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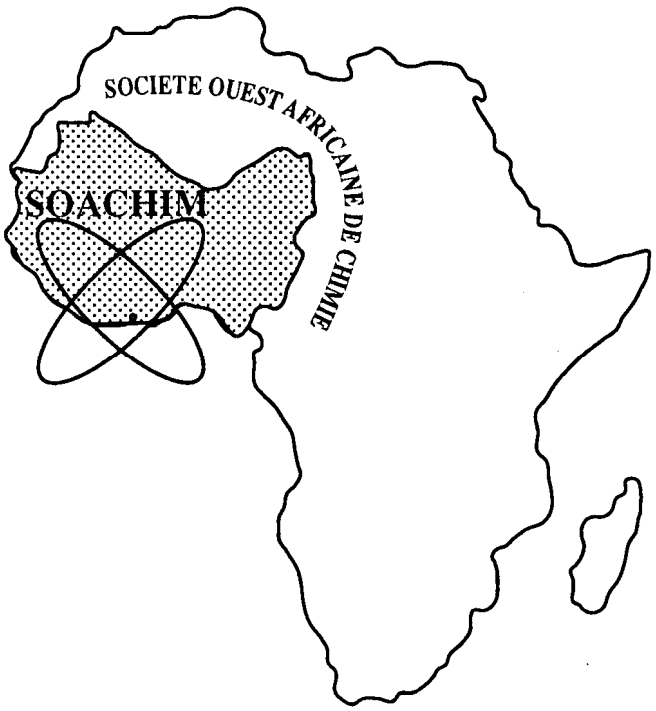

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Physico-chemical and structural properties of clay-based ceramic filters from Côte d'Ivoire

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Abstract : Two clays materials denoted D and Y were physico-chemically and structurally characterized by ICP-AES, XRD and DTA-TGA. For clay D they consisted mainly of 29.92% of kaolinite, 55.95% of quartz, 13.6% of illite and for clay Y, 41.9% of kaolinite, 42.41% of quartz, 10.65% illite and 4.25% of goethite. From these two clays D, Y and corn flour, ceramic filters were made by calcination at 1000°C. Scanning electron microscopy (SEM) revealed a network of interconnected pores in the material. Mercury porosimetry revealed that the pore diameter is predominantly 1 µm. The ceramic filters produced with 75% D + 25% F and 75% Y + 25% F respectively had an open porosity of 52.8% and 50.6%. On the other hand, those produced with 50% D + 50% F and 50% Y + 50% F had an open porosity of 66.6% and 68.2%, respectively, similar to that of the standard reference ceramic filter (66.5%). The specific surfaces of the filters produced are much higher than that of the standard reference filter (2.1 m^2 / g). After 60 days of immersion in water at different pH values, the produced ceramic filters do not disintegrate.

Key words: Clays; Clay minerals; Ceramic filters; Open porosity; corn flour.

Propriétés physico-chimiques et structurales de filtres céramiques à base d'argile de Côte d'Ivoire

Résumé : La caractérisation physico-chimique et structurale de deux argiles D et Y a été réalisée par ICP-AES, DRX et ATD-ATG. Elles sont constituées majoritairement de 29,92% de kaolinite, 55,95% de quartz, de 13,6% d'illite pour l'argile D et de 41,9% de kaolinite, de 42,41% de quartz, de 10,65% d'illite et 4,25% de goethite pour l'argile Y. A partir de ces deux argiles D, Y et de la farine de maïs, des filtres céramiques ont été élaborés par consolidation thermique à 1000°C. La microscopie électronique à balayage a mis en évidence un réseau de pores interconnectés dans le matériau. La porosimétrie au mercure a révélé que le diamètre des pores est majoritairement de 1 µm. Les filtres céramiques élaborés avec 75% D + 25% F et 75% Y + 25% F ont respectivement une porosité ouverte de 52,8% et 50,6%. Par contre, ceux élaborés avec 50% D + 50% F et 50% Y + 50% F ont respectivement une porosité ouverte de 66,6% et 68,2% proche de celle du filtre céramique de référence (66,5%). Les surfaces spécifiques des filtres élaborés sont largement plus élevées que celle du filtre de référence (2,1 m2/g). Après 60 jours d'immersion dans l'eau à différentes valeurs de pH, les filtres céramiques élaborés ne se désagrègent pas.

