

CHARACTERIZATION OF NATURAL LEBANESE CLAYS FOR THE PREPARATION OF CERAMIC MEMBRANES DESIGNED TO WATER FILTRATION

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ABSTRACT

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The potentiality of natural Lebanon minerals for the fabrication of ceramics membranes has been investigated for the first time, opening new perspectives for the development of local, low-cost and sustainable processes for water filtration. Natural clay deposits, originated from North (Kousba, El-Koura), South (Hasbaya) and East (Rashaya, south of the Beqaa valley) regions of Lebanon were collected and investigated in terms of chemical, mineralogical and thermal features. The phase and chemical transformations occurring during heat treatments of these clays were studied by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron spectroscopy (SEM), and X-ray fluorescence (XRF), in view of their uses as membranes for water purification. Flat membranes were prepared by roll-pressing of clay pastes followed by pyrolysis. The mineral membranes were characterized in terms of porosity and water flux.

Keywords: Clay, Lebanon, Membrane, Water, Kaolinite, Mullite.

INTRODUCTION

Clays and clay-based natural minerals are important and versatile raw materials for a wide range of applications going from traditional industry like pottery to agriculture and construction. Industrial processes usually take benefits of the plasticity of clay pastes which facilitates their shaping into green bodies, the latter can be converted into ceramic pieces by convenient thermal treatment. Beside the intrinsic properties of clay-based products after firing, both low-cost and local accessibility are the most important factors of choice that motivate the common use of these natural materials worldwide. More recently, the interest in sustainable and green chemistry process has encouraged the use of natural materials for some low-volume and high-added value applications, like for instance cosmetics, pharmaceuticals and environmental science issues (Silva et al., 2011; Oti et al., 2012; Figueiredo et al., 2007; Grifa et al., 2009; Meseguer et al., 2010). The local availability of clays together with their non-toxicity, abundance and low-cost are the engine of this increasing interest (Nandi et al., 2008; Bun et al., 2011; Baccour et al., 2008; Nayak et al., 2007; Kinuthia et al., 2012; Vasanth et al., 2011; Ekosse et al., 2012). However, high-value applications can be highly sensitive to small fluctuations in terms of mineralogical and chemical compositions (Gao et al., 2011). Industrial processes need therefore to be adapted to each variety of clay-based materials, whose chemical composition should be previously deeply investigated. Due to its geographic and climatic position, Lebanon is considered as one of the richest Mediterranean countries in soil variety, such as terra-rosa and terra-fesca, which are known to contain kaolin and montmorillonite (Darwish et al., 1997). In the present study, natural clay deposits from Lebanon, originated from North (Kousba, El-Koura), South (Hasbaya) and East (Rashaya, south of Beqaa valley) regions were collected and investigated in terms of chemical, mineralogical and thermal features.

In environmental science, the access to drinkable non-polluted water for the entire world population is one of the key challenges of the XXIst century. In the field of water purification, the interest of membrane materials and processes is clearly established for a sustainable development (Anbri et al., 2008; Bouzerara et al., 2006; Palacio et al., 2009; Somen et al., 2010; Khemakhem et al., 2006). Polymeric materials are presently dominating the membrane market, because of both economic and technological criteria, but the main challenge of the polymeric materials is their lack of durability. Thus, inorganic/ceramic materials have recently motivated strong R&D efforts due to their higher chemical, thermal stability, mechanical strength and durability of porosity. Ceramic materials involved in a membrane system are usually asymmetric and made of a porous support, a membrane of large porosity, holding an active membrane layer of thinner porosity. The supports will be in direct contact with the flux of polluted water and their expected main features are their mechanical properties, chemical stability and porosity distribution (to improve the water flux through the whole membrane system). Ceramic/inorganic membranes are usually prepared by chemical route, like sol-gel, for a better control of their features and a better reproducibility during industrial

manufacturing. Beside these thin membranes, their ceramic supports represent the main weight part of the filtration materials. In a sustainable development strategy and more especially in third-countries, it is obvious that using local natural clay products will permit to reduce the global cost of the filtration systems, including the reduction of the transport cost of commercial artificial supports, which are usually manufactured in large scale in developed countries.

In the present study, Lebanon clays were investigated as candidates in view of their possible use as membranes for water filtration. It is obvious that the preparation of ceramic membranes from natural minerals is well-documented for a wide range of natural clays (Nandi et al., 2008; Bouzerara et al., 2006; Yingchao et al., 2007; Zhou et al., 2010; Seffaj et al., 2005), but it is to our knowledge the first study on Lebanese natural deposits. Membrane supports manufacturing requires the preparation of a clay paste with the convenient rheological properties, the shaping of this paste by roll-pressing (for flat supports) or extrusion (for tubular supports), the thermal conversion of the ensuing green bodies into ceramic materials exhibiting convenient porosity and mechanical properties. For the last step, the thermal treatment experimental conditions are a key-step to ensure the convenient properties to the support. In this context, the relationship between the characteristics of clay minerals, which refers to its mineralogical composition, with the transformation of phases during the sintering process will be presented.

