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1                   Effect of variability of hemp shiv on the setting of lime hemp concrete

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6

7                   **Abstract**

8                   Lime hemp concrete (LHC) is one of the most environmentally friendly alternatives to traditional  
9                   building materials, which is normally used as an insulation material. The lime hemp concrete is  
10                  made up of hemp shiv and aerial (or hydraulic) lime and has the ability to offer better thermal and  
11                  acoustic performances. However, it is reported that the shiv/matrix reaction does not always meet  
12                  the expectations, thus the properties of hemp concrete may be affected by certain characteristics,  
13                  such as origin, retting time, harvest time, etc. of the used hemp. During this work, the authors  
14                  have studied the influence of variability of hemp shiv on the setting of LHC. The results depicted  
15                  that the soluble components (e.g., organic acids, simple sugars, etc.) from hemp shiv had a  
16                  significant impact on the setting and hardening of mortars. This study also proved that hemp  
17                  containing more soluble components tends to involve a longer setting time and hinders long-term  
18                  carbonation reaction of binders. Furthermore, the experimental results also showed that water  
19                  treatment can effectively remove these soluble agents from hemp shiv and improve the  
20                  compatibility between shiv and binder in the composite.

21                  **Keywords:** Hemp shiv; setting time; carbonation reaction; retting; hemp shiv leachate

22 **1. Introduction**

23 The **production of cement** contributes about 5-7% to global CO<sub>2</sub> emissions and 2% to overall  
24 energy consumption (Benhelal et al., 2013; Worrell et al., 2001), so it is necessary to develop  
25 cement substitutes having low environmental impact. The binder such as cement is considered to  
26 be the main contributor to the environmental impact as demonstrated by the life cycle assessment  
27 (Prétot et al., 2014). Therefore, alternative binder materials (e.g., geopolymers, lime, pozzolans,  
28 etc.) are attracting increasing interests in research and development during the past decades. At  
29 the same time, recent investigations indicated that plant aggregates have interesting  
30 environmental and economic benefits (Sanjay et al., 2018; Sáez-Perez et al., 2020), and they  
31 could be used to replace conventional aggregates. Hemp shiv is the byproduct of hemp fibers  
32 production, which is the most widely used plant aggregate of lightweight concretes. Hemp shiv is  
33 derived from woody core (composed of xylem and pith), whereas the bark (composed of  
34 epidermis, bast fibers and cambium) is considered as principal source of hemp fibers (Sáez-Perez  
35 et al., 2020). **LHC**, was reported to possess excellent thermal and acoustic performances e.g.,  
36 thermal isolation, sound absorption, soundproofing, etc. (Elfordy et al., 2008) , which could be  
37 effectively employed as an insulation material, coating, and even bricks. Owing to the carbon  
38 storage effect of lime carbonation and hemp cultivation, **LHC** has a weaker ecological impact  
39 compared to traditional building materials (Ip and Miller, 2012; Hirst et al., 2010). Keeping in  
40 view its excellent thermal insulation property, the application of LHC can reduce long-term  
41 energy consumptions of the building.

42 Despite these advantages of hemp concrete, the wide-use of LHC is still limited due to certain  
43 drawbacks. An essential disadvantage of LHC is **its** poor strength performance, thus limiting its  
44 use as a load-bearing material (Tronet et al., 2016). The poor mechanical performance is mainly  
45 triggered by the intrinsic mechanical properties of aggregates (hemp shiv). Another problem  
46 which affects the application of LHC is the incompatibility that exists between hemp shiv and

47 binder (lime, cement), thus leading to a setting delay and a large variability of thermal and  
48 acoustic properties. The previous works have illustrated that the various factors such as origin  
49 (Diquélou et al., 2015), harvest time, field retting (Li et al., 2009) of hemp shiv, binder types  
50 (Walker et al., 2014) can influence the compatibility. It was reported that thermal and chemical  
51 treatments might enhance the compatibility between plant aggregates and the binder (Bilba et al.,  
52 2003; Khazma et al., 2012; Sedan et al., 2008), but this will result in an increase in costs and  
53 carbon emissions. It is therefore important to find an economic and ecological approach for the  
54 treatment of hemp to meet the application needs of bio-aggregate based building materials.

