

Research paper

Physico-mechanical and gas permeability characteristics of kaolin based ceramic membranes prepared with a new pore-forming agent



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ABSTRACT

The objective of this study was to prepare low-cost macroporous ceramic membranes using natural kaolin obtained from deposits in Nigeria and Ghana, and powdery high density polyethylene (PHDPE) as porogen agent. The ceramic membranes have been prepared with porogen content wt% between (0 and 20)% by die pressing. Pellets were fired at 1150 °C and soaking time of 4 h. The raw materials were characterized using TG/DTA, particle size distribution (PSD) and Zeta potential. The membranes cast as circular disks were subjected for characterization studies using XRD and SEM analysis. In a bid to correlate the physico-mechanical properties vis-à-vis pore former content, the effect of the sintering temperature and pore former (PHDPE) content on porosity, density, water absorption and mechanical strength were evaluated. The membrane corrosion resistance was found to be unaltered with experimental conditions. Obtained membranes showed good porosity with maximum at about 62% with a mechanical strength that does not exceed 18 MPa. These membranes can be considered as efficient regarding the results shown in the gas permeation tests at different sintering temperatures. A PHDPE percentage of 20% and a sintering temperature of 1150 °C were chosen as the optimum for gas permeation based on enlarged pore diameter of sintered membranes.

1. Introduction

Ceramic membranes are more favourable than their polymeric counterparts, especially in gas applications, due to its high thermal stability, good chemical compatibility and exceptional flexion and compressive strengths (Kingsbury and Li, 2009; Wang and Lai, 2012). By virtue of having such characteristics that require no maintenance, the production of ceramic supports has gained attention widely among researchers. Also, ceramic membranes which can be utilized at relatively higher temperatures are finding increasing relevance, because it is more realistic to carry out many chemical reactions and separation at elevated temperatures (Mizukami et al., 1992; Xu and Anderson, 1993; Church et al., 1994; Lin et al., 1994; LeDuc et al., 1996). However, because ceramic membranes have higher cost than polymeric counterparts, their applications have been retarded in some traditional industries such as food, beverage, and pharmaceutical. Also, limited types of membrane materials (such as Al₂O₃, ZrO₂, TiO₂, and their composite oxides) hinder their further applications (Pandey and Chauhan, 2001;

Khemakhem et al., 2009; Hamad et al., 2013). In light of this, it is imperative to find more low-cost alternatives. A significant effort has been provided in the field of membrane technology in order to find new low-cost ceramic materials (Li et al., 2001; Benito et al., 2007). Recent research in the fabrication of inorganic membranes is focused towards the utilization of cheaper raw materials such as apatite powder (Masmoudia et al., 2007), fly ash (Saffaj et al., 2004a, 2004b), natural raw clay (Saffaj et al., 2005, 2006), dolomite, kaolin (Almandoz et al., 2004; Bouzerara et al., 2006). Of these inorganic precursors, research is devoted to other raw materials that would be of low cost and suitable as a standard raw material replacement. Clays have been identified as the best cost-effective raw materials for membrane applications (Weir et al., 2001; Saffaj et al., 2004a, 2004b; Khemakhem et al., 2006). Precisely, kaolin appears to be an important inexpensive raw material that can be studied for the fabrication of durable micro-filtration range inorganic membranes at a lesser cost. In addition, kaolin is also one of the cheapest and the most abundant support raw material and it is easily obtained.

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Porosity is known to be an important characteristic as far as ceramic membranes for industrial applications are concerned. One of the basic methods to produce porous ceramics membranes is by using pore-forming agents (PFAs) (Liu, 1996; Rice, 1998; Rice, 2003; Scheffler and Colombo, 2006; Studart et al., 2006). Porous ceramics are nowadays being investigated for a variety of applications due to their specific properties like high surface area, high temperature stability, high permeability, low weight and low thermal conductivity.

Characterization of particle dispersion is important to optimize and control, for example, ceramic forming processes, etc. (Somasundran et al., 1997). Two very significant characteristics of aqueous dispersions are particle size distribution (PSD) and zeta potential (ξ -potential). The effect of the particle charge of clay minerals on the aggregation behaviour, sedimentation or filtration is the main object of several researches (Alkan et al., 2005a,b; Kosmulski, 2003; Hang et al., 2007).

A wide variety of natural (i.e. biogenic) and carbon based pore-forming agents (also called sacrificial templates or fugitive materials) have been tested or used so far, including saw dust (Saggio-Woyansky et al., 1992; Sheppard, 1992; Liu, 1996; Rice, 1998; Ducman and Kopar, 2001; Scheffler, 2005; Studart et al., 2006), wheat particles (Prabhakaran et al., 2007a, 2007b), carbon fibers (Isobe et al., 2007), cotton (Zhang et al., 2001), peas and seeds (Luyten et al., 2003), including poppy seed (Gregorová and Pabst, 2007).

A recent study (Obada et al., 2016a, 2016b), the potentials of fabricating porous ceramics bodies from kaolin clay mined from deposits in Nigeria and Ghana using different pore formers was investigated. Therefore, the objective of this study was to fabricate ceramic membranes from kaolin clay/powdery high density polyethylene mixture with varying ratios by weight to prepare macroporous membranes to improve the potential competitiveness of the low-cost ceramic membranes. The physical and mechanical properties of the kaolin based ceramic membranes and gas permeability test results are also presented.

2. Materials and methods

2.1. Processing of raw materials

The raw materials used in this study are kaolin and powdery high density polyethylene. The kaolin was obtained from Kankara and Kibi deposits in Nigeria and Ghana respectively. The powdery high density polyethylene powder was processed at the Materials Laboratory of the University of Ghana. The kaolin was beneficiated as reported in our previous studies (Obada et al., 2016a). Moreover, the raw materials used in this work serve for different functional attributes. The kaolin was the base material while the powdery high density polyethylene (PHDPE) serves as a pore-forming agent.

The kaolin clay was mixed with the powdery high density polyethylene in four different ratios (clay-to-pore formers) by weight (Table 1). The XRF and XRD of the kaolin clay used for membrane fabrication in this present study have been presented in our previous works (Obada et al., 2016a, 2016b). It was observed that the composition of the kaolin consists of kaolinite, illite, mica and montmorillonite.

Table 1
Composition of test samples by weight (total weight = 100 g).

