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Elaboration of a new ceramic membrane support from Cameroonian clays, coconut husks and eggshells: application for *Escherichia coli* bacteria retention

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Abstract

In this work, the feasibility to elaborate a membrane support for water treatment from Cameroonian clays, coconut husks and eggshells was assessed. Twenty-five plastic formulations with different percentage of raw materials were tested and consolidated by thermal treatment to get the membrane supports. Mercury porosimetry allowed to select five supports potentially eligible for water filtration since their porosities were higher than 50%. Mechanical resistance and water absorption studies then allowed to choose the best ceramic membrane support S1510 (made from clays 75%, coconut husks 15% and eggshells 10% after sintering at 900°C). EDX, XRD, TGA/DSC, FTIR and SEM characterizations techniques were used to characterize the raw materials and selected membrane support. The selected support has 52% of porosity, a mean pore diameter of 0.08 µm and a water permeability of 14 013 L/h/m²/bar. The ability of the support to retain *E. coli* bacteria present in a contaminated water was finally assessed. Retention tests showed 90%

of *E. coli* removal, making this membrane support interesting for microfiltration purpose.

Keywords: Membrane support; Clays; Coconut husks; Eggshells; *E. coli* retention.

1. Introduction

The main microbial risks on health are generally associated with the ingestion of water contaminated by human or animal (including birds) feces which are a source of pathogenic bacteria, viruses, protozoa and helminths (WHO, 2008). Among pathogenic microorganisms present in water, *E. coli* is the most common indicator for faecal contamination in drinking water (Ashbolt, 2015). Chemical disinfection is effective against many pathogens (especially bacteria). But the use of physical barriers such as membranes to remove pathogens is particularly interesting since it is efficient and lowers the chemical demand EPA, 2012). Membrane limitations lie nevertheless on damages that can occur during water treatment and thus alter their retention performances. Compared to polymeric membranes, inorganic porous membranes are more robust. They are commonly used to filter colloidal suspensions, to remove natural organic matter and pathogenic microorganisms contained in surface waters (Burggraaf and Cot, 1996).

Ceramic membranes are a class of inorganic materials which have specific properties such as chemical stability, thermal and mechanical resistance, wide diversity of microstructures, porosities and accessible geometries (Burggraaf, 1996). They are prepared by deposition of one or several active layer of desired materials (TiO_2, ZrO_2, $ZnAl_2O_4$, zeolite, etc.) on an inorganic membrane support which could be elaborated with mineral clays (Saffaj et al., 2004; Achiou et al., 2018). Nowadays, various membrane supports have been elaborated for microfiltration and ultrafiltration

using different local mineral clays from Moroccan (Saffaj et al., 2006; Saja et al., 2018; Majouli et al., 2011), Tunisia (Masmoudi et al., 2007; Khemakhem et al., 2009), China (Kumar et al., 2019), Algeria (Bouzerara et al., 2006) with specific properties (porosity and pores diameter). These works have used Methocel^{TM} as a plasticizer agent, gelatin as a gelling agent as well as amijel, amidon and calcium carbonate as pore-forming agents. The porosity can also be generated by using porogens arisen from natural wastes, which makes the membrane conception environmentally friendly (Burggraaf and Cot, 1996). That is the case of ashes obtained from animal bones, rice husk wastes (Hubadillah et al., 2018) and sugarcane bagasse (Jamalludin et al., 2018) or banana peel powders (Mouiya et al., 2019) that are added to the mineral clays to create porosity and then make membrane supports used for microfiltration and ultrafiltration purposes.

In the specific context of Cameroon, the most abundant wastes available to generate porogens for membrane elaboration from local clays are coconut husks and eggshells. The eggshells contain about 94% of calcium carbonate and are similar to the ceramic formed at low temperature (Nys et al., 2010). The addition of calcium carbonate in clay also contributes to increasing its mechanical strength (Suresh and Pugazhenthi, 2016). In the same way, coconut husks were used to activate charcoal which results in a good porosity (mixture of meso and micropores) and specific surface areas between 500 m^2/g and 1300 m^2/g (Bamba et al., 2009). Considering these specific properties, coconut husks and eggshells could be good candidates as additives to create pores and to ensure a good mechanical resistance of the composite material. This all the more relevant that these natural wastes accumulate in nature which can induce environmental concerns. To the best of our knowledge,

none membrane support elaborated from a mixture of clays, coconut husks and eggshells was reported yet.

