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Porous ceramic from Moroccan natural phosphate and raw clay for microfiltration applications

Mossaab Mouiya[a,b,*], Abdelkrim Abourriche[a], Abdelaziz Benhammou[a], Youssef El Hafiane[a], Younes Abouliatim[a], Lahbib Nibou[a], Mina Oumam[b], Hassane Hannache[b,d], Agnès Smith[c]

[a]*Laboratoire de Matériaux, Procédés, Environnement et Qualité, École Nationale des Sciences Appliquées, B.P. 63 46000 Safi, Morocco, Tel. +212 24 66 91 55, email: mossaab.mouiya@gmail.com (M. Mouiya), krimabou@hotmail.com (A. Abourriche), benhammou_ab@yahoo.fr (A. Benhammou), youssef.elhafiane@unilim.fr (Y. El Hafiane)*
[b]*Laboratoire des Matériaux Thermostructuraux, Faculté des Sciences Ben M'sik, B.P. 7955 Casablanca, Morocco, Tel. +212 615 124178, email: hannache.hassan@gmail.com (H. Hannache)*
[c]*Laboratoire Science des Procédés Céramiques et de Traitements de Surface, UMR CNRS 7315 – Université de Limoges, Centre Européen de la Céramique, 12 rue Atlantis 87065 Limoges Cedex, France, Tel. +33 5 87 50 25 50, email: agnes.smith@unilim.fr (A. Smith)*
[d]*Center for Advanced Materials Université Mohammed VI Polytechnique, Lot 660 – hay Moulay Rachid 43150 Ben Guerir, Morocco*

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ABSTRACT

Porous ceramics were prepared by the dry compaction process by combining raw clay and Moroccan natural phosphate, which is rich in organic matter. The phosphate was used as a natural pore-forming agent. Compacted pallets were sintered at 1100°C. The samples were characterized by XRD, TG-DTA, Archimedes's principal and Brazilin test. The porosity and the tensile strength were strongly influenced by the concentration of natural phosphate (10–40 wt. %). An increase in the amount of natural phosphate led to an increase the open porosity while the tensile strength was decreased. In order to get porous materials (28 vol% porosity) with a sufficient tensile strength (11 MPa), the optimal clay to natural phosphate mass ratio was found to be 1.5.

Keywords: Clay; Natural phosphate; Porous ceramic; Porosity

1. Introduction

Ceramics are mostly used in totally dense form, but porous ceramics can also be useful due to their low density and good strengths [1]. Materials generally produced in porous form include synthetic oxides such as alumina and zirconia, as well as carbides and nitrides along with organic additives as pore forming agents. These porous materials are not suitable for large-scale production because the raw materials can be very expensive [2–4]. Attention has been paid in the last ten years to the development of porous ceramic based on natural minerals due to their abundance and low cost [4–9].

Porous ceramic materials can provide physical barriers and act as an important exchange surface area for chemical reactions, liquid permeability and interaction between cells and biomaterials. Therefore, these materials are increasingly used in many different fields such as wastewater treatment, thermal insulation, selective filtration and pollution control technologies [9–11]. This study investigates the possibility of developing low cost porous ceramic from natural resources.

Different authors described the development of porous ceramics using natural minerals and synthetic additives as organic pore-forming agents. Palacio et al.

*Corresponding author.

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[4] developed ceramic membranes from Moroccan natural clay and phosphate for industrial water treatment. Barrouk et al. [9,12] described and characterized the ceramic membranes made from natural and synthetic phosphates and their application in filtration of chemically pretreated textile effluent.

In this work, porous ceramics have been developed by solid-state reaction technique using only two Moroccan natural materials: red clay (RC) from Safi and Youssoufia natural phosphate (NPh). This phosphate is highly rich in organic matter, which could potentially act as a natural pore-forming agent during its thermal decomposition.

2. Experimental procedure

2.1. Raw materials

The raw clay (RC) in the raw state is a natural rock extracted from the Safi region, located in western Morocco on the Atlantic Ocean. This locally abundant clay is used mainly in the industry of brick and handmade pottery. The Youssoufia natural phosphate deposit consists of two types of ores; phosphate "clear" containing little organic matter and phosphate "black" (NPh) in turn is rich in organic matter, mainly humic-like substances [13,14]. This material is found 100 km from Marrakech and 230 km south of Casablanca.

