Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.986536

56 (2015) 3561–3567
December

Taylor & Francis
Taylor & Francis Group

Performance of zeolite membrane (ZSM-5/γ-Alumina) in the oil/water separation process

Janaína Rafaella Scheibler*, Everton Ranny Ferreira Santos, Antusia Santos Barbosa, Meiry Gláucia Freire Rodrigues

Academic Unit of Chemical Engineering, Federal University of Campina Grande, Av. Aprígio Veloso, 882 – Bodocongó, CEP 58109-970, Campina Grande, Brazil, Tel. +55 83 2101 1488; emails: janainarafaella@hotmail.com (J.R. Scheibler), everton.ufcg@gmail.com (E.R.F. Santos), antusiasb@hotmail.com (A.S. Barbosa), meirygfr@hotmail.com (M.G.F. Rodrigues)

Received 15 July 2014; Accepted 3 November 2014

ABSTRACT

There are several technologies for the treatment of oily wastewater generated by the oil industry, not only to separate the emulsified oil in water, but also to reduce its concentration in the aqueous effluent. Among the processes of separation, the separation using membranes should be highlighted when they become an effective material and it also resistant to high temperatures, have good corrosion resistance, easy to clean, and have long life operation, among others. This work aims to synthesize the material (ZSM-5, γ-alumina membrane, and zeolite membrane ZSM-5/γ-alumina) and to evaluate the membranes in the oil/water separation in a continuous flow system. From the XRD results of the individual materials, it can be observed the formation of all the characteristic peaks for each material. The EDX analysis of zeolite ZSM-5 showed the formation of this material with a Si/Al = 19. From the SEM image of these materials, it can be seen that the surface of the γ-alumina is completely covered with ZSM-5 zeolite crystals. The oil/water removing, using ZSM-5 γ-alumina membrane, showed high retention of the oil, obtaining a higher performance in relation to γ-alumina membrane. This reveals that the insertion of ZSM-5/γ-alumina in the material makes that this new material acquires a lower porosity, obtained by decreasing the passage of oil molecules through the membrane structure.

Keywords: ZSM-5; γ-alumina; Zeolite membrane; Oil/water separation

1. Introduction

The oil/water emulsion is an aqueous solution that is present in a variety of industrial applications, such as the petroleum, steel industries, and related ones, among others. The oil/water emulsion is generated as waste in industries, or it serves the purposes of lubrication, cooling, cleaning, and corrosion prevention in the manufacturing process where it is used. And thus, every year, large quantities are generated by many industries worldwide [1,2].

Membrane processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are

*Corresponding author.

Presented at the IX Ibero-American Congress on Membrane Science and Technology (CITEM 2014), 25–28 May 2014, Santander, Spain

1944-3994/1944-3986

increasingly applied to the treatment of oily wastewater. There are three broad categories of oily waste: the oil free ones, the unstable oil/water emulsions, and the highly stable oil/water emulsions. The membranes are useful to more stable emulsions, in oily residues, which are partially dissolved in water and have been used extensively for removing oil and grease from water produced [3–5].

The zeolite membranes, which are described as a crystalline zeolite layer, deposited on porous inorganic supports. These membranes have a uniform pore size (molecular scale), and they can separate molecules based on differences in the properties of absorption and the properties of diffusion of these molecules. They are used to separate or to fractionate the components of wastewater flows and to produce fewer pollutants, but without altering them chemically, reducing transportation costs and removal, making the permeate flow ready to be properly disposed. In comparison with other methods of treatment, the results of membrane technology produce effluents of good quality, it is a simple operation which requires a small area of operation, and the results are usually immediate and without the need for additional chemicals, reducing risk of incrustation [3,6].

The main disadvantage of this method of separation is the incrustation in which the particles are deposited on the membrane surface or in their pores. This problem can be solved by frequent cleaning of the membrane or it can be reduced depending on the type of pretreatment used to the residue [7,8].

The technique, used in order to obtain the zeolite membrane (ZSM-5/γ-alumina), is the mechanical mixing. This is an advantageous method compared with the methods using hydrothermal synthesis because it is relatively simple, low operating cost, and requires low energy consumption. The zeolite membrane obtained by the mechanical mixing allows the membrane to be completed in less than four h after the synthesis of the materials, while in other growth methods, wherein the zeolite is deposited on the porous environment by hydrothermal synthesis requires at least three syntheses until a satisfactory zeolite layer on the support so that the cost becomes higher.