Sample code	Kaolin (g)	Plasticizer (Kibi kaolin) (g)	High density polyethylene (HDPE) (g)
0% CS	80	20	–
5% HDPE	75	20	5
10% HDPE	70	20	10
15% HDPE	65	20	15
20% HDPE	60	20	20

2.2. Materials characterization

2.2.1. Thermal analysis

In order to know the thermal behaviour of the kaolin and more information about its composition, a thermogravimetric analysis has been performed between 100 and 700 °C. This was studied by TG/DTA/DTG under air flow of 50 ml/min. The samples were thermally analysed by placing $\approx$ 25 mg of the specimens in an alumina (Al_2O_3) crucible (100 mg capacity), subjected to a linear heating ramp between 100 °C and 700 °C at a rate of 20 °C/min in NETZSCH, STA 449C Jupiter TG/DTA instrument. The test measurements were made for the mass change (loss) of the sample as a function of the temperature and the phase changes by the adsorption or the emission of energy.

2.2.2. Particle size distribution (PSD) and zeta potential

The essential properties of the raw materials (kaolin and powdery HDPE) such as particle size ranges were experimentally determined in a wet dispersion mode. A laser method, low-angle laser light scattering (LALLS), was used for the particle size analysis with levels of sensitivity in the 0.3 nm to 8000 nm range using a Horiba Scientific, SZ-100 nanoparticle analyzer. 10 mg of the kaolin samples and pore formers which were prepared using an analytical mill to reduce the sizes, were dispersed in freshly deionized water and subjected to continuous ultrasound treatment in an ultrasonic bath for 30 min to ensure dilution and homogenous dispersion. The zeta potential of dispersed kaolin was also performed on the same equipment as discussed for PSD. After 15 min ultrasonication of the suspension, the zeta potential was measured as a function of pH by titration with HCL and NaOH.

2.3. Membrane fabrication

The raw materials as listed in Table 1 were mixed in a ball mill at 50 rpm for 30 min. The resulting powdery mix was then compacted in a hydraulic pressing machine at a pressure of 3.5 MPa with the help of stainless steel die. The membranes were shaped as disks of 5 cm in diameter and 0.5 cm thicknesses. The obtained circular shaped membranes were first dried at ambient temperature before further drying at 150 °C for 24 h in a hot air oven. This was to remove moisture and also reduce any thermal stress which may hamper the successful fabrication of the ceramic membranes. Subsequently, the membranes were sintered at 1150 °C for 4 h in a muffle furnace at 5 °C/min. The sintering process was run in two steps; firstly, sintering temperature was setup at 500 °C at a rate of 2 °C/min and held for 2 h so that the pore former (PHDPE) would be burnt off. Then, the sintering temperature was increased up to 1150 °C at a rate of 5 °C/min and held for 4 h to produce ceramic membranes for the physical and mechanical tests, and up to 850 °C, 1000 °C, 1150 °C at a rate of 5 °C/min and held for 4 h to produce ceramic membranes for the gas permeation tests. Finally, temperature was then reduced to room temperature at a rate of 5 °C/min. After sintering, the compact and porous ceramic membranes were polished on both sides using silicon carbide abrasive paper to obtain ceramic membranes with uniform surface and considerably free from defects. These membranes were washed with deionized water in an ultrasonic for 15 min to remove the loose particles adhered on the surface of membranes.

For the mechanical properties testing of the membrane formulations, the kaolin and pore former mixture was completely filled into a rectangular mold and pressed to the same level to ensure compactness and dimensional homogeneity using a hydraulic pressing machine with pressure corresponding to 3.5 Mpa. The as-prepared green body samples were removed from the mold and dried at room temperature on boards for three (3) days after which they were further dried at 150 °C for 24 h in a hot air oven to remove moisture. The dried batch-formulated green bodies were then sintered at 1150 °C for 4 h in an electric muffle furnace at a heating rate of 5 °C/min after the systematic pore former oxidation process which was set at 500 °C at a rate of 2 °C/min and held for 2 h.

2.3.1. Characterization of ceramic membranes

2.3.1.1. Apparent porosity, apparent density and water absorption. The apparent porosity (the amount of void or pores within a volume of porous solid) of the as-sintered membranes was calculated using Eq. (1):

$$\text{Apparent porosity} = \left(\frac{W - D}{W - S} \right) \times 100 \quad (1)$$

Their respective apparent density and percentage water absorption were also calculated using the formulae as proposed (Chesti, 1986):

$$\text{Apparent density} = \frac{D}{(D - S)} \times 100(\text{g/cm}^3) \quad (2)$$

$$\text{Water absorption} = \frac{W}{(W - S)} \times 100 \quad (3)$$

where: D = weight of fired specimen, S = weight of fired specimen suspended in water, and W = weight of soaked specimen suspended in air.

2.3.1.2. Mechanical strength. Mechanical properties tested for were cold compression and flexural strengths. The compressive strength is an indication of the membranes' probable performance under load. The membrane samples were dried in an oven at a temperature of 110 °C and allowed to cool. The compressive strength testing was carried out on an hydraulic testing machine (Carver Press, USA). The compressive strength of the porous clay ceramics were obtained by compressive loading of samples and the strength of standard and conditioned samples were calculated from the equation:

$$CS = \frac{P}{BW} \quad (4)$$

where P = load at failure and B and W are the respective breadth and width of the specimens.

The flexural strength of the membranes was tested with three-point bending, with rectangular bars using Universal Testing Machine. The flexural strength was evaluated by the expression.

$$\sigma = \frac{3Fl}{2bt} \quad (5)$$

where σ is the flexural strength (Pa), F is the load at the fracture point (N), l is the span length (m), b is the width of the sample (m), and t is the thickness of the sample (m).