2.2. Porous ceramic membrane synthesis

After crushing and grinding the raw material is sieved to a mesh size of 150 µm. The fine powders (<150 µm separated during sieving) are dry blended using a rotary mixer for 1 h. Then the mixture is uniaxially pressed at 150 MPa in a mold with a diameter of 22 mm and a thickness of 5 mm. Later, the compacted pellets were sintered at 1100°C for 2 h with a heating ramp of 5°C/min.

2.3. Characterization techniques

Inductively Coupled Plasma (ICPE-9000) was used to determine the elemental compositions of starting materials. ICP-MS consisting of ions, electrons and neutral particles, is formed from Argon gas which is then utilized to atomize and ionize the elements in the sample matrix.

The D2 Phaser is a powder diffractometer (Bragg-Brentano fixed sample theta-theta geometry) was used to identify different phases of raw clay, using CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA, with 2θ ranging from 10° to 100°.

The thermogravimetric (TG) and differential thermal analyses (DTA) of mixture were carried by Setaram SETSYS 24 apparatus using α-Al_2O_3 as a reference. Samples were heated from ambient temperature to 1100°C and a heating rate of 10°C/min.

The apparent porosity and density of each sintered sample was measured three times by the Archimedes' principle using water as the fluid.

The Brazilian test was performed at ambient temperature on cylindrical samples with a diameter of 22 mm and a thickness of 6 mm using a universal testing machine (Ametek Lloyd Instruments).

3. Results and discussion

3.1. Characterization of raw materials

The chemical analysis of the raw clay and natural phosphate was determined by ICPE-9000 and the results are shown in Table 1.

It appears that the clay fraction is silica rich and silica is mainly in the form of quartz, followed by kaolinite as shown by XRD (Fig. 1). Muscovite and calcite are also present in small proportions. Almost similar phases have been reported by other authors [15].

The mass loss of (NPh) at 1100°C is 22% which corresponds to carbonate and mainly organic matter loss.

3.2. Thermal analysis (DTA/TG)

Thermal analyses (DTA and TG) carried out on natural phosphate/raw clay mixtures. The data for a mix containing 20 wt. % of NPh are presented in Fig. 2. The TG curve exhibits four losses of mass. The first weight loss corresponds to dehydration of the mixture which is expressed in DTA by an endothermic peak at 100°C. The second loss, from 312 to 430°C, is combination of two exothermic, peaks one centered at 342°C corresponding to the thermal decomposition of organic matter contained in the (NPh) and other loss around 423°C attributed to the beginning of dehydroxylation of the clay minerals. The third loss between 525 and 573°C is due to the dehydroxylation of kaolinite ($Si_2O_5Al_2(OH)_4$) [16]. The last weight loss from 712°C to 813°C accounts for the thermal decomposition of mineral carbonates.

3.3. Effect of natural phosphate addition

To assess the potential of natural phosphate as a natural pore-forming agent, three samples containing 10 wt. %, 20 wt. % and 40 wt. % of (NPh) were prepared under the conditions described in the experimental procedure.

3.3.1. Mass loss

The weight loss rate of each sample was evaluated by measuring the mass loss once the samples are treated at 1100°C. The results reported in Table 2 show that the mass loss rates for sintered samples increase from 14.6 to 17.7% with the addition of natural phosphate (10, 20, and 40 wt.%); It can be linked to an increase of organic matter decomposition contained in the natural phosphate (Fig. 2).

Table 1
Chemical compositions of raw clay and natural phosphate (wt. %)

	Raw clay	Natural phosphate
MgO	2.24	2.3
SiO_2	52.79	9.26
Al_2O_3	17.44	0.58
Fe_2O_3	5.08	0.28
P_2O_5	0.17	19.94
K_2O	1.70	0.083
Na_2O	0.39	0.97

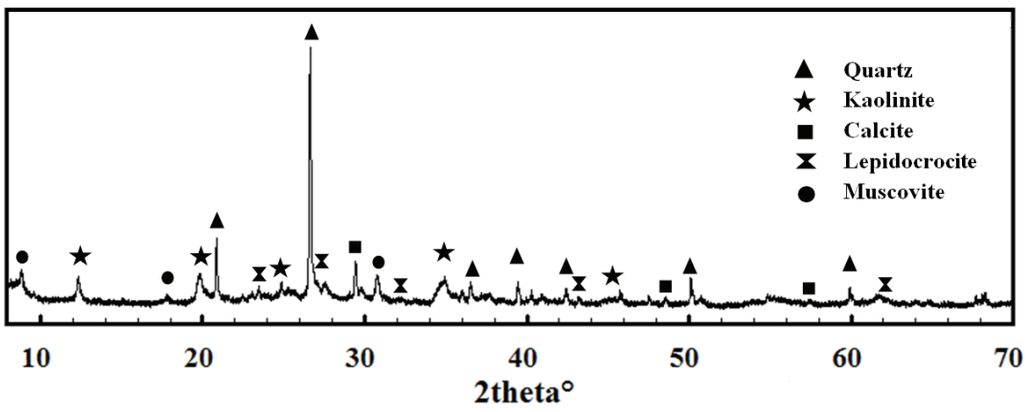

Fig. 1. XRD patterns of natural raw clay (RC) at 25°C.

