



# Development of a new high porosity ceramic membrane for the treatment of bilge water

J.M. Benito, M.J. Sánchez, P. Pena, M.A. Rodríguez\*

*Instituto de Cerámica y Vidrio (CSIC), C/ Kelsen 5, 28049 Cantoblanco, Madrid, Spain  
Tel. +34 (91) 735-5840; Fax: +34 (91) 735-5843; email: [mar@icv.csic.es](mailto:mar@icv.csic.es)*

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## Abstract

Bilge waters with different oil-emulsion droplet sizes can be treated successfully using ultrafiltration processes with ceramic membranes. The structure of these membranes has been designed to obtain high permeate fluxes and increase the efficiency of the process. Membranes with very high porosity (about 70%) have been obtained. Using water permeation experiments, it was shown that the permeate fluxes obtained using this membrane configuration are higher when compared to membranes with similar structural characteristics. The kind of the fouling process (internal or external) was evaluated to understand the filtration mechanisms of membrane. These phenomena are very affected by the transmembrane pressure used in each case. Using a multilayer system with a membrane of 6 nm and transmembrane pressures between 0.2 and 0.5 MPa, the oil content in the permeate fluxes can be decreased to below 15 ppm. For the elimination of internal fouling, a membrane regeneration process is proposed. This process consists of a thermal treatment to volatilize the oil droplets deposited on the pore walls of membrane. Using N<sub>2</sub> permeation measurements, an absence of any residue into the membrane and the stability of the membrane structure after the thermal treatment were demonstrated.

**Keywords:** Bilge; Ceramic; Membrane; Porosity; Oil-emulsion; Regeneration

## 1. Introduction

The use of ceramic membranes for treatment of wastewaters is growing in certain applications and above all in those filtration processes where polymeric membranes cannot be applied. Also,

ceramic membranes present some disadvantages, and all of them are related with their relatively high cost because of the expensive raw materials, the fabrication of a complex multilayer system and the low membrane surface.

One of the most important conditions to make a filtration process with ceramic membranes economically viable is that the membrane must be

\*Corresponding author.

able of treating large amounts of effluents. According to this, the main industrial applications can be found in the treatment of waters such as regeneration processes, wastewaters with oily emulsions, recycling of solids in suspensions, treatment of semi-solids products, etc [1].

Nowadays, ceramic membranes can be obtained with high separations coefficient, but at the same time, this fact supposes low permeate fluxes. For each application, it is necessary to look for the adequate combination between selectivity and permeation.

Oil is a common pollutant of wastewaters, and it can be found in a wide range of industries such as general metal-working, food processing, textile, leather, etc. But oily waters from onshore and offshore industry and from engine rooms of ships (bilge waters) are the effluents which have higher levels of oil. Also suspended solids with very different sizes can be found in this kind of waters. These pollutants must be reduced to acceptable levels before the water can be poured [2,3].

In relation with bilge waters and according to the current regulations, the concentration of oil in waters discharges cannot overcome a level of 15 ppm, especially in seagoing. Usually, the oil present in these kinds of waters is found as emulsion because of the presence of detergents. Conventional separation technology consists of a chemical treatment to break oil emulsions followed by a gravity separation. To fulfill the current legislation, a second step of processing, which consists in a separation process of the before-treated water, is necessary. Normally, this purification process is carried out using absorption columns which are removed after their saturation. These columns must be treated after that.

In the present work, for the second step, a membrane system has been used. This one could be used as alternative process since it does not need space requirements. Of course the membrane must treat successfully produced waters

(fulfilling the present legislation), and it must be capable of generating high permeate fluxes (to make the process profitable).

In the literature, there are excellent works about of the treatment of oily wastewaters with ceramic membranes. All of them successfully reduce the oil concentration in water. The reported studies mainly focus the filtration of oily waters for industrial applications from refinery processes [2,4,5], aluminum cutting process[6], steel factory[7,8], bilge water [9–12], etc. But in many cases, the low permeate fluxes obtained impede its application in industrial processes.

In the present study the membrane used for the treatment of bilge waters has been designed taking into account two important things [13]: the membrane must have a suitable pore size to decrease the oil concentration below of 15 ppm (current legislation), and it must have a high porosity. Increasing the porosity of the membrane, the problem associated with its low efficiency could be avoided, since a higher volume of permeate flux can be obtained.