55 Empirical observations indicate that "rotten" hemp shiv (or other byproducts of plant fibers  
56 production) tend to have better aggregate/matrix interaction (i.e., shorter setting time and better  
57 mechanical performance). Depending upon industrial requirements, a certain level of retting may  
58 be required. Retting is a critical step in the production of fiber from plant material (Martin et al.,  
59 2013). The most widely used method of retting is the field retting which requires the action of  
60 micro-organisms and moisture on plants to dissolve or rot away the stem material surrounding the  
61 fiber bundles. However, field retting is highly climate-dependent, and its mechanism has not yet  
62 been completely understood by the researchers. It has been reported that as the retting time  
63 increases, the color of the hemp fiber becomes darker and the tensile strength increases (Mazian  
64 et al., 2018). Meijer et al. (1995) found that the degradation of pectin is the key process in retting  
65 and can be used as a measure of the degree of retting. At the same time, the colorimeter,  
66 thermogravimetric analysis (TGA), and FT-IR spectrum analyses were also reviewed to evaluate  
67 the retting degree (Sedan et al., 2008; Martin et al., 2013). However, until now, no indicator or  
68 method is sensitive enough to determine the variability of the degree of retting of hemp shiv  
69 available in the market.

70 So, the current work focuses on the influence of hemp variability on the setting of the matrix.  
71 Four samples of hemp shiv were analyzed for producing water leachate and the hemp shiv

72 through water treatment which were characterized and added to the lime binder. During this  
73 process , setting time and the carbonation reaction of mortars have been monitored.

## 74 **2. Materials and methods**

### 75 **2.1 Raw materials**

76 Hemsps utilized in the present study were grown in France, and these were pulled and dew-retted  
77 in the field during September. This process took 30 to 40 days as it was dependent on the climate  
78 and experience of farmers. Due to the fact that field retting involves complex biochemical  
79 reactions, and the retting degree is strongly affected by climatic conditions, the relation between  
80 the retting process (i.e., retting time and retting method) and retting degree was not discussed  
81 during our study. Four types of hemp shiv (i.e., B1-B4), with different localisation origins, were  
82 included in current research and are presented in section 2.2. The choice of samples was made on  
83 the basis of their color, whereas, the variability of shiv was analyzed and compared by the color,  
84 leachate concentration, infrared spectrum analysis and biochemical composition.

85 The binder employed in this study was Tradical PF70 of Lhoist, an air lime pre-formulated  
86 binder, which is widely used for the manufacture of hemp concrete blocks and insulation in  
87 Europe. Tradical PF70 consists of 75 wt% hydrated lime, 15 wt% hydraulic binder and 10 wt% of  
88 the pozzolanic material. The purpose of the hydraulic binder (e.g., Portland cement) is to improve  
89 early age properties such as setting time and strength development, whilst the pozzolans can  
90 reduce the use of cement (Walker and Pavía, 2014).

### 91 **2.2 Sample preparation and experimental methods**

92 The schematic presentation of the sample preparation process is shown in Fig. 1. Hemp shiv were  
93 ground to 2 mm particles, then submerged in water for 24 hours (water treatment), under  
94 mechanic agitation. After this water treatment, the shiv and leachate were separated by filter

95 paper having pore size of 10  $\mu\text{m}$ . The shiv before (B) and after (C) water treatment are shown in  
96 Fig. 2, which indicate that the 24 hours of water treatment had no significant effect on the color of  
97 hemp shiv. Since the hemp shiv has a strong water absorption performance, after preliminary  
98 tests, the water ratio was set to 1:20 to ensure that a sufficient and suitable concentration of the  
99 leachate was obtained. It is worth noting that the weight of the leachate (D) in Fig. 2 was the  
100 theoretical value, the real weight which was obtained during the analysis was less than 201g due  
101 to filtration and drying.

102 *Location of Figure 1*

103 *Location of Figure 2*

#### 104 **2.2.1 pH and conductivity analysis of leachate**

105 The leachate (D1-D4) of hemp shiv were analyzed by pH-meter and conductivity using a  
106 THERMO Orion Star A11 equipment.

#### 107 **2.2.2 Infrared spectrum analysis of hemp shiv**

108 Fourier Transform Infrared Spectrometry (FT-IR) in transmission mode with a Nicolet iS10 FT-  
109 IR spectrometer was used to analyze solid samples. The transmission spectra were recorded with  
110 a resolution of 2  $\text{cm}^{-1}$  and a wavenumber range of 4000-650  $\text{cm}^{-1}$ .