The aim of this work was consequently to elaborate and characterize ceramic membrane supports based on kaolinite clays from Cameroon, coconut husks and egg shells. The obtained membrane supports were fully characterized using scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA)/Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and mercury porosimetry. A non-pathogenic strain of *E. coli* was chosen in this study as a model for bacterial contamination since its exhibit similar morphology and biochemical structure than pathogenic *E. coli* strains (Ahmetagic and Pemberton, 2011). The ability of the membrane support to retain *E. coli* bacteria from water was finally assessed.

2. Materials and methods

2.1 Raw materials

Two kaolinite clays were used for this work. These clays were sampled in West-Cameroon at a depth of 1.8 m using hand augers. The first clay was collected in Mayouom and the second one in Koutaba. Coconut husks were collected nearby a coconut market in Edea (Littoral-Cameroon) and eggshells were collected in several cafeterias in Yaounde (Centre-Cameroon).

2.2 Elaboration of porous ceramic supports

Coconut husks and eggshells were firstly washed several times with distilled water. They were then dried with mineral clays in an oven (VT5042 EK, Heraeus) at

100°C for 48 hours. Each sample was thereafter powdered in a porcelain mortar until full passage through 100 µm mesh opening sieve.

25 plastic formulations with variable percentages of Mayouom clay (35–75% *w/w*), coconut husks (0–25% *w/w*) and eggshells (0–25% *w/w*) were tested; each formulation contained 25% of Koutaba clay and 15% of deionized water (i.e. 15 mL of deionized water for 100 g of plastic powder).

Ceramic membrane supports were elaborated according to the following sequence: (i) preparation of a plastic powder with different percentages of raw materials; (ii) shaping the plastic powder (physical mixture) by a hydraulic press (FED S. CARVER INC Menomonee Falls Wisconsin 53051) at 3.5 tons to obtain ceramic disks of 4 cm diameter and 2 mm thickness; (iii) drying the supports obtained for 48 h at room temperature to reach maturity and (iv) consolidation of the dried supports by thermal treatment at different temperatures: 800°C, 900°C or 1000°C. The implemented temperature program consisted in heating the supports from room temperature to 500°C with a heating speed of 1°C min^{-1}, and then increasing to the final temperature desired with a heating speed of 2°C min^{-1}. Finally, supports were cooled until room temperature with a 5°C min^{-1} cooling speed.

2.3 Materials characterizations

Different techniques were used to characterize raw materials and the elaborated supports. X-ray diffraction (XRD) measurements were carried out on raw powders with a Bruker D5000 X-ray powder diffractometer employing Cu-Kα radiation of the wavelength of 1.5406 Å at room temperature at 40 kV and 30 mA in a 2θ range from 2 to 80° with scanning rate of 0.5/min and step of 0.02°. Energy Dispersive X-ray (EDX) analysis on powder using Zeiss EVO HD15 allowed to

125 determine the chemical composition. A Fourier transform infrared spectrophotometer
126 (FTIR) Nexus was used to identify the chemical function groups of clays.
127 Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were
128 carried out under air with a temperature rise of 5°C.min^{-1} up to 1000°C. α-Al_2O_3 was
129 used as a reference. Scanning electron microscopy (SEM) using a Hitachi S4800
130 was used to check the presence of possible defects in the prepared membrane
131 supports. XRD, EDX, FITR, TGA/DSC and SEM analyses were carried out once. The
132 porosity and the mean pore diameter were determined using a mercury porosimeter
133 (Auto Pore IV 9500 Micromeritics). Porosimetry analyses were done once, except for
134 the finally selected support whose measures were reproduced.

135 With the aim to use these membrane supports for water filtration, their
136 resistance to water and their water absorption were determined. To do so, the
137 supports were boiled in distilled water for 4 h and then let at room temperature for 24
138 h in distilled water. Water absorption (WA) was calculated according to **Eq. (1).**

139 $$\mathrm{WA} = \frac{(M_f - M_i)}{M_f} \times 100 \qquad \textbf{Eq. (1)}$$

140 where M_i is the initial mass of the support and M_f the mass after the treatment of the
141 membrane supports in water. WA measurements were reproduced (2 samples per
142 support tested).