MATERIALS AND METHODS

Sample preparation

For the selection of the collecting area for natural materials sampling, we have chosen three of the most commonly used and accessible clay deposits. Clay samples C1 is coming from Rashaya, known as Rashaya al Wadi located in the South of the Beqaa valley of Lebanon. C2 was obtained from Hasbaya, located in the South of Lebanon, closed to Rashaya. Both of them were recovered at 10 m height in order to get the clay mineral and represent the most commonly used clays in the traditional Lebanese pottery industry. These collected samples were ground prior to use in a ball miller for 4 hours.

For sample C3, a soil was collected in Kousba, located in the Koura region along the coast from Batroun to Tripoli, in the North of Lebanon. The as-collected soil was suspended in water and sieved successively at 400 μm , 200 μm , and 50 μm in order to eliminate sand and silt. Finally, it was oven-dried at 110°C during 24 hours and then ground in a ball miller for 4 hours, yielding sample C3.

Ceramic paste formulation

To elaborate plane or tubular supports from clays C1, C2 and C3, ceramic pastes with adequate plasticity and rheology were prepared. The manufacturing steps of the ceramic pastes and supports are shown in figure 1.

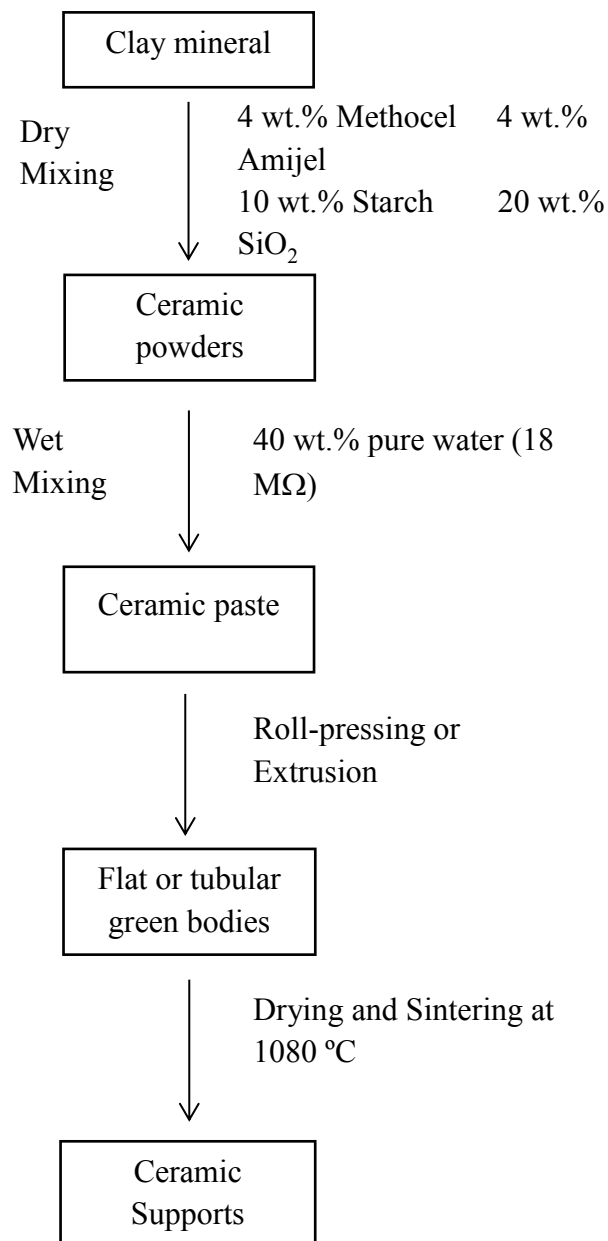


Figure 1. Manufacturing steps of Lebanese clay ceramic supports

In a first step, the different clay powders were dry mixed for 30 min with some solid additives, as porosity agent, binder and plasticizer (corn starch (RG 03408, Cerestar); amijel (Cplus 12072, Cerestar); methocel, (Dow Chemical Company)) and silica as chamotte (Fluka, chemika 83345). The mixture was mechanically stirred during 30 min to ensure a good homogeneity. In a second step, water was added and the mechanical stirring was maintained until the formation of a plastic, non-sticky clay paste. The latter was further processed either by roll-processing to get green flat supports or by extrusion to obtain green tubular supports. Finally, a sintering thermal treatment up to 1080°C (heating rate 5°C.h⁻¹ with 2 h dwelling step) was applied under air atmosphere to allow the consolidation of the supports and the appearance of the porosity. Two dwelling steps at 250°C (1 h) and 700°C (1 h) were applied to allow the elimination of organic additives and the structural water present in the clay, respectively.