#### 111 **2.2.3 Spectrocolorimetry of hemp shiv**

112 Color determination of hemp shiv powders was carried out using a spectrophotometer (CM-  
113 2300d, Konika Minolta, Japan). Color was measured by means of CIELab coordinates (ISO  
114 11664-4:2008):  $L^*$  (whiteness ( $L^*=0$ ) or brightness ( $L^*=100$ )),  $a^*$  (redness ( $a^*>0$ ) or greenness  
115 ( $a^*<0$ )) and  $b^*$  (yellowness ( $b^*>0$ ) or blueness ( $b^*<0$ )). Hemp shiv powders were obtained after  
116 milling of hemp shiv (previously dried until constant weight at 40°C) employing a micro impact

117 mill (Culatti, Switzerland). The rotor speed was adjusted to 7 and a standard sieve of 1 mm mesh  
118 size was employed. Color of untreated hemp (B1-B4) and treated hemp shiv (C1-C4) was  
119 determined. Each sample was measured at least in triplicate. The maximum of standard deviation  
120 associated with the mean of measured values are, respectively, 3% for L\* values, 6% for a\*  
121 values and 5 % for b\* values.

#### 122 **2.2.4 Biochemical composition of hemp shiv**

123 Biochemical composition of plant samples (B1-B4), ash content, lignin, cellulose, hemicellulose  
124 and soluble contents, were determined following the method given by Van Soest method (NF  
125 V18-122; Viel et al., 2018; Carrier et al., 2011) employing an adapted machine (FibercTR 8000,  
126 Foss, Denmark). To carry out this measurement, all samples were previously dried until constant  
127 weight at 40°C and then milled with the procedure described in section 2.2.3. All measurements  
128 were carried out at least in triplicate.

#### 129 **2.2.5 Vicat test**

130 The setting time of mortars was determined according to NF EN 196-3 using a manual Vicat  
131 apparatus at room temperature. The shiv were ground to 2mm in order to make sure that the  
132 aggregate will not interfere with the penetration of the Vicat needle. Thirteen samples were  
133 prepared for the Vicat test, and the detail of the tested samples are given in Tab. 1. After  
134 preliminary tests, it was found that when the water to binder ratio was 0.6 (e.g., water = 120g,  
135 binder = 200g), the mortar had the best workability. Empirical observations indicated that water  
136 treatment could effectively eliminate soluble components; therefore 6g of hemp shiv without  
137 water treatment (i.e., shiv B in Fig. 1) and 120g of leachate (i.e., leachate D in Fig. 1)  
138 theoretically contained the same quantity of soluble components. In addition, for each sample  
139 shown in Tab. 1, a measure of penetration (at a random point) was made every 30 minutes by

140 recording the penetration depth of the needle into the paste. The Vicat test was repeated a total of  
 141 three times, and the experimental results were the average value of these three repetitions.

142 **Table 1** Details of the tested samples. (B, C, and D correspond to the symbols in Fig. 1)

Symbol	Brief Introduction	Binder (g)	Shiv (g)	Water or Leachate* (g)
R	Reference (100% binder)	200	0	120
B1	Hemp shiv 1	194	6	120
B2	Hemp shiv 2	194	6	120
B3	Hemp shiv 3	194	6	120
B4	Hemp shiv 4	194	6	120
C1	Treated shiv 1	194	6	120
C2	Treated shiv 2	194	6	120
C3	Treated shiv 3	194	6	120
C4	Treated shiv 4	194	6	120
D1	Leachate 1	200	0	120*
D2	Leachate 2	200	0	120*
D3	Leachate 3	200	0	120*
D4	Leachate 4	200	0	120*

143

#### 144 2.2.6 Thermogravimetric analysis

145 The thermogravimetric analysis (TGA) can be used to determine the Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> content  
 146 of the sample. The aim of this experiment is to evaluate the long-term influence of hemp shiv  
 147 leachate (i.e., D1-D4 in Tab. 1) on the carbonation process. Five samples (i.e., R, D1, D2, D3,  
 148 and D4 in Tab. 1) were prepared at the same time and stored indoors under controlled conditions  
 149 of temperature (20±2°C) and relative humidity (50±5%). For each sampling time (1 hour, 3 hours,  
 150 7 hours, 1 day, 3 days, 7 days, 14 days, 28 days), 15g of the sample was gathered and stored in  
 151 three sealed plastic tubes. Since the TGA test usually takes a long time (i.e., 2 hours for each  
 152 sample), it was not possible to test all the samples at each sampling time. The sealed plastic tubes  
 153 were soaked in liquid nitrogen (-196°C) for 30 seconds then stored in a -81°C freezer. This  
 154 process was proved to be able to inhibit and even stop the hydration and carbonation reaction of  
 155 the sample (Diquélou et al., 2015).



