Cross-flow microfiltration with microporous tubes chemically treated for desemulsifying mixtures of water and sunflower oil

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Abstract. *A tubular microstructure composed of alumina (Al_2O_3) and chemically treated was used in the desemulsifying by microfiltration process for mixtures of water and sunflower oil in the form of a stable emulsion. The tubes were sintered at a final temperature of 1450°C and showed average pore size of 0.5 μm. After it burns the tubes were treated by chemical impregnation using a solution of citrate of zirconium, in the form of metallic precursor. Soon after the impregnation, the tubes tubes were sintered at a temperature of 600°C or 900°C for the formation of agglomerates of nanoparticles of zirconia in the support tubular of alumina. Results are presented for the microporous medium what was characterized by mercury porosimetry and by scanning electron microscopy (SEM). For studied the performance of microporous tube in the desemulsifying process, the cross-flow was analyzed from to unit of laboratory equipped with a pump of positive displacement of transmembrane flux in ranging from 200kPa to 800kPa. Experiments accomplished for stable emulsions of water and sunflower oil subjects to pressures transmembrane of 200kPa; 300kPa; 400kPa and 500kPa in the regime turbulent larger than Re= 20.000. The quality of the permeate flux as the retention of phase oil was analyzed with measurements of total organic carbon (TOC), with retention of carbon larger than 98%.*

Palavras Chave: *Tube microporous; Microfiltration; Zirconia; Sunflower oil, Emulsion.*

1. Introduction

Porous ceramic are usually used as filters, refractory and support for the inorganic membranes. Inorganic commercial membranes are commonly made of synthesis of fine particles of alumina (Al_2O_3) with homogeneous and controlled size. The morphology of the middle and the definition of the size of pores in the personal computer-porous way, come from the sinterização the high temperature, starting from the half produced by the classic method of precipitation by collage (Deng, Fukasawa and Walks, 2001).

The cross-flow microfiltration has as driving power the difference of pressure transmembrane, which submits the mixture in parallel circulation to the surface of membrane. This process has emerged as a viable and efficacious for the concentration of suspensions, the production of pure liquids, and the regeneration of emulsions in the process of separation (Cheryan, 1998 and Ripperger and Altmann, 2002).

Zirconia is very interesting material in the composition of inorganic membranes. The qualities of zirconia membranes are: high chemical resistance that allows steam sterilization; acceptable in procedures in the pH range 0-14; good water permeability and high membrane flux in separation and filtration due to their specific surface properties, and high thermal stability which is very attractive for catalytic membrane reactors. Some studies on zirconia membranes show better separation performance with high transmembrane flux, less fouling and higher oil rejection, compared with other membranes. In the work of Yang *et al.* (1998), the higher and more stable flux was observed through zirconia composite MF membrane.

Inorganic membranes are stable in non-aqueous solutions. Guizard *et al.* (1993) applied alumina, silica and zirconia for the ultrafiltration membranes to separation of crude oil in the temperature range of 155-180ºC, and found that zirconia membranes showed higher transmebrane flux than alumina and silica membranes because of lower level of interaction with asphaltene (result in agreement with Tsuru *et al.*, 2001). In the work of Köseoglu *et al.* (1990), was examined the feasibility of use the membrane to remove the solvent from crude vegetable oil. The ceramic membrane was also attractive in the separation and dissolution of hexane (Wu and Lee, 1999).

Emulsions of water/oil are formed in several industrial process (food and chemical) where immiscible organic and aqueous phase are in emulsification. Oil vegetal or mineral in mixture with water are frequently presented as waste streams. The emulsification and demulsification process of oil/water mixtures occurs according to the physical interaction of each phase of the biphasic mixture with the inorganic surface, and depends of the pore-size distribution and interfacial tension between the two liquids (Joscelyne and Trägardh, 2000). The used a tubular microstructure porous of ceramic has been an economic and good alternative form in the substitution the membranes (Gregg and Sing, 1982).

In this paper, alumina (Al_2O_3) was used as primary matter in the production of microporous tubes. The tubes sintered in the temperature of 1450°C were taken as support and chemically treated with a solution of citrate of zirconium, in order to get aggregated of nanoparticles of zirconia in alumina. The performance of the impregnation was investigated with analysis of permeate and in different conditions fluid dynamics in the process of demulsification of mixtures of water and sunflower oil. The results indicated satisfactory conditions with the presence of zirconia.

