

© 2024 Universidad Nacional Autónoma de México, Facultad de Estudios Superiores Zaragoza.
This is an Open Access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).
TIP Revista Especializada en Ciencias Químico-Biológicas, 27: 1-9, 2024.
<https://doi.org/10.22201/fesz.23958723e.2024.649>

Reduction of water hardness with porous membranes made with Mexican clays

Víctor Pérez-Moreno¹, Miriam Martínez-González²,
Miguel Angel Ramos-López¹, Juan Campos-Guillén¹, José Santos-Cruz¹,
José Alberto Rodríguez-Morales³ and Carlos Eduardo Zavala-Gómez^{3*}

¹Faculty of Chemistry, ²Faculty of Administration, ³Faculty of Engineering, Autonomous University of Queretaro, Cerro de las Campanas s/n, Colonia Las Campanas, Santiago de Querétaro 76010, Querétaro, México. E-mail: *ezavala2@gmail.com

ABSTRACT

Based on the properties that clays have, they are considered as raw material for membrane preparation. It is reported that these materials agglomerate easily and possess ion exchange characteristics as well as adsorption capacity for water treatment. The aim of this study was to use Mexican clays to obtain porous membranes to decrease water hardness. The technique used to elaborate the membranes developed during this study consists of the compaction of clay and its subsequent sintering. In the pressing of the raw material, additives were used as lubricants and binders. The pressing was performed in a hydraulic press with a pressure of 150 to 300 Kg/cm². The sintering was conducted in a muffle at 500 °C, 800°C and 1,000°C. The raw material was characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF) as well as Nitrogen physisorption. Using X-ray fluorescence, it was determined that the samples of Mexican clay are mainly composed of oxides containing Silicon, Aluminum, Iron, Calcium, and Potassium. Through nitrogen physisorption of the calcined clay, it was inferred that the clay is a mesoporous material. The material exhibits a unimodal distribution; the average pore diameter is 3.42 nm and the specific surface area was 48.8 m²/g. Heat treatment caused chemical changes in the material, which were detected and analyzed by X-ray diffraction. The membrane obtained was characterized using X-ray diffraction (XRD), Nitrogen physisorption, and Scanning Electron Microscopy (SEM). The result of these techniques corroborated that the membrane obtained can be used in filtration processes and was able to remove over 40% of water hardness.

Keywords: mexican clay, membrane, filtration, sintering, water hardness.

Disminución de la dureza del agua con membranas porosas elaboradas con arcillas mexicanas

RESUMEN

Las arcillas por sus propiedades, son empleadas como materia prima en la elaboración de membranas, debido a que se aglomeran fácilmente y poseen características de intercambio iónico, así como capacidad de adsorción para el tratamiento del agua. El objetivo de este estudio fue utilizar las arcillas mexicanas para obtener membranas porosas y con ellas disminuir la dureza del agua. La técnica utilizada consistió en la compactación de la arcilla y su posterior sinterización. En el prensado de la materia prima se usaron aditivos como lubricantes y aglomerantes, además de una prensa hidráulica con una presión de 150 a 300 Kg/cm². La sinterización se realizó en una mufla a 500 °C, 800 °C y 1,000 °C. La materia prima se expuso a la difracción y a la fluorescencia de los rayos X (XRD) y X (XRF), respectivamente, así como a la fisisorción de nitrógeno. Mediante la fluorescencia de los rayos X se vio que las muestras de arcilla mexicana están compuestas principalmente por óxidos que contienen silicio, aluminio, hierro, calcio y potasio. A través de la fisisorción de nitrógeno de la arcilla calcinada, se comprobó que es un material mesoporoso, por presentar una distribución unimodal; el diámetro del poro promedio es de 3.42 nm y el área superficial específica de 48.8 m²/g; con el tratamiento térmico hubo cambios químicos que fueron detectados y analizados por difracción de rayos X (XRD). La membrana estuvo además sujeta a la fisisorción de nitrógeno y microscopía electrónica de barrido (SEM). Los resultados de estas técnicas corroboraron que se puede emplear en los procesos de filtración y con la capacidad de eliminar más del 40% de la dureza del agua.

Palabras clave: arcilla mexicana, filtración, membrana, sinterización, dureza del agua.

Artículo recibido el 05 de diciembre del 2023.

Artículo aceptado el 03 de junio del 2024.

INTRODUCTION

Clay is a material comprised of hydrated aluminum silicates aggregates originating from the decomposition of rock containing feldspar. The clay used in this study is employed in the manufacturing of ceramics (bricks, pottery, etc.) X-Ray Fluorescence (Silva *et al.*, 2020) determined its composition. This has several colorations depending on the impurities, which range from red-orange to white when pure. Physically, it is considered a colloid of extremely small particles with a smooth surface. The diameter of the clay particles is less than the particles that make up the soil vary in size, between very broad limits, the smallest being those of the clay fraction (Mora & Tejeira, 2019). The textural clay fraction may not be composed of mineral particles. Chemically, it is a hydrous silicate of alumina, whose formula is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. This material is characterized by acquiring hardness when heated above 500 °C. Hardened clay pottery was first made by humans and is still an inexpensive and widely used for the preparation of various artisanal objects (Bensoain, 1969). During the past 25 years, there has been impressive development in technological processes based on the use of membranes (Yusuf *et al.*, 2020).

This has resulted in interdisciplinary technologies with a wide scope, covering various areas such as osmosis, reverse osmosis, dialysis, microfiltration, ultrafiltration, gas separation reactors, and separators (catalytic membranes). These filtration processes are applied in industries such as: chemical, petrochemical, biochemical, nuclear, and food (Nunes *et al.*, 2020). The membranes that are generally used in these processes can be classified into two groups according to the nature of the material: organic or inorganic (Zhang *et al.*, 2022).