Characterization techniques

As the three clay samples were collected from three different deposits, it was important to analyze their chemical composition as well as their particle size distribution after ball milling. Concerning the chemical composition, two complementary techniques were used to identify precisely all the elements present in the samples. X-ray fluorescence (XRF, Thermo Fisher 9900 XP) was the main technique used to determine the amount of the different oxides composing the clays, and especially silica SiO₂, which is not accessible by other techniques. Before analysis, the as-grounded samples were heated up to 950°C to evaluate the loss on ignition (LOI), then the treated powders were melted with lithium borate using the fused bead technique in a 1/11 ratio (Claisse type 4). The second technique used to analyze the chemical composition of the clay powders was the inductively coupled plasma mass spectroscopy (ICP-MS).

The particle size distribution of the different samples was determined using a Horiba LA 950 laser diffraction system that provides a measurement in the range 0.01 to 3000 µm. The thermogravimetric (TGA) and differential thermal (DTA) analyses were performed using a SETARAM apparatus (TA instrument SDT 2960) under air from room temperature up to 1200°C at a heating rate of 10°C/min. The mineralogical analysis of clay samples was carried out by X-ray diffraction using a Philips PAN analytical X'Pert PRO diffractometer operating at 40 kV and 20 mA, using the Cu K α radiation. The diffraction patterns were obtained in the 2 θ range of 5° to 80° with a 0.0334° step. The identification of mineral phases was carried out by using the Eva software and the powder diffraction files database of the International Center for Diffraction Data (ICDD).

Infrared spectroscopy was performed using the Attenuated Total Reflectance (ATR) technique at room temperature with a Spectrum BX Perkin Elmer apparatus, in the range 4000 cm⁻¹ to 450 cm⁻¹. The morphology of the raw clays as well as the sintered flat supports obtained after pastes processing was observed by Scanning Electron Microscopy (SEM) using a HITACHI S4800 microscope. The median pore size and

global porosity of the fired clay supports were characterized by Hg porosimetry using a Micromeritics, Autopore IV 9500.

RESULTS AND DISCUSSION

Clay minerals characterization

The as-collected samples C1 and C2 were ground in a ball miller to yield light brown powders. As-collected sample C3 was first dispersed in water before sieving to 50 μm , dried then ball-milled yielding to a red powder. The particle size distribution of clay powders is presented in figure 2. This parameter is a key-point for the reproducibility of the paste formulation process and therefore for the manufacturing of green clay bodies.

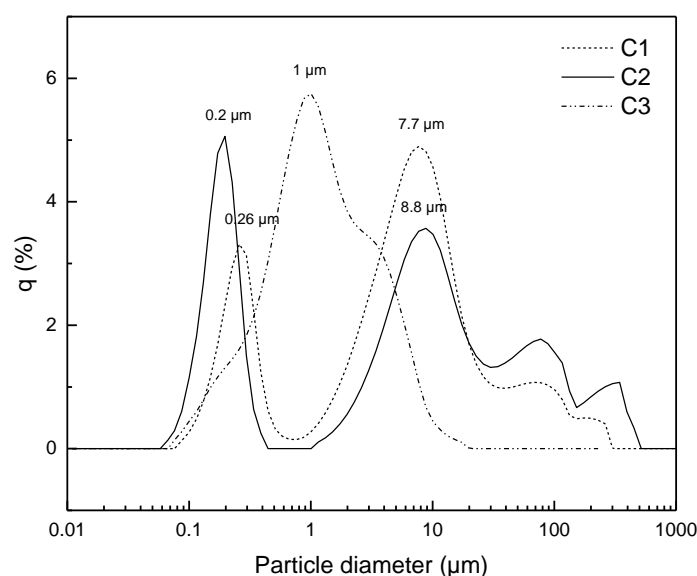


Figure 2. Particle size distribution of clay samples C1, C2 and C3.

Samples C1 and C2 show a wide range of size distribution with two main families centered at $\sim 0.2\mu\text{m}$ and $\sim 8\mu\text{m}$. Clay sample C3 exhibits a more narrow distribution around $\sim 1\mu\text{m}$. The strong difference between these two series can be either interpreted in terms of chemical composition, which affected the effect of ball milling via intrinsic hardness and brittleness, and in terms of manufacturing conditions since C3 has been dispersed, filtered and dried before milling. The chemical composition of the different clay minerals was examined by the means of XRF and ICP-MS. Table 1 summarizes the data collected by these two techniques.