2.3.1.3. X-ray diffraction and SEM analyses of sintered ceramic membranes. X-ray diffraction analysis (XRD) of the ceramic membranes at the sintering temperature (1150 °C) was conducted to evaluate the extent of phase transformations during sintering by collecting on an Empyrean diffractometer (Panalytical BV, Netherlands) with theta/theta geometry, operating Cu K α radiation tube ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 45 mA. To investigate the morphology, scanning electron microscopy analysis was conducted to study the morphological features of the various layers of the ceramic membranes using an ultra-high vacuum and high resolution FEI, XI-30 scanning electron microscope. Samples were metalized with gold/platinum coating prior to the analysis. Images were acquired at magnifications of 201 $\times$, 500 $\times$, 2000 $\times$ and 5000 $\times$ for sintered samples. Furthermore, scanning electron microscopy was performed to provide additional qualitative data on the pore geometry and interconnectivity of polished sections of ceramic membrane at different magnifications. Fine polishing of the ceramic membrane surface was conducted using graded ferric oxide suspensions in water. It was done on a rotating wheel with a layer of fluid on the surface of the polishing cloth using automatic wheels (Finchley polishing tool, UK). The specimen was evaluated by SEM at 228 $\times$, and 413 $\times$.

2.3.1.4. Chemical stability. Chemical stability of the membranes was

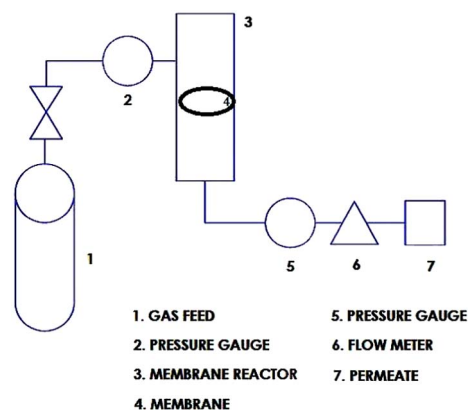


Fig. 1. Schematic of gas permeation testing of ceramic membrane with PHDPE as porogen.

determined by subjecting the membrane separately into acid (pH 4) and alkali (pH 12) solutions. The pH of the solution was adjusted using HCl solution and NaOH pellets. The stability was measured in terms of mass loss before and after corrosion. For this, the membrane was placed in acid and alkali solutions for one week at an atmospheric condition. Then the membranes were taken out from the solution, washed with deionized water, and dried at 110 °C for 6 h. The mass loss of the membrane characterizes the chemical stability.

2.3.1.5. Permeability tests. The permeability of the porous membranes obtained was tested using N₂ as permeate with a laboratory designed set up. The schematic of experimental set up is shown in Fig. 1. For this experimentation, the membranes were sintered at 850, 1000 and 1150 °C for 4 h in a muffle at 5 °C/min. This was to investigate the effects of sintering temperatures on gas permeability through the membranes. The gas cylinder was connected to a permeate flow tube which was in turn connected to a mass flow controller and the set point was such that 10 ml/min of gas was released at the out flow. The mass flow controller was connected to the end of the membrane reactor and connected to valves for the control of inlet and outlet. The pressure supplied was varied as the gas permeance was obtained from the following expression:

$$Q = \frac{q}{A \cdot \Delta P} \quad (6)$$

where Q is the permeance (ml cm⁻² min⁻¹ Pa⁻¹); q is the gas flux (ml/min); A is the membrane area (cm⁻²); and ΔP is the pressure difference (Pa) across the membrane.

3. Results and discussion

3.1. TG/DTA analyses

The objective of thermal analysis is to identify temperature regimes where predominant weight losses (and hence transformations) occur in the membrane. Thereby, an understanding could be developed for analyzing the effect of various temperature regimes on the porous structure, pore diameter and mechanical strength of the membrane. Fig. 2 conveys that a non-linear variation exists due to the presence of complex phase transformations and interactions. The TG curves show the weight loss associated with thermal treatment of the kaolin up to 700 °C. It can be observed that the remarkable loss occurred between 450 °C and 600 °C and stabilized at about 700 °C for the thermal treatment of the kaolin considering the clays from the two deposits (Kankara and Kibi) as used in this study. The endotherm as shown in Fig. 2, corresponds to the kaolinite dehydroxylation temperature range and the formation of metakaolin (Dodson, 1957; Sonuparlak et al., 1987; Sayin, 2007; Štuboa and Trník, 2007). The dehydroxylation

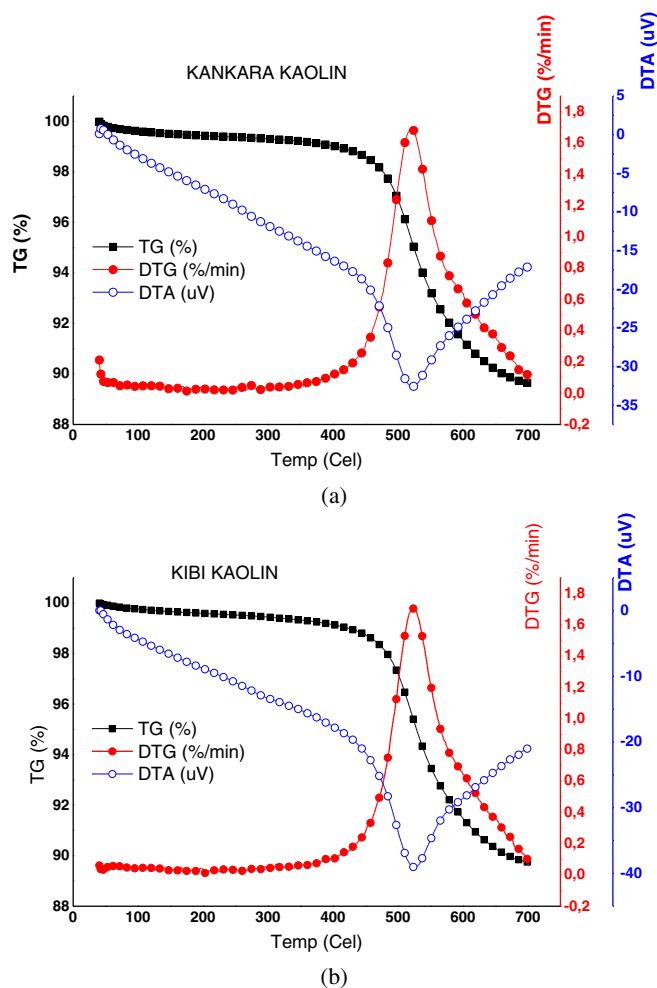


Fig. 2. Thermal analyses (TG, DTG and DTA) of the two kaolin types (Kankara (a) and Kibi (b)).

temperature of the Kankara and Kibi kaolin are 526.2 and 521.3 °C at enthalpies of $-39.07 \mu\text{V}$ and $-32.60 \mu\text{V}$ respectively.