The system of oil/water separation, used in this work, had a continuous flow of emulsion through a constant flow through the membrane to evaluate the quality of the permeate in the separation process. The tests performed in the laboratory simulated emulsions in real conditions.

2. Experimental

2.1. Materials

Aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) P.A. (A 1000 5G (Almatis, Inc.)), sodium aluminate (50–56% Al_2O_3, maximum 0.05% Fe_2O_3, 40–45% Na_2O, Riedel-deHaen), sodium hydroxide (NaOH—97%, Merck), deionized water, silica aerosil (SiO_2-Aerosil 200, Degussa), hexamethyleneimine (HMI 99%, Aldrich), oleic acid, PABA (para-aminobenzoic acid), and ethyl alcohol (Vetec, P.A. ACS (ethanol) C_2H_6O).

2.2. Synthesis of the ZSM-5 zeolite

The ZSM-5 zeolite was synthesized by hydrothermal synthesis, with a source of Si and Al. Concentrated sulfuric acid was used to adjust the pH of the gel. Tetrapropylammonium bromide (TPABr) was used as a structure for the agent (organic model). Initial blends were formed using the following procedures [9,10] TPABr and reagents for the formation of zeolite ZSM-5 were first dissolved in deionized water from separate solutions under stirring at room temperature. A mixture of the mineralizing agent (NaOH) was also dissolved in deionized water with stirring. The ethanol was then added dropwise to the mixture, acting as a codirecionador. The final pH of the mixture was adjusted with sulfuric acid (final pH 11). After stirring for one h at room temperature, the mixture was placed in a stainless steel autoclave of 70 mL and allowed to react in an oven at 443 K for 48 h. After crystallization, the solid product was centrifuged and washed thoroughly with deionized water. A product was obtained by drying the solid at 343 K for 24 h, followed by calcination at 823 K for six h under an air atmosphere to remove the organic model, producing ZSM-5.

2.3. γ-Alumina membrane preparation

Initially, the thermal decomposition of aluminum sulfate ($Al_2(SO_4)3 \cdot 16\ H_2O$) PA was carried out in a muffle furnace at a temperature 1,275 K, using a heating rate of 280 K/min for two h to obtain γ-alumina crystal phase. There was a mixture of alumina with additives in a total of 200 ml of dispersion in the following composition: 40% of alumina obtained above; 0.2% of para-aminobenzoic acid (dissolved in ethanol), 0.5% oleic acid (lubricant), and 59.3% ethyl alcohol. The mixture was ground for one h in a ball mill, and then placed in an oven for 24 h at 333 K for drying. Exactly 3 g of the material was inserted into a stainless steel mold and pressed for two min with 4 ton. The ceramic membrane was submitted to a heat treatment at 823 K for 4 h, to acquire the requisite mechanical strength. It was obtained a ceramic flat membrane (γ-alumina), with the dimensions: diameter 28 mm and thickness of 3.2 mm.

2.4. Preparation of zeolite membrane ZSM-5/γ-alumina

For membrane preparation, the method of mechanical mixing was applied. In this process, 1.5 g of ZSM-5 zeolite was added to 1.5 g of γ-alumina powder. The mixture was mechanically inserted into a stainless steel mold, which was compressed with 4 ton for 2 min. After that the membrane was submitted to a heat treatment at 550℃ for 4 h, with the purpose of improving its mechanical strength. After these steps, it was obtained a planar inorganic membrane (ZSM-5/γ-alumina) with the following dimensions: 28 mm diameter and 3.2 mm thick.

This method has some advantages over the hydrothermal process, once is not necessary a source of thermal energy and it is a process of rapid preparation, consequently, it has a very low cost compared with other synthesis methods.

2.5. Membrane microfiltration treatment of oil-in-water emulsions

To achieve the separation tests, a sample of emulsion oil/water with a concentration of 600 mg/L was produced. The oil used was Lubrax lube oil. It was added to the sodium emulsions chloride at a concentration of 2,500 mg/L to simulate the salinity of the seawater. The emulsions were prepared under intensive stirring, 17,000 rpm, sufficient for the formation of emulsions during 20 min of rotation. The oil/water emulsion was fed to the separation system under conditions of 298 K and 5 mL/min. Inorganic membranes (γ-alumina and ZSM-5/γ-alumina) were inserted into the separation column to evaluate their performances in continuous system for the removal of oil.