As mentioned in the experimental part, the samples were first heated up to 950°C to evaluate the loss on ignition (LOI) before further analysis. The values obtained for the three samples are quite comparable and will be discussed below with the

thermogravimetric analysis. According to XRF measurements, samples C1, C2 and C3, after firing up to 950°C, are mainly composed of SiO₂, Al₂O₃, Fe₂O₃, CaO and TiO₂. Traces of K₂O, MgO, MnO, P₂O₅, SO₃, Na₂O and Cr₂O₃ have also been detected but their concentration is below 1wt.%. By comparing C1 and C2, from the Beqaa and South region, the first one has a higher iron oxide content, which is confirmed by its darker coloration. The main difference between these two samples and C3 stays in their different alumina proportion. This value appears to be much higher in the C3 sample from the North region. The iron oxide content is also very high in C3, also correlated to its reddish coloration. A second analysis technique, ICP-MS, was used in order to cross the results. The preparation of the samples before analysis is different since they are not fired and melted but digested in acidic solution.

The results obtained by XRF can therefore be slightly different from the ICP-MS data. For comparison, the elemental analysis of the samples C1 to C3 was calculated from the XRF measurements. The results of the two analytical techniques are in good agreement concerning the Al and Fe contents. For Ti and Ca, the contents for each sample are close to the detection limit thus it is difficult to conclude. It is also possible to notice an experimental scattering of the Ca content calculated by XRF or ICP-MS in the C1 sample. The value of Ca content for C1 sample by ICP-MS is presumably overestimated.

The identification of minerals in C1, C2 and C3 was conducted on the basis of the identification of the peaks obtained by X-ray diffraction. With the aim of preparing clay-based membrane supports for water purification, we also investigated the evolution of the diffraction patterns, recorded at room temperature, with different temperatures of firing (300°C, 600°C, 900°C and 1200°C). Figure 3 presents the different diffractograms recorded for sample C1.

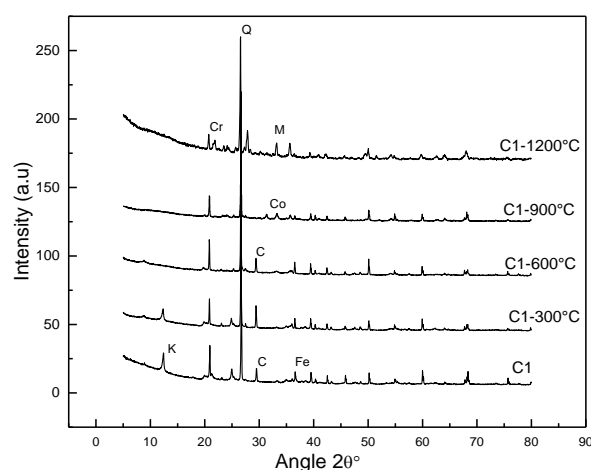
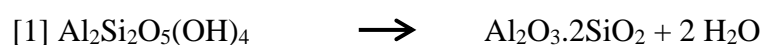


Figure 3. X-ray diffraction patterns of sample C1 for different firing temperatures. K: Kaolinite, C: Calcite, Co: Calcium oxide, Q: Quartz, M: Mullite, Cr: Cristobalite, Fe: Hematite.

According to XRD results, crude sample C1 is containing quartz ($2\theta_{\max}=26.61^\circ$), kaolinite ($2\theta_{\max}=12.33^\circ$), calcite ($2\theta_{\max}=29.39^\circ$) and hematite ($2\theta_{\max}=35.6^\circ$). This result is consistent with the chemical composition obtained from XRF and ICP-MS analyses. During the thermal treatment of C1, some changes are occurring in the diffractograms due to the chemical evolution of the sample. First of all, the peak featuring the presence of kaolinite disappeared above 300°C . According to the literature, kaolinite is known to undergo phase transformation upon heating to form metakaolinite by deshydration reactions [Eq. 1] (Castelein et al., 2001; Ptáček et al., 2010; Benazzouz et al., 2012). The formation of metakaolinite is usually not observed by XRD in the literature, in good agreement with our observations.



Another interesting result is the formation of mullite ($2\theta_{\max}=33.15^\circ$) from a heating temperature of 900°C . At 1200°C , a second phase of mullite, namely the secondary mullite (Gridi-bennadji et al., 2007), is also appearing. Finally, it is possible to observe the degradation of calcite into calcium oxide, CaO ($2\theta_{\max}=29.39^\circ$), above 600°C [Eq. 2] and the phase transformation of quartz into cristobalite ($2\theta_{\max}=19.89^\circ$) above 1200°C .



The X-ray diffraction patterns of sample C2 (Figure 4a) are very similar to those recorded for sample C1.