2. Experimental

Alumina (Al_2O_3) kindly supplied in tubes by Cetebra-Tecnicer Ltda. was used in the present paper. Tubular microstructure with 250 mm long and 7.8 mm internal diameter was produced by precipitation method. The tubes microporous were sintered from the environment temperature (30 °C) until to reach temperatures of 1430, 1450, 1470 and 1490 ºC during one hour, with a cooling rate of 10 ºC/min until environment temperature. After this synthesis the ceramic tubes were submitted to the chemical impregnation using a solution of citrate of zirconium in the concentration of 3.38×10^{-5} mol/l (Fig. 1).

In the sequence, the tubes were sintered until to reach temperatures different temperatures (600 and 900°C), with variable times in the heating. This treatment in the ceramic tubes has the objective of to eliminate the organic matter of the solution of citrate of zirconium, and to carry the impregnation of nanoparticles of metallic oxide or zirconia.

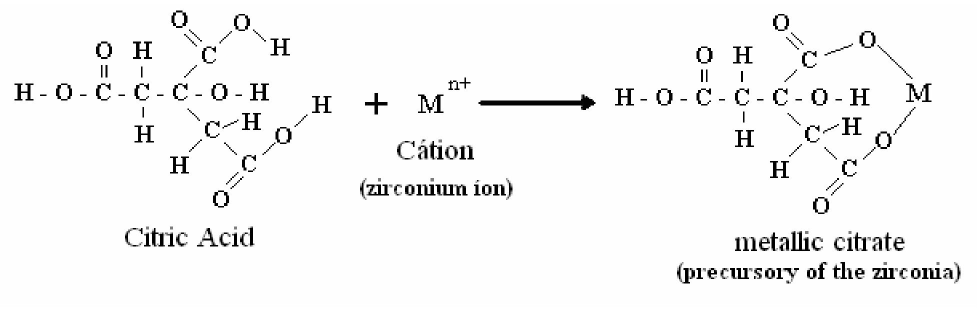


Figure 1. Chemical reaction for production of the metallic citrate (M=Zr) in porous tube.

For to obtain different concentration of zirconia in the microporous tubes, its already impregnated go by a new impregnation and are submitted to a heating at 600 and 900°C. After that process, the ceramic tubes were studied in an experimental apparatus of process de microfiltration, to evaluate the performance of the same in the demulsification of stable emulsions of water and sunflower oil.

The demulsifying process occurs according to the physical interaction of each phase of biphasic mixture with the inorganic surface. Water has an affinity for mass transfer at microporous surfaces; hence, it is hydrophilic to permeable the porous surface. However, the dispersed phase (oil) is hydrophobic to permeable surfaces. Figure 2 illustrates the mass transfer at the permeable surface of each phase of the biphasic mixture confined in the microporous tube and subjected to a transmembrane pressure (ΔP) of over 100 kPa and shows a water/oil droplet interacting superficially with the permeable surface. The water phase (hydrophilic) has an affinity for transferring through the permeable surface due to interfacial and superficial stresses, which differ substantially from the physical properties of the oily phase (hydrophobic).

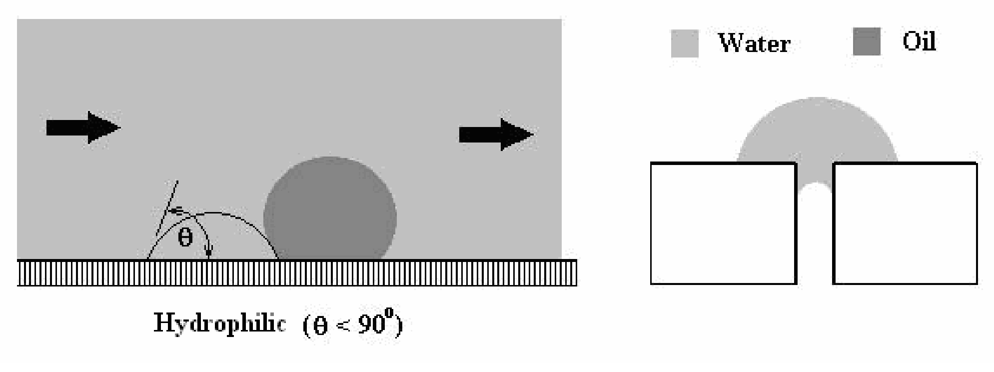


Figure 2. Microfiltration demulsifying process (adapted of Fontes *et al.*, 2005).