Fig. 1 shows the system of water separation from the oil/water system, which was used in this work. The components of the system are: (1) solution oil/water (600 mg/L); (2) peristaltic pump-Cole-Parmer-(flow rate set to 5 mL/min); (3) membrane separation column. In this system, the emulsion passes through the membrane and the permeate is collected at the end of the process.

The oil/water emulsion was fed to the separation system under conditions of 298 K and 5 mL/min. Inorganic membranes (γ-alumina and ZSM-5/alumina) were inserted into the separation column to evaluate their performances in continuous system for the removal of oil. Thus, it was evaluated the performance of inorganic membranes (γ-alumina and ZSM-5/γ-alumina) in the continuous system for the removal of oil.

Oil–water separation test: The concentration of oil present in the aqueous phase was determined by absorption analysis using a spectrophotometer (UV–visible/UV Shimadzu 1800). A calibration curve of absorbance vs. concentration, using various oil concentrations varied from 0 to 600 ppm was built. The chloroform was used as solvent for the extraction, because of its excellent response (significant peak) at a wavelength of 262 nm for the samples. The absorbance at this wavelength is commonly used to estimate the concentration of oil in water samples [11,12] and also in the water produced. This wavelength is measured by aromatic CH band in the medium. This application procedure was designed to standardize the determination of oil and grease.

The permeate flow was calculated by dividing the volume of permeated by the product of the membrane area, and the sample of time and the oil rejection coefficient R was calculated as a percentage according to the following expression:

$$\%R = \left(\frac{C_f - C_p}{C_f}\right) \times 100 \quad (1)$$

where C_f is the concentration of oil in the feed and C_p is the concentration of oil in the permeate [2].

2.6. Characterization

2.6.1. Diffraction (XRD)

The powder method was used, through which the samples were sieved, ABNT No. 200 (0.074 mm) sieve, and then placed in an aluminum sample holder by X-ray diffraction, using Shimadzu XRD 6000 equipment. Operational details of the technique are defined as follows: copper Kα radiation at 40 kV/30 mA, goniometer with a speed of 2˚/min, and a step of 0.02˚ in 2θ scanning range 2˚–70˚.

2.6.2. X-ray spectroscopy energy dispersive rays (EDX)

The surface composition of the samples was determined with a Shimadzu EDX-700 X-ray Energy Dispersion Spectrophotometer (EDX).

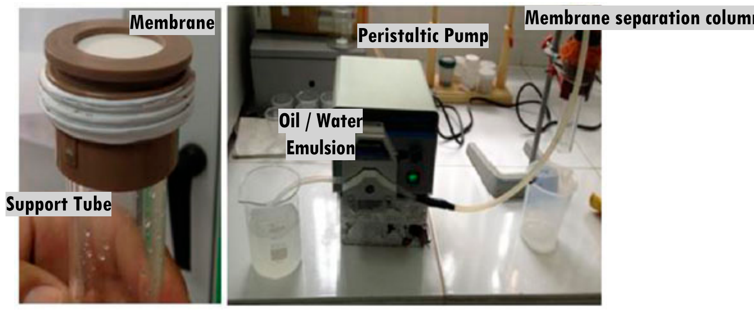

Fig. 1. Column for insertion into the membrane, and a continuous flow system used for separating oil/water emulsions.

2.6.3. Scanning electron microscopy (SEM)

The powder samples were recovered with a thin layer of gold, due to the high electron conductivity of this metal, fixed in the alumina sample door by an adhesive carbon tape. The micrographs necessary to analyze the morphology of the samples were obtained using a scanning electron microscope Philips XL 30 EDAX equipped with X-ray energy dispersive spectrometer (EDS).

The determination of the concentrations of oil and grease were obtained by chloroform method [1,12].