156 TGA analysis was carried out with the TG 209 F1 Iris Libra thermogravimetric analyzer  
157 (produced by NETZSCH company). All experiments were conducted at temperature ranging from  
158 25°C to 800°C with a heating rate of 10 °C/min under argon flow. Fig. 3 shows two examples of  
159 the TGA curve. It is clear that sample weight changes occur in three areas, i.e., I, II, III in Fig. 3.

160 *Location of Figure 3*

161 Weight loss from 25°C to 380°C is mainly due to the loss of water from the pore and some  
162 hydrate products (e.g., calcium silicate hydrate). While the reduction in weight from 380°C to  
163 510°C and 510°C to 800°C are due to the decomposition of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> (Diquélou et al.,  
164 2015), respectively. According to Fig. 3, it is observed that when the sampling time is 28 days,  
165 the carbonation level of the sample prepared with leachate D3 is significantly lower than that of  
166 the reference. This phenomenon will be analyzed in section 3.2.

167 The dry weight of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> (wt%) was calculated according to Eq. 1 and Eq. 2,  
168 respectively, where LCO<sub>2</sub> represents the weight loss of CO<sub>2</sub> between 510°C and 800°C. LH<sub>2</sub>O  
169 and LH<sub>2</sub>O' are the weight losses of water taking place between 25°C - 380°C and 380°C - 510°C.

170 
$$Ca(OH)_2(wt\%) = LH_2O'(wt\%) \times \frac{MW(Ca(OH)_2)}{MW(H_2O)} \times \frac{1}{1 - LH_2O(wt\%)} \quad (Eq. 1)$$

171 
$$CaCO_3(wt\%) = LCO_2(wt\%) \times \frac{MW(CaCO_3)}{MW(CO_2)} \times \frac{1}{1 - LH_2O(wt\%)} \quad (Eq. 2)$$

172 Here, MW is the abbreviation used for molecular weight, e.g., MW(CaCO<sub>3</sub>) and MW(Ca(OH)<sub>2</sub>)  
173 represent the molecular weights of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>, respectively i.e., 100.087g/mol and  
174 74.093g/mol.

175

176

177 **3. Results and discussion**

178 **3.1 Setting time analysis**

179 The effect of hemp shiv and its leachate on the setting time of lime-based binders is shown in Fig.  
180 4. The setting time of LHC using the hemp shiv without treatment is presented in Fig. 4a. Among  
181 them, B3 and B4 had obvious delay effects on the setting. The delay was considerable, even  
182 though the shiv dosage was significantly lower than that in a conventional LHC. Fig. 4b depicts  
183 the setting time of the LHC using hemp shiv with water treatment and shows that after 24 hours  
184 of water treatment, hemp shiv can significantly reduce the setting time. It is worth noting that all  
185 treated hemp shiv accelerates the setting of LHC. Fig 4c describes the setting time of the LHC  
186 using hemp shiv leachate and some of the leachate (e.g., D1, D2 in Fig. 4c) accelerates the setting  
187 too. The mechanism of the accelerating effect was not studied in this work, which needs further  
188 investigation on the chemical reaction of carbonation and hydration. The trends of the curves in  
189 Fig 4a are similar to that of Fig 4c. The similarity of results between Fig. 4a and Fig. 4c indicate  
190 that the retarding effect is mainly caused by the soluble components from hemp shiv (the leachate  
191 contains mainly the soluble components like sugar and organic acids). The overlay of curves C1,  
192 C2 and C3 are noticed and the shift of curve C4 implies that all soluble components from hemp  
193 shiv B4 were not solubilized, and more than 24h of water treatment would have been required.