143 The mechanical resistance of the supports was also assessed and measured
144 by the three points mechanical test (LLOYD Instrument) applied to sintered
145 parallelepiped test bars. The distance (*L*) separating the two extremities of the test
146 bar was 40 mm. Compressive strength (σ) was calculated using **Eq. (2).**

147 $$\sigma = \frac{3\,\mathrm{PL}}{2\mathrm{bh}^2} \qquad \textbf{Eq. (2)}$$

where: σ is the compressive strength (MPa), P the total charge applied to the flexural fracture (N), L the distance between the two extremities of the test bar (L = 40 mm), b the material width (b = 40 mm) and h the material thickness (h = 9 mm). For each support tested, compressive strengths were measured twice (2 samples per support).

2.4 Permeability of the membrane support

Permeability is the ability of the membrane support to be crossed by a liquid under pressure. A filtration system for flat sheet membranes was used for the flow measurements that were performed in a dead-end mode and at a constant transmembrane pressure (ΔP). The elaborated membrane support was used as a membrane and three ΔP were implemented: 0.1, 0.2 and 0.3 bar. A filtration cell (Millipore, France, Model 8050) without stirring and with a membrane surface *S* of about 12.5 cm^2 was employed. **Fig. 1** illustrates the membrane system.

Fig. 1. Filtration system

This filtration cell was connected to a feed tank (1 L) containing either deionized water or Phosphate-Buffered Saline (PBS) at 12.9 mM, pH = 7.0 ± 0.1 to allow longer filtration times. PBS is a water-based salt solution made of KH_2PO_4 1.06 g/L and $Na_2HPO_4.12H_2O$ 4.34 g/L.

For each ΔP, the permeate flow was monitored over time (every 5 s) with an electronic balance until to reach a constant value. For the support finally selected, the permeate flow was measured twice independently; the data were then smoothed and averaged. The stabilized permeate flows were then normalized by the membrane surface to get the corresponding flow densities (J, L/h/m^2). Flow densities were finally

reported against ΔP to obtain the mean support permeability (L_p, L/h/m^2/bar) according to Darcy's law (**Eq. (3)**).

$$L_p = \frac{\mathrm{J}}{\Delta \mathrm{P}} \qquad \textbf{Eq. (3)}$$

2.5 Assessment of the bacterial retention

2.5.1 Preparation of the bacterial suspension

A non-pathogenic Gram-negative *Escherichia coli* bacterium (K12 DSM 423, from DSMZ, Germany) was used for the retention tests. A ready-to-use Lysogeny Broth (LB) Miller culture medium was used for growth and counting (Sigma, France). The bacterial cultures were prepared from frozen aliquots of *E. coli* stored at -20°C. The aliquots were inoculated into fresh LB medium (4% *v/v*) and incubated for 18 h at 30°C under constant stirring (180 rpm), until the optical density at 600 nm (OD_{600nm}) of the bacterial culture reached nearly 5 (which corresponds approximately to 10^9 CFU/mL). In these conditions, bacteria were in a stationary phase. Once prepared, the bacterial culture was diluted by decades in PBS (12.9 mM, pH = 7.0 ± 0.1) prepared in deionized water and exempt of nutriments to reach a bacterial concentration of about 10^2 CFU/mL. PBS allows maintaining the bacteria cells in life while avoiding their growth.

2.5.2 Bacterial counting

The bacterial concentrations in liquid samples were measured by the conventional plaque assay method. For that, liquid samples (400 µL each) were spread onto LB agar plates obtained by adding 15 g/L of microbiological agar (Sigma, France) into LB solution. All plates were then incubated for 48 h at 37°C. Once the cultivable bacteria had grown on plates, the colonies were counted,

knowing that each colony stemmed from one initial bacterium. The concentrations of bacteria in the samples were calculated as the average number of the colonies divided by the volume inoculated (i.e., 400 µL). Each counting was duplicated. The quantification limit was 3 CFU/mL. Negative controls (i.e., without bacteria) were always run in parallel to check the sterility.

2.5.3 Filtration of the bacterial suspension

Filtration was carried out in the filtration cell presented in **Fig. 1.** Before bacteria filtration, the whole filtration system without membrane was disinfected with ethanol (70% in water) and then massively washed with sterile ultrapure water. A bacterial suspension at about 10^2 CFU/mL, prepared according to section 2.5.1, was used as the feed. The bacterial concentration of the suspension was initially enumerated (section 2.5.2). Filtration was performed with a transmembrane pressure ΔP fixed to 0.2 bar and the permeate flow (Q, L/h) was monitored over time with an electronic balance. At the end of the filtration, the bacteria concentration was measured in the permeate (**Fig. 1**) by the plaque assay method (section 2.5.2). The bacterial retention of the support that was finally selected was assayed twice.