Based on the properties that clays and zeolites (silico-aluminates) have, they are considered as raw materials for the development of membranes. According to literature these materials agglomerate easily and possess ion exchange characteristics as well as adsorption capacity for water treatment, their disadvantage is that they become saturated over time. (Hristov, Yoleva, Djambazov & Dimitrov, 2012; Fakhfakh, Baklouti, Baklouti & Bouaziz, 2010; Liang, Huang, Zhang, Fu, Zhang & Chen, 2021). For the development of membranes based on silico-aluminates, the objectives pursued were create a structure with homogeneous distribution of pores, obtain adequate physicochemical stability, define porosity that allows for the selective separation of a mixture, and obtain high permeability (Harabi, Bouzerara & Condom, 2009; Bouzerara, Boulanacer, Harabi, Boudaira, Achour & Condom, 2009; Adam *et al.*, 2022). The characterization of materials involves the establishment of the structural properties and physical-chemical characteristics (Sapag, Solar, Ricardo, Oliveira & Lago, 2013; Amin & Subri, 2018; Belgada *et al.*, 2021). The aim of this study was to characterize and use Mexican clays to obtain and describe porous membranes to decrease water hardness.

MATERIALS AND METHODS

This study presents the characterization of Mexican clay obtained from La Solana, Querétaro, Mexico (20°44.303'N-100°23.342'W). The techniques used for the characterization of the Mexican clay were as follows: X-Ray Diffraction, X-Ray Fluorescence, and Nitrogen Physisorption. These techniques were used to determine the composition and structure of the raw material as well as the membrane preparation techniques implemented.

X-Ray diffraction

The compounds present in the Mexican clay were determined through X-Ray Diffraction and through diffractograms on a Bruker brand D8 Advance diffractometer using Cu-K α radiation ($\lambda=0.15406$ nm) with a range of 10-80° in 2 θ . The particle sizing was performed using the Scherrer equation. For the analysis of the sample there was no need for special preparation, since it is not required for the X-ray diffractometer.

X-Ray fluorescence

For X-ray fluorescence there were two types of sample preparation: First. Loose powder. The clay was ground into samples of sizes less than 60 micrometers. The powders were placed in a glass for liquid samples, using a 6-micron thick Mylar film as a carrier with an area of analysis of approximately 30 mm in diameter. Second. Cast bars. The samples were analyzed for their loss on ignition (LOI) by melting 1 g of sample in 6 grams of lithium tetraborate flux ($\text{Li}_2\text{B}_4\text{O}_7$), to ensure that flux to sample ratios reflects only non-volatile elements that will be present after fusion (Zipkin, Ambrose, Lundstrom, Bartov, Dwyer & Taylor, 2020). To analyze this process, an Axios brand advanced model with analytical PAN wavelength sequential spectrometer equipped with an X-ray tube containing Rhodium anode was used. For analysis, a sequential spectrometer wavelength PAN analytical brand Axios Advanced model with X-ray tube with Rhodium anode was used.

Nitrogen physisorption

By Nitrogen physisorption the textural properties of the Mexican Clay were determined from the Nitrogen adsorption isotherms recorded at 77 K with a Quantachrome iQ2 apparatus. The samples were previously degassed at 423 K for 24 h under a vacuum (10-4 mbar) to ensure a clean, dry surface, free of any loosely bound adsorbed species. The specific area of the sample was calculated according to standard BET procedure using nitrogen adsorption data collected in the relative equilibrium pressure interval of $0.03 < P/P_0 < 0.3$. Pore size distributions were calculated from the desorption branches of the corresponding nitrogen isotherm using the BJH method (Betancourth, Gómez, Mosquera & Mejía, 2010). The total pore volume (V_{total}) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99.

Membrane preparation

Mexico is facing water scarcity problems that will increase in the coming years. The selected site in Querétaro (La Solana), where sampling and characterization were done, is a suitable place to collect clay for membrane preparation due to its low price and availability (industrial zone of San Nicolás) as well as its composition (silico-aluminates), which allows chemical affinity. For membrane preparation using the pressing technique, a series of steps were required to obtain a proper membrane with suitable physical and chemical properties. First, milling and sieving of the clay was performed. Followed by the selection of the binder, selection of the lubricant, pressing, heat treatment, and finally the membrane was obtained. The mold used was designed with flat type steel using the following dimensions: length = 2 cm, outer diameter = 5 cm, and inner diameter = 3 cm. The membrane preparation technique that was developed in this study was through compaction and subsequent sintering of the clay. In the pressing of the clay, additives such as lubricants and binders were necessary for obtaining a proper membrane. To evaluate the efficiency of the membranes in reducing water hardness, acrylic reactor was constructed. In this reactor, the membrane was mounted in the central point using an O-ring to avoid leakage.

Scanning electron microscopy (SEM)

For scanning electron microscopy, a JEOL-JSM-7800F was used. It was necessary to split the membrane and mount it in the sample holder, which was covered with a layer of graphite (because the sample is not electrically conductive). The accelerating voltage used in the microscope was 20 kV and the images were formed from secondary electrons. The samples were coated by an amorphous carbon thin film to avoid electrostatic charge accumulation using an EMS 150T sputter. Finally, the sample holder was placed in the scanning electron microscope to be observed.

Membrane evaluation

Figure 1 shows the diagram used in the study to filtrate the water. To evaluate the membrane, three separate readings for each sample and blank were taken. The method consisted of an assay using a visual indicator endpoint, the eriochrome black T, which is red in the presence of Calcium and Magnesium and turns blue when they are bound or absent. The analysis of water hardness was conducted in accordance with the provisions of the Official Mexican Regulations and Standards NMX-AA-072-SCFI-2001. This draft Mexican standard establishes the analysis method for determining total hardness in natural and wastewater. Finally, using the membrane obtained the analysis of water samples and quantitative calculations were made as established by the Official Mexican Regulations and Standards. The pump used was a ProMinent, Model GALA1801PPB200UD012000 (Heidelberg - Germany).