3.2. Particle size distribution and zeta potential

3.2.1. Particle size

The particle size distribution analysis of the kaolin, and the pore former used for the membrane fabrication process are shown in Fig. 3. The average particle size of kaolin and PHDPE are $1.97 \mu\text{m}$, and $6.4 \mu\text{m}$, respectively. It can be seen that both kaolin types showed unimodal distribution of kaolin particle size, which is in line with work carried out by Lungu et al. (2012).

3.2.2. Zeta potential

The slurries stability is linked to the surface charge of the kaolinite particles and in particular to the Zeta potential (ζ). It is well documented that in kaolinite particles, there are basal plane surfaces with permanent negative charges, while the edges can be positively or negatively charged, depending on the pH of the suspending medium (Andreola et al., 2000). Fig. 4 shows the zeta potential of kaolin used for membrane fabrication as a function of the pH of dispersant (H_2O). It is known that to obtain dense ceramic components, a number of stages, including mixing, incorporating additives, shape forming, drying and sintering are required. Water (H_2O) has been used as a binder and dispersant, hence, a need to evaluate dispersion stability by the zeta potential measurements. Particles in aqueous solution become charged, the charge, measurable by the zeta potential, is an important parameter

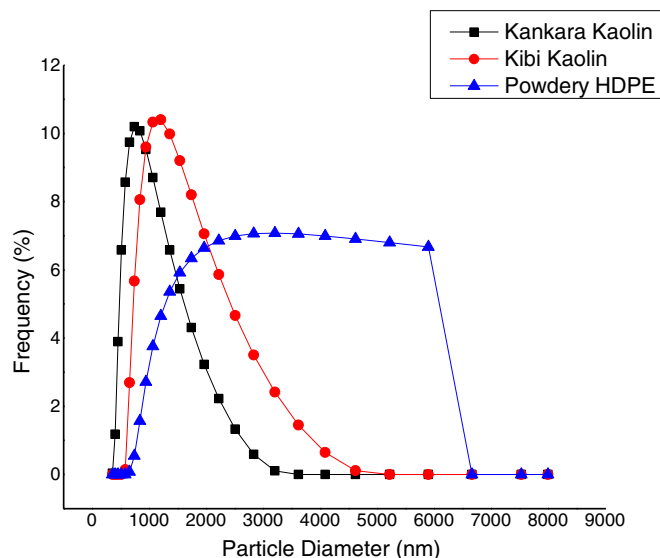


Fig. 3. Particles size distribution of raw materials.

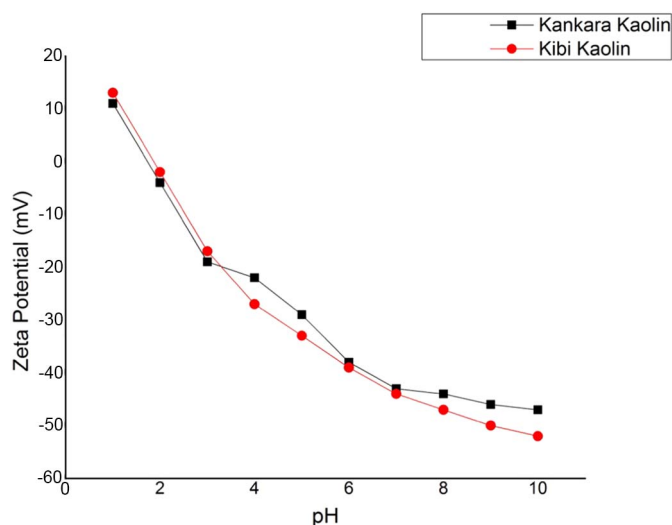


Fig. 4. The zeta potential of kaolin in H_2O as a function of pH.

in determining the stability of dispersion. If the particles have a large zeta potential they will repel each other and the dispersion is stable. If they have low zeta potential values, then there is no force to prevent the particles from coming together, meaning the dispersion is unstable and particles aggregate (Dohnalová et al., 2008). The curves (Fig. 4) show mostly a negative zeta potential in the pH range from 2 to 10. The isoelectric point (the point where the value of the zeta potential is zero) is about pH 2 for the kaolin types used in this study. Dispersions with a pH near the isoelectric point are unstable, thus, in pH range of 2, particles are oppositely charged and dispersion flocculates. The interaction is very strong and in this range it is impossible to disperse mixture of kaolin powder and to obtain slurry of good quality without any additives.

Fig. 5 presents the XRD patterns of raw and thermally treated clay. It shows that kaolinite (K), illite (I) and quartz (Q) are the main minerals present in the raw clay. After calcination of the sample at 600°C , all the reflections in the diffractogram due to kaolinite are almost not visible, this is due to the transformation of the kaolinite mineral to amorphous metakaolinite (Saadi et al., 1991; Lahsini et al., 1998; Kakali et al., 2001). On the contrary, the reflections of quartz and illite do not change, that means the kaolinite phase is only affected by the

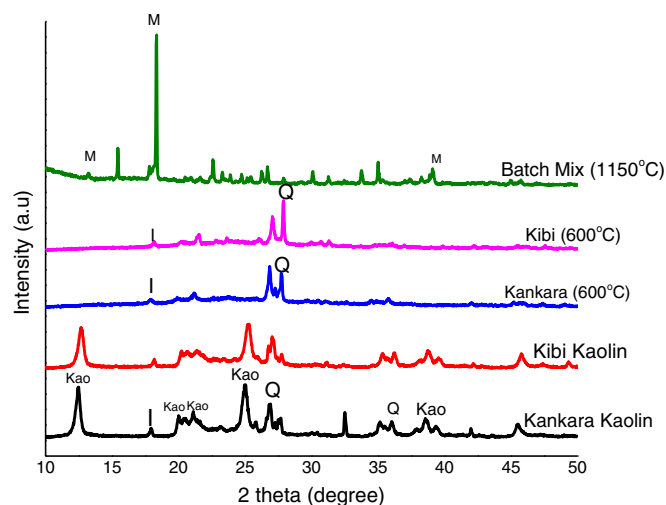


Fig. 5. XRD patterns of the pretreated clay samples and sintered mix (Kao: kaolinite, I: illite, M: mullite, Q: quartz).

thermal treatment at 600 °C. In a study by Araujo et al. (2004), it was observed that the onset of thermal structural decomposition of illite occurred at 800 °C. Normally, there should be loss of constituted water, however, it is suggested that illite decomposition depends on its composition which varies considerably and is strongly dependent on their origin. At a temperature of 1150 °C, reflections of illite (I) are not seen, whereas reflections of mullite (M) appear due to the transformation of kaolin under thermal treatment at high temperatures. The reflections of quartz remain without change in the diffractogram which confirms the thermal stability of this phase.