Previous studies performed on bilge water used in this study have demonstrated that at least an ultrafiltration process (membrane with a pore size between 1 and  $10^2$  nm) is necessary to separate the oil emulsions. Two different membrane system have been used, one of them with a separation membrane of  $\alpha$ - $\text{Al}_2\text{O}_3$ , and with a pore size and a porosity of 98 nm and 38% respectively [14]. The second one (“system 2”) consists in a separation membrane of  $\gamma$ - $\text{Al}_2\text{O}_3$ , a pore size of 6 nm and a porosity of 70% [14].

Regarding the operation conditions of the separation process, only high transmembrane pressures have been used. Thus, high permeate fluxes can be obtained. The characterization of membrane fouling has been carried out using a resistance model which analyzes the flux-decline as total resistance versus time [3,15].

Finally, a membrane regeneration process by means of oil volatilization is proposed.

## 2. Experimental

### 2.1. Bilge water

The bilge water was prepared according to a composition supplied by Detegasa S.A. (Spain). This water consists of two different hydrocarbons: fuel and diesel. Both of them have been mixed with an amount of surfactant (sodium dodecylbenzenesulfonate, SDBS) of 0.02 g per liter of produced water. The synthetic bilge water was prepared mixing these compounds with tap water using a high shear rotor mixer (Silverson, UK) at a velocity of 2500–3000 rpm during 15 min. The bilge water has been prepared with an oil emulsions concentration of 4000 ppm where 2000 ppm corresponds to the fuel and 2000 ppm to the diesel.

The oil-emulsion droplet size distributions were determined using dynamic light scattering. For that, a Zetasizer Nano ZS (Malvern, England) was used.

### 2.2. Membranes

The membranes used correspond to a multi-layer asymmetric system, which consists of a tubular cordierite support where an  $\alpha$ - $\text{Al}_2\text{O}_3$  layer has been deposited on its outer surface. This system is named as “System 1”. And for the second one, on the previous system, a  $\gamma$ - $\text{Al}_2\text{O}_3$  layer has been deposited (named as “System 2”).

Cordierite supports have been obtained by extrusion using a reactive mix (Vicar S.A., Spain) plus 30 wt.% of distilled water. The extrudate was dried for 24 h at room temperature and sintered vertically in a electrical furnace at 1200°C for 2 h, using heating and cooling rates of 300°C/h. The tubular supports have an external diameter of 0.8 cm, an internal diameter of 0.4 cm, a pore size of 2.7  $\mu\text{m}$  and a porosity of 41%. Pieces of 10 cm of length have been obtained from the initial piece for the deposition of the different layers.

In system 1, the deposition of the  $\alpha$ - $\text{Al}_2\text{O}_3$  layer on the cordierite supports was performed by dipping. This involves the preparation of stable suspensions, which has been prepared using  $\alpha$ - $\text{Al}_2\text{O}_3$  (HPA05, Condea, USA). The suspension was prepared adding 0.75 wt.% of deflocculant (Dolapix CE64, Zschimmer & Schwarz, Germany) and 1 wt.% of a binder (Optapix C12G, Zschimmer & Schwarz, Germany), both with respect to the solids content. The layer has been deposited on the outer surface of support. For that, one of the ends was closed before introducing vertically the support into the suspension. After a dipping time of 1 min, the support was withdrawn at a velocity of 4 cm/s. The system support-layer was dried vertically for 24 h at room temperature and was sintered vertically at 1100°C (kept for 2 h) with heating and cooling rates of 200°C/h. This layer has a thickness of 6  $\mu\text{m}$  and a porosity of 38%. The pore size calculated by  $\text{N}_2$  permeation of the supported membrane is around 98 nm [14].

In system 2, the  $\gamma$ - $\text{Al}_2\text{O}_3$  high porosity layer was prepared via a sol-gel process. For that, the process developed by Yoldas [16] has been followed. It started from an aluminum alcoxide (Aluminumtri-sec-butylate, Merck, Germany), which has been hydrolyzed totally with water above 90°C in a proportion of 2 L of  $\text{H}_2\text{O}$  per mole of alcoxide. The obtained precipitate was peptized with 0.07 moles of  $\text{HNO}_3$  per mole of alcoxide. The suspension was maintained at reflux conditions for 16 h and at 90°C. Boehmite sols with a concentration 0.72 M plus an amount of polyvinylalcohol (PVA) (Optapix PAF 35, Zschimmer & Schwarz, Germany) of 40 wt.% with respect to the sol weight were prepared.