Figure 3 consists of a schematic drawing of the experimental setup in inox. The system, which was manufactured with positive-displacement pump of the Netzsch of Brazil Ltda, and has one module with a 207mm long and 7.9mm internal diameter of porous tube (filtration area = $5.14 \times 10^{-3} m^2$). The solutions or stable mixture in the 30-liter feed tank was circulated, and the retention flux was returned to the feed tank, while the permeate flux was measured volumetrically and stored for analysis of electrical conductivity, pH and TOC. This procedure causes the concentration of the retained material to increase over time.

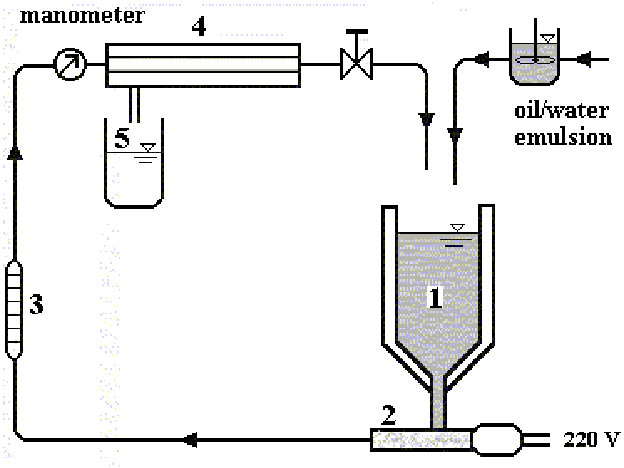


Figure 3. Schematic drawing of the experimental apparatus (1) jacketed fluid container;

(2) pump; (3) flowmeter; (4) covering module with tubular microstructure; (5) outflow of the permeate.

Several experiments were conducted for oil/water (sunflower oil) in 1% of volume in water. A refrigeration system was set up with a centrifugal pump to stabilize the solutions' temperature using circulating water to cool the jacketed feed tank. The temperature during the experiments was kept at 25°C ± 0.5°C.

The mixtures were produced with intense agitation in blender in the concentration volumetric of 1% of oil in water. The total time of the process was of 200 minutes, varying the pressure transmembrane without interruption of the process, with samples of collected permeate of 5 in 5 minutes, in the constant temperature of 25 ºC ± 0,5 ºC. The experiments were accomplished with the tube produced to chemical impregnation procedure. The transmembrane flux or permeate outflow was measured in all the experiments using a precision balance of two significant digits. The mass transmembrane flux was transformed into volumetric transmembrane flux based on the measurements of the permeate's density using a densitymeter at the temperature of the permeate. The permeate's physicochemical properties were investigated based on measurements of the total organic carbon (TOC), conductivity measured and the pH measured, respectively, with a Shimadzu (TOC 5000A), Orion model 115A conductivity meter and an Orion model 290A pH meter, after a standard equipment calibration procedure.

The microstructure porous tube was regenerated between experiments, using the 60 minutes of flow washing with a special detergent NaOH in aquous solution. The pressure in the filtration module was controlled with a special valve, installed in the end of the hydraulic circuit. A clear permeate flow into the shell side of the porous tube module was obtained, with the permeate viscosity and density equaling the pure water.

3. Results and discussion

3.1. Characterization of the microporous environment

The tubes were characterized by mercury intrusion porosimetry (Autopore II/9220 - Micrometrics Instruments Corporation) and electronic microscopic. Samples of the extremity of each tube were selected for porosimetry analysis.

In the preliminary heating the microporous tubes had as objective to verify changes in the porosity and pore size distributions of the ceramic material due to the temperature variation during the synthesis. In agreement with the literature (Chang *et al.*, 1994), the morphology and the structure of pores in porous ceramics is sensitive with the temperature during to the heating or phase transformation.