3. Results and discussion

3.1 Raw materials characterizations

Two natural clays were used in this study. Their crystalline phase was investigated by X-ray diffraction. **Fig. 2** presents the XRD patterns of Mayouom and Koutaba clays, either non-sintered or sintered at 900°C.

Fig. 2. XRD patterns of Mayouom (a) and Koutaba (b) clays, either non-sintered (dark curves) or sintered at 900°C (red curves).

According to the International Centre for Diffraction Data (ICDD), non-sintered Mayouom (**Fig. 2a**) and Koutaba (**Fig. 2b**) clays exhibit the peaks corresponding to kaolinite (ICDD 01-083-0971), illite (ICDD 00-015-0603), quartz α (ICDD 00-005-0490) and anatase (ICDD 01-071-1167). Goethite (ICDD 01-073-6522) appears only for Koutaba clay (**Fig. 2b**)**.**

After sintering at 900 °C, kaolinite and illite disappear to give mullite (ICDD-98-02-8246), quartz α gives quartz β (ICDD-00-005-0490) and anatase gives rutile (ICDD-01-076-0324) in both cases.

Chemical analyses of clays, coconut husks and eggshells were carried out by EDX analysis (**Fig. S1**). The major phase in Mayouom clay and Koutaba clay contains aluminum and silicon suggesting the presence of kaolinite. The presence of silicon can be also attributed to quartz evidenced by DRX (**Fig. 2**). Coconut husks are constituted exclusively of carbon and oxygen, reflecting organic matter. Eggshells contain exclusively carbon, oxygen and calcium that can be attributed to calcium carbonates.

FTIR spectra of Mayouom and Koutaba clays, either non-sintered or sintered at 900°C are presented in **Fig. 3**.

Fig. 3. FTIR spectra of Mayouom clay (a) and Koutaba clay (b), either non-sintered (dark curves) or sintered at 900°C (red curves).

The FTIR spectra of raw Mayouom clay presented in **Fig. 3a** show absorption bands located at 3693 cm^{-1} and 3620 cm^{-1} that can be attributed to the O-H bond vibration of hydroxyl groups (El Qacimi et al., 2019).

According to Masmoudi et al. (2007) and Majouli et al. (2011), the bands located at 1003 cm^{-1} and 1088 cm^{-1} are attributed to symmetrical and asymmetrical elongation vibrations of the Si-O-Si bond; the vibration band observed at 910 cm^{-1} corresponds to the deformation of the Al-OH bond while the other one observed at 750 cm^{-1} corresponds to the different modes of Si-O-Al bond (where Al is tetracoordinate).

The presence of O-H groups, Si-O-Si, Al-OH and Si-O-Al bonds can be referred to the presence of kaolinite and illite shown by XRD patterns of Mayouom clay (**Fig. 2a**).The bands located at 675 cm^{-1} are attributed to Ti-O (El Qacimi et al., 2019) which can be correlated to the presence of anatase.

After sintering Mayouom clay at 900°C (**Fig. 3a**), only two bands appear at 1055 cm^{-1} and 773 cm^{-1} corresponding to Si-O-Si and Si-O-Al bonds respectively. These groups can be attributed to the presence of mullite shown by XRD patterns of sintered clays.

The FTIR spectra of raw Koutaba clay presented in **Fig. 3b** exhibit similar absorption bands as raw Mayouom clay. The bands located at 3690 cm^{-1} and 3620 cm^{-1} can be attributed to the O-H bond vibration of hydroxyl groups while the bands located at 1010 cm^{-1} are attributed to Si-O-Si bond. The vibration band observed at 910 cm^{-1} corresponds to Al-OH bond and the bands observed at 777 cm^{-1} correspond to Si-O-Al bond. The other ones located at 677 cm^{-1} can be attributed to Fe-O and Ti-O bond. The presence of O-H groups, Si-O-Si, Al-OH, Si-O-Al, Ti-O and Fe-O bonds can be correlated to the presence of kaolinite, illite and goethite seen by XRD (**Fig. 2b**). After sintering Koutaba clay at 900°C (**Fig. 3b**), only two bands

appear at 1051 cm^{-1} and 779 cm^{-1} corresponding to Si-O-Si and Si-O-Al bonds respectively, which can be linked to the presence of mullite shown by XRD (**Fig. 2b**).