The deposition of this membrane to obtain the system 2 consists in three necessary dipping procedures: deposition of the membrane by dipping for 45 s, first reparation by dipping for 30 s and second reparation for 30 s. Between step and step the membrane has been dried and calcined. The

used conditions for the deposition process were the same ones that in the case of system 1. The drying was performed vertically at a temperature of 40°C and 60% of relative humidity in a climate chamber. The resulting gel was calcined at 600°C (kept for 3 h) at a rate of 60°C/h in an electric furnace. This layer has a thickness of about 5 µm and a porosity of 70% [14]. The pore size obtained by N<sub>2</sub> permeation of the supported membranes is 6 nm approximately [14].

### 2.3. Experimental apparatus and procedures

The crossflow experiments were performed using the apparatus shown in Fig. 1. It is capable of operating at transmembrane pressures between 0.1 and 0.7 MPa. The pump circulates the feed flux from the feed tank to the membrane module. The transmembrane pressure was controlled by the valve 2, which is found at the exit of the membrane module. The permeate flow was measured volumetrically. The retentate flux is recycled to the feed tank. The membrane system was sealed with a resin to a brass pieces to avoid whatever leak. One of the ends was closed with

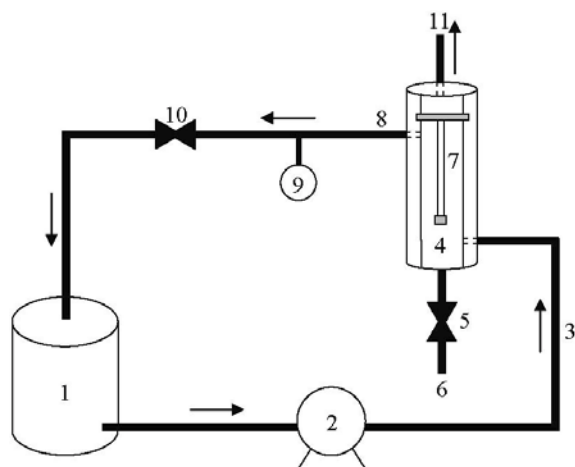


Fig. 1. Filtration equipment. (1) feed tank, (2) centrifugal pump, (3) feed line, (4) membrane module, (5) valve 1, (6) drainage, (7) tubular membrane, (8) retentate line, (9) pressure transducer, (10) valve 2, (11) permeate line.

one of the brass pieces to cause that the feed flow goes through membrane. The other end was left opened and was isolated of rest of membrane module.

Before permeation experiments, the membrane systems were immersed in tap water during 24 h with the objective to reach a stable flux at the beginning of the experiment [17]. Permeation experiments with water and bilge waters were carried out with both systems, and during an operation time of 1 h. The flux measurements were per unit of pressure, time and surface ( $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ). The determination of the tap water permeation was carried out at a transmembrane pressure of 0.5 MPa. The study of the filtration of bilge waters with the different membrane system was performed at different transmembrane pressures.

### 2.4. Resistance model

To evaluate the fouling membrane, a theoretical model was used. Two different kinds of fouling mechanisms can be found in a separation process by membranes. One of them is related with the deposition of material (in this case small amounts of oil), on the pore walls. This phenomenon is known as internal fouling and it produces a big drop pressure across membrane because of clogging process of pores. Normally it is an irreversible process and it determines the lifetime of the membrane. The second fouling mechanism is known as external fouling and it is characterized by the formation of a “cake layer” of material at the entrance of pores. Both of them produce the flux decline during the filtration operation. To know which kind of fouling process is produced on the membrane, Darcy’s law can be used [3,15]:

$$J = \frac{\Delta P}{v_p R_t} = \frac{\Delta P}{v_p (R_i + R_e)} \quad (1)$$

where  $J$  is the permeate flux ( $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ),  $\Delta P$  is the transmembrane pressure (Pa),  $\nu_p$  is the permeate kinematic viscosity,  $R_t$  the total resistance to flow,  $R_i$  the internal resistance and  $R_e$  the external resistance. As the kinematic viscosity, it has been taken the corresponding one to the pure water at 25°C ( $8.97 \cdot 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ ).

