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

4  
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7  
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12  
13        **Abstract**

14        In this work, the feasibility to elaborate a membrane support for water  
15        treatment from Cameroonian clays, coconut husks and eggshells was assessed.  
16        Twenty-five plastic formulations with different percentage of raw materials were  
17        tested and consolidated by thermal treatment to get the membrane supports. Mercury  
18        porosimetry allowed to select five supports potentially eligible for water filtration since  
19        their porosities were higher than 50%. Mechanical resistance and water absorption  
20        studies then allowed to choose the best ceramic membrane support S1510 (made  
21        from clays 75%, coconut husks 15% and eggshells 10% after sintering at 900°C).  
22        EDX, XRD, TGA/DSC, FTIR and SEM characterizations techniques were used to  
23        characterize the raw materials and selected membrane support. The selected  
24        support has 52% of porosity, a mean pore diameter of 0.08 µm and a water  
25        permeability of 14 013 L/h/m<sup>2</sup>/bar. The ability of the support to retain *E. coli* bacteria  
26        present in a contaminated water was finally assessed. Retention tests showed 90%

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

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

30

## 31 **1. Introduction**

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

45 Ceramic membranes are a class of inorganic materials which have specific  
46 properties such as chemical stability, thermal and mechanical resistance, wide  
47 diversity of microstructures, porosities and accessible geometries (Burggraaf, 1996).  
48 They are prepared by deposition of one or several active layer of desired materials  
49 ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnAl}_2\text{O}_4$ , zeolite, etc.) on an inorganic membrane support which could be  
50 elaborated with mineral clays (Saffaj et al., 2004; Achiou et al., 2018). Nowadays,  
51 various membrane supports have been elaborated for microfiltration and ultrafiltration

52 using different local mineral clays from Moroccan (Saffaj et al., 2006; Saja et al.,  
53 2018; Majouli et al., 2011), Tunisia (Masmoudi et al., 2007; Khemakhem et al., 2009),  
54 China (Kumar et al., 2019), Algeria (Bouzerara et al., 2006) with specific properties  
55 (porosity and pores diameter). These works have used Methocel™ as a plasticizer  
56 agent, gelatin as a gelling agent as well as amijel, amidon and calcium carbonate as  
57 pore-forming agents. The porosity can also be generated by using porogens arisen  
58 from natural wastes, which makes the membrane conception environmentally friendly  
59 (Burggraaf and Cot, 1996). That is the case of ashes obtained from animal bones,  
60 rice husk wastes (Hubadillah et al., 2018) and sugarcane bagasse (Jamalludin et al.,  
61 2018) or banana peel powders (Mouiya et al., 2019) that are added to the mineral  
62 clays to create porosity and then make membrane supports used for microfiltration  
63 and ultrafiltration purposes.

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

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

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

88

## 89 **2. Materials and methods**

### 90 **2.1 Raw materials**

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

96

### 97 **2.2 Elaboration of porous ceramic supports**

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

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

102 25 plastic formulations with variable percentages of Mayouom clay (35–75%  
103 w/w), coconut husks (0–25% w/w) and eggshells (0–25% w/w) were tested; each  
104 formulation contained 25% of Koutaba clay and 15% of deionized water (i.e. 15 mL of  
105 deionized water for 100 g of plastic powder).

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

117

### 118 **2.3 Materials characterizations**

119 Different techniques were used to characterize raw materials and the  
120 elaborated supports. X-ray diffraction (XRD) measurements were carried out on raw  
121 powders with a Bruker D5000 X-ray powder diffractometer employing Cu-Kα  
122 radiation of the wavelength of 1.5406 Å at room temperature at 40 kV and 30 mA in a  
123 2θ range from 2 to 80° with scanning rate of 0.5/min and step of 0.02°. Energy  
124 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<sup>-1</sup> up to 1000°C. α-Al<sub>2</sub>O<sub>3</sub> 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)**.

$$139 \quad WA = \frac{(M_f - M_i)}{M_f} \times 100 \quad \text{Eq. (1)}$$

140 where M<sub>i</sub> is the initial mass of the support and M<sub>f</sub> 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)**.

$$147 \quad \sigma = \frac{3 PL}{2bh^2} \quad \text{Eq. (2)}$$

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

152

## 153 **2.4 Permeability of the membrane support**

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

161

### 162 **Fig. 1.** Filtration system

163

164 This filtration cell was connected to a feed tank (1 L) containing either deionized  
165 water or Phosphate-Buffered Saline (PBS) at 12.9 mM,  $\text{pH} = 7.0 \pm 0.1$  to allow longer  
166 filtration times. PBS is a water-based salt solution made of  $\text{KH}_2\text{PO}_4$  1.06 g/L and  
167  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  4.34 g/L.