Mots clés: Argiles; Minéraux argileux; filtres céramiques; porosité ouverte; farine de maïs.

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1. Introduction

One of the major issues concerning the future of humanity is the availability of quality water that has become even more valuable than oil [1]. In many developing countries, about 1.1 billion people have no access to safe drinking water, causing several million deaths per year, especially among children in poorer countries of Asia and Africa. [2]. As a result, halving the proportion of people without access to safe drinking water reduced by halve becomes one of the major goals of the Millennium Development Goals. Across the world, water level is thus subjected to increasingly heavy pressure. These natural reservoirs, which contain nearly one third of the world's freshwater reserves, is over utilized in some parts of the world by man, industry and agriculture utilization. The groundwater level in the world is declining and constitutes a threat to about 1.5 billion inhabitants of the planet [3].

In Côte d'Ivoire, the demand for drinking water by the Ivorian population is in perpetual increase which is by far exceeds the available water supply. In the district of Abidjan, drinking water requirements is estimated at 170 million m3 / year, while the maximum possible volume of water withdrawal from the groundwater is 130 million cubic meters [4]. Considering the ever growing population and the increasing depletion of groundwater, the development of surface water is becoming a necessity to meet up with the drinking water needs. However, before any consumption, this water must respect certain quality standards. Several methods of water treatment are being used in particular: coagulation-flocculation [5,6], adsorption on activated carbon and more recently electrocoagulation [7] which are certainly effective but very expensive for the developing countries. It is therefore urgent to develop new methods of water treatment process that are more environmentally friendly and at low cost. Ceramic materials of synthetic origin (alumina and zirconia) or natural (clay), less studied than polymers or metals with high porosity, are attracting more attention by the scientific researchers owing to their multifunctionality [8- 10]. Their porous phase can in fact provide, apart from being light, an important exchange surface for chemical reactions or for filtration. The aim of the present work was to characterize two clays from Côte d'Ivoire and on the other hand to produce from these clays ceramic filters using corn flour as pore-forming agents, and to be used as adsorbent and filter suitable for domestic water purification.

2. Experimental materials and methods

2.1. Materials

Two clay materials D and Y from Dabou and Yaou sites in southern Côte d'Ivoire were used. The Yaou site is located at the geographical coordinates 5 ° 19'70"North and 4 ° 22'80"West while that of Dabou is located at geographical coordinates 8 ° 08'42" North and 5 ° 06'12 " West. These sites are located in a sedimentary basin containing clay formations, particularly kaolinitic, resulting from a ferralitic alteration in a tropical humid climate. Residues of ferruginous sand and oxides or oxyhydroxides of iron or aluminium are also present. All analyzes were carried out on 100 µm sieved samples.

2.2. Experimental methods

The chemical analysis was carried out by ICP-AES plasma atomic emission spectrometry after a microwave assisted chemical solution (CEA, MARS5). The samples were first dried at 110 ° C. for 24 hours and dissolved using a multiwave Pro microwave of the ANTON brand under acidic conditions (4 mL hydrofluoric acid and 2 mL nitric acid) and at high pressure (Maximum pressure 60 bar). Dissolution was carried out after a 50-minute cycle: a 10-minute temperature rise followed by a 40-minute plateau at maximum temperature (Tmax = 260°C) and cooling to 35°C.

The X-ray diffractograms were obtained using a Bruker D8 ADVANCE multifunctional diffractometer. The analyzes were carried out in a sweeping mode on non-oriented preparations in the form of powder with a grain size of less than 100 µm in the range 2 ° <2θ <60 ° with a pitch of 0.01 ° and a counting time of 10.1 seconds by step. Phase identification was performed by comparing the X-ray diffraction patterns with the International Center for Diffraction Data (ICDD) using the EVA (Bruker AXS) software.

The thermograms of the clays were produced using the SETSYS Evolution apparatus of the company SETARAM in the temperature range of 30°C.- 1100°C under a dry air atmosphere with a rising temperature rate of 5°C/min . The alumina powder, previously calcined at 1500°C for 1 hour, was used as reference material.

The microstructural observation of the ceramic filters produced was carried out using a scanning electron microscope of the "FEI, Quanta FEG 450, Environmental" type. SEM images were performed on fractures of massive sample. The samples were

glued with the silver plate on the sample holder and then metallized by platinum (Pt) deposit before observation.