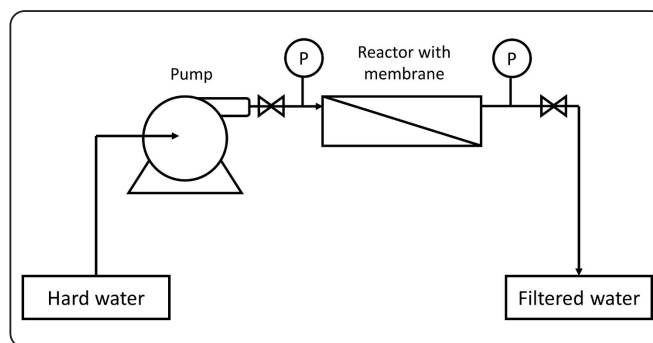


Figure 1. Diagram of the equipment used in the study.

Total hardness expressed as where:

$$\text{CaCO}_3 \text{ (mg / L)} = \frac{(A - B) \times C \times 1,000}{D}$$

A are the mL of EDTA titration spent on the sample;

B mL of EDTA spent on the titration in the blank;

C mg CaCO₃ equivalent to 1 mL of EDTA;

D mL of the sample.

RESULTS AND DISCUSSION

The properties physico-chemical of membrane composed of this material was evaluated through X-Ray Diffraction, X-Ray Fluorescence, and Nitrogen Physisorption to determine whether it is a useful raw material for membrane preparation.

Mexican clay characterization

X-Ray diffraction

The raw material was characterized by X-ray diffraction at four different temperatures (25, 500, 800, and 1,000 °C). The Mexican clay used in this study was basically composed of feldspars [K (AlSi₃O₈)] corresponding to the series of plagioclase mainly andesine. It also contains Fe₂O₃ and SiO₂ (tridymite and quartz) (Figure 2). The heat treatment causes a phase transition from andesine to anorthite. At high temperatures the formation of anorthite is favored, but it depends on the amount of Calcium or Sodium present in the sample. Moreover, there is a phase transition due to heat treatment with SiO₂ minerals. Quartz has a higher thermodynamic temperature stability at low temperatures, (present in the sample at 25 and 500 °C), and it transformed to tridymite at high temperatures (Figure 3).

The heat treatment caused the removal of some amorphous compounds, possibly of an organic nature (Lahsini, Bentama, Addaou & Rafiq, 1998). This is observed in the change of the shape of the base line of the diffractograms at 25 °C and 500 °C. In these diffractograms, few curves were observed

between 10-15° and 20-30° in 2θ, and similarly were not present in the diffractograms of 800 °C and 1,000 °C. The heating phase transitions originated in the andesite state, which then transformed into anorthite, however, Quartz, became tridymite. In Potassium feldspar and Iron oxide compounds, no changes occurred due to heat treatment (Figure 4 and Figure 5).

X-Ray fluorescence

The results showed that this clay is mainly composed of silica and alumina (56%). Moreover, the presence of Iron oxide (8.28%) indicates color oxide in clay (López, Etcheverry &

Botto, 2013). Table I gives the mass percentages of different oxides composing the Mexican clay.

In Mexico and North Africa (Morocco and Tunisia) clays are abundant and inexpensive. Previous studies on the characterization of clays for the preparation of membranes based on these materials are compared with this study. Mexican clay contained a higher percentage of organic matter (29%) when compared to African clay (15%) (Bentama, Ouazzani & Schmitz, 2002; Anbri, Tijani, Coronas, Mateo, Menéndez & Bentama, 2008). The amount of alumina was similar in both clays and silica was slightly lower in the Mexican clay. However,

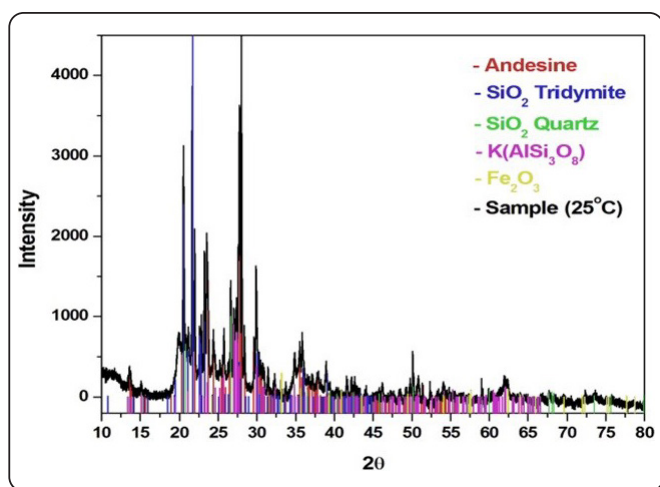


Figure 2. XRD spectrum of Mexican clay (25 °C).

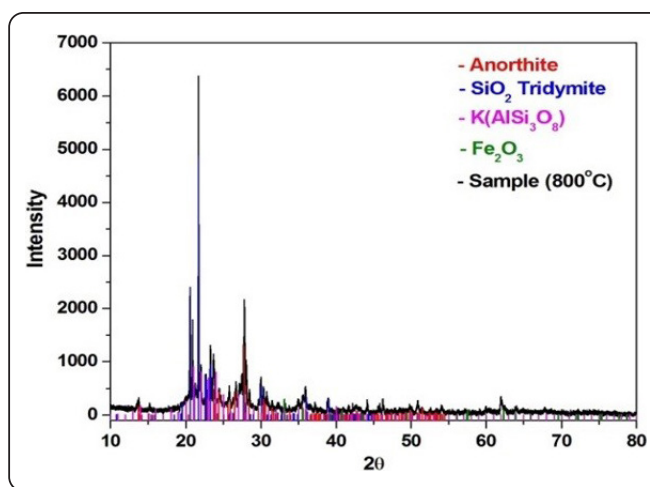


Figure 4. XRD spectrum of Mexican clay (800 °C).