3. Results and discussion

The diffraction analyzes (XRD) were performed on zeolite ZSM-5, the γ-alumina membrane and the zeolite membrane ZSM-5/γ-alumina. In Fig. 2 the zeolite ZSM-5 structure can be seen, through the five main peaks, more intensive, identified by the symbol (*). Two peaks are located at $2\theta = 07.09^\circ$ (doublet) and three peaks at $2\theta = 23–25^\circ$ (triplet). It is also observed that the structure analyzed does not show the presence of secondary phases, only the characteristic peaks of zeolite ZSM-5 phase [13].

From the analysis of Fig. 2, it is noted that there is the formation of specific peaks of γ-alumina phase, marked with the symbol (°) obtained after decomposition of aluminum sulfate. The presence of impurities or other phases are not observed, which indicates a pure material [14,15].

Fig. 2 also shows the confirmation of the formation of zeolite structure in the membrane (ZSM-5/γ-alumina), developed in this work, due to mechanical mixing. It can be clearly noticed the identification of the peaks related to the phase ZSM-5 zeolite (°) peaks related to the phase corresponding of γ-alumina (*) [16].

Table 1 shows the results of chemical composition of the zeolite ZSM-5 sample. The data were obtained

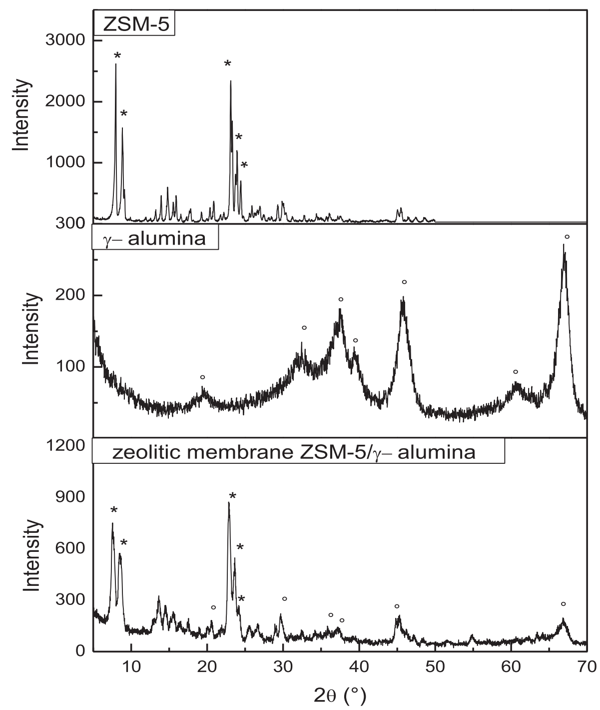

Fig. 2. XRD patterns of samples: ZSM-5 zeolite, γ-Al_2O_3, and membrane zeolite (ZSM-5/γ-Al_2O_3).

from the analysis of Energy Dispersive Spectrometry analysis of X-ray (EDX).

According to the data in Table 1, it can be seen that ZSM-5 has a high percentage of silicon oxide (SiO_2) and low content of aluminum oxide (Al_2O_3), which results in a high ratio of SiO_2/Al_2O_3 approximately 19. The ratio SiO_2/Al_2O_3 for the synthesis of ZSM-5 zeolite should be between 15 and infinity [17].

The SEM images of the ZSM-5 zeolite, γ-alumina, and zeolite membrane (ZSM-5/γ-alumina) which were synthesized are given in Fig. 3.

Through (Fig. 3(a)) where the scale is 20,000 times, it was observed that the sample consists of spherical

Table 1
Chemical composition of the zeolite ZSM-5 sample

Sample	SiO_2 (%)	Al_2O_3 (%)	Impurities (%)	SiO_2/Al_2O_3
Zeolite ZSM-5	91.62	4.67	3.71	19.0