The open porosity measurements of the ceramic filters produced were carried out by intrusion of mercury using a MICROMERITICS AUTOPORE IV 9510 Porosimeter - internal code: POR 4. The maximum intrusion pressure of the mercury is approximately 413 MPa that means a minimum size of the detectable pores are in the order of 0.0035 µm.

The procedure for the production of ceramic filters is based on three basic steps of ceramic technology: mineral mixture process, shaping and heating [11, 12]. Thus, in this study, the clay was finely ground and then sieved to 100 µm. The resulting clay powder was mixed with corn flour in different proportions. Two types of compositions were studied: 50% clay + 50% flour and 75% clay + 25% flour. The mixture was moistened in the order of 37% in water and kneaded in a mixer of the Winkworth brand for 30 min. The plastic paste obtained made it possible to produce cylindrical tubes. After drying at room temperature for one week, these cylindrical tubes were calcined at 1000 ° C. for one hour in a Naberthem oven at a heating rate of 5 ° C. /min. This calcined temperature was chosen so as not to densify the material (harmful to the porosity) while giving it an acceptable mechanical strength. A commercial ceramic filter marked FC was used as a reference filter

3. Results and Discussion

3.1. Physico-chemical characterization of the clays used

The chemical composition of the clays used, expressed as a percentage by weight of oxide, is given in **Table I**. Silica and alumina are the major oxides constituent in both samples. The SiO_2 / Al_2O_3 mass ratios are 4.48 for clay D and 3.24 for clay Y instead of about 1.18 for pure kaolins. These high values suggest the presence of a large amount of free silica and clay of type 2/1. Indeed, in clays of type 2/1, the values of the ratio SiO_2/Al_2O_3 are generally between 2 and 4, because of the numerous substitutions [13]. The iron oxide content is quite high in clay Y whereas it remains low in clay D. According to the literature [14, 15], iron is found in soils in the form of oxy- Hydroxides, namely goethite (FeOOH), and / or oxides such as hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3). Finally, the K_2O and TiO_2 content are relatively low while Na_2O, CaO and MgO are present in trace amounts in both samples.

Fig. 1 shows the diffraction patterns of the different samples. The characteristic peaks of kaolinite (12.30 °, 19.85 °, 24.85 °), illite (8.70 °, 18.70 °, 29.36 °) and quartz (21.50 °, 26, 50 °, 43,30 °) are mainly observed on the two diffractograms. The characteristic peaks of goethite (21,12 °, 36,57 °) and rutile (25,32 °, 26,12 °) are also shown on the diffractograms of clay Y and clay D .

Fig. 2 shows the thermograms of the different clays used. The low intensity endothermic peak observed at 80 ° C is associated with a loss in mass ($\leq$ 1%). It corresponds to the depletion of the hygroscopic water. An endothermic peak visible at 265 ° C on the thermogram of clay Y is associated with a mass loss of about 1.5%. It occurs in a temperature domain where the decomposition of goethite into hematite is generally observed [16] (Eq.1).

$$2FeOOH \rightarrow Fe_2O_3 + H_2O \quad (\mathbf{1})$$

Between 400°C-550°C, an endothermic phenomenon of very marked intensity is associated with a mass loss of approximately 6%. This phenomenon is due to the superposition of two phenomena, namely the dehydroxylation of kaolinite (Eq.2) and illite (Eq.3) [17].

$$Si_2Al_2O_5(OH)_4 \rightarrow Si_2Al_2O_7 + 2H_2O \quad (\mathbf{2})$$

$$Si_3Al_3O_{10}(OH)_2K \rightarrow Si_3Al_3O_{11}Al_3K + H_2O \quad (\mathbf{3})$$

Around 573 ° C, an endothermic phenomenon of low intensity with no effect on the thermogravimetric curve is observed. It corresponds to the allotropic transformation of quartz α in quartz β [13].

Around 950 ° C, an exothermic phenomenon is associated with no mass loss. It is characteristic of the structural reorganization of the products of the dehydroxylation of the clay minerals present in the different samples.

The latter phenomenon is generally affected by the presence of Fe^{3+} ions in the clay minerals or ferric compounds on the surfaces. The peak exothermic then widens towards the lower temperatures [15].