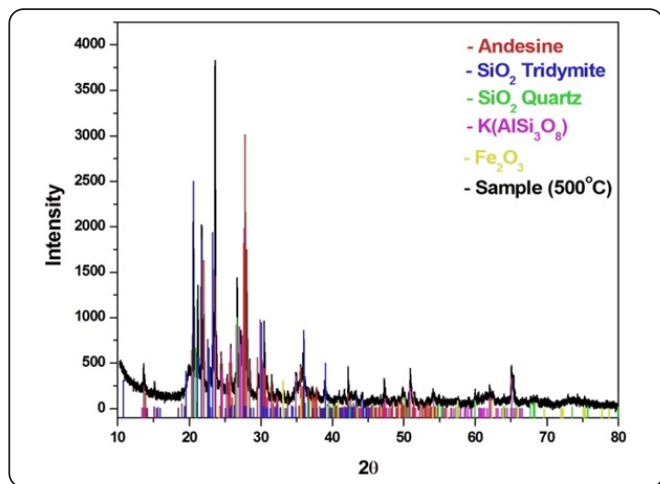


Figure 3. XRD spectrum of Mexican clay (500 °C).

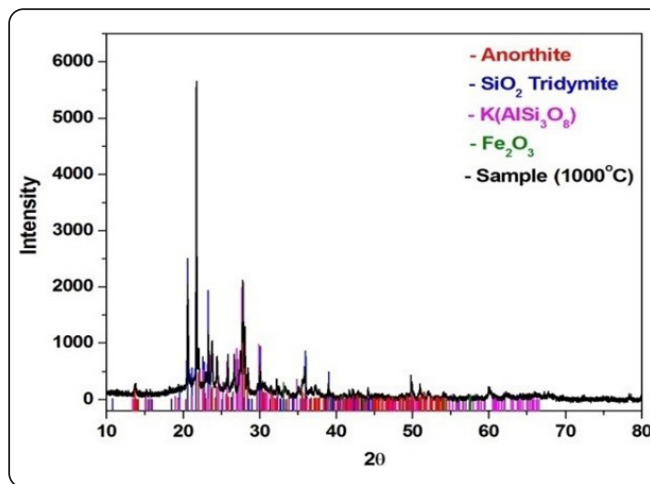


Figure 5. XRD spectrum of Mexican clay (1,000°C).

Table I. Chemical composition of natural Mexican clay.

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	MgO	TiO ₂
%	44.63	11.64	8.28	1.72	1.7	1.4	0.92	0.79

Iron oxide was superior and Calcium oxide was lower in the Mexican clay. The remaining oxides were similar in both clays. The Mexican clays mainly contained Al_2O_3 and SiO_2 , which have capacity for chemical affinity. This makes them potentially attractive for membrane preparation.

Nitrogen physisorption

The N_2 adsorption-desorption isotherms of the Mexican clay corresponded to the type II isotherms according to IUPAC classification (Zelenka, Horikawa & Do, 2023). The isotherm was reversible at low relative pressures and hysteresis loop at higher relative pressures, which corresponded to the H3 type hysteresis loop. This type of hysteresis loop is characteristic for aggregated and agglomerated plate particles forming slit shape pores (Vuković, Milutinović-Nikolić, Krstić, Abu-Rabi, Novaković & Jovanović, 2005). The enlargement of the hysteresis loop implies no uniformity in shape and size of the pores (Gelves, Monroy, Sánchez & Ramírez, 2013). The clay exhibited a unimodal distribution; the average pore diameter was 3.42 nm, and the specific surface area was 48.801 m^2/g . In Figure 6 adsorption isotherm types are showed (Zelenka *et al.*, 2023).

Membrane preparation

The technique developed during this study for the preparation of the membrane was through the pressing the raw material. Posteriorly, the membrane was treated at different temperatures allowing it to harden to obtain the final membrane (Pérez-Moreno, Arellano & Ramirez, 2004). First, the Mexican clay was crushed and screened. During the pressing of the raw material (clay), it was necessary to take additives into consideration, such as choosing adequate lubricants and binders (stearic acid and alumina). When additives were not used, the membranes broke easily. However, when stearic acid and alumina were used, good textural property membranes

were obtained. The global density was determined against the uniaxial pressure for the combination of stearic acid and alumina with the clay. The best properties for obtaining the membranes (membranes without rupture problems) were found using stearic acid (5%) and alumina (15%), taking into consideration the influence of the clay granule (300 μm of size particles). Anbri *et al.* (2008) reported 56% of silico-aluminate in the clay of Meknes (Morocco), the same percentage as the one reported in the present study. Also, Bentama *et al.* (2002) reported the same average of silico-aluminate in Fés (Morocco).

Membrane characterization

X-Ray diffraction

Figure 7 shows the diffractogram of the membrane made of Mexican clay and shows that the reflections present are consistent with the applicable standards of the following phases: Sodium anorthite, potash feldspar [$K(AlSi_3O_8)$] and two polymorphs of SiO_2 (quartz and tridymite). This indicates that the nature of the sample is fiery in nature. They are composed of mostly tectosilicates group, plagioclase and orthoclase. The presence of the mixture of quartz and tridymite is because the sample was thermally treated and moderately cooled.

Scanning electron microscopy (SEM)

In Figure 8, the membrane made from Mexican clay (80%), alumina (15%), stearic acid (5%), compacted to 300 Kg/cm^3 and sintered at 800 $^{\circ}C$ is shown. In the figure crystals presented are pooled. The pores are estimated to be 1 μm . This is in accordance with the results of the X-ray diffraction performed at different temperatures with clay calcination. The material undergoes changes in its structure and therefore its morphology. Pérez-Moreno *et al.* (2004) show that as the sintering temperature increases the pore size decreases, thus the temperature of 800 $^{\circ}C$ used in this study was suitable for the preparation of membranes.