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



173 reported against  $\Delta P$  to obtain the mean support permeability ( $L_p$ , L/h/m<sup>2</sup>/bar)  
174 according to Darcy's law (**Eq. (3)**).

$$175 \quad L_p = \frac{J}{\Delta P} \quad \text{Eq. (3)}$$

176

## 177 **2.5 Assessment of the bacterial retention**

### 178 **2.5.1 Preparation of the bacterial suspension**

179 A non-pathogenic Gram-negative *Escherichia coli* bacterium (K12 DSM 423,  
180 from DSMZ, Germany) was used for the retention tests. A ready-to-use Lysogeny  
181 Broth (LB) Miller culture medium was used for growth and counting (Sigma, France).  
182 The bacterial cultures were prepared from frozen aliquots of *E. coli* stored at -20°C.  
183 The aliquots were inoculated into fresh LB medium (4% v/v) and incubated for 18 h at  
184 30°C under constant stirring (180 rpm), until the optical density at 600 nm (OD<sub>600nm</sub>)  
185 of the bacterial culture reached nearly 5 (which corresponds approximately to 10<sup>9</sup>  
186 CFU/mL). In these conditions, bacteria were in a stationary phase. Once prepared,  
187 the bacterial culture was diluted by decades in PBS (12.9 mM, pH = 7.0 ± 0.1)  
188 prepared in deionized water and exempt of nutriments to reach a bacterial  
189 concentration of about 10<sup>2</sup> CFU/mL. PBS allows maintaining the bacteria cells in life  
190 while avoiding their growth.

191

### 192 **2.5.2 Bacterial counting**

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

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

203

### 204 **2.5.3 Filtration of the bacterial suspension**

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

215

## 216 **3. Results and discussion**

### 217 **3.1 Raw materials characterizations**

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

221

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

224

225 According to the International Centre for Diffraction Data (ICDD), non-sintered  
226 Mayouom (**Fig. 2a**) and Koutaba (**Fig. 2b**) clays exhibit the peaks corresponding to  
227 kaolinite (ICDD 01-083-0971), illite (ICDD 00-015-0603), quartz  $\alpha$  (ICDD 00-005-  
228 0490) and anatase (ICDD 01-071-1167). Goethite (ICDD 01-073-6522) appears only  
229 for Koutaba clay (**Fig. 2b**).

230 After sintering at 900 °C, kaolinite and illite disappear to give mullite (ICDD-98-02-  
231 8246), quartz  $\alpha$  gives quartz  $\beta$  (ICDD-00-005-0490) and anatase gives rutile (ICDD-  
232 01-076-0324) in both cases.

233

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

241 FTIR spectra of Mayouom and Koutaba clays, either non-sintered or sintered at  
242 900°C are presented in **Fig. 3**.

243

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

246

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

250 According to Masmoudi et al. (2007) and Majouli et al. (2011), the bands located at  
251  $1003\text{ cm}^{-1}$  and  $1088\text{ cm}^{-1}$  are attributed to symmetrical and asymmetrical elongation  
252 vibrations of the Si-O-Si bond; the vibration band observed at  $910\text{ cm}^{-1}$  corresponds  
253 to the deformation of the Al-OH bond while the other one observed at  $750\text{ cm}^{-1}$   
254 corresponds to the different modes of Si-O-Al bond (where Al is tetracoordinate).

255 The presence of O-H groups, Si-O-Si, Al-OH and Si-O-Al bonds can be referred to  
256 the presence of kaolinite and illite shown by XRD patterns of Mayouom clay (**Fig.**  
257 **2a**). The bands located at  $675\text{ cm}^{-1}$  are attributed to Ti-O (El Qacimi et al., 2019)  
258 which can be correlated to the presence of anatase.

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

262 The FTIR spectra of raw Koutaba clay presented in **Fig. 3b** exhibit similar  
263 absorption bands as raw Mayouom clay. The bands located at  $3690\text{ cm}^{-1}$  and  $3620$   
264  $\text{cm}^{-1}$  can be attributed to the O-H bond vibration of hydroxyl groups while the bands  
265 located at  $1010\text{ cm}^{-1}$  are attributed to Si-O-Si bond. The vibration band observed at  
266  $910\text{ cm}^{-1}$  corresponds to Al-OH bond and the bands observed at  $777\text{ cm}^{-1}$   
267 correspond to Si-O-Al bond. The other ones located at  $677\text{ cm}^{-1}$  can be attributed to  
268 Fe-O and Ti-O bond. The presence of O-H groups, Si-O-Si, Al-OH, Si-O-Al, Ti-O and  
269 Fe-O bonds can be correlated to the presence of kaolinite, illite and goethite seen by  
270 XRD (**Fig. 2b**). After sintering Koutaba clay at  $900^{\circ}\text{C}$  (**Fig. 3b**), only two bands