Table I: Chemical composition of the clays used (% by weight of oxides).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	SiO_2/Al_2O_3
D	75.88	16.94	3.48	0.12	1.57	0.28	0.9	0.83	4.48
Y	66.61	20.57	9.27	0.05	1.23	0.18	0.57	1.52	3.24

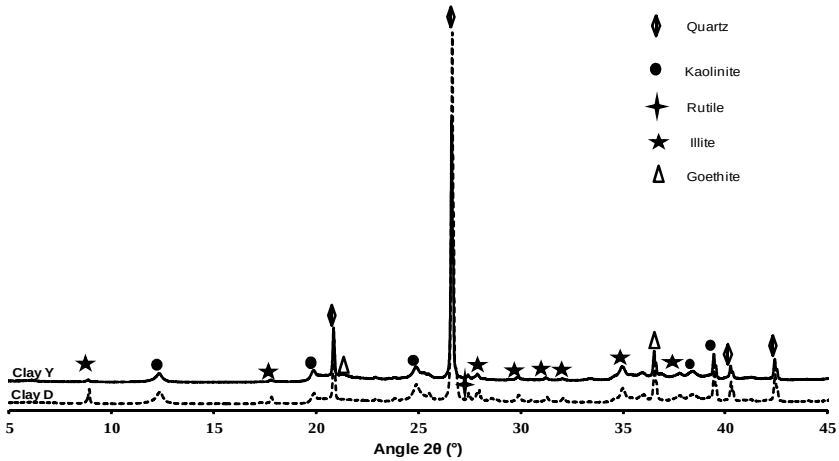

Fig. 1: X-ray diffraction of the clays D and Y

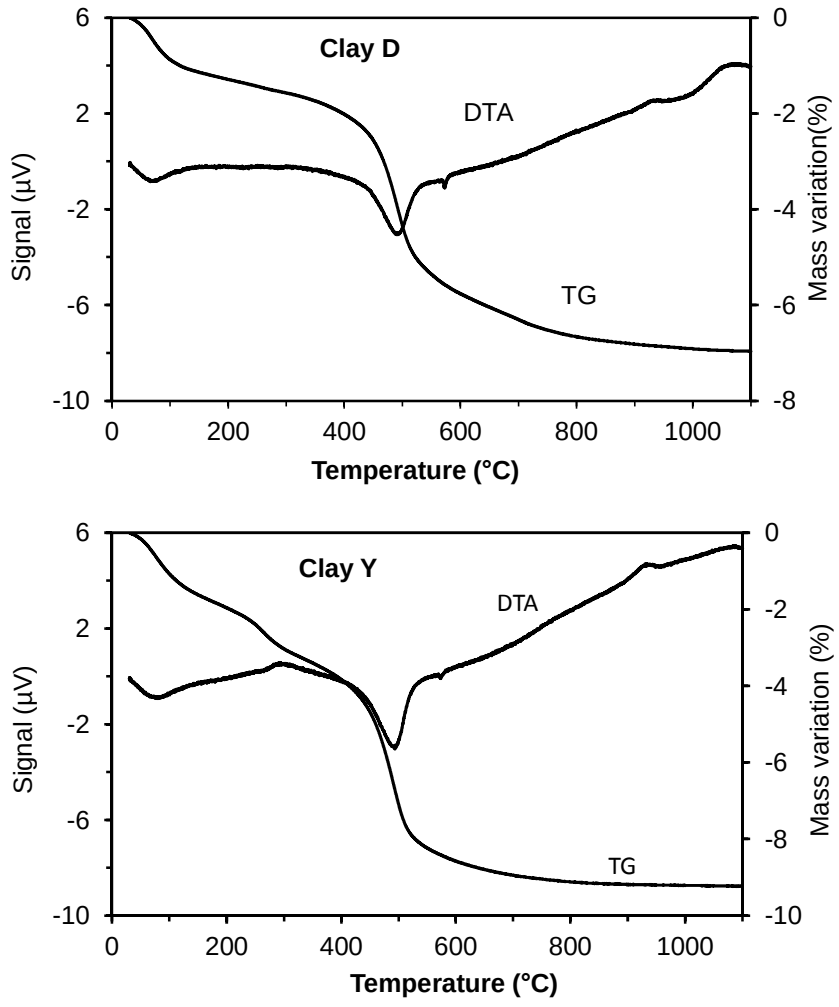

Fig. 2: Thermograms of the clays D and Y

Calculations as described by Njopwouo [18] were carried out using the results obtained from the chemical analysis, thermal analysis and the ideal chemical composition of the mineralogical phases detected by X-ray diffraction. To estimate the mineralogical compositions of the various clays used (Table II).