The analysis of the porosimetry for mercury intrusion is illustrated in Fig. 4, through the graphical of the variation of the volume rate of Hg in function of medium size of pore. In the studied temperature interval it is observed that for all the synthesis temperature the medium size of pores in the tubular microporous material is of approximately 0.5 µm, indicating what in this temperature interval there is not influence of temperature.

An intermediary temperature of 1450ºC was chosen for the heating of tubes used in the demulsifying process.

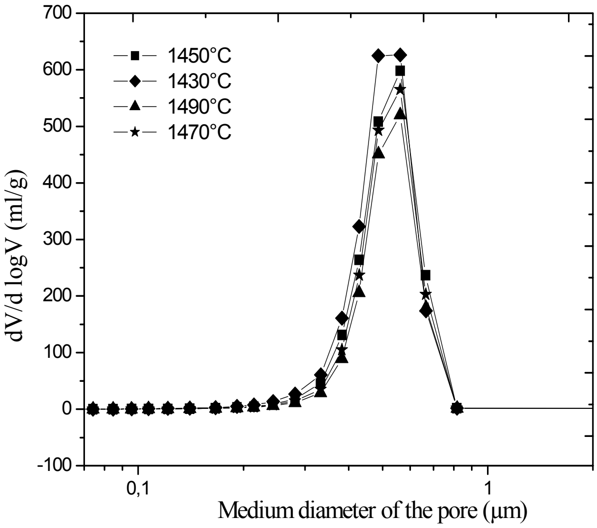
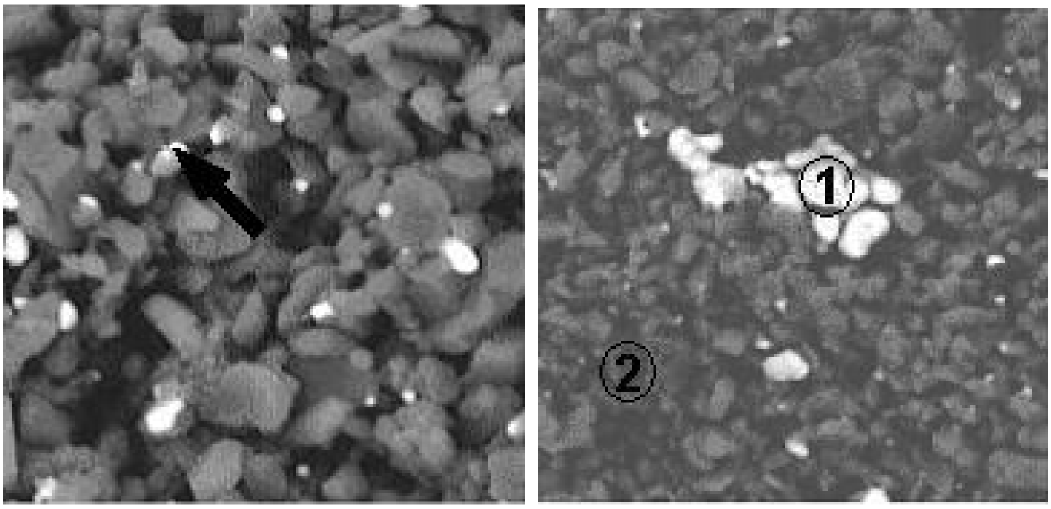


Figure 4. Analysis by mercury porosimetry of the tubes ceramics sinterized at different temperatures.

The Figure 5 presents the visualization of morphology of surface and qualitative chemical composition of the microstructure porous, obtained with the technique of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. The morphologic analysis of the tubular porous microstructure impregnated in different concentrations, it was accomplished through the map of zirconium on the surface of ceramic material.

The Fig. 5.a (black arrow) and the Fig. 5.b (number one) illustrate the presence of the oxide of zirconium in the structure microporous ceramic with the formation of some agglomerates in the material impregnated once (Fig. 5.a) and impregnated twice (Fig. 5.b). In the point "2" (Fig. 5.b) the portion of aluminum is larger (45.52 %), it also meets: magnesium (0.26%); oxygen (48.13%) and carbon (6.09 %).

The chemical composition for the tube impregnated twice suggests a larger amount of zirconia in the agglomerate form. In the sample of the tube impregnated once (Fig. 5a), the zirconia is more evenly distributed on the support (alumina).