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

273

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

275

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

278

279 Mayouom clay curves (**Fig. 4a**) show an exothermic peak at  $260^{\circ}\text{C}$  with a mass loss  
280 of 2% which corresponds to the organic matter decomposition (Khemakhem et al.,  
281 2009). At  $500^{\circ}\text{C}$ , an endothermic peak is observed with a mass loss of 9%  
282 corresponding to the deshydroxylation of kaolinite into metakaolinite (Saffaj et al.,  
283 2006; El Qacimi et al., 2019).

284 Koutaba clay curves (**Fig. 4b**) show an endothermic peak at  $70^{\circ}\text{C}$  with a mass loss of  
285 2% which corresponds to the elimination of the free water on the material surface  
286 (Masmoudi et al., 2007; Majouli et al., 2011; El Qacimi et al., 2019). An exothermic  
287 peak is observed at  $260^{\circ}\text{C}$  with a mass loss of 3% corresponding to the organic  
288 matter decomposition (Khemakhem et al., 2009). At  $460^{\circ}\text{C}$ , an endothermic peak is  
289 observed with a mass loss of 11% corresponding to the dehydroxylation of kaolinite  
290 into metakaolinite. At  $930^{\circ}\text{C}$ , an exothermic peak is observed, without any mass loss,  
291 corresponding to the structural reorganization of metakaolinite into spinel phase  
292 (primary mullite) (Majouli et al., 2011; El Qacimi et al., 2019).

293 The coconut husks curve (**Fig. 4c**) shows an endothermic peak at  $40^{\circ}\text{C}$  with a mass  
294 loss of 4% which corresponds to the elimination of the free water. At  $320^{\circ}\text{C}$ , an  
295 exothermic peak is observed with a mass loss of 50% corresponding to the pyrolysis

296 of hemicellulose. Another exothermic peak is observed at 440°C with a mass loss of  
297 46% corresponding to the pyrolysis of cellulose (Liyanage and Pieris, 2015).

298 Eggshells curves (**Fig. 4d**) show an exothermic peak at 340°C with a mass loss of  
299 6% corresponding to the organic matter decomposition (Khemakhem et al., 2009). At  
300 720°C, an endothermic peak with a mass loss of 42% is observed corresponding to  
301 the decomposition of calcium carbonate into calcium oxide (Périnet, 1962). In fact,  
302 the TGA/DSC curves of pure calcium carbonate exhibited an endothermic peak at  
303 higher temperatures, i.e., between 900°C and 1000°C (Klosek-Wawrzyn et al., 2013).  
304 This temperature difference could be explained by the presence of organic matter  
305 residue on eggshells which act as an impurity.

306

### 307 **3.2 Elaboration and choice of the porous supports**

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

311

312 **Fig. 5.** General physical aspects of supports after sintering at 800°C, 900°C and  
313 1000°C.

314

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

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

323

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

326

327 Water absorption ability and mechanical properties of the 5 selected supports  
328 sintered at 900°C were assessed. To do so, the supports were boiled in distilled  
329 water during 4 h and then let at room temperature for 24 h in the same distilled water.

330 S1520, S2015 and S2020 crumbled while S1510 and S2010 kept their integrity even  
331 after 48 h in distilled water. The water absorption (WA) of these both supports were  
332 measured. It appears that WA is higher for S2010 ( $31.1 \pm 0.2$  %) than for S1510  
333 ( $26.1 \pm 0.3$  %). It is worth noticing that the same values are reached after only  
334 immersing 4 h the supports in distilled water at room temperature.

335 Mechanical tests were then performed on S1510 and S2010. The compressive  
336 strength of support S1510 is twice as much as S2010 ( $2.04 \pm 0.06$  Mpa vs.  $1.30 \pm$   
337  $0.03$  Mpa). This induced that support S2010 broke when it was set up inside the  
338 filtration cell making water flow measurements impossible with this support. For this  
339 reason, the membrane support S1510 was selected as the most suitable for water  
340 filtration applications.