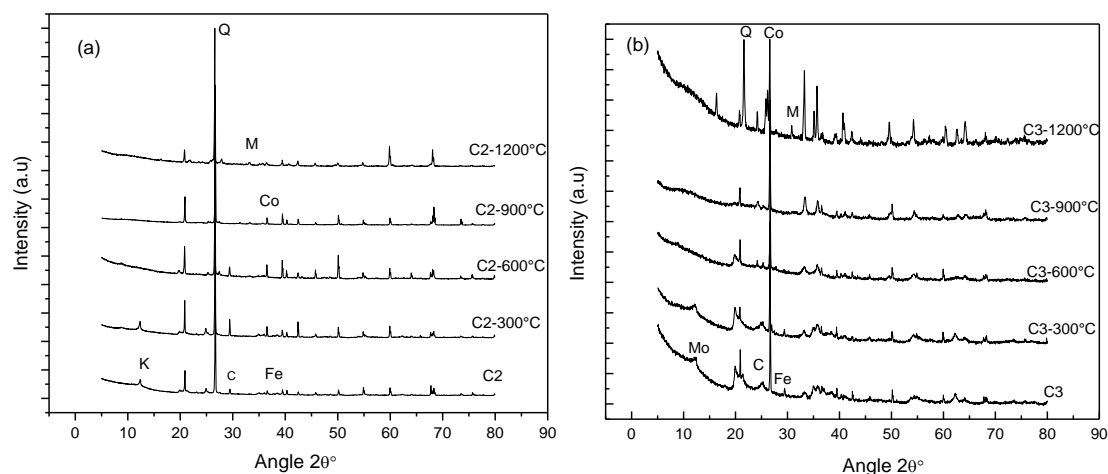


Figure 4. X-ray diffractograms for samples C2 (a) and C3 (b) for different firing temperatures. K: Kaolinite, C: Calcite, Co: Calcium oxide, Q: Quartz, M: Mullite, Cr: Cristobalite, Fe: Hematite, Mo: Montmorillonite.

The main differences are the variation of the relative peak intensities, underlying their differences in chemical composition. The crystallization of quartz into cristobalite is not observed by XRD for sample C2. Sample C3, originating from a different region of Lebanon, is significantly different in term of mineralogical composition. The diffractograms of C3 (Figure 4b) show the presence of Montmorillonite ($2\theta_{\max}=23.69^\circ$) and only traces of calcite, consistently with the results of the chemical analysis of C3. The chemical evolution of the different samples C1-C3 was also studied by infrared spectroscopy.

Figure 5 shows the IR spectra recorded for the different samples heated at various temperatures up to 1200°C. The IR spectra of the different samples are almost similar, emphasizing the similarity in the nature of the chemical bonds in these three natural materials. The crude products are featuring OH bonds vibration at $\sim 3600\text{cm}^{-1}$ (not shown in figure 5).