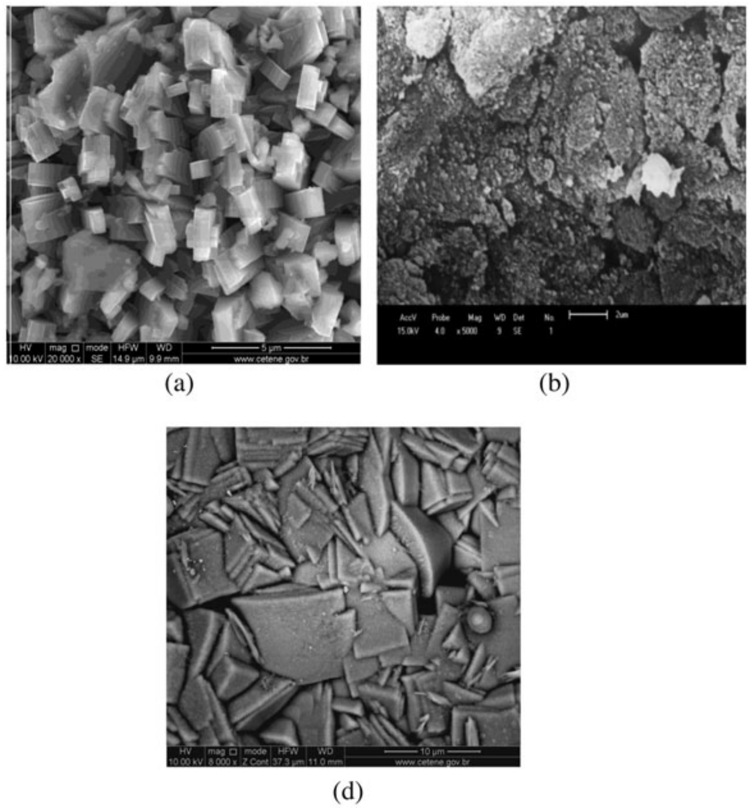

Fig. 3. SEM images of the zeolite ZSM-5 (a), γ-alumina membrane (b), and zeolite membrane (ZSM-5/γ-alumina) (c).

agglomerates of small crystals which have a cubic shape.

The micrograph (Fig. 3(b)) shows the morphology of the γ-alumina. In general, this material has a morphology made up of agglomerates of particles also being possible to observe the presence of homogeneous pores and structure [18].

From the SEM image (Fig. 3(c)), it can be seen that the surface of the γ-alumina is completely covered with ZSM-5 zeolite crystals. Maybe this can be explained by the fact that a zeolite powder is less dense than the support powder of γ-alumina and because of this the volume of the zeolite is greater than the support, and the 1:1 ratio makes that the volume occupied by the zeolite is enough to be predominant on the surface of the support.

The efficiency of the oil/water separation process of the emulsion using inorganic membranes: γ-alumina, ZSM-5/γ-alumina, using the experiments of continuous filtration in the system, as described in the methodology. The concentration of the permeate with respect to time for the filtration experiment with γ-alumina membrane is shown in Fig. 4. The inorganic membranes (γ-alumina and ZSM-5/γ-alumina) were used for the filtration of contaminated water (600 mg/L theoretical), noting a significant regression of the oil concentration. So, there is a great efficiency in the oil removal for the two membranes. However, there is an emphasis on ZSM-5/γ-alumina membrane, which reached permeate with a concentration of 56.04 mg/L, which is the better removal compared with the γ-alumina membrane, which reached a concentration of 220.52 mg/L. The

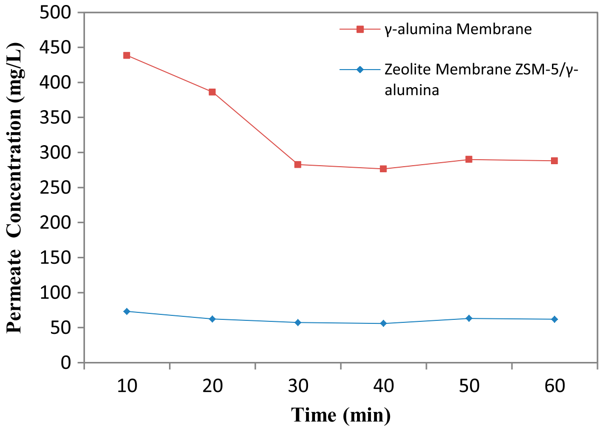

Fig. 4. Figure removing oil/water emulsion over time of the inorganic membrane filtration to γ-alumina membrane and zeolite membrane ZSM-5/γ-alumina.

lower the concentration of the permeate, the more efficient is the separation. With this, it is possible to notice that the performance of zeolite membrane ZSM-5/γ-alumina is much higher than that of γ-alumina membrane without the inclusion of zeolite.