341

### 342 **3.3 Characterizations of the selected support S1510**

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

345

346

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

349 According to the International Centre for Diffraction Data (ICDD) and **Fig. 6a**, peaks  
350 corresponding to quartz  $\beta$  (ICDD 00-005-0490), mullite (ICDD 98-02-8246),  
351 anorthite (ICDD 00-041-1486) and rutile ICDD 00-015-0603) are identified. The  
352 formation of mullite at low temperature (900°C) is due to the presence of anorthite. In  
353 fact, the heating of kaolinite (main phase of raw clays used) gives metakaolinite (**Fig.**  
354 **4a and 4b**) which in presence of calcium oxide (**Fig. 4d**) gives anorthite. Then, the  
355 heating of the overage of metakaolinite mixed to anorthite for a longer time at 900°C  
356 promotes the formation of mullite (Traoré et al., 2003; Klosek-Wawrzyn et al., 2013).

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

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



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

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

375

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

378

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

385

### 386 **3.4 Permeability of the selected support SN1510**

387 **Fig. 8** shows the flow densities measured over time with deionized water (**Fig. 8a**)  
388 and PBS (**Fig. 8b**) for different transmembrane pressures ( $\Delta P$ ), and the  
389 corresponding permeability curves obtained with deionized water (**Fig. 8c**) and PBS  
390 (**Fig. 8d**) for the selected support S1510.

391

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

394

395 Prior to permeability tests, the support was conditioned by immersion in deionized  
396 water for 4 h at room temperature to saturate the pores of the support with water.  
397 Then, the flow densities were measured for different pressures (0.1; 0.2 and 0.3 bar).  
398 Whatever the matrix (either deionized water or PBS), the flow density stabilized  
399 quickly, i.e., after 2 min for each pressure. As expected, experiments showed that the  
400 flow density through the support increased proportionally with the pressure (**Fig. 8a**  
401 **and 8b**). Increasing the pressure increases indeed the convective driving force  
402 across the membrane support (Mohamed Bazin et al., 2019). In addition, the  
403 permeability tests showed that the flow densities obtained with deionized water (**Fig.**  
404 **8a**) were significantly higher than the ones obtained with PBS (**Fig. 8b**). In fact, the  
405 presence of salts in PBS may induce a concentration polarization near the membrane  
406 support, i.e., a salt concentration gradient at the membrane/solution interface (laich  
407 and Messaoudi, 2014). This concentration gradient of salts formed on the membrane  
408 support becomes an additional resistance to the mass transfer that reduces the flow  
409 density. As a consequence, the mean support permeability for PBS ( $7259 \pm 774$   
410  $\text{L/h/m}^2/\text{bar}$ , **Fig. 8d**) is lower than the one measured for deionized water ( $14013 \pm$   
411  $1251 \text{ L/h/m}^2/\text{bar}$ , **Fig. 8c**). It is worth highlighting that the water permeability reached  
412 with the elaborated support S1510 is higher than the water permeability reported in  
413 other works for microfiltration ceramic membranes elaborated by natural mineral  
414 clays (**Table 3**). ~~867  $\text{L/h/m}^2/\text{bar}$ , Khemakhem et al., 2009; 1434  $\text{L/h/m}^2/\text{bar}$ , Saja et~~  
415 ~~al., 2018; 121  $\text{L/h/m}^2/\text{bar}$ , El-Qacimi et al., 2019).~~

416

417 **Table 3.** Comparison with other works reported in literature.

418

### 419 **3.5 Bacterial retention of the selected support S1510**

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

427

428 **Table 2.** Counted bacteria in the feed and permeate.

429

430 The concentration of bacteria in the permeate was reduced by a factor 10  
431 compared to the feed (**Table 2**): 32 vs 307 CFU/mL corresponding to  $8 \times 10^3$  vs.  $8 \times$   
432  $10^4$  CFU since 250 mL of bacterial suspension were filtrated. This means that the  
433 selected ceramic support S1510 retains about 90% of bacteria, corresponding to 1  
434 log-removal. The selected support allows thus a significant bacterial retention (WHO,  
435 2008) **that is consistent with the bacterial retention reported by Kaetzi et al. (2020) for**  
436 **Miscanthus-biochar filters (Table 3)**. Knowing that the usual *E. coli* bacteria size is  
437 about 0.6–4  $\mu\text{m}$  (Sayato, 1989), retention can be explained by steric considerations  
438 since the support pores range from 0.03  $\mu\text{m}$  to 2.32  $\mu\text{m}$  and even up to 0.01  $\mu\text{m}$  (**Fig.**  
439 **7e**). The pore size distribution also explains the presence of bacteria in the permeate  
440 since the bacteria meeting the biggest pores can pass through the support.

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

444 in PBS (1198 L/h/m<sup>2</sup>) 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/m<sup>2</sup>/bar and 7258 L/h/m<sup>2</sup>/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

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

470

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474

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