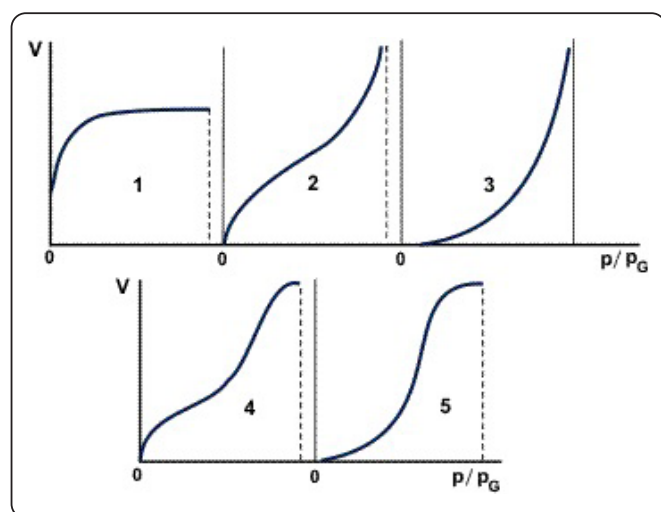


Figure 6. Adsorption isotherm types.

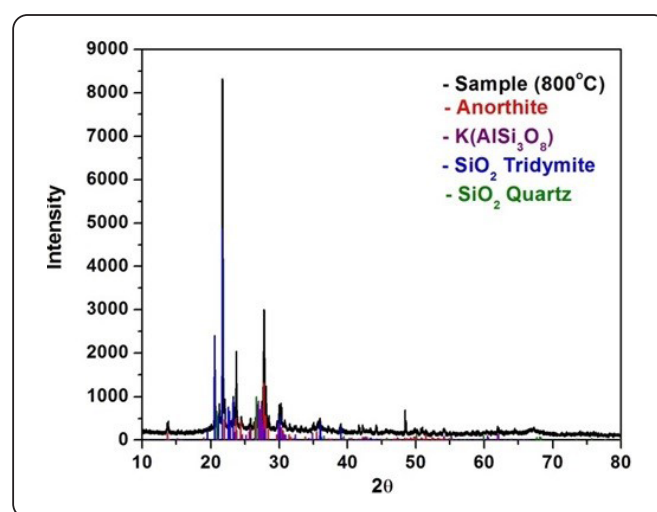


Figure 7. XRD spectrum of membrane made of Mexican clay.

Nitrogen physisorption

The adsorption-desorption isotherms of Nitrogen of the Mexican clay present in the main formulation of the membrane are shown in Figure 9. The curve corresponded to the type II isotherms according to the IUPAC classification. The isotherm had a reversible relative low-pressure part and the hysteresis loop at high relative pressures corresponding to an H3 type hysteresis loop. This type of hysteresis loop is characteristic for aggregated and agglomerated plate particles forming slit shape pores (Rouquerol *et al.*, 1994). The elongation of the hysteresis loop implied the presence of non-uniform pore shape and size. The clay exhibited a unimodal distribution; the average pore diameter is 3.408 nm, total pore volume of de 0.096 cm³/g and the specific surface area was 55.922 m²/g. The specific areas of the samples were calculated by

applying the BET method to the adsorption branch of the nitrogen isotherm within the 0.005 <P/P0< 0.25 range. The pore size distribution and cumulative pore volume were obtained by the Barret-Joyner-Halenda method (BJH) and from the isotherms at P/P0 = 0.99, respectively. This slight increase in the surface area in the membrane compared to clay is due to the generation of textural porosity (interparticles), during the process of sintering in the membrane preparation (Bouzerara, Harabi, Achour & Larbot, 2006; Saffaj, Persin, Younsi, Albizane, Cretin & Larbot, 2006; Yoshino, Suzuki, Nair, Taguchi & Itoh, 2005).

Membrane evaluation

The membrane was washed for 24 h in a solution of 10% hydrochloric acid then rinsed with distilled water, then further