The evolution of densification and surface quality of membranes sintered at 1150 °C were also followed by scanning electron microscopy. The formation of grain boundaries (Fig. 6) shows SEM images of sintered ceramic bodies with the new pore former (HDPE) at different

magnifications (201 ×, 500 ×, 2000 ×, and 5000 ×). It can be observed that the higher the magnification the more visible the pore diameter. It is also seen that both macropores and micro pores are interconnected. Also, to allow for a better view of the porous network, Fig. 7 shows the SEM images of the polished sections of fabricated membranes which were taken at 228 × and 413 ×. It was observed that the porous network of interconnected pores were quite visible. It can be also be noticed that a continuous porous structure was created. The addition of the pore generator (PHDPE) increases porosity and pore size as well as pore connectivity, owed to the increase in the amount of interconnected pores created by pore former burnout, which should result in an increase in permeability as it will be explained in Section “Chemical stability and permeability tests of ceramic membranes”.

3.3. Physical and mechanical properties of membranes

The porosity (ϵ) of the membrane was determined by the Archimedes principle. Figs. 8–11 presents the correlation of the physico-mechanical properties: porosity, density, water absorption, and compressive and flexural strengths of the membranes with varying pore former addition investigated in this study. Standard deviation values of the physical and mechanical tests of the membranes are presented (see Tables 2–6) after five (5) measurements.

Fig. 8 shows the variation of membrane porosity and apparent density of membrane with varying pore former addition. The membrane porosity increases from 47.52% to 62.10% whereas apparent density decreases from 1.97 g/cm³ to 1.92 g/cm³ when pore former content varies from 5 to 20%. This is due to the fact that with increase in pore former content, porosity of the structure increase thereby reducing the densification of the porous membrane structure.

The porosity and water absorption rate, which are the void contents and the weight of the moisture in the pores as a fraction of the weight of the sintered membranes, is an effective index of the quality of porous ceramic membranes. From Fig. 9, the effect of increase in pore former content on the apparent porosity and water absorption of the sintered

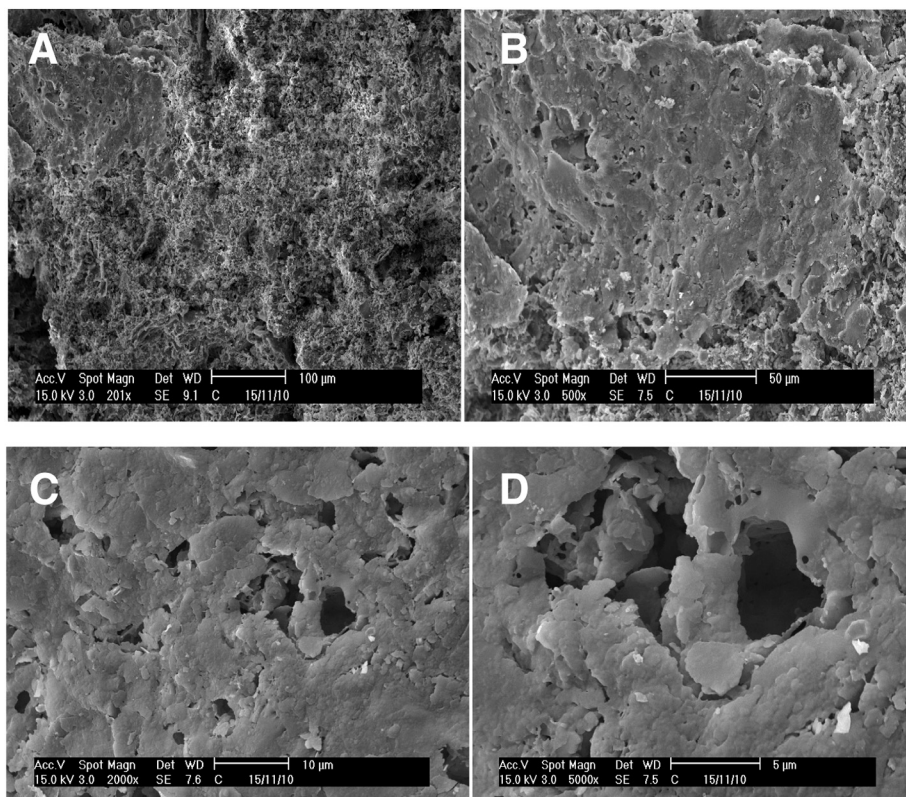


Fig. 6. SEM images of sintered membranes with HDPE as pore former at 20 wt%: a) 201 ×, b) 500 ×, c) 2000 ×, d) 5000 ×.

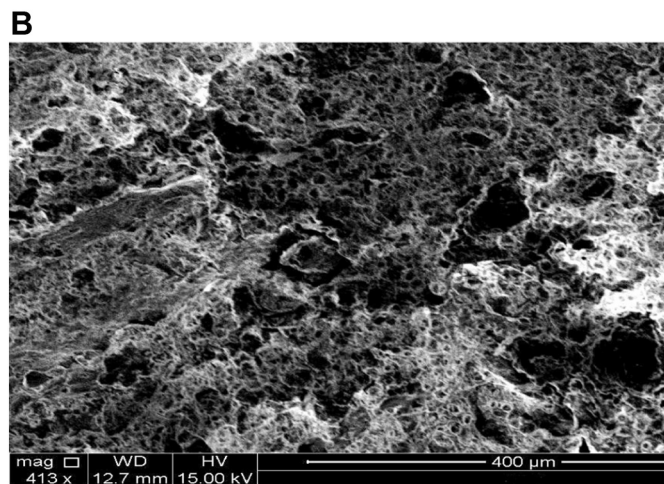
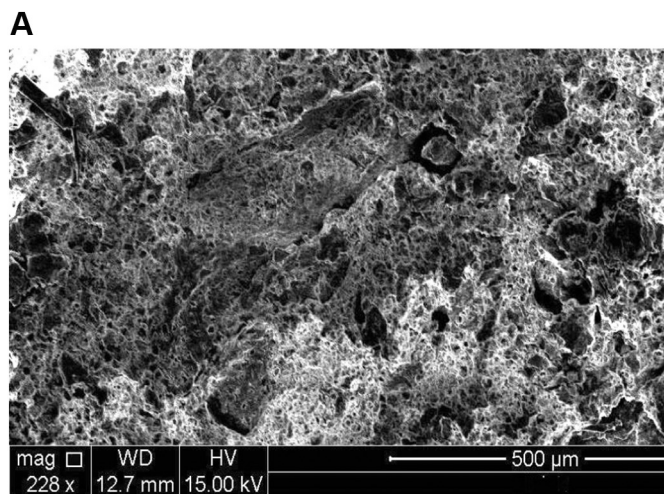