Fig. 5 shows the flow for zeolite membrane ZSM-5/γ-alumina.

From the data, presented in Fig. 5, it is possible to observe a decrease in flow through the zeolite membrane ZSM-5/γ-alumina as time goes by. This shows that the flow of the oil/water emulsion through the membrane becomes less in the course of time. There was a decrease in 23.12 L/m^2 h, in the first 20 min, and afterward, the decreasing in the flow becomes more pronounced 30 min, with a flow decreased in 93.37 L/m^2 h, in relation to the initial time and it keeps decreasing until the end of the test. This decrease in flux through the membrane is observed by several investigators, because the particles of oil are deposited on the membrane surface or in its pores. This problem can be solved with frequent cleaning or can be reduced depending on the type of pretreatment used for residue [7,8]. However, as shown in Fig. 4, the removal results are very satisfactory throughout the test and are not affected by the flow decrease up to the first 50 min of the test.

Fig. 6 presents the oil content in the permeate stream and the calculated oil rejection coefficient, *R*. The membrane results of oil/water separation to γ-alumina membrane and zeolite membrane ZSM-5/γ-alumina made in a continuous system, where the values of the permeate concentration over time through each membrane and the removal percentage for each material.

It can be noticed, in Fig. 6, that the removal of the ceramic membrane in the permeate in ceramic membrane decreased by 39% in 10 min. Between 20 and 30 min a steeper decrease in the concentration of the permeate occurs. After 30 min, the filter reaches stability at a level of satisfactory 62.32%.

The results of the experiment using membrane of zeolite ZSM-5/γ-alumina show that, after 30 min, there is no almost change in the concentration, and this remained stable and satisfactory during the time interval, as shown in Fig. 6.

When comparing the inorganic membranes (γ-alumina and ZSM-5/γ-alumina), it is possible to check that with the insertion of ZSM-5 to the ceramic membrane (γ-alumina), using the technique of mechanical mixing occurred a better results in the separation of oil in the permeate. Observed that the best result for (ZSM-5/γ-alumina), in 91.33%, compared with the best result of the ceramic (γ-alumina) membrane with 62.32%.

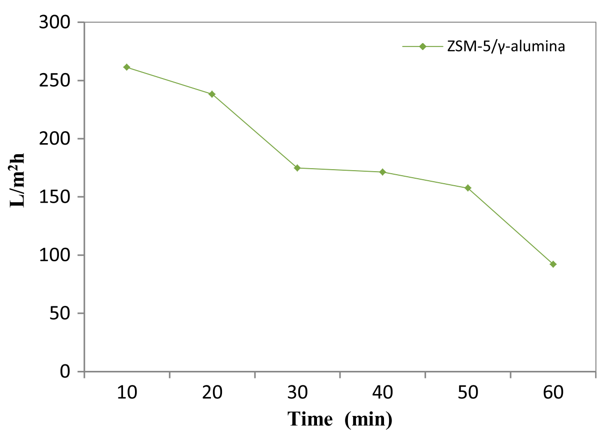

Fig. 5. Flow along the filtration time for the zeolite membrane ZSM-5/γ-alumina.

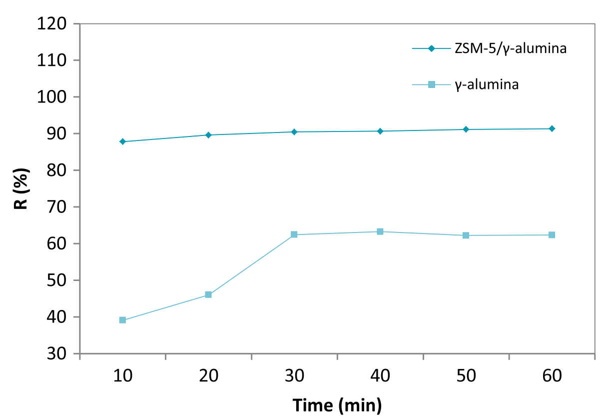

Fig. 6. Oil rejection coefficient, *R* of inorganic membranes (γ-alumina and ZSM-5/γ-alumina), over the flow time.

From the data cited, it was observed that the membrane had a great time over 60 min performance showing that the damage to the membrane and the adhesion of organic material in your pores, was not enough to cause a significant decrease in removal. This reinforces the fact that the membrane is a very advantageous option in oil/water separation.