The results obtained revealed that clay Y is much richer in kaolinite and goethite than clay D. This explains the high value of the surface area observed in clay Y (41.61m^2 / g). The density values obtained correspond to those generally observed for kaolinitic clays [13].

3.2. Structural and microstructural properties of elaborated filters

Fig. 3 shows the photograph of the elaborated filters compared to the reference filter. The ceramic filters all have a homogeneous surface and a good intergranular cohesion similar to that of the standard commercial filter (FC). These ceramic filters have an average circumference of 15.71 cm while the inner circumference was 6.28 cm.

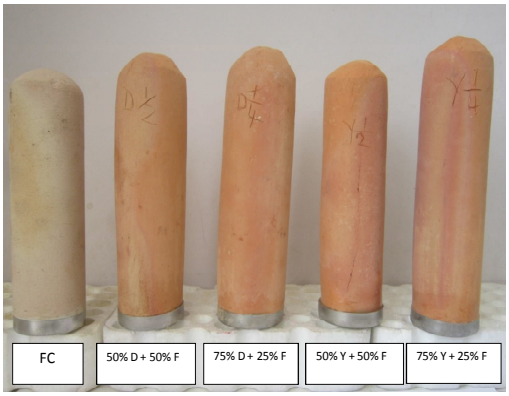

Figure 3: Photograph of the elaborated ceramic filters

Fig. 4 shows the microstructure of the elaborated ceramic filters. The images made it possible to demonstrate the presence of numerous pores of predominantly spherical shape and of variable sizes in the various filters. A decrease in the porosity with the decrease in the amount of blowing agent was observed. The presence of organic matter in the material causes the creation of pores within the material. Therefore, the smaller the amount of pore-forming agent (organic material) the fewer pore in the material.

Fig. 5 shows the distribution curves of the volume of pore of the ceramic filters as a function of the size of the pores. In all samples a single pore population was observed. They are pores with an average diameter of 1 µm, greater than 0.05 µm. This suggests that the elaborated filters are made up mainly of macropores [12]. The cumulative volume of pores is higher in ceramic filters containing more of corn flour. Furthermore, the pore diameter decreases as the amount of blowing agent in the mixture decreases. This is again with the images observed under the scanning electron microscope.

The open porosity, specific surface area and density values of the elaborated ceramic filters and that of the standard reference filter are given in **Table III**.

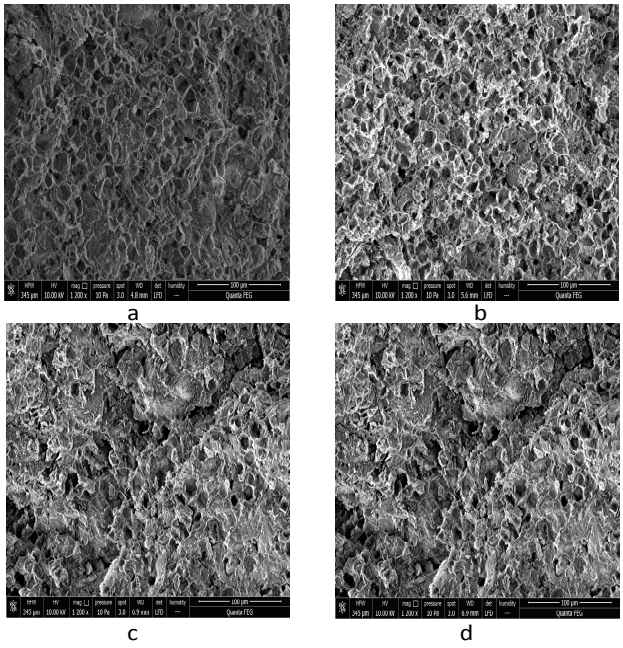

Fig. 4: SEM images of elaborated ceramic filters (**a** = 50% D + 50% F; **b** = 50% Y + 50% F; **c** = 75% D + 25% F; **d** = 75% Y + 25% F)

Table II. Mineralogical proportions (%) and physical parameters of the used clays