Fig. 7. SEM images of polished sections of sintered membranes with HDPE as pore former at 20 wt%: a) 223 ×, b) 413 ×.

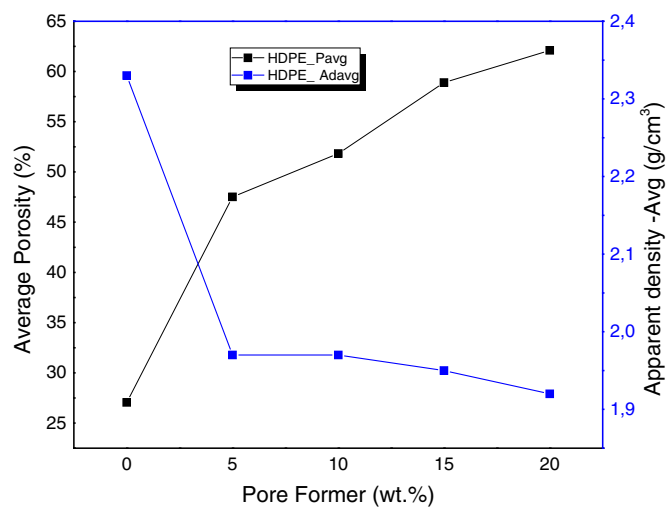


Fig. 8. Porosity and apparent density of sintered membranes with varying pore former content.

ceramic membranes are clearly shown. The plots show a similar trend, which is an increasing porosity and water absorption trend with pore former content. In other words, a linear relationship exists between these two physical properties.

Fig. 10 shows that the compressive strength is higher for the control

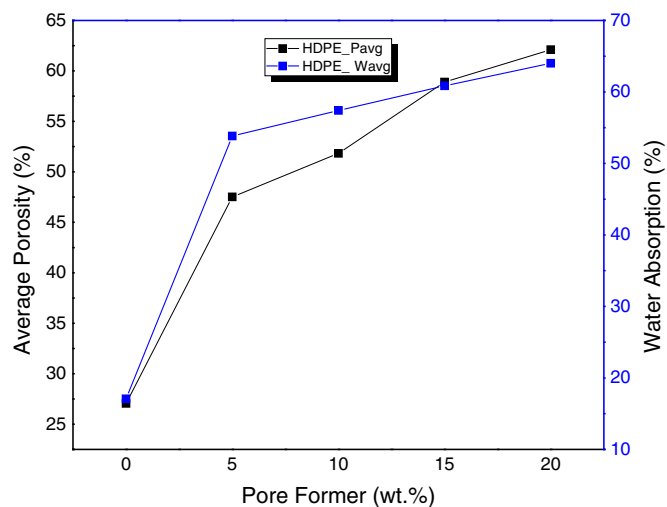


Fig. 9. Porosity and water absorption of sintered membranes with varying pore former content.

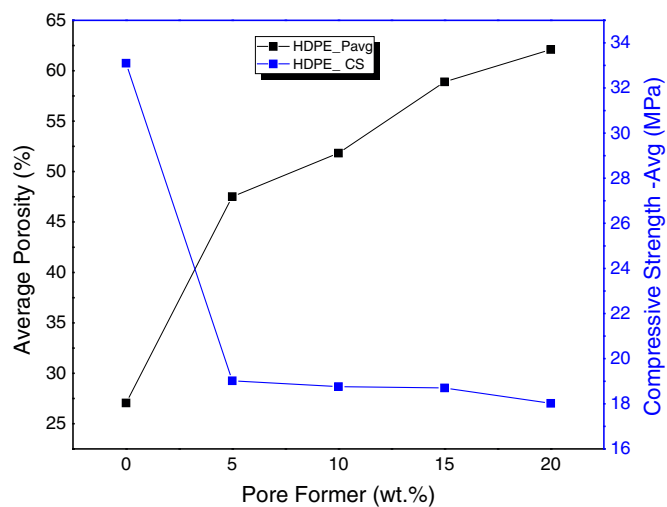


Fig. 10. Porosity and compressive strength of sintered membranes with varying pore former content.

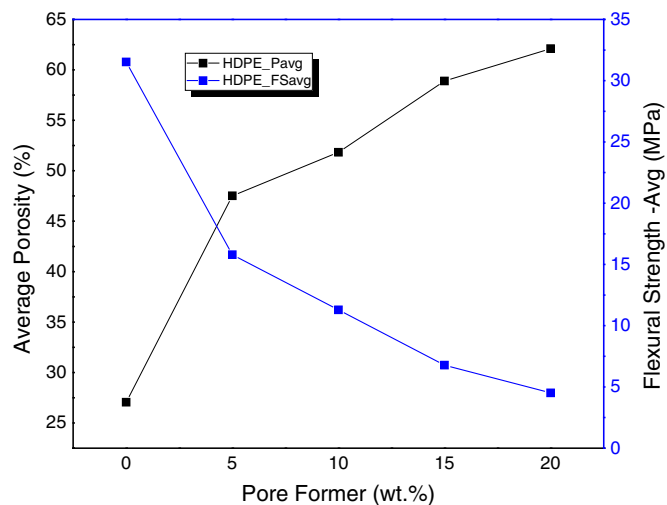


Fig. 11. Porosity and flexural strength of sintered membranes with varying pore former content.

Table 2
Values of porosity and standard deviation for ceramic membranes.