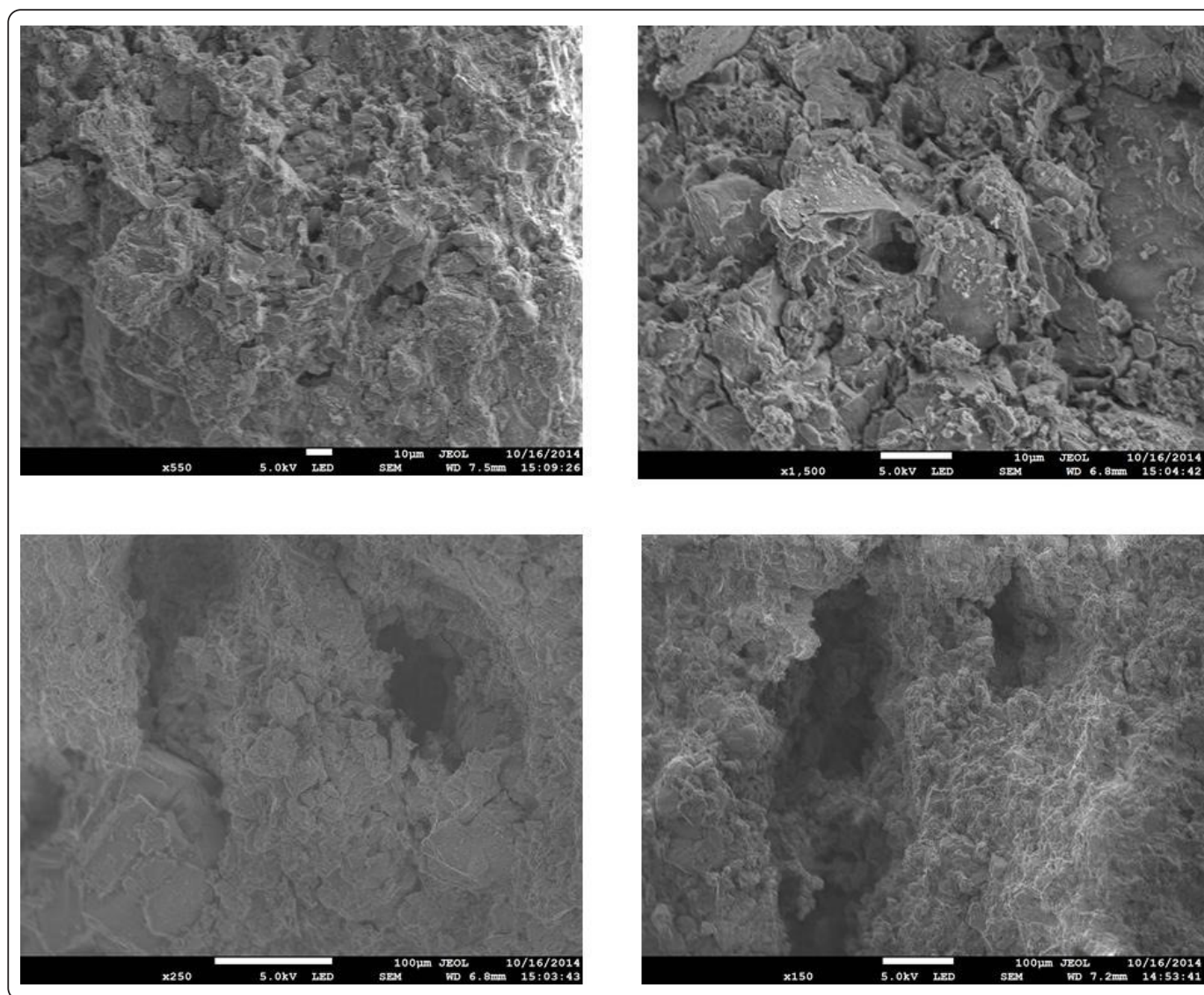


Figure 8. Scanning electron microscopy of the membrane made of Mexican clay.

washed for 30 min in a solution of 10% sodium hydroxide and finally rinsed for 30 min with distilled water.

After the membrane was washed, it was placed in the center of two acrylic molds and then applying a pressure gradient, water was passed through it. The flux was 28 mL/min.; the membrane area was 7.07 cm² and the transmembrane pressure of 1.1 bar. The water was assessed before and after passing through the reactor containing the membrane to determine the total hardness by means of the technique specified by Official Mexican Regulations and Standards (NMX-AA-072-SCFI-2001). According to this procedure the initial hardness of the water was 280 mg/L of CaCO₃. After passing the water through the reactor containing the membrane, the total hardness decreased by over 40%. This is shown in Figure 10 where the graphical evaluation is presented of how hardness in water decreased using the membrane elaborated in this study.

CONCLUSIONS

This study successfully characterized and evaluated Mexican clay from the city of Querétaro, México, and determined that the material contained mainly aluminum oxide and silicon, which have capacity for chemical affinity. Through X-ray diffraction (XRD) characterization, the crystalline structure of the clay was observed when it was subjected to sintering treatment in the range of 500 to 1,000 °C resulting in significant structural changes. Through X-Ray fluorescence, it was determined that the raw material contained Al₂O₃ and SiO₂ (56%). From the results of pore distribution, it was concluded that clay is a mesoporous material (average pore diameter is 3.42 nm and a specific surface area of 48.8 m²/g), which has, based on the results, filtration properties.

In the characterization of the membranes by XRD, it was observed that there were phase transformations in two of the clay components when it was thermally treated in the range of 800 to 1,000 °C. This transformation resulted in significant structural changes and crystalline quality improvement in the clay. So far only one membrane (sintered at 800 °C) has been tested and presented. From the results of the size pore, it was concluded that the membrane made of clay is a mesoporous material (average pore diameter is 3.408 nm total pore volume of 0.096 cm³/g and a specific surface area of 55.922 m²/g). By direct measurement in the SEM, the images analyzed displayed that the pore diameters are on the order of one micron, which has, based on the results, filtration properties.

In the membrane evaluation, it was concluded that the filtration membranes obtained were able to remove Ca²⁺ and Mg²⁺ ions, which are responsible for hardness in water. The membranes developed were able to decrease water hardness by over 40%.

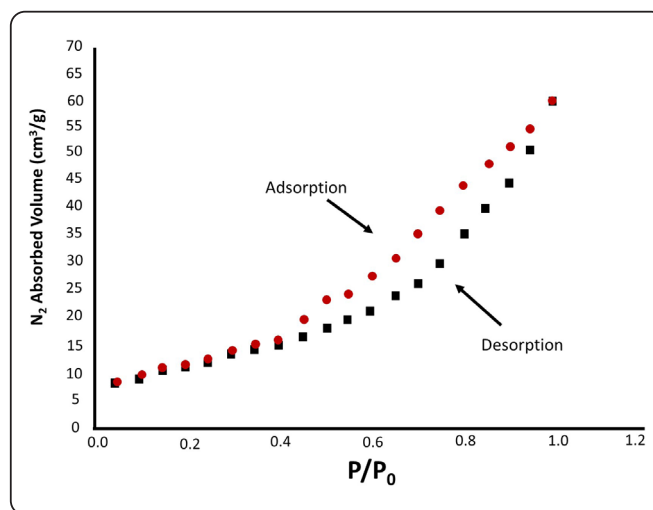


Figure 9. Nitrogen physisorption of membrane made of Mexican clay.

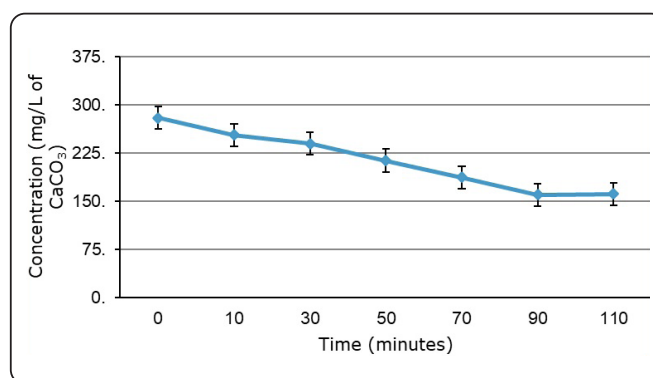


Figure 10. Graphical evaluation of hardness in water of membrane made of Mexican clay.