According to this model, if the variation of the  $R_t$  versus operation time has a concave-shaped, this tendency will correspond to an internal fouling phenomenon. On the other hand, a convex-shaped curve will correspond to an external fouling phenomenon.

### 2.5. Determination of oil concentration

The oil in the permeate fluxes was determined using infrared spectrophotometry since all oils and greases present an absorption band at  $2930 \text{ cm}^{-1}$  [18]. To avoid interferences with the bands of water, the oil has been extracted with a solvent (tetrachloroethylene). The extraction was performed adding solvent to the collected volume of permeate and by means of vigorous stirring with a high shear rotor mixer (Silverson, UK) at a velocity of 2500–3000 rpm during 15 min. The amount of oil was calculated by representation of the absorption intensity at  $2930 \text{ cm}^{-1}$  in a calibration curve previously obtained. The calibration curve has been obtained measuring the absorption intensity of prepared solutions using known amounts of oil (fuel and diesel) and solvent.

### 2.6. Regeneration membrane process

The membrane regeneration was performed via a thermal treatment after the filtration process with the objective to produce the total volatilization of oils. This process is performed extracting the membrane of the membrane module and introducing it in a furnace. First of all, thermogravimetric (TG) measurements (STA 409, Netzsch, Germany), were carried out on the different oils to know the volatilization temperature of

both. A heating rate of  $1^\circ\text{C}/\text{min}$  was used. After this thermal treatment,  $\text{N}_2$  permeation measurements were performed. This method is very useful to determine any change in the porous structure of membrane and any clogging process of pores. It can be described as follows [19–22]:

$$F = a + bP_m \quad (2)$$

where  $F$  is the  $\text{N}_2$  permeation,  $a$  is a constant corresponding to Knudsen diffusion transport,  $b$  a constant representing viscous flow transport and  $P_m$  the mean pressure. Carrying out the representation of  $\text{N}_2$  permeation as a function of the mean pressure, both constants ( $a$  and  $b$ ) can be obtained.

The Knudsen diffusion transport represents the gas permeation through the mesoporous structure of membrane and it is produced only by pores sizes between 2 and 100 nm. Instead, the viscous flow transport is produced by pore sizes above 20 nm.

Starting from the obtained data of  $a$  and  $b$ , the pore radius can be estimated ( $r_p$ ), which would be given by:

$$r_p = \frac{16b\eta}{3a} \sqrt{\frac{8RT}{\pi M}} \quad (3)$$

where  $\eta$  is the viscosity of the gas (in this case  $\text{N}_2$ ),  $R$  the gas constant,  $T$  the temperature and  $M$  the molecular weight of the gas.

To calculate the pore radius of the each supported layer, a previous characterization of the preceding layer must be performed. These gas permeation measurements are subtracted from the total characterization of the asymmetric system, obtaining by this way the characterization of the top layer. These calculations were performed using the method described in reference [21]. This previous characterization will not be necessary when the rest of the layers do not generate a pressure drop gas flow. =

### 3. Results and discussion

#### 3.1. Water permeation

Fig. 2 represents the variation of the water permeate flux during the operation time. For systems 1 and 2, it can be observed the water permeation decline. This fact is produced because by the existence of small particles in the tap water. These small particles cause a fouling process on the membrane. If both representations are compared, in the case of the system 1, a gradual flux decline can be observed. However for the system 2, the flux decline has been produced at very low operation times, and after that, a steady flux of  $7.4 \times 10^{-9} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  was reached. The reason of these different behaviors resides in the pore size of both systems. For the membrane with an average pore size of about 98 nm (system 1), the tap water pollutants are deposited little by little on the pore walls. Due to this, the water flux will decrease until a total saturation of the pores of membrane. In the case of the membrane with an average pore size of 6 nm (system 2), also the pollutants are deposited, but now, this deposition process on the pore walls finishes after an operation time of 300 s, since the pore size is smaller. At this moment, it is considered that the membrane has achieved a steady flux. After this saturation process, the water flux continues decreasing through a very slow process, because now the accumulation of pollutants is produced at the entrance of pores and on the membrane surface.