TGA and DSC curves obtained for the raw materials are shown in **Fig. 4.**

Fig. 4. TGA/DSC curves for Mayouom clay (a), Koutaba clay (b), coconut husks (c) and eggshells (d).

Mayouom clay curves (**Fig. 4a**) show an exothermic peak at 260°C with a mass loss of 2% which corresponds to the organic matter decomposition (Khemakhem et al., 2009). At 500°C, an endothermic peak is observed with a mass loss of 9% corresponding to the deshydroxylation of kaolinite into metakaolinite (Saffaj et al., 2006; El Qacimi et al., 2019).

Koutaba clay curves (**Fig. 4b**) show an endothermic peak at 70°C with a mass loss of 2% which corresponds to the elimination of the free water on the material surface (Masmoudi et al., 2007; Majouli et al., 2011; El Qacimi et al., 2019). An exothermic peak is observed at 260°C with a mass loss of 3% corresponding to the organic matter decomposition (Khemakhem et al., 2009). At 460°C, an endothermic peak is observed with a mass loss of 11% corresponding to the dehydroxylation of kaolinite into metakaolinite. At 930°C, an exothermic peak is observed, without any mass loss, corresponding to the structural reorganization of metakaolinite into spinel phase (primary mullite) (Majouli et al., 2011;El Qacimi et al., 2019).

The coconut husks curve (**Fig. 4c**) shows an endothermic peak at 40°C with a mass loss of 4% which corresponds to the elimination of the free water. At 320°C , an exothermic peak is observed with a mass loss of 50% corresponding to the pyrolysis

of hemicellulose. Another exothermic peak is observed at 440°C with a mass loss of 46% corresponding to the pyrolysis of cellulose (Liyanage and Pieris, 2015).

Eggshells curves (**Fig. 4d**) show an exothermic peak at 340°C with a mass loss of 6% corresponding to the organic matter decomposition (Khemakhem et al., 2009). At 720°C, an endothermic peak with a mass loss of 42% is observed corresponding to the decomposition of calcium carbonate into calcium oxide (Périnet, 1962). In fact, the TGA/DSC curves of pure calcium carbonate exhibited an endothermic peak at higher temperatures, i.e., between 900°C and 1000°C (Klosek-Wawrzyn et al., 2013). This temperature difference could be explained by the presence of organic matter residue on eggshells which act as an impurity.

3.2 Elaboration and choice of the porous supports

All supports were elaborated by the method described in section 2.2. After sintering at 800°C, 900°C and 1000°C, all supports exhibit similar physical aspects for a same sintering temperature (**Fig. 5**)

Fig. 5. General physical aspects of supports after sintering at 800°C, 900°C and 1000°C.

At 800°C and 1000°C, almost all supports were crumbled due to the non-grain cohesion within the material. But at 900°C, all formulations exhibited a good physical aspect. Supports sintered at 900°C were thus considered for the rest of the study. In order to have supports with good water permeability, 5 membrane supports sintered at 900°C were chosen among the 25 supports elaborated on the basis of their porosity (**Table 1**). The 5 selected supports, marked in bold in **Table 1**, have

porosities higher than 50%. The formulation composition and particularly the porogens content appear thus to be a key element regarding material porosity.

Table 1. Porosities and average pore size diameters of the elaborated membrane supports**.**

Water absorption ability and mechanical properties of the 5 selected supports sintered at 900°C were assessed. To do so, the supports were boiled in distilled water during 4 h and then let at room temperature for 24 h in the same distilled water. S1520, S2015 and S2020 crumbled while S1510 and S2010 kept their integrity even after 48 h in distilled water. The water absorption (WA) of these both supports were measured**.** It appears that WA is higher for S2010 (31.1 ± 0.2 %) than for S1510 (26.1 ± 0.3 %). It is worth noticing that the same values are reached after only immersing 4 h the supports in distilled water at room temperature.