	D	**Y**
Kaolinite	30	42
Quartz	56	42
Illite	14	11
Rutile	-	2
Goethite	-	4
Specific surface (m2/g)	16.51	41.61
Density	2.65	2.65

For the same type of clay, the open porosity in the material increases while the specific surface area decreases as the level of blowing agent increases. This could be explained by the fact that: as the

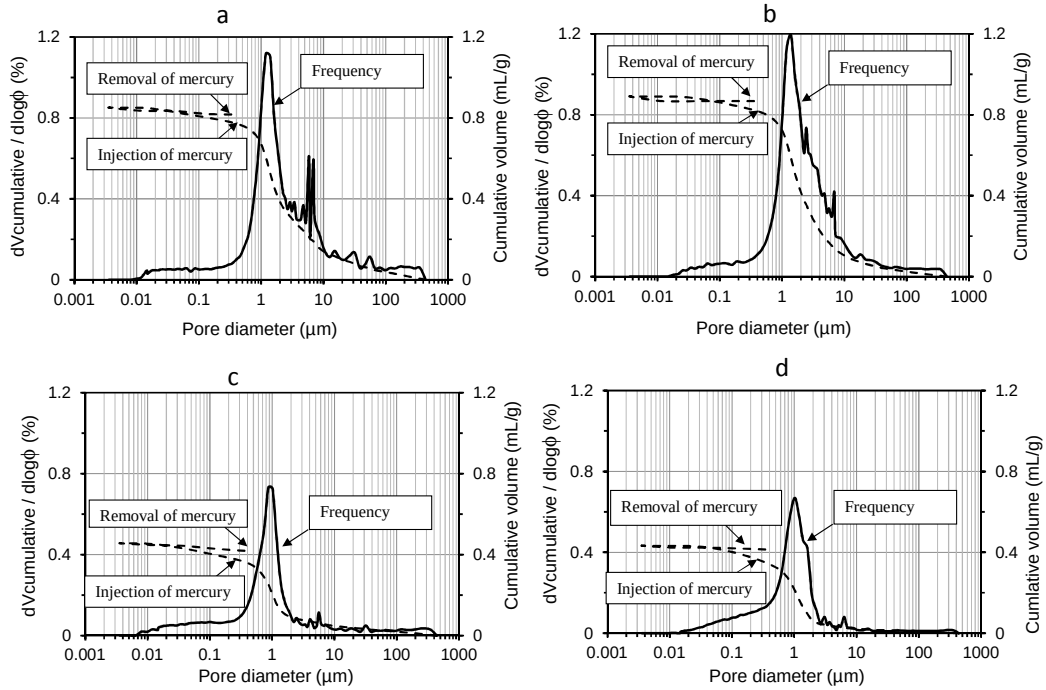

Fig. 5: Distribution of the pore volume based on the pore size of the elaborated ceramic filters (**a** = 50%D + 50%F; **b** = 50%Y + 50%F; **c** = 75%D + 25%F; **d** = 75%Y + 25%F)

amount of pore-forming agent increases, the amount of clay material decreases in the mixture. The density values are similar and lower (2.7), which is generally observed for materials with high porosity [19]. Ceramic filters made with 50% clay and 50% corn flour have an open porosity ratio closer to that of the standard reference filter (66.5%). The specific surface area of the elaborated filters, the place of chemical exchange and adsorption between the fluid and the matrix, is higher than that of the standard reference filter (2.1 m^2 / g). This could be explained by the presence in significant quantities of iron oxide in clay Y.

The filtration flow rates measured on the filters are recorded in the table III. The filters elaborated from clay Y have a higher average flow rate than the filters obtained with the clay D. However, these filters have a higher average flow rate than the commercial filter. Several elements can be the basis of the difference in flow rate observed between these filters. It's about the variation in composition in clay, in corn flour, but also the heterogeneity in the porosities.

Fig. 6 shows the variation curves of the mass of elaborate filters as a function of the immersion time in a solution with different pH values. The curves all have a similar appearance regardless of the immersion medium. The first period where an increase in the mass of the ceramic filters as a function of the immersion time is observed. This could be explained by the penetration of water molecules into the porous space of the filters. Indeed, in the presence of water, the hydration energy of the cations allows the water molecules to occupy the pores present in the ceramic filters [20]. A second period where, despite the immersion in the water, which continues, the mass of the different filters did not vary. This suggests that the observed pores are all saturated with water. The absence of mass loss in spite of a long immersion time (60 days) in the water clearly showed that the elaborated ceramic filters maintained their cohesion in the water regardless of the pH of the solution.