These membranes can be used as home filters to decrease minerals salts as well as for industrial processes.

ACKNOWLEDGEMENTS

We would like to thank Universidad Autónoma de Querétaro for the Institutional Program for Research FOFI-UAQ (FCQ-201228) for supporting this study. We would also like to thank Heberto Balmori Ramirez of Centro de Nanociencias y Micro y Nanotecnologías (Instituto Politécnico Nacional) for Scanning Electron Microscopy images, to Francisco Enrique Longoria of Centro de Investigación en Materiales Avanzados, S.C. (CIMAV) for the XRD analysis, to the Dirección de Materiales de Referencia of Centro Nacional de Metrología (CENAM) for XRF analysis, and M. in S. Mercy Lea Dinwiddie for English edition.

REFERENCES

- Adam, M. R., Othman, M. H. D., Kurniawan, T. A., Puteh, M. H., Ismail, A. F., Khongnakorn, W., Rahman, M. & Jaafar, J. (2022). Advances in adsorptive membrane technology for water treatment and resource recovery applications: A critical review. *Journal of Environmental Chemical Engineering*, **10**(3), 107633. <https://doi.org/10.1016/j.jece.2022.107633>
- Amin, M. & Subri, M. (2018). Preparation and Characterization of Porous Ceramic Membranes for Micro-Filtration from Clay/CuZn Using Extrusion Methods. In MATEC Web of Conferences (Vol. 156, p. 08015). EDP Sciences. <https://doi.org/10.1051/mateconf/201815608015>
- Anbri, Y., Tijani, N., Coronas, J., Mateo, E., Menéndez, M. & Bentama, J. (2008). Clay plane membranes: development and characterization. *Desalination*, **221**(1), 419-424. <https://doi.org/10.1016/j.desal.2007>
- Belgada, A., Achiou, B., Younssi, S. A., Charik, F. Z., Ouammou, M., Cody, J. A., Benhida, R. & Khaless, K. (2021). Low-cost ceramic microfiltration membrane made from natural phosphate for pretreatment of raw seawater for desalination. *Journal of the European Ceramic Society*, **41**(2), 1613-1621. <https://doi.org/10.1016/j.jeurceramsoc.2020.09.064>
- Bentama, J., Ouazzani, K. & Schmitz, P. (2002). Mineral membranes made of sintered clay: application to crossflow microfiltration. *Desalination*, **146**(1), 57-61. [https://doi.org/10.1016/S0011-9164\(02\)00479-4](https://doi.org/10.1016/S0011-9164(02)00479-4)
- Besoain, E. M. (1969). Clay mineralogy of volcanic ash soils, Panel of Volcanic ash soils in Latin America, Soil B. 1.1-B. 1.16. Turrialba, Costa Rica.
- Betancourth, D., Gómez, J. F., Mosquera, J. C. & Mejía, L. T. (2010). Análisis por difracción de rayos x de rocas provenientes de región esmeraldífera. *Scientia et Technica*, **1**(44), 409-413. <https://dialnet.unirioja.es/servlet/articulo?codigo=4587146>
- Bouzerara, F., Boulanacer, S., Harabi, A., Boudaira, B., Achour, S. & Condom, S. (2009). Preparation and characterization of macroporous ceramic supports for membranes. *Physics Procedia*, **2**(3), 1449-1453. <https://doi.org/10.1016/j.phpro.2009.11.115>
- Bouzerara, F., Harabi, A., Achour, S. & Larbot, A. (2006). Porous ceramic supports for membranes prepared from kaolin and dolomite mixtures. *Journal of the European Ceramic Society*, **26**(9), 1663-1671. <https://doi.org/10.1016/j.jeurceramsoc.2005.03.244>
- Fakhfakh, S., Baklouti, S., Baklouti, S. & Bouaziz, J. (2010). Elaboration and characterisation of low cost ceramic support membrane. *Advances in Applied Ceramics*, **109**(1), 31-38. <https://doi.org/10.1179/174367609X422234>
- Gelves, J. F., Monroy, R., Sánchez, J. & Ramírez, R. P. (2013). Estudio comparativo de las técnicas de extrusión y prensado como procesos de conformado de productos cerámicos de construcción en el Área Metropolitana de Cúcuta. *Boletín de la Sociedad Española de Cerámica y Vidrio*, **52**(1), 48-54. <https://boletines.secv.es/upload/2013021891143.20135248.pdf>
- Harabi, A., Bouzerara, F. & Condom, S. (2009). Preparation and characterization of tubular membrane supports using centrifugal casting. *Desalination and Water Treatment*, **6**(1-3), 222-226. <https://doi.org/10.5004/dwt.2009.646>
- Hristov, P., Yoleva, A., St. Djambazov, I. C. & Dimitrov, D. (2012). Preparation and characterization of porous ceramic membranes for micro-filtration from natural zeolite. *Journal of the University of Chemical Technology and Metallurgy*, **47**(4), 476-480. https://journal.uctm.edu/node/j2012-4/18-Preslav_476-480.pdf
- Lahsini, A., Bentama, J., Addaou, A. & Rafiq, M. (1998). Caractérisation physico-chimique et étude du frittage d'une argile destinée à l'élaboration de membranes de filtration tangentielle. *Journal de Chimie Physique et de Physico-Chimie Biologique*, **95**(5), 1001-1019. https://www.researchgate.net/profile/Jilali-Bentama/publication/243665668_Caractrisation_physico-chimique_et_tude_du_frittage_d'une_argile_destine_laboration_de_membranes_de_filtration_tangentielle/links/577eed0208ae5f367d33e415/Caractrisation-physico-chimique-et-tude-du-frittage-dune-argile-destine-laboration-de-membranes-de-filtration-tangentielle.pdf
- Liang, D., Huang, J., Zhang, H., Fu, H., Zhang, Y. & Chen, H. (2021). Influencing factors on the performance of tubular ceramic membrane supports prepared by extrusion. *Ceramics International*, **47**(8), 10464-10477. <https://doi.org/10.1016/j.ceramint.2020.12.235>
- López, K., Etcheverry, R. & Botto, I. (2013). Estudios Morfológicos y Composicionales por Microscopía Electrónica y Edax en Depósitos Sedimentarios de Tandilla, Buenos Aires, Argentina. *Revista Tecnológica-ESPOL*, **20**(1), 115-121. https://www.researchgate.net/publication/309615269_Estudios_Morfologicos_y_Composicionales_por_Microscopia_Electronica_y_Edax_en_Depositos_Sedimentarios_de_Tandilla_Buenos_Aires_Argentina
- Mora Solís, F. A. & Tejeira, R. (2019). Determinación mineralógica de la fracción arcilla en suelos de importancia agrícolas de la república de Panamá mineralogical determination of the clay fraction of soils of agricultural. *Revista Investigaciones Agropecuarias*, **2**(1), 1-10. <http://portal.amelica.org/ameli/jatsRepo/222/222973003/index.html>
- Norma Mexicana NMX-AA-072-SCFI-2001 (2001). "Análisis de agua - determinación de dureza total en aguas naturales, residuales y residuales tratadas". Available at: www.conagua.gob.mx/CONAGUA07/Noticias/NMX-AA-072-SCFI-001.pdf Accessed on 18/09/2014.
- Nunes, S. P., Culfaz-Emecen, P. Z., Ramon, G. Z., Visser, T., Koops, G. H., Jin, W. & Ulbricht, M. (2020). Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes.