Mechanical tests were then performed on S1510 and S2010. The compressive strength of support S1510 is twice as much as S2010 (2.04 ± 0.06 Mpa *vs.* 1.30 ± 0.03 Mpa). This induced that support S2010 broke when it was set up inside the filtration cell making water flow measurements impossible with this support. For this reason, the membrane support S1510 was selected as the most suitable for water filtration applications.

3.3 Characterizations of the selected support S1510

Fig. 6 shows the XRD patterns of the membrane support S1510 sintered at 900°C and the TGA/DSC curves of the support before sintering.

Fig. 6. XRD patterns of the membrane support S1510 sintered at 900°C (a) and TGA/DSC curves of the support before sintering (b).

According to the International Centre for Diffraction Data (ICDD) and **Fig. 6a**, peaks corresponding to quartz β (ICDD 00-005-0490), mullite (ICDD 98–02–8246), anorthite (ICDD 00-041-1486) and rutile ICDD 00-015-0603) are identified. The formation of mullite at low temperature (900°C) is due to the presence of anorthite. In fact, the heating of kaolinite (main phase of raw clays used) gives metakaolinite (**Fig. 4a and 4b**) which in presence of calcium oxide (**Fig. 4d)** gives anorthite. Then, the heating of the overage of metakaolinite mixed to anorthite for a longer time at 900°C promotes the formation of mullite (Traoré et al., 2003; Klosek-Wawrzyn et al., 2013).

Chemical analyses of selected membrane support S1510 were carried out by EDX analysis (**Fig. S1**). The major phase contains aluminum, silicon and calcium suggesting the presence of anorthite evidenced by XRD. The presence of aluminum and silicon can be also attributed to mullite and to quartz.

TGA and DSC curves of the raw plastic powder formulation used to make the membrane support are shown in **Fig. 6b.** At 50°C, an endothermic peak is observed with a mass loss of 7% which corresponds to the elimination of free water on the material surface (Masmoudi et al., 2007;Majouli et al., 2011). At 340°C, an exothermic peak is observed with a mass loss of 15% which corresponds to the decomposition of organic matter from eggshells and coconut husks (cellulose and hemicellulose) (Liyanage and Pieris, 2015). At 500°C, an endothermic peak is observed with mass losses of 6% corresponding to the dehydroxylation of kaolinite into metakaolinite (Saffaj et al., 2006;El Qacimi et al., 2019). At 700°C, an

endothermic peak is observed with a mass loss of 4% which corresponds to the transformation of metakaolinite mixed to calcium oxide (due to the decomposition of eggshells) into anorthite (Périnet, 1962; Traoré et al., 2003).

SEM pictures and pore size distribution of the S1510 membrane support are presented in **Fig. 7.**

Fig. 7. SEM pictures at different magnifications (a, b, c, d) and pore size distribution (e) of the support SN1510.

Both top and cross views of the membrane support S1510 show that the grains are interconnected each other forming a compact structure (**Fig. 7a to d**). The pore size distribution within the support was investigated by mercury porosimetry for filtration purpose (**Fig. 7e**). The distribution shows that the membrane support contains a mixture of macropores and mesopores with mean diameters of 2.32 µm and 0.03 µm respectively which makes the support eligible for microfiltration.

3.4 Permeability of the selected support SN1510

Fig. 8 shows the flow densities measured over time with deionized water (**Fig. 8a**) and PBS (**Fig. 8b**) for different transmembrane pressures (ΔP), and the corresponding permeability curves obtained with deionized water (**Fig. 8c**) and PBS (**Fig. 8d**) for the selected support S1510.

Fig. 8. Flow density and permeability curves obtained with deionized water (a, c) and PBS (b, d) respectively.