In the case of the system 1, still the saturation process has not been achieved and therefore the steady flux has not been reached during the water permeation experiment.

Both processes, the initial membrane saturation (internal fouling) and the deposition process of pollutants on the surface of membrane (external fouling), are frequent processes in many filtration experiments.

Considering the water flux for the system 2 (with a membrane with a pore size of 6 nm), it

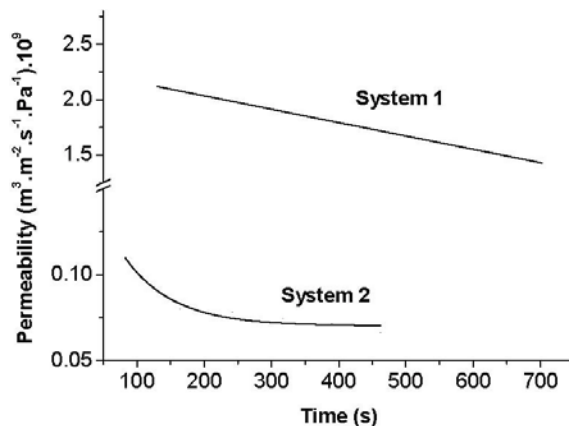


Fig. 2. Variation of water flux during the operation time for systems 1 and 2.

can be seen that this flux is very high if it is compared with systems with the same pore sizes in the top-layer and similar structural characteristics, even using a water (tap water) without any purification process [23–27]. This way, it is demonstrated that using high porosity membranes (with porosities around 70%), the liquid flux through membrane can be increased and as a result the efficiency of a filtration process. Also, these porosity values have been demonstrated by recent studies thanks to  $\text{N}_2$  permeation measurements [28].

#### 3.2. Bilge water experiments

It is necessary to characterize water which is going to be treated. In Fig. 3a, it is shown the oil-emulsion droplet size distribution of the prepared water. Three different droplet sizes can be found. Most of the volume of droplets has an average diameter of about 4  $\mu\text{m}$ . Otherwise, a small percentage of the total volume corresponds to droplets with an average diameter of about 300 nm and 90 nm. According to these results, the membrane corresponding to system 1 might be enough to decrease the oil concentration from 4000 ppm (prepared bilge water) to a concentration below 15 ppm (current legislation).

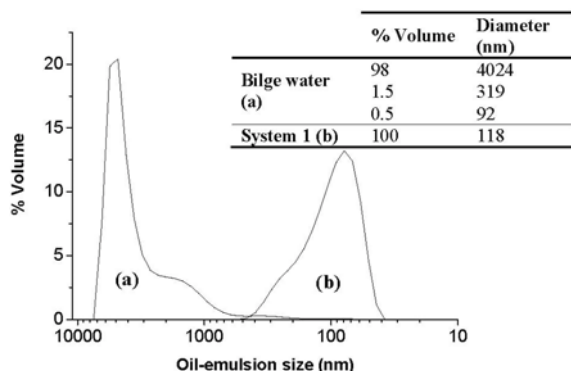


Fig. 3. Oil-emulsion droplet size distribution of prepared bilge water (a), and the permeate flux obtained with the system 1 at a transmembrane pressure of 0.2 MPa (b).

The variation of the permeate flow and the total resistance in the filtration experiments using system 1 can be seen in Figs. 4 and 5 respectively. Equally that in the water permeation experiments, at the beginning of the process, membranes experiment a flux decline due to the adsorption of oil droplet on the material membrane and due to the pollutants of the tap water (Fig. 4). After the flux decline, the steady flux is achieved. For a transmembrane pressure of 0.2 MPa, still the flux decline has not finished during the operation time. This fact is due to the slow accumulation process of material at low pressures. On the other hand, it can be observed that the steady flux is higher when the transmembrane pressure used is higher too.