Sample code	% P ₁	% P ₂	% P ₃	% P ₄	% P ₅	% P _{avg}	SD
0% CNS	27.03	27.03	27.04	27.03	27.05	27.04	0.01
5% HDPE	47.54	47.51	47.52	47.53	47.52	47.52	0.01
10% HDPE	51.83	51.81	51.82	51.84	51.81	51.82	0.01
15% HDPE	58.88	58.90	58.94	58.89	58.90	58.90	0.02
20% HDPE	62.12	62.10	62.11	62.10	62.09	62.10	0.01

% P_{1–5} = percentage porosities of the 5 samples for each batch formulation.
SD = standard deviation.

Table 3
Values of water absorption and standard deviation for ceramic membranes.

Sample code	% WA ₁	% WA ₂	% WA ₃	% WA ₄	% WA ₅	% WA _{avg}	SD
0% CNS	17.05	17.07	17.06	17.04	17.13	17.07	0.04
5% HDPE	53.86	53.85	53.80	53.85	53.84	53.84	0.02
10% HDPE	57.43	57.40	57.43	57.40	57.39	57.41	0.02
15% HDPE	60.87	60.84	60.83	60.85	60.86	60.85	0.02
20% HDPE	64.03	64.02	64.04	63.95	64.01	64.01	0.04

% WA_{1–5} = percentage water absorption of the 5 samples for each batch formulation.
SD = standard deviation.

Table 4
Values of apparent density and standard deviation for ceramic membranes.

Sample code	% AD ₁	% AD ₂	% AD ₃	% AD ₄	% AD ₅	% AD _{avg}	SD
0% CNS	2.34	2.32	2.30	2.36	2.33	2.33	0.02
5% HDPE	1.95	2.01	1.95	1.97	1.97	1.97	0.02
10% HDPE	1.94	1.95	2.02	1.97	1.97	1.97	0.03
15% HDPE	1.92	1.99	1.96	1.94	1.94	1.95	0.03
20% HDPE	1.90	1.92	1.92	1.95	1.91	1.92	0.02

% AD_{1–5} = percentage apparent density of the 5 samples for each batch formulation.
SD = standard deviation.

Table 5
Values of compressive strength and standard deviation for ceramic membranes.

Sample code	% CS ₁	% CS ₂	% CS ₃	% CS ₄	% CS ₅	% CS _{avg}	SD
0% CNS	33.10	33.09	33.10	33.09	33.11	33.10	0.01
5% HDPE	19.00	19.01	19.03	19.02	19.05	19.02	0.02
10% HDPE	18.78	18.74	18.74	18.78	18.77	18.76	0.02
15% HDPE	18.69	18.69	18.72	18.71	18.70	18.70	0.01
20% HDPE	18.01	18.04	18.02	18.01	18.02	18.02	0.01

% CS_{1–5} = percentage compressive strength of the 5 samples for each batch formulation.
SD = standard deviation.

Table 6
Values of flexural strength and standard deviation for ceramic membranes.

Sample code	% FS ₁	% FS ₂	% FS ₃	% FS ₄	% FS ₅	% FS _{avg}	SD
0% CNS	31.51	31.54	31.54	31.57	31.49	31.53	0.03
5% HDPE	15.76	15.82	15.78	15.81	15.78	15.79	0.02
10% HDPE	11.26	11.27	11.26	11.29	11.37	11.29	0.05
15% HDPE	6.76	6.74	6.89	6.76	6.75	6.78	0.06
20% HDPE	4.54	4.53	4.52	4.45	4.51	4.51	0.04

% FS_{1–5} = percentage compressive strength of the 5 samples for each batch formulation.
SD = standard deviation.

sample (0% pore former content) in comparison to samples with pore formers due to higher porosity in the latter samples. Higher porosity implies fewer load bearing capacity. Therefore, the strength decreases at higher pore former content. However the value of compressive strength (18.02 Mpa) obtained at maximum pore former content (20%)

at the sintering temperature used in this study (1150 °C) is considered to be within tolerable limits.

The obtained resistance of the membranes to flexion at different pore former content is shown in Fig. 11. It can be seen that the flexural strength decreases (15.79 MPa at 5%) with increasing pore former content (4.51 MPa at 20%). The decrease in flexural strength is attributed to the reduced densification of the clay materials with increasing pore former content of the samples. This result is in good agreement with the trends found in literature (Saffaj et al., 2004a, 2004b; Bouzerara et al., 2006).

In terms of correlating the porosity of the membranes vis-à-vis the mechanical strength, it can be noted that the porosity increases with the percentage of PHDPE to reach up to 62.10% with 20% of pore former addition. On the other hand, the mechanical strength has an opposite behaviour and it decreases with the percentage of PHDPE up to 18.02 and 4.51 MPa with 20% of pore former for compressive and flexural strengths respectively. The loss of the inorganic material at higher temperatures is the origin of the porosity. The higher porosity that follows the increase of the percentage of pore former makes the membrane mechanically less resistant. These results suggest a compromise to obtain macroporous support with high porosity but also with a good mechanical strength. It was necessary to raise the sintering temperature to 1150 °C to get a higher mechanical strength. It can be noted that porosity decreases with the temperature which is due to the transformation of the clay and the formation of the glassy phase. On the other hand, the mechanical strength improves with the temperature because of the transformation of the kaolin and the presence of glassy phase at high temperature.

3.4. Chemical stability and permeability tests of ceramic membranes

The chemical stability of the membranes was evaluated in terms of mass loss after keeping the membrane in contact with acid and alkali solutions separately. As the pore former content increased, the weight loss of the membranes due to the corrosion of acid decreased from 6 to 3%, while the weight loss of the membrane due to alkali solution attack was found to be around 2% for all the membranes as depicted in Tables 7 and 8. The results reveal that the membranes exhibit good corrosion resistance in both acidic medium and basic medium. The obtained results are comparable with alumino silicate microfiltration membranes (Almandoz et al., 2004; Suresh and Pugazhenth, 2016).