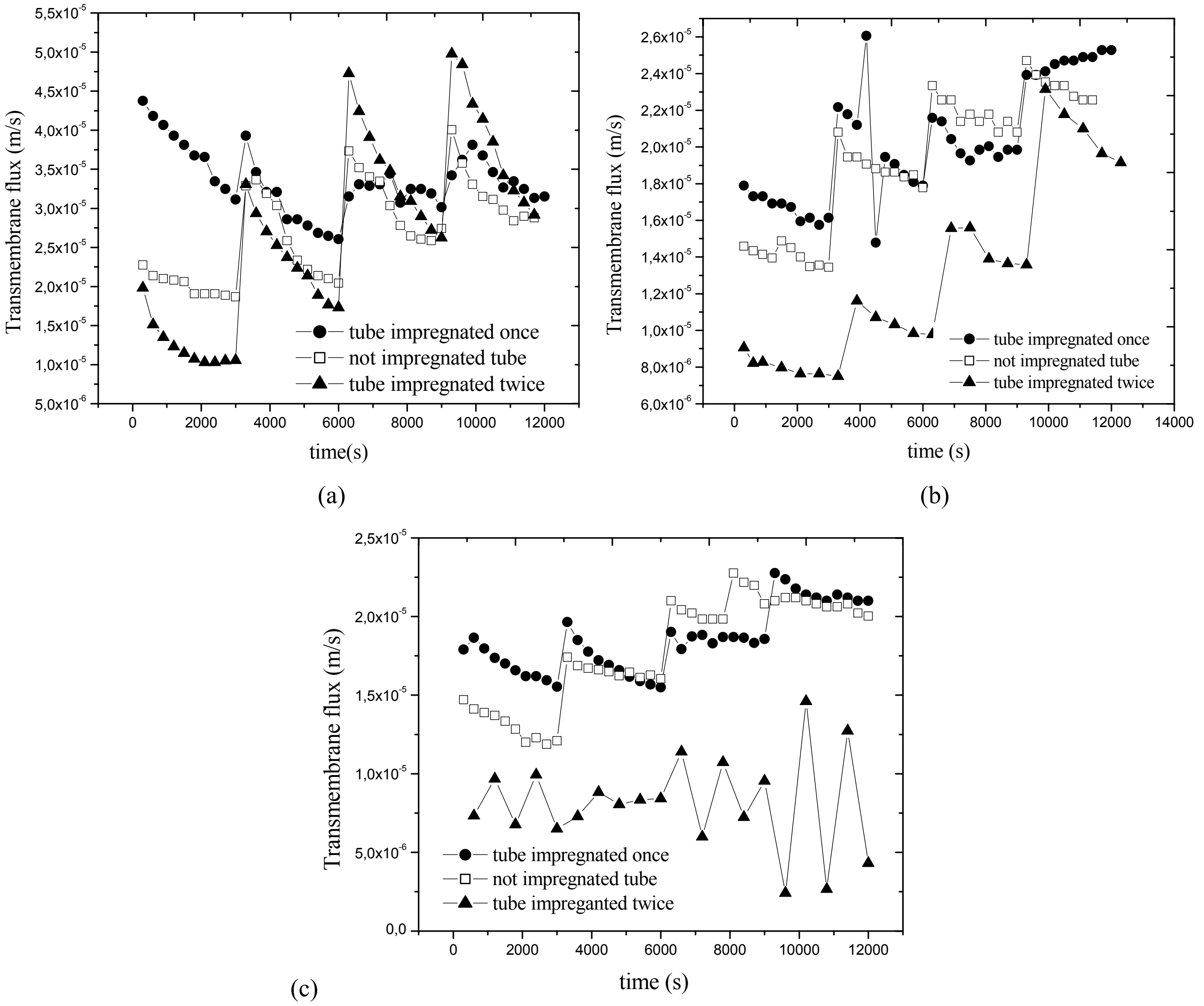
(a) (b)

Figure 5. Images obtained through scanning electron microscopy (SEM). (a) tube microporous ceramic impregnated once; (b) tube microporous ceramic impregnated twice.

