeate was almost the same with the two membranes: the COD and color removal was 75% and 90%, respectively.

These experimental results show that mineral coal fly ash is an appropriate material for the development of microfiltration membranes which could be applied to the industrial wastewater treatment.

Table 3 Characteristics of the effluent before and after microfiltration at 1 bar with the fly ash and the alumina membranes.

Sample	Conductivity (μS cm^{-1})	Turbidity (NTU)	COD (mg l^{-1})	Absorbance at 600 nm
Raw effluent	6.16	45.5	3440	0.104
Fly ash membrane permeate	5.38	0.58	880	0.010
Alumina membrane permeate	5.6	0.62	834	0.013

Acknowledgements

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