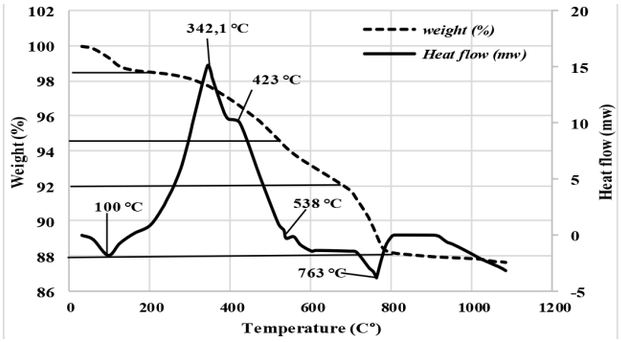

Fig. 2. DTA/TG curves of mixture (RC) and (NPh).

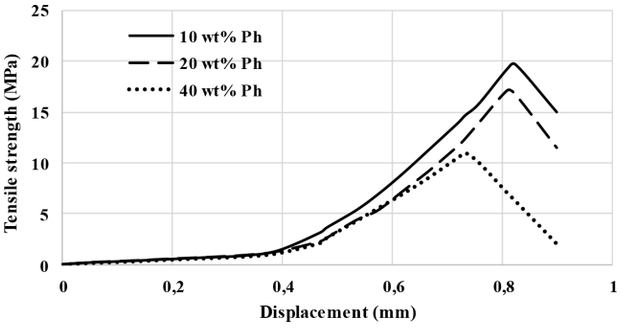

Fig. 3. Effect of natural phosphate addition on the tensile strength of RC/NPh samples sintered at 1100°C.

Table 2
Effects of (NPh) addition on the weight loss of materials prepared by mixing (RC) and (NPh)

Natural phosphate addition (wt. %) in the RC/NPh mixtures	Mass loss (%)
10	14.6
20	15.9
40	17.7

Table 3
Effects of (NPh) addition on Apparent porosity and density of materials prepared by mixing (RC) and (NPh)

Sample	Apparent porosity (%)	Apparent density (g/cm^3)	Bulk density (g/cm^3)
10 wt. %	4.1	2.2	2.1
20 wt. %	14.6	2.3	2.0
40 wt. %	28.1	2.8	2.0

3.3.2. Apparent porosity and density

The porosity and density were measured by the Archimedes' principal. The natural phosphate addition has a significant effect on porosity and apparent density of the materials obtained from clay and natural phosphate mixtures (Table 3). Indeed, the porosity was increased from 4.1 to 28.1% when the amount of NPh in the mix goes from 10 to 40 wt.%. This value of porosity is relatively lower than that of porous ceramic prepared from natural clay minerals without synthetic additives reported in previous works [6,15].

3.4. Tensile strength

The tensile strength of sintered samples at 1100°C containing different proportion of natural phosphate (10–40 wt.%) were measured by the Brazilian tests.

Fig. 3 illustrates the curves of the tensile strength versus displacement. Beyond a displacement of 0.4 mm, the curves showed a linear behavior which could be due to an elastic behavior of the samples. On the other hand, it can be seen that the tensile strengths values decrease from19.6 MPa to 11 MPa with increasing the amount of natural phosphate. This can be due to the increase in porosity (Table 3) [17].

4. Conclusion

Porous ceramics were prepared by solid state using Moroccan natural raw clay and phosphate. Porosity formation is largely caused by the thermal degradation of organic matter originally existing in the natural phosphate. The porosity significantly increases from 4.1% to 28.1%

with addition of natural phosphate from 10 to 40 wt.%. A good compromise between porosity (28 vol%) and tensile strength (11 MPa) has been found for a mixture containing 60 wt.% of clay and 40 wt.% of NPh (apparent density: 2.01 g/cm^3). The natural phosphate, highly rich in organic matter, can be used as natural and low-cost porogen agent for the development of porous ceramics.

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