3.2. Characterization of the microporous environment in the microfiltration process

For characterization of the process of cross-flow microfiltration, dynamic experiments were accomplished with variation of transmembrane pressure between 2.10^5 and 5.10^5 Pa and of Reynolds (Re) number. In the Figure 6 are presented results of transmembrane flux in function of time of processing. To each interval of 50 min. (or 3000 seg.), it was made the respective change of transmembrane pressure, of 200 kPa for 300 kPa, of 300 kPa for 400 kPa and of 400 kPa for 500 kPa. This fact is observed in the experimental results of the Figure 6, where exists an abrupt increase in the transmembrane flux in the interval of time mentioned (50 min. or 3000 seg.). The results are presented for experiments accomplished for tubes without impregnation; impregnated once and impregnated twice, and respectively for the Re= Re = 21194 (Fig.6a), Re = 16182 (Fig. 6b) and Re = 13032 (Fig. 6c).

In the Fig. 6 is observed that for the cases of larger numbers of Reynolds (Fig. 6.a and 6.b), and in the end of each interval of time of 50 min. and to each pressure, the transmembrane flux is larger in the process studied with the tube impregnated once, except for 400 kPa in the condition of Fig. 5.b.



(a)

(b)

(c)

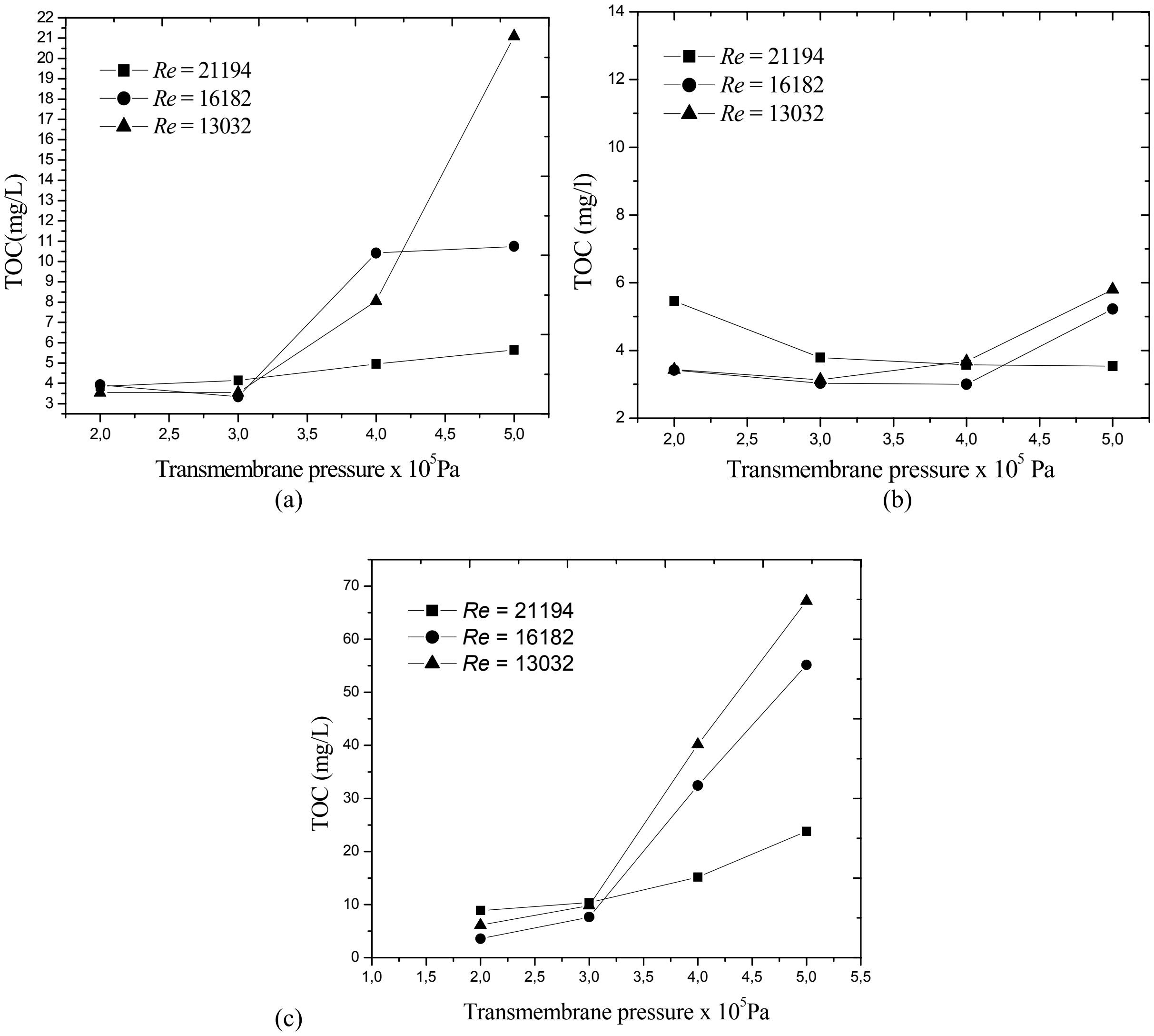
Figure 6. Transmembrane flux (m/s) in function of the time (s) for the emulsions water/sunflower for three ceramics tubes with different flows (a) *Re* = 21194; (b) *Re* = 16182; (c) *Re* = 13032.