194 *Location of Figure 4*

195 It was found that there is a linear relation between hemp color and the retting degree, more the  
196 hemp is rotten, the darker will be the color (Martin et al., 2013) for hemp shiv originating from  
197 the same production batch. In this study, 4 different hemp shiv resulted from 4 production  
198 batches. So, the prediction of the setting time of LHC by color analysis was not easy. However,  
199 through visual observation, it was noticed that B4 is greener than other hemp shiv, and its LHC  
200 has the longest setting time. In addition, no difference between untreated hemp shiv (B) and

201 treated hemp shiv (C) was visible whereas a difference in setting time was observed. Color  
202 analysis was performed on powders of untreated hemp shiv (B1-B4 in Fig 5) and treated hemp  
203 shiv (C1-C4 in Fig 5), as shown by results given in Fig. 5.

#### 204 *Location of Figure 5*

205 The luminance (L) is a parameter which can vary from 0 to 100 and define respectively the  
206 whiteness and the brightness. The mean for our L\* values in Fig. 5 was 75. Martin et al. (2013)  
207 observed a decrease of L\* values from 70 to 50 progressively with the retting duration in case of  
208 flax fibers. As all the values observed in our results were higher, it can be inferred that used hemp  
209 shiv are probably all low retted. L\*a\*b\* values were very similar for each hemp shiv, untreated or  
210 treated, which supports our visual observation. However, values \*b always decrease from B to C  
211 samples, particularly for hemp shiv 3 and 4, from about 18 to 15. A decrease of parameter b  
212 suggests an impact of treatment on color hemp and is an indicator of retting degree, as identified  
213 by Martin et al. (2013) with flax fibers where a decrease of parameter b from 25 to 13 was  
214 observed in 20 days of retting. The retting is a degradation of pectin through enzymes actions  
215 produced by fungi (Meijer et al.,1995). The change of parameter b\* between untreated and  
216 treated hemp shiv suggests that hemp shiv 3 and 4 are less retted than hemp shiv 1 and 2. The  
217 water treatment normally simulates the retting and is also involved in the release of pectin.  
218 Investigations were also carried out to characterize hemp shiv for biochemical composition and  
219 results are presented in Fig 6.

#### 220 *Location of Figure 6*

221 Soluble fraction, hemicellulose, cellulose and lignin contents varied from 5.5 to 19,7 %, 16.2 to  
222 20.7%, 53.9 and 62.4%, 9.4 to 15.4%, respectively. Which correspond to previous literature  
223 studies (Diquélou et al., 2015; Viel et al., 2018). Hemp shiv B4 demonstrated a slightly different  
224 composition from the others with the highest fraction of soluble compounds. The composition of

225 this fraction includes different soluble compounds such as fat, wax, pectin, proteins and  
226 polysaccharides (Viel et al., 2018). So, hemp shiv B4, comprising the higher fraction of pectin is  
227 probably the less retted.

228 Due to cost and time consumption aspects, spectrophotometry and Van Soest methods are not  
229 considered to be feasible for application at industrial scale. It is necessary to find a simple and  
230 sensitive method to predict the setting time and the compatibility of LHC, therefore we studied  
231 the leachate using pH and conductivity analysis.

232 The hemp shiv leachate (i.e., D1-D4 in Tab. 1) is shown in Fig. 7. It was found that the color of  
233 leachate D4 was significantly darker than the others. For leachate D1-D3, even though the color  
234 of hemp shiv (i.e., B1-B3 in Fig. 1) is different, their leachate appears identical. For further  
235 evaluation of the leachate, pH and conductivity analysis were performed for D1-D4 leachate. The  
236 results of the pH and conductivity analysis are shown in Tab. 2.

237 *Location of Figure 6*

238 **Table 2** pH and conductivity of the leachate D1-D4. (The weight loss is the weight reduction of  
239 10g hemp shiv after water treatment)

Sample	pH	Conductivity (mS/cm)	Weight loss (g)
Water	6.946	0.003	-
D1	6.797	1.472	0.77
D2	7.673	0.949	0.43
D3	7.127	1.853	1.25
D4	5.49	3.54	1.41

240

241 It can be seen from Table. 2 that D3 and D4 present the highest weight loss and conductivity  
242 values. The leachate concentration suggests a mass concentration based on the difference of hemp  
243 masses before and after water treatment. The weight loss of the hemp shiv has a linear correlation

244 with the concentration of leachate substance. It was found that the conductivity and the loss  
245 roughly correspond to the setting time (Fig. 4c), higher the weight loss (or conductivity) longer  
246 the setting time. Usually, farmers control the duration of field retting based on the color changes  
247 and their experiences. This experiment result indicated that the weight loss could be a helpful  
248 indicator for the industry to predict the setting time of LHC and test the retting degree. To reveal  
249 the mechanism of the setting retardation, the leachate was analyzed by infrared spectrum.