Table III: Physical properties of elaborate ceramic filters

	75% D+25% F	**50% D+50% F**	**75% Y+25% F**	**50% Y+50%F**	**FC**
Density	2.7 ± 0.1	2.7 ± 0.1	2.7 ± 0.1	2.8 ± 0.1	2.8 ± 0.1
Specific Surface (m^2/g)	10.6 ± 0.1	5.1 ± 0.1	17.9 ± 0.1	16.7 ± 0.1	2.1 ± 0.1
Open Porosity (%)	52.8 ± 0.1	66.6 ± 0.1	50.6 ± 0.1	68.2 ± 0.1	66.5 ± 0.1
Average flow rate (L/h)	1.0	1.1	2.8	3.0	0.3

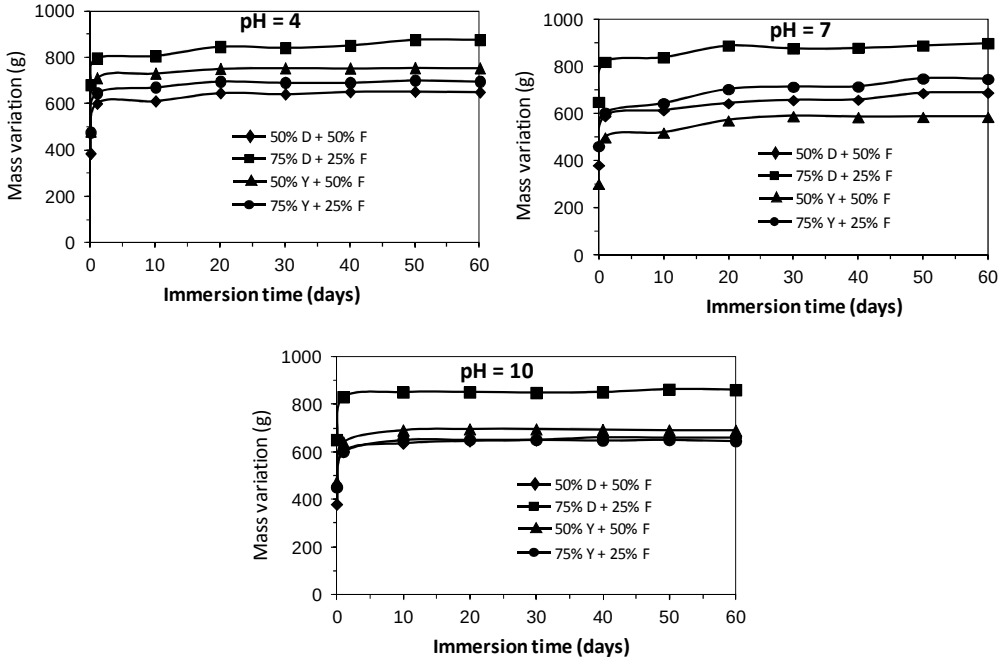

Fig. 6: Variations in mass of the filters as a function of the time of immersion in water

4. Conclusion

The two local clays D and Y used in this study composed mainly of kaolinite, quartz and illite. The mixtures of clays and corn flour in different proportions were prepared for the production of elaborate ceramic filters. The porosity tests carried out have shown that these ceramic filters are constituted predominantly of macropores. Those obtained with 75% clay and 25% corn flour had a porosity of 52.8% and 50.6% respectively for clays D and Y. Whereas those produced with 50% clay and 50% corn flour had a porosity of 66.6% and 68.2% respectively for clays D and Y, values closer to those of the commercial reference filter (66.5%). The majority of the pores having a diameter of 1 µm, the elaborated ceramic filters can be characterized as ceramic membranes. Moreover, the specific surface area of the elaborated filters is by far superior to that of the standard reference filter. The values of the pores, the elementary cells of the fluid flow and the specific surface area, the place of chemical exchanges and of the adsorption, suggests that the elaborated ceramic filters can combine the fixing of dissolved pollutant and filtration, which is necessary for drinking water purification. The elaborate ceramic filters do not lose their cohesion after 60 hours of immersion in solutions with different pH values.

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