A similar behavior is observed among the processes in the tubes impregnated once and in not impregnated tube (Fig. 6c). In the Fig. 6c, the dynamic process to the tube impregnated twice introduces behavior different of the others. In this case (Fig. 6c, tube impregnated twice), the values of transmembrane flux are variable, and there is not in process the typical stabilization of cake layer or polarisation layer (Zeman and Zydney, 1996). The transmembrane flux present abrupt variations in all the investigated conditions. Probably due to superficial interactions between the emulsion and the microstructure (with zirconia) are predominant in relation to the shear stress.

These results indicate that the process with the tube microporous impregnated once has the best performance to the permeate, with significant influence of zirconia in the microporous structure.

In the Figure 7 are presents results of concentration of total carbon (TOC, mg/l) of permeate collected in the processes described in the Fig. 6. To analyze the quality of permeate in relation to the concentration of carbon in the dinamics of process; the values are presented in function of transmembrane pressure and of number of Reynolds of flow.

It is observed in the Fig.7 that the smaller value of TOC is due to the process with tube impregnated once (Fig. 7.b), in the condition of transmembrane pressure, ΔP_{tm} = 500 kPa and Re=21194 (Fig. 7.b). This condiction corresponds to the larger transmembrane flux in the end of process in the value of $3.2x10^5$ m/s (Fig. 6.a).



(a)

(b)

(c)

Figure 6. Total carbon - TOC (mg/l) in function of transmembrane pressure of permeate of microfiltration of emulsion water/sunflower using tube: (a) microporous without chemical impregnation; (b) tube microporous impregnated once and (c) tube microporous impregnated twice.

However the largest values of TOC in the permeate are due to the process with tube impregnated twice (Fig. 7.c). It is also observed that the transfer process is governed by a balance of forces among transmembrane pressure and shear stress. In all the cases, in the pressure of 500 kPa, the TOC decreases in function of increase of Reynolds.

Measurement of TOC of initial mixture between water and sunflower oil was of 5410 mg “C"/l. In relation to better condition for the process for the fluid dynamics and selected tube microporous (Fig. 7.b), the reduction of TOC corresponds at 99%, being the permeate a water of very good quality.

The results for the higher TOC (Fig. 7.c) regarding the process with the tube impregnated twice, indicates that the physical-chemical properties of the zirconia (Nabi *et al.*, 2000) in larger concentration, present in the microporous structure, probably increase the interfacial tension between the aqueous phase and the phase oil, facilitating the passage of the phase oil for the microporous structure. The surface interactions (superficial tension) between phase oil and the ceramic surface are larger than between the aqueous phase and the ceramic surface, turning the ceramic tube impregnated once highly hydrophilic or more permeable to the water.

4. Conclusions

The following conclusions can be drawn from the results of this experimental study:

i)The impregnation procedure was satisfactory, being possible the aggregation of nanoparticles in the tube of alumina.

ii)The microporous tubes performed well in the process with emulsions; the largest values of transmembrane flux were observed in the process with the tube impregnated once.

iii)The best condition of retention of the phase oil (or smaller TOC) went to the largest pressure transmembrane of the process, 5 bar and Re=21194 in the tube impregnated once. The value of TOC in permeate was of an excellent recycled water.

5. Acknowledgements

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