250 As the concentration of the leachate was too small to be tested, it was necessary to concentrate the  
251 soluble component, thus the freeze-drying method was used to get the components in the  
252 leachate. The dehydrated soluble components are shown in Fig. 8. Colors and textures of  
253 dehydrated soluble components are different, suggesting a variability in their content and  
254 chemical composition.

255 *Location of Figure 8*

256 The freeze-drying substances of the leachate (Fig. 8) were analyzed by FT-IR spectrum (Fig. 9).

257 *Location of Figure 9*

258 The most diagnostic FT-IR bands were  $1050\text{ cm}^{-1}$  (C-O stretch),  $1404\text{ cm}^{-1}$  (O-H), and  $1558\text{ cm}^{-1}$   
259 (in-plane  $\text{NH}_2$  scissoring), the first two bands correspond to the carbohydrate (Dorado et al.,  
260 2001) whilst the second corresponds to amides. The intensity of band  $1050\text{ cm}^{-1}$  had a positive  
261 correlation with the field retting duration (Walker et al., 2014), which indicated that the sample  
262 having low retting degree (B3 in Fig. 1) comprised more carbohydrates. The intensity of band  
263  $1558\text{ cm}^{-1}$  of D4 spectrum meant hemp shiv B4 contained amide functions. The amides in plants  
264 are mainly derived from asparagine and glutamine, which are formed through photosynthesis in  
265 plants. Other main sources of these amides are plant proteins and some co-enzymes.

266 It is a well-known fact that saccharides could delay the setting time (Wang et al., 2019) of cement  
267 and that hemp leachates were rich in some monomeric sugars (e.g., galactose, glucose, fructose)  
268 (Tronet et al., 2016; Kochova et al., 2017; Delannoy et al., 2020), which could explain the  
269 retarding effect of hemp shiv B3, B4 and its leachate D3, D4 (Fig. 4). However, the hemp shiv B4  
270 and its leachate D4 obviously contain more soluble fraction than other hemp shiv samples, as  
271 shown in Fig. 6 and Fig. 7. Therefore, the 24h water treatment may not be long enough, resulting  
272 in a longer setting time for the treated hemp shiv C4 than other hemp shiv samples (Fig. 4b). The  
273 high intensity of spectrum band  $1050\text{ cm}^{-1}$  and the low pH (Tab. 2) indicated that the leachate D4  
274 was rich in carboxylate group (COOH) originating from galacturonic acids, which in turn are  
275 probably derived from pectin. Kochova et al. (2017) proved that the pH of the leachate could be  
276 used as an indicator of the cement-plant aggregates compatibility, and acid admixture might slow  
277 down the cement setting (Uchikawa et al., 1995; Gori et al., 2011). Bruere (1966) and Smith et al.  
278 (2011) found that the set-retarding saccharides (e.g., maltose, lactose, glucose) either contain the  
279 OH-C-C=O group or can be converted by dilute alkali into saccharides acids containing this  
280 group. The oxygen molecules of this particular group can approach each other and adsorb on the  
281 surface of  $\text{Ca}(\text{OH})_2$  or cement particles by a chelation reaction (Young 1972; Juenger and  
282 Jennings, 2002; Thomas et al., 2009).

283 The hemp leachate influenced not only the setting time of the lime-based matrix, but section 3.2  
284 indicated that the carbonation reaction was also affected by the leachate. It can be supposed that  
285 not only the cement particle, but the calcium hydroxide particle was chelated or complexed with  
286 organic components. It is well known that popular cement retarders such as sodium gluconate and  
287 lignosulfonate can form complexes with  $\text{Ca}^{2+}$ , reduce the concentration of calcium ions in the  
288 solution, and the presence of these complexes on the surface of the cement particles inhibit  
289 cement hydration. Since there is a large amount of  $\text{Ca}(\text{OH})_2$  in the lime-based matrix, there is no  
290 shortage of  $\text{Ca}^{2+}$  ions, so a more reasonable explanation is the chelate formed by the organic

291 matter (i.e., sugar and amide) and  $\text{Ca}^{2+}$  precipitates and adheres to the cement and calcium  
292 hydroxide particle.