According to the total resistance plot obtained (Fig. 5), the high initial permeate flux decline corresponds to an external fouling process. This phenomenon is produced by the adsorption of oil onto membrane surface, since the most of the oil-emulsion droplets have a size higher than the pore size of membrane (Fig. 3). This fouling process is more severe when higher transmembrane pressures are used. This tendency is associated with the crossflow velocity. At high pressures, the flux velocity increases, and as a result, the accumulation process of oil onto the membrane surface

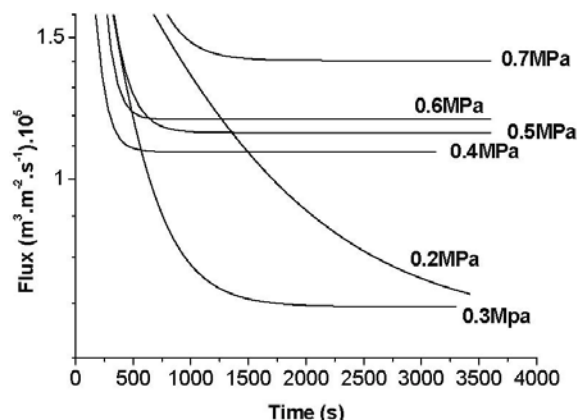


Fig. 4. Variation of the permeate flux during the filtration experiment using system 1.

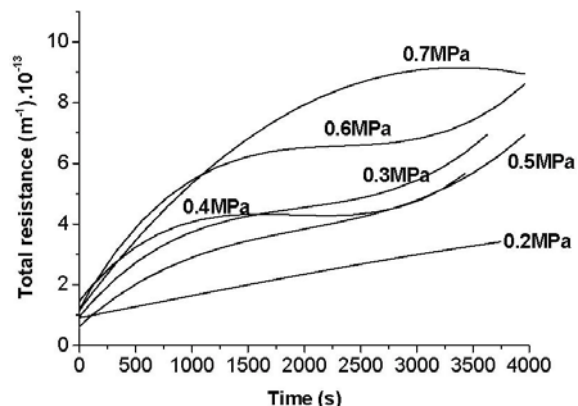


Fig. 5. Variation of the total resistance during the filtration experiment using system 1.

increases too. In this case, the internal fouling produced at very early stages by the adsorption of pollutants of the tap water and by the smaller oil droplets can not be observed, since the external fouling process is predominant; however, at the same time this internal fouling process is produced.

The internal fouling is become in the predominant one after 2000 s and with transmembrane pressures between 0.3 and 0.6 MPa (Fig. 5). Also this internal fouling is more severe at higher transmembrane pressures. This phenomenon is responsible of the flux decline at the stage named

as steady flux and it is produced by the introduction of droplets inside membrane. The droplet can enter the membrane due to a deformation process caused by the transmembrane pressure. This process is very slow and for this reason, it does not generate big flux declines.

At very high pressures (0.7 MPa), the predominant fouling process in the period of the operation time is an external one. The internal fouling process cannot be observed because the contribution of the external one to the total resistance is very high.

Analyzing the oil concentration in the permeate flux (Table 1), it can be seen that the retention percentage is lower when the used transmembrane pressure is higher. This behavior suggests that the smaller droplets can go through the membrane by a deformation process of its shape when the transmembrane pressure increases. This fact makes the oil concentration overcomes the limit of 15 ppm for all the used transmembrane pressures.

The oil-emulsion size distribution of the permeate fluxes (Fig. 3) shows exactly that all the droplets which have gone through membrane, have an average diameter of 118 nm. This result corresponds to the permeate flux obtained using a transmembrane pressure of 0.2 MPa. This oil-emulsion size is in concordance with the pore size of the membrane of system 1 (98 nm). So, these oil-emulsions can come from the initial bilge water directly or they have been produced when big oil emulsions go through membrane. If the oil-emulsions found in the permeate flux correspond to this last case, oil concentrations below 15 ppm could be obtained if very low transmembrane pressures were used. But this way, the permeate flux would be so low that the process would not be profitable.

These last results conclude that the use of membranes with smaller pore sizes is necessary. Also, preliminary studies performed on bilge waters have demonstrated that many times suspended solids, such as  $\text{Fe}_3\text{O}_4$ , with sizes below

100 nm can be found. This fact indicates that at least, membranes with pore sizes below 100 nm are necessary to avoid the internal fouling of the membrane with these solids. These facts justify the use of system 2. Thanks to its high porosity, the permeate flux is very high without detriment to its structural characteristics.