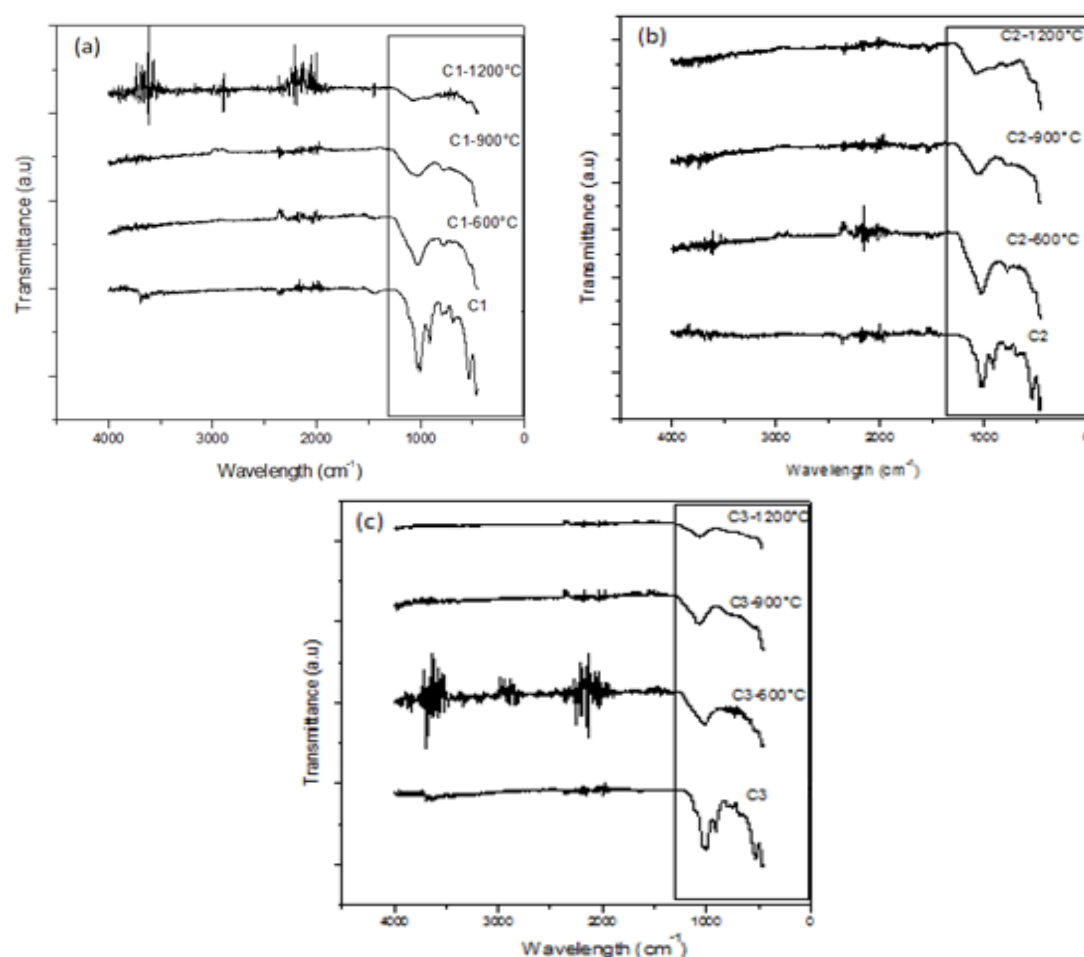


Figure 5. ATR-IR spectra for samples C1 (a), C2 (b) and C3 (c) for different firing temperatures.

The main bands observed are at 1032, 1008, 465 cm^{-1} (Si-O bonds), 913 cm^{-1} (Al-OH bond) and 538 cm^{-1} attributed to Si-O-Al bond. Upon heating up to 1200 $^{\circ}\text{C}$, the vibration bands related to the OH groups disappeared together with the band corresponding to Al-OH groups. A new band at 800 cm^{-1} can be observed, which can be related to the change from octahedral coordination of Al in kaolinite to tetrahedral coordination in metakaolinite (Meseguer et al., 2011). This observation is in good agreement with the XRD data.

The thermogravimetric (TG) and differential thermal (DT) analyses of the clay samples are presented in figure 6. The measured total weight loss for C1, C2 and C3 are 8.9%, 7.2% and 15.4%, respectively.