Prior to permeability tests, the support was conditioned by immersion in deionized water for 4 h at room temperature to saturate the pores of the support with water. Then, the flow densities were measured for different pressures (0.1; 0.2 and 0.3 bar). Whatever the matrix (either deionized water or PBS), the flow density stabilized quickly, i.e., after 2 min for each pressure. As expected, experiments showed that the flow density through the support increased proportionally with the pressure (**Fig. 8a and 8b**). Increasing the pressure increases indeed the convective driving force across the membrane support (Mohamed Bazin et al., 2019). In addition, the permeability tests showed that the flow densities obtained with deionized water (**Fig. 8a**) were significantly higher than the ones obtained with PBS (**Fig. 8b**). In fact, the presence of salts in PBS may induce a concentration polarization near the membrane support, i.e., a salt concentration gradient at the membrane/solution interface (Iaich and Messaoudi, 2014). This concentration gradient of salts formed on the membrane support becomes an additional resistance to the mass transfer that reduces the flow density. As a consequence, the mean support permeability for PBS (7259 ± 774 L/h/m²/bar, **Fig. 8d**) is lower than the one measured for deionized water (14013 ± 1251 L/h/m²/bar, **Fig. 8c**). It is worth highlighting that the water permeability reached with the elaborated support S1510 is higher than the water permeability reported in other works for microfiltration ceramic membranes elaborated by natural mineral clays (Table 3). ~~867 L/h/m²/bar, Khemakhem et al., 2009; 1434 L/h/m²/bar, Saja et al., 2018; 121 L/h/m²/bar, El Qacimi et al., 2019).~~

Table 3. Comparison with other works reported in literature.

3.5 Bacterial retention of the selected support S1510

In order to assess the ability of the selected support to retain bacteria, a bacterial suspension at about 10^2 CFU/mL in PBS was filtrated at 0.2 bar in a dead-end filtration cell (**Fig. 1**). PBS was chosen as a matrix to avoid osmosis phenomena that could lyse bacteria cells; besides, this matrix is more representative of real water in terms of ionic force. Bacteria were counted in the feed suspension and the permeate (**Fig. 1**) by the plaque assay method (section 2.5.2). **Table 2** shows the results obtained.

Table 2. Counted bacteria in the feed and permeate.

The concentration of bacteria in the permeate was reduced by a factor 10 compared to the feed (**Table 2**): 32 *vs* 307 CFU/mL corresponding to 8 x 10^3 *vs.* 8 x 10^4 CFU since 250 mL of bacterial suspension were filtrated. This means that the selected ceramic support S1510 retains about 90% of bacteria, corresponding to 1 log-removal. The selected support allows thus a significant bacterial retention (WHO, 2008) that is consistent with the bacterial retention reported by Kaetzl et al. (2020) for Miscanthus-biochar filters (Table 3). Knowing that the usual *E. coli* bacteria size is about 0.6–4 µm (Sayato, 1989), retention can be explained by steric considerations since the support pores range from 0.03 µm to 2.32 µm and even up to 0.01 µm (**Fig. 7e**). The pore size distribution also explains the presence of bacteria in the permeate since the bacteria meeting the biggest pores can pass through the support.

In addition, it is worth noticing that the permeate flow density at 0.2 bar did not exhibit any decrease during the filtration of the bacterial feed (**Fig. 9**). Besides, the flow densities obtained with PBS alone (1384 L/h/m^2) and with the bacterial feed prepared

444 in PBS (1198 L/h/m^2) did not show significant difference. This means that little or no
445 fouling occurred during the filtration. Longer filtration time will be further implemented
446 to study the fouling.

447

448 **Fig. 9.** Permeate flow densities at 0.2 bar with PBS and bacterial feed.

449

450 **4. Conclusions**

451 A new ceramic membrane support was elaborated in this work from natural sources
452 including low-cost organic wastes. The formulation composition and the sintering
453 temperature were evidenced to impact the material porosity and mechanical
454 resistance. It was prepared from a plastic powder containing 75% of natural
455 Cameroonian clays, 15% of coconut husks and 10% of eggshells. The elaboration
456 protocol was quite simple since the powder was shaped (disk sheet) by pressing and
457 then sintering at 900°C. The structural properties of the ceramic support elaborated
458 are satisfying for microfiltration use in terms of porosity (52%) and pore distribution
459 (with a mean pore diameter of 0.08 µm). Its water and PBS permeabilities are
460 respectively 14013 L/h/m²/bar and 7258 L/h/m²/bar. Compared to other studies in
461 which local natural clays have been used with or without organic wastes to make
462 ceramic membranes, the resulting porosity and permeability were among the highest
463 ones reported, which could make possible an application at a larger scale. In
464 addition, this membrane support has the ability to retain 90% of *E. coli* bacteria and
465 can be considered for a preliminary water treatment. Work is in progress in order to
466 deposit an additional ceramic membrane layer to improve the bacteria retention.
467 Membrane fouling will also be further investigated. As a perspective, a multi-tubular

geometry of the support could be envisaged for the scale-up and to work in a parallel flow mode to contribute to reduce the fouling during operation.

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