293 Hydroxycarboxylic acid, provided by the leachate solution has both carboxylic and hydroxyl  
294 groups. Carboxylic group  $\text{COO}^-$  adsorbs on the surface of mineral particles through forming a  
295 complex with  $\text{Ca}^{2+}$  by electrostatic interaction. However, high  $\text{COO}^-$  content might lead to higher  
296 water bleeding and a long setting time of the concrete (Young 1972; Sha et al., 2020). Hydroxyl  
297 group would interact with surface  $\text{Ca}^{2+}$  ions, while the latter could bond simultaneously to  
298 adjacent  $\text{O}^{2-}$  ions (Young 1972). In addition,  $\text{Ca}^{2+}$  forming ligands with nitrogen atoms in amide  
299 structure, decreases the concentration of available  $\text{Ca}^{2+}$  ions (Liu et al., 2014). Thus, the  
300 formation of calcium hydroxide and C-S-H gel were delayed, and the good flowability of cement  
301 pastes maintained a longer time (Sha et al., 2020). Diquélou et al. (2015) demonstrated that strong  
302 retarding agents and a reduction in the number of hydrates (C-S-H and portlandite) were  
303 observed. This considerable modification of the setting and hardening process is further  
304 illustrated with the loss of mechanical properties.

305 The above explanation interpreted the mechanism that the less rotten hemp shiv delays the setting  
306 of LHC. Both the saccharides and organic acids from hemp shiv might have delayed the setting  
307 and decreased the compatibility of LHC. Experiments showed that 24 hours of water treatment  
308 could effectively eliminate these substances. However, it was not clear through which mechanism  
309 the hemp leachate (i.e., hemp leachate D1 and D2 in Fig. 4) accelerated the setting time. So, the  
310 long-term influence of the hemp shiv leachate on the binder was explored in the following section  
311 [3.2](#).

### 312 **3.2 Carbonation reaction**

313 The lime carbonation reaction is a chemical reaction in which calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )  
314 reacts with carbon dioxide ( $\text{CO}_2$ ) and forms insoluble calcium carbonate ( $\text{CaCO}_3$ ). The

315 mechanism and the kinetics of the carbonation depend strongly on the CO<sub>2</sub> concentration and the  
316 moisture (Despotou et al., 2016). Fig. 10 (a and b) showed the results of thermogravimetric  
317 analysis (the calculation method is in 2.2.6), which highlight the change of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>  
318 contents in the presence of hemp shiv leachate at different sampling times (1h, 3h, 7h, 1d, 3d, 7d,  
319 14d, 28d and 90d).

320 *Location of Figure 10*

321 It was found that the contents of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> were negatively correlated, but the change  
322 of Ca(OH)<sub>2</sub> content was relatively complicated. The main reason is that the content of calcium  
323 hydroxides was affected by carbonation reaction, cement hydration and pozzolanic reaction. Fig.  
324 10 depicted that during the first 7 hours, the Ca(OH)<sub>2</sub> content of D4 was lower than others, which  
325 was mainly because of the low pH of leachate D4. In the first 7 hours, the sample D1 and D2  
326 (Fig. 4c) almost finished the setting while their CaCO<sub>3</sub> content had no apparent difference with  
327 other samples. This phenomenon indicated that the carbonation reaction had no significant effect  
328 on the setting time (in fact the carbonation reaction is a long-term reaction which takes several  
329 months). It was the hydration of the cement that determines the setting time.

330 As far as the long-term carbonation reaction is concerned, it was observed that from the seventh  
331 day that the CaCO<sub>3</sub> content of D3 and D4 were significantly lower than that of other samples. It  
332 was recognized that leachate D3 and D4 have higher mass loss and conductivity (Tab. 2), which  
333 revealed that the conductivity of the leachate and weight loss of the hemp could be an indicator to  
334 predict the carbonation rate of the LHC. We proposed the hypothesis that setting retarder  
335 (leachate D3 and D4 in Fig. 4c) tends to have lower carbonation levels, which mean that the  
336 hemp shiv which retarded the setting could prevent the carbonation reaction and even influence  
337 the mechanical performance.