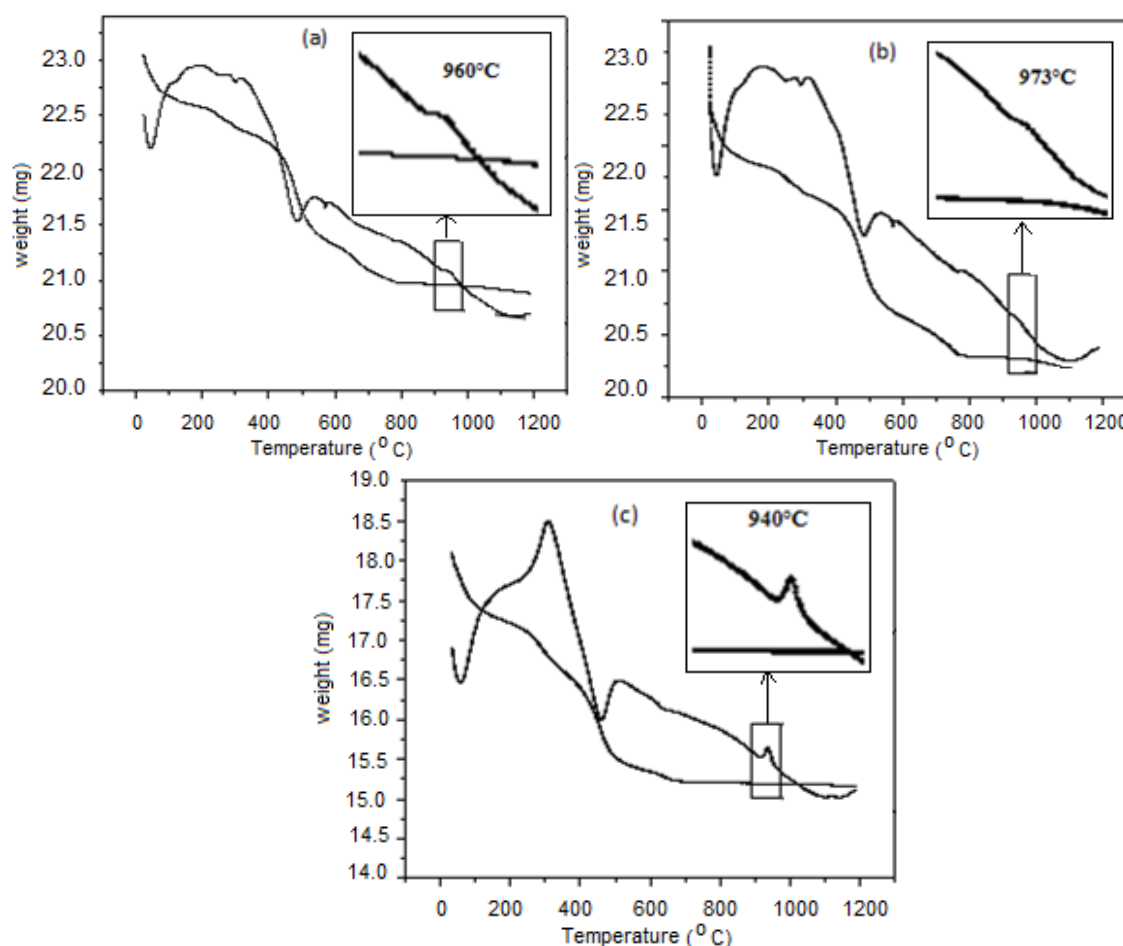


Figure 6. Thermogravimetric analysis (TGA) combined with differential thermal analysis (DTA) of samples C1 (a), C2 (b), and C3 (c).

These results are in good agreement with the LOI obtained from the XRF analysis. The TGA/DTA curves are also in good agreement with the literature (Ptáček and al.; 2010). For all samples, the first weight loss in the range 40°C – 100°C is attributed to the elimination of physical water within the samples (drying step). The next weight loss appearing up to 250°C is related to the pre-dehydroxylation of the samples. These two phenomena are accompanied by an endothermic effect. At higher temperatures, there is an intensive weight loss correlated with a strong endothermic effect in the range 400 °C - 600 °C. This phenomenon is attributed to the loss of the hydroxyl groups present at the surface of the alumino silicate layers (dehydroxylation). At a higher temperature (above 800°C), the weight loss is attributed to the decomposition of calcite into calcium oxide. In addition, we obviously note the existence of an exothermic peak without any weight loss at 960°C, 973°C and 940°C for C1, C2 and C3, respectively.

This exothermic effect can be associated with the formation of a spinel phase from the metakaolinite. We can also envisage the crystallization of mullite and cristobalite but this occurs preferentially at temperature above 1050°C (Ptáček et al., 2010; Doğan et al., 2008; Ilić et al., 2010; Toraj et al., 2003).

These TGA data can be exploited for the formation of membrane supports since the gas evolved during calcite decomposition can allow to improve the porosity of the support. The final temperature of firing needed in the porous membrane support preparation should be therefore chosen around 1000°C to prevent the formation of vitreous mullite phase, which would decrease the effective porosity. In the porous membrane support preparation should be therefore chosen around 1000°C to prevent the formation of vitreous mullite phase, which would decrease the effective porosity.

Scanning electron microscopy observations were performed for all the samples treated at different temperatures (Figure 7).

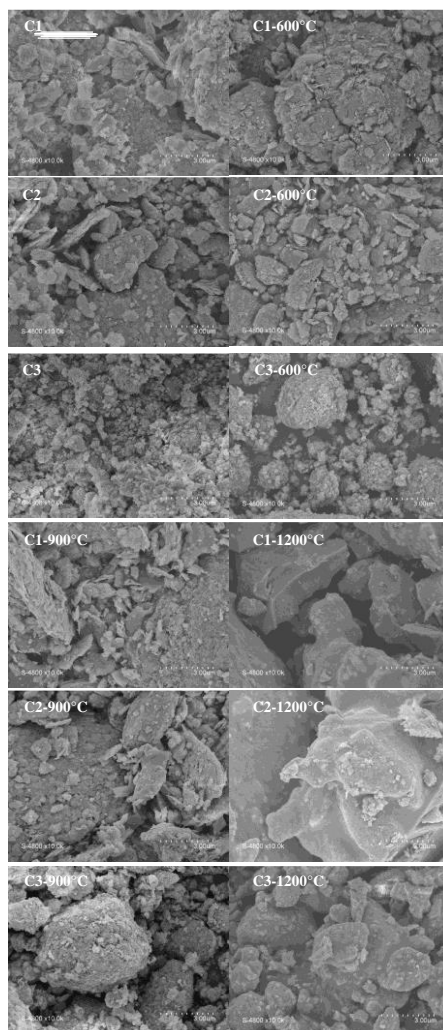


Figure 7. SEM images of samples C1, C2 and C3 heated at different temperatures (white bar is 3.0 μm).

For the crude samples, the layered structure of clays is observed. With the temperature, an evolution of the appearance of the powders can be observed. The thermal treatment at 1200°C induces the formation of dense glassy particles. These observations are in good agreement with the formation of mullite detected by XRD analysis. This result allows us to determine that the temperature to be reached for the firing of the clay-based porous supports must be below 1200°C to improve the porosity and preclude any formation of a dense glassy material.