4. Conclusions

From the analysis of the high quality of the permeate obtained from the filtration of two membranes evaluated in the process, it was noticed a good performance both when compared with traditional separation methods. The insertion of zeolite ZSM-5 to γ-alumina improved the ability of zeolite membrane (ZSM-5/γ-alumina) in removing oil emulsions, with a percentage of removing of 91.33%, showing an efficiency and a good result as expected due to the characteristic of opening the pores of ZSM-5, and the ability to retain and to stop the passage of most oil molecules of smaller size. Thus, it can be concluded that the membrane (ZSM-5/γ-alumina) is a good alternative to the treatment of aqueous effluents.

Acknowledgments

The authors gratefully acknowledge PRH-25/ANP/UFCG, Petrobras e CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior).

References

[1] S.H. Lin, W.J. Lan, Waste oil/water emulsion treatment by membrane processes, J. Hazard. Mater. 59 (1998) 189–199.

[2] J. Cui, X. Zhang, H. Liu, S. Liu, K.L. Yeung, Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water, J. Membr. Sci. 325 (2008) 420–426.

[3] M. Cheryana, N. Rajagopalan, Membrane processing of oily streams. Wastewater treatment and waste reduction, J. Membr. Sci. 151 (1998) 13–28.

[4] A.S.C. Chen, J.T. Flynn, R.G. Cook, A.L. Casaday, Removal of oil, grease, and suspended solids from produced water with ceramic crossflow microfiltration, SPE Prod. Eng. 6 (1991) 131–136.

[5] A. Zaidi, K. Simms, S. Kok, The use of micro/ultrafiltration for the removal of oil and suspended solids from oilfield brines, Water Sci. Technol. 25 (1992) 163–176.

[6] T.C. Bowen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, J. Membr. Sci. 245 (2004) 1–33.

[7] N. Kubota, Polymer membranes, filtration membranes for water treatment, Purasuch. Eji 56 (2010) 72–75.

[8] S. Rezaei, M.R. Abadi, M.R. Sebzari, M. Hemati, F. Rekabdar, T. Mohammadi, Ceramic membrane performance in microfiltration of oily wastewater, Desalination 265 (2011) 222–228.

[9] H. Feng, C. Li, H. Shan, In situ synthesis and catalytic activity of ZSM-5 zeolite, Appl. Clay Sci. 42 (2009) 439–445.

[10] Y.L.Lam, Processo de preparação de zeólito tipo ZSM-5, Petrobras, BR no. PI 8506248 (1987) (in Portuguese).

[11] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for Examination of Water and Wastewater. twentieth ed., American Public Health Association, Baltimore, MD, 1999.

[12] S.B. Henderson, S.J.W. Grigson, P.E. Johnson, B.D. Roddie, Potential impact of production chemicals on the toxicity of produced water discharges from North Sea oil platforms, Mar. Pollut. Bull. 12 (1999) 1141–1151.

[13] M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites, fourth ed., Elsevier, Amsterdam, 2001.

[14] M.G. Ma, Y.J. Zhu, Z.L. Xu, A new route to synthesis of γ-alumina nanorods, Mater. Lett. 61 (2007) 1812–1815.

[15] M.S. Ghamsari, Z.A.S. Mahzar, S. Radiman, A.M.A. Hamid, Sh.R. Khalilabad, Facile route for preparation of highly crystalline γ-Al_2O_3 nanopowder, Mater. Lett. 72 (2012) 32–35.

[16] V. Parvulescu, C. Tablet, B.L. Su, Zeolite membrane with orientation-controlled hexagonal crystals from a mesostructured gel supported on γ-Al_2O_3, Colloids Surfaces A: Physicochem. Eng. Aspec. 300 (2007) 94–98.

[17] G.P. Gianneto, Zeolitas: Características, Propriedades y Aplicaciones Industriales, Ediciones Innovación Tecnológica, Caracas, 1990.

[18] S. Abedini, N. Parvin, P. Ashtari, Preparation, characterization and microstructural optimization of a thin γ-alumina membrane on a porous stainless steel substrate, Mater. Sci. Eng. 533 (2012) 1–8.