- Journal of Membrane Science*, **598**, 117761. <https://doi.org/10.1016/j.memsci.2019.117761>
- Peréz-Moreno, V., Arellano, J. C. & Ramirez, H. B. (2004). Characterization and preparation of porous membranes with a natural Mexican zeolite. *Journal of Physics: Condensed Matter*, **16(22)**, S2345. <https://doi.org/10.1088/0953-8984/16/22/037>
- Rouquerol, J., Avnir, D., Everett, D. H., Fairbridge, C., Haynes, M., Pernicone, N. & Unger, K. K. (1994). Guidelines for the characterization of porous solids. *Studies in Surface Science and Catalysis*, **87**, 1-9. (Vol. 87, pp. 1-9). Elsevier. [https://doi.org/10.1016/S0167-2991\(08\)63059-1](https://doi.org/10.1016/S0167-2991(08)63059-1)
- Saffaj, N., Persin, M., Younsi, S. A., Albizane, A., Cretin, M. & Larbot, A. (2006). Elaboration and characterization of microfiltration and ultrafiltration membranes deposited on raw support prepared from natural Moroccan clay: application to filtration of solution containing dyes and salts. *Applied Clay Science*, **31(1)**, 110-119. <https://doi.org/10.1016/j.clay.2005.07.002>
- Sapag, K., Solar, C., Ricardo, J. L., Oliveira, L. C. A. & Lago, R. M. (2013). Síntesis y caracterización de materiales porosos a partir de arcillas montmorilloníticas naturales. In *Anales AFA*, **13(1)**, 218-224. <https://anales.fisica.org.ar/index.php/analesafa/article/view/710>
- Silva, S. H. G., Weindorf, D. C., Pinto, L. C., Faria, W. M., Junior, F. W. A., Gomide, L. R., Marcio de Mello, J., Linares de Pádua Junior, A., de Souza, A., dos Santos Teixeira, F., Guimarães Guilherme, L. & Curi, N. (2020). Soil texture prediction in tropical soils: A portable X-ray fluorescence spectrometry approach. *Geoderma*, **362**, 114136. <https://doi.org/10.1016/j.geoderma.2019.114136>
- Vuković, Z., Milutinović-Nikolić, A., Krstić, J., Abu-Rabi, A., Novaković, T. & Jovanović. (2005). The influence of acid treatment on the nanostructure and textural properties of bentonite clays. In *Materials Science Forum*, **Vol. 494**, 339-344. Trans Tech Publications Ltd. <https://doi.org/10.4028/www.scientific.net/MSF.494.339>
- Yoshino, Y., Suzuki, T., Nair, B. N., Taguchi, H. & Itoh, N. (2005). Development of tubular substrates, silica based membranes and membrane modules for hydrogen separation at high temperature. *Journal of Membrane Science*, **267(1-2)**, 8-17. <https://doi.org/10.1016/j.memsci.2005.05.020>
- Yusuf, A., Sodiq, A., Giwa, A., Eke, J., Pikuda, O., De Luca, G., Luque Di Salvo, J. & Chakraborty, S. (2020). A review of emerging trends in membrane science and technology for sustainable water treatment. *Journal of Cleaner Production*, **266**, 121867. <https://doi.org/10.1016/j.jclepro.2020.121867>
- Zelenka, T., Horikawa, T. & Do, D. D. (2023). Artifacts and misinterpretations in gas physisorption measurements and characterization of porous solids. *Advances in Colloid and Interface Science*, **311**, 102831. <https://doi.org/10.1016/j.cis.2022.102831>
- Zhang, Z., Huang, G., Li, Y., Chen, X., Yao, Y., Ren, S., Li, M., Wu Y. & An, C. (2022). Electrically conductive inorganic membranes: A review on principles, characteristics and applications. *Chemical Engineering Journal*, **427**, 131987. <https://doi.org/10.1016/j.cej.2021.131987>
- Zipkin, A. M., Ambrose, S. H., Lundstrom, C. C., Bartov, G., Dwyer, A. & Taylor, A. H. (2020). Red earth, green glass, and compositional data: a new procedure for solid-state elemental characterization, source discrimination, and provenience analysis of ochres. *Journal of Archaeological Method and Theory*, **27(4)**, 930-970. <https://link.springer.com/article/10.1007/s10816-020-09448-9>