Membrane supports formation and characterization

As an illustration of the potentiality of the Lebanese natural minerals for the manufacturing of membrane supports for water purification, flat and cylindrical macro porous ceramic supports were manufactured starting from sample C1. The formulation of a paste from the crude C1 powder was performed on the basis of results obtained in the group for similar natural materials (Seffaj et al., 2005; Khemakhem et al., 2004). Figure 8 shows images of flat and cylindrical supports prepared from C1-based paste by roll-pressing and extrusion processes, respectively, followed by a convenient high temperature treatment.

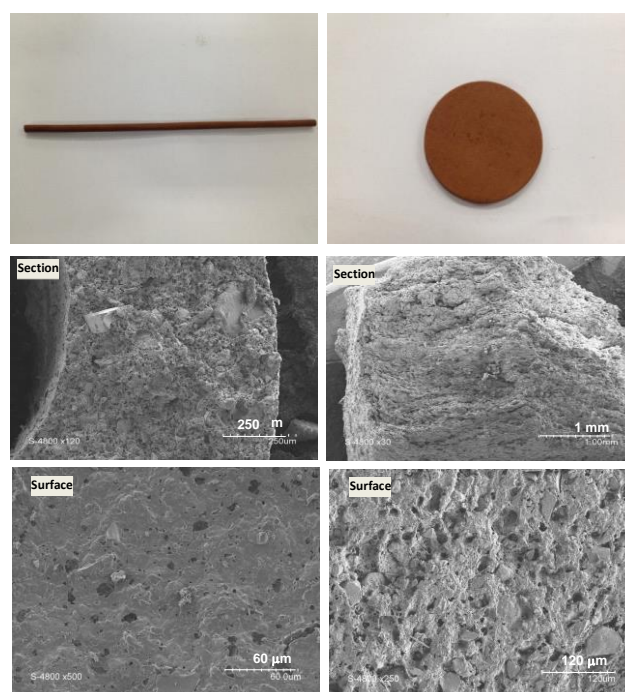


Figure 8. Images of plane and cylindrical supports (section and surface) prepared from C1-based paste by roll-pressing and extrusion processes.

Porosity of the supports was evaluated using the mercury intrusion technique. A mean pore size diameter of $4.5\mu\text{m}$ was measured with 33% of porosity for tubular membrane and a diameter size of $12\mu\text{m}$ with 35% of porosity for plane membrane. These values of porosity and permeability are not very high compared to the literature ((Yingchao et al., 2007; Zhou et al., 2010; Khemakhem et al., 2004). In addition, the permeability of capillary support was measured at $\sim 125\text{ L/h.m}^2\text{.bar}$. Figure 9 shows the water flux through the clay-based support as a function of the applied pressure.

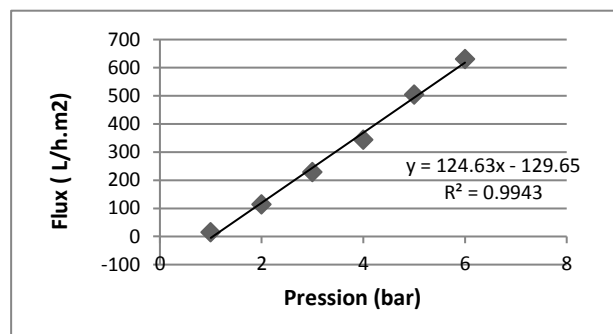


Figure 9. Permeability test using the cylindrical clay support.

These results underline all the potentialities of Lebanese clay-based support for the treatment of water.

CONCLUSION

Natural clay deposits from Lebanon, originated from North (Kousba), South (Hasbaya) and the Beqaa valley (Rashaya) regions were collected and investigated in terms of chemical, mineralogical and thermal features. The effect of thermal treatment up to 1200°C was studied in view of their utilization as membrane supports for water purification. The samples have been characterized as a mixture of quartz, calcite and hematite with kaolinite (C1 and C2) or Montmorillonite (C3). The study of their thermal behavior shows the formation of a dense glassy-like solid at 1200°C, which has been related to the formation of mullite. Calcite present in the samples undergoes decomposition into calcium oxide above 600°C.

These two results allow us to determine a convenient temperature for the elaboration of membrane supports, which is in the range 800°C-1200°C. Membrane supports for water filtration were elaborated from a clay-based paste. Mean pore diameter sizes of 4.5 μm and 12.4 μm were measured with 33% and 35% of total porosity, for flat and tubular support, respectively.

The potentiality of Lebanon minerals for the fabrication of water treatment system has been clearly demonstrated for the first time, opening new perspectives for the development of local, low-cost and sustainable processes for water purification.

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