The permeate fluxes using system 2 are shown in Fig. 6. It can be appreciated that only at high transmembrane pressures (0.6 and 0.7 MPa), the steady flux has been achieved. At lower pressures, the flux did not reach steady state. Equally that in system 1, at higher pressures, the external fouling (Fig. 7) is produced very fast since the crossflow velocity is very high and therefore the steady state is reached very soon. This process is more severe when the transmembrane pressure increases.

After the external fouling process, the internal one is not observed using pressures between 0.2 and 0.6 MPa, since the pore size of this system is smaller than the oil-emulsion droplets. Therefore, only by a deformation process at high pressures, the oil could go through the membrane and

Table 1  
Oil retention as a function of transmembrane pressure using systems 1 and 2

	Transmembrane pressure (MPa)	Oil conc. (ppm)	Retention (%)
System 1	0.2	27	99.3
	0.3	36	99.1
	0.4	36	99.1
	0.5	37	99.1
	0.6	38	99.1
	0.7	46	98.9
System 2	0.2	11	99.7
	0.3	11	99.7
	0.4	10	99.8
	0.5	10	99.8
	0.6	31	99.2
	0.7	37	99.1

deposit on the pore walls. At transmembrane pressures not very high, the internal fouling only will be produced by the pollutants of tap water. So, in this case the oil-emulsion will be deposited onto membrane above all.

At very high pressures (0.7 MPa), an internal process is becoming in the predominant one after the external process (Fig. 7), since at high transmembrane pressures a deformation process of droplets is produced. In this case, the internal fouling is predominant because the oil-emulsions adsorbed on the walls of pores produce a big flux decline.

Using a transmembrane pressure of 0.7 MPa, the oil concentration in the permeate flux surpasses the limit of 15 ppm (Table 1). Even using 0.6 MPa, the oil concentration is 31 ppm. At pressures between 0.2 and 0.5 MPa an amount of oil below 15 ppm is obtained.

### 3.3. Membrane regeneration

The total membrane regeneration is a very interesting alternative, above all in those processes where an internal fouling process is produced. The deposition of oil into membrane produces a flux decline which increases during

the filtration process, and many times it cannot be eliminated. Besides, it is very difficult to recover the initial flux in ultrafiltration process, since the pore sizes used are very small (below 100 nm). So, this kind of fouling phenomenon is usually an irreversible process.

With regard to the external fouling, (reversible process), there are different ways to eliminate it successfully, as using the backpulsing method [29] by means of cleaning solutions [17] and with the movement of baffles inside the membrane module [30].

The total volatilization of oil can be a solution for the internal fouling process in ceramic membranes. A thermogravimetric study performed on

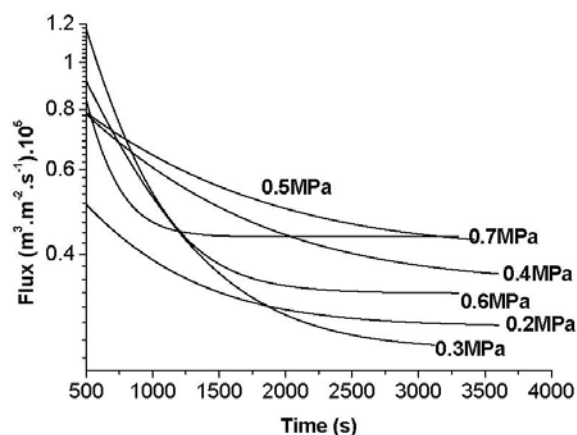


Fig. 6. Variation of the permeate flux during the filtration experiment using system 2.

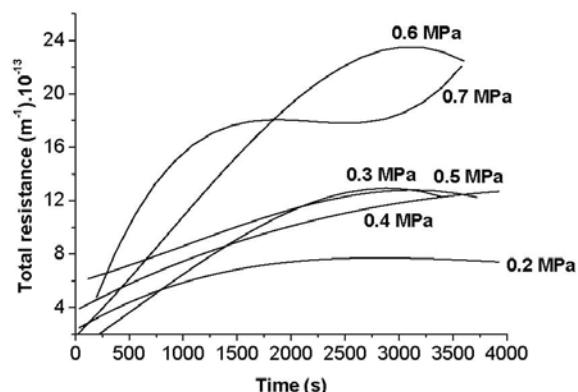


Fig. 7. Variation of the total resistance during the filtration experiment using system 2.