Fig. 12 shows the gas flux with variation in applied pressure for membranes heated at 850 °C, 1000 °C and 1150 °C. It should be noted that for the purpose of this experimentation, the membranes were sintered at different temperatures to allow for comparison. A near linear evolution of the flow vs. pressure can be noted with the sintering temperatures. The gas flux was around 31 ml/min under a pressure of 3 bar for the membrane sintered at 850 °C, a value of gas flux of around 35.50 ml/min under a higher pressure of 3.5 bar for the membrane sintered at 1000 °C and 42.50 ml/min for the membrane sintered at 1150 °C. At a maximum pressure of 5 bar, the flow evolution was 40.10 ml/min, 44.30 ml/min and 49.50 ml/min at 850 °C, 1000 °C and 1150 °C respectively. These values of gas flux are different from the expected results considering that porosity should decrease with sintering temperature. The outcome could be directly related to the bigger pore size generated by the higher sintering temperature. It is known

Table 7
Chemical stability data for acid attacks on ceramic membranes.

Sample code	Weight before	Weight after	% mass loss
5% HDPE	1.3108	1.2330	6
10% HDPE	1.1342	1.0824	4
15% HDPE	0.7359	0.7100	3.5
20% HDPE	0.6969	0.6750	3

Table 8
Chemical stability data for alkali attacks on ceramic membranes.

Sample code	Weight before	Weight after	% mass loss
5% HDPE	1.3105	1.2850	2
10% HDPE	1.1341	1.1085	2
15% HDPE	0.7359	0.7200	2
20% HDPE	0.6969	0.6820	2

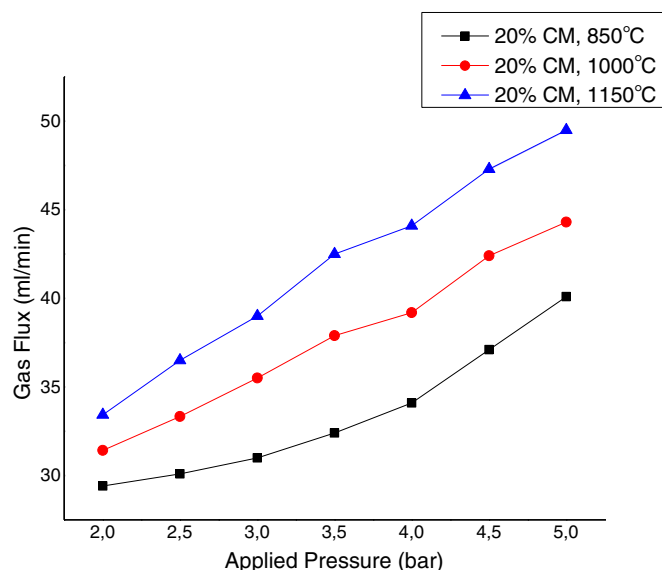


Fig. 12. Gas flux through membranes at different sintering temperature.

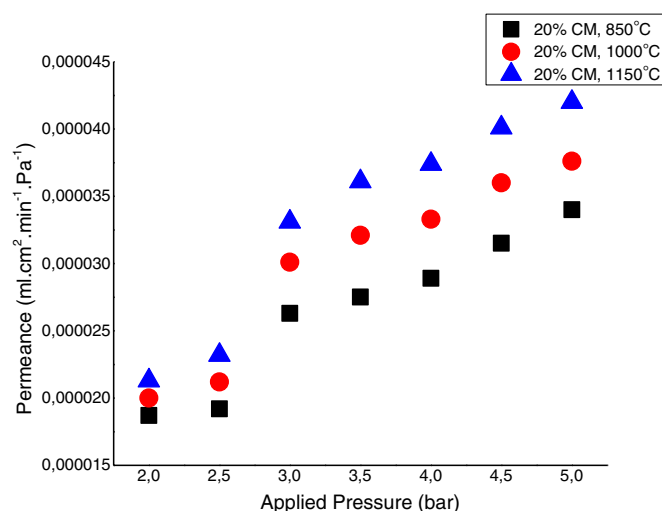


Fig. 13. Permeate flux through membranes at different sintering temperatures.

that pore nucleation or cavitation precedes pore growth in ceramics at high temperature. This result confirms that the pore size is more important for the gas flux than the total pore volume. The increase of the heating temperature closes the porosity and also induces the pore coalescence which engage a bigger pore size. Usually, average pore diameter of the membrane increases with increasing sintering temperature due to which membrane permeability also increases. Similar trends are reported in literature (Saffaj et al., 2005; Bouzerara et al., 2006) for the other type of clay based inorganic membrane fabrication.

The permeate flux also increases due to enhancement of the driving force across the membrane. At maximum applied pressure of 5 bar, the permeability of gas (N_2) through the membranes using Eq. (6) at the

different sintering temperatures (850, 1000 and 1150 °C) as used in this study are $3.40E-05$, $3.76E-05$ and $4.20E-05$ $ml\ cm^{-2}\ min^{-1}\ Pa^{-1}$ respectively. The addition of the pore former (PHDPE) to the initial composition improves the permeability, because compositions with the pore former mix at increased sintering temperature should have higher slopes than those at lower sintering temperature as can be seen in Fig. 13. The results are consistent with the microstructure observed in Section “X-ray diffraction and SEM analyses of sintered ceramic membranes”, where it has been stated that the addition of PHDPE to the membrane's composition increase the pore size and the connectivity of the pores, owed to the porosity created when the pore former is burnt out during the sintering step, increasing the membrane's permeability. This is especially effective for PHDPE percentage of 20 wt%, since a connected coarse pore network is developed.

4. Conclusions

A new inorganic formulation is tested for the fabrication of ceramic membranes. This study indicates that a ceramic membrane can be fabricated with higher content of kaolin (80%) and pore formers. Thermal characterization and XRD study provided information about changes in phase of precursor materials and sintered membranes for the chosen temperature of sintering 1150 °C. The distribution of pore sizes based on SEM showed the inclusion of macropores and at larger magnification, enlarged pore diameters. The membranes provided good mechanical strength and chemical stability in both acid and base media. The evaluation of the performance of the membranes has been made through gas permeation tests. The obtained values show an increase in permeability with increase in sintering temperature of membranes and applied pressure. The permeate flux is increased due to enhancement of the driving force across the membrane. At maximum applied pressure of 5 bar, the permeability of gas through the membranes considering the sintering temperatures are $3.40E-05$, $3.76E-05$ and $4.20E-05$ $ml\ cm^{-2}\ min^{-1}\ Pa^{-1}$ respectively. These results suggest that these membranes could also be tested to evaluate their performance for liquid permeation. These results provide significant opportunities to develop ceramic micro-filtration membranes with flexible pore sizes for industrial applications.

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