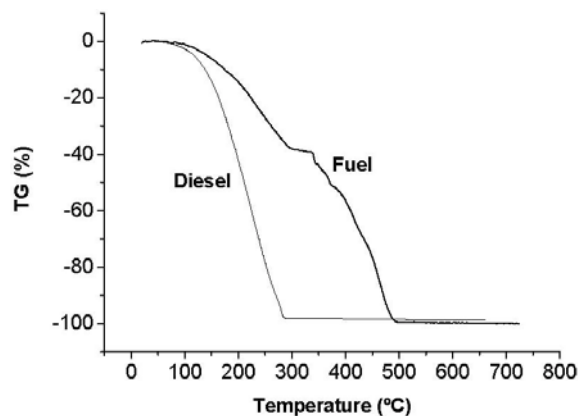


Fig. 8. TG curves for systems 1 and 2.

Table 2

Knudsen diffusion and viscous flow transports and pore size obtained by measurements of N<sub>2</sub> permeability of systems 1 and 2 before and after filtration experiments

Membrane		Knudsen diffusion transport (mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> ).10 <sup>6</sup>	Viscous flow transport (P = 10 <sup>5</sup> Pa) (mol.m <sup>-2</sup> .s <sup>-1</sup> .Pa <sup>-1</sup> ).10 <sup>6</sup>	Pore size (nm)
System 1	B.f.	10.3	1.1	98.3 ± 3.0
	A.f.	9.7	1.1	95.8
System 2	B.f.	9.6	0.1	6.3 ± 1.1
	A.f.	7.1	0.1	7.0

B.f. = before filtration process.

A.f. = after filtration and regeneration processes.

the different oils (Fig. 8) shows that it should be possible to volatilize totally both oils at a temperature of 500°C.

Before carrying out the calcination of the used systems in the filtration process, it is necessary to take into account that this process could generate changes in the membrane structure. Using N<sub>2</sub> permeation measurements, the Knudsen transport and viscous flow for systems 1 and 2 were compared before the filtration experiment and after the filtration experiment and the regeneration process at 500°C. The presence of defects can be evaluated by means of viscous flow gas transport [14], since this transport is predominant when defects appear on the structure. The presence of some carbonaceous residue which clogged the pore (internal fouling) can be detected by a decreasing in the Knudsen diffusion transport, since this kind of transport is proportional to the pore size of membrane.

So, systems 1 and 2 have been subjected to a calcination process at 500°C during 2 h using heating and cooling rates of 1°C/min. In Table 2, the Knudsen diffusion and viscous flow for both systems are shown before filtration experiments and after filtration and regeneration processes. For both systems, variations of the viscous flow cannot be observed. This fact indicates that after thermal treatment, no cracks or defects have been produced on the structure of the systems. On the

Knudsen diffusions, some differences can be observed. In both cases, they are slightly smaller after the regeneration process. However, the pore sizes calculated by permeation show that both values are the same. So, it can be concluded that no carbonaceous residue is present after the thermal treatment.

#### 4. Conclusions

Two different membrane systems have been obtained for the treatment of bilge water with oil-emulsion droplets diameters between 4 µm and 90 nm. The membrane of system 1 has a pore size of about 100 nm, and the membrane of system 2 has a pore size of 6 nm. This last membrane has been designed with the objective of obtaining high permeate fluxes (porosities of about 70%). By means of water permeation it has been demonstrated that the permeate flux across this membrane is higher if it is compared with membranes with similar characteristics.

The filtration experiments have shown that using system 1 and transmembrane pressures between 0.2 and 0.7 MPa, the oil content in the permeate flux overcomes the limit of 15 ppm imposed by the current legislation. Instead with the system 2, oil concentrations below this limit can be obtained with transmembrane pressures between 0.2 and 0.5 MPa.

By means of a process of volatilization of the oil adsorbed on the membrane at a temperature of 500°C for 2 h, membranes can be regenerated without undergoing any change in their structures.

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