338 **4. Conclusion**



339 This research evaluated the influence of different hemp shiv on the setting time and the  
340 carbonation of lime-based binder. Empirical observations and experimental results showed that  
341 the low rotten shiv tend to have compatibility problems with the binder and prolong the setting  
342 time. The Vicat test proved that it was due to the soluble components (e.g., organic acids, simple  
343 sugars, proteins) of the shiv which influenced the hydration and carbonation reactions. In general,  
344 the color was considered an effective way to assess the degree of retting, but the present study  
345 revealed that the color was not linearly related to the setting time of LHC. In this research, we  
346 found that water treatment can effectively remove the retarding agent. These findings indicated  
347 the potential use of water treatment to improve the compatibility between hemp shiv and lime  
348 matrix. The weight loss of hemp shiv after water treatment can be a useful indicator to evaluate  
349 the retting degree and predict the setting delay. Considering the pH and conductivity of leachate,  
350 the prediction can be more accurate. However, there are still many phenomena (e.g., some  
351 leachates accelerate solidification and hardening) and mechanisms (e.g., mechanism of the effect  
352 of leachate on carbonation) that cannot be explained now, as this requires further investigation.

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438 **Figure 1** Schematic diagram of the material preparation process

439 **Figure 2** Photographs of the tested hemp shiv before and after water treatment. B1-B4: hemp shiv  
440 before water treatment; C1-C4: hemp shiv after water treatment

441 **Figure 3** Thermogravimetric curves of samples D3 and R at 28 days

442 **Figure 4** Setting time of lime-based binder with the addition of (a): hemp shiv without water  
443 treatment; (b): hemp shiv after water treatment; (c): hemp shiv leachate. (The symbols B1-B4,  
444 C1-C4, and D1-D4 correspond to the symbols shown in Tab. 1)

445 **Figure 5** Color analysis of untreated hemp shiv (B1-B4) and treated hemp shiv (C1-C4)

446 **Figure 6** Biochemical composition of 4 different hemp shiv

447 **Figure 7** Leachates D1-D4 of the hemp shiv

448 **Figure 8** Soluble components in leachates after freeze-drying

449 **Figure 9** The infrared spectrum of the leachates after freeze drying.

450 **Figure 10** (a) The change in  $\text{CaCO}_3$  content of the lime-based binder in the presence of hemp  
451 leachate D1-D4. (b) The change in  $\text{Ca(OH)}_2$  content of lime-based binder in the presence of hemp  
452 leachate.

453 **Table 1** Details of the tested samples. (B, C, and D correspond to the symbols in Fig. 1)

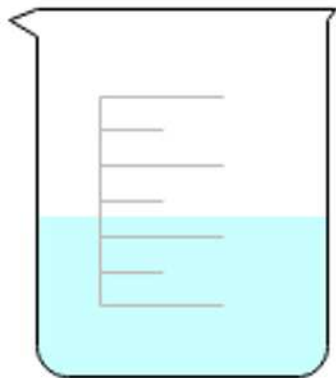
454 **Table 2** pH and conductivity of the leachate D1-D4. (The weight loss is the weight reduction of

455 10g hemp shiv after water treatment)

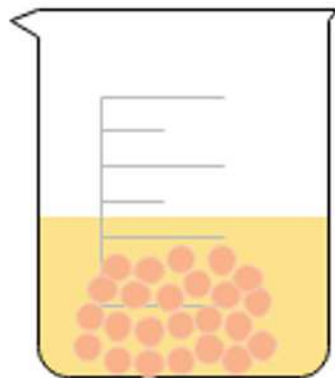
B: 10g hemp shiv



+



A: 200g water

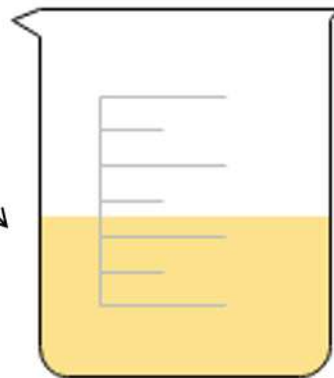


210g Mixture.  
20°C, 24h

Filtration

Drying  
60°C, 24 h

C:  $\approx 9$ g treated hemp  
shiv



D:  $\approx 201$ g  
leachate



B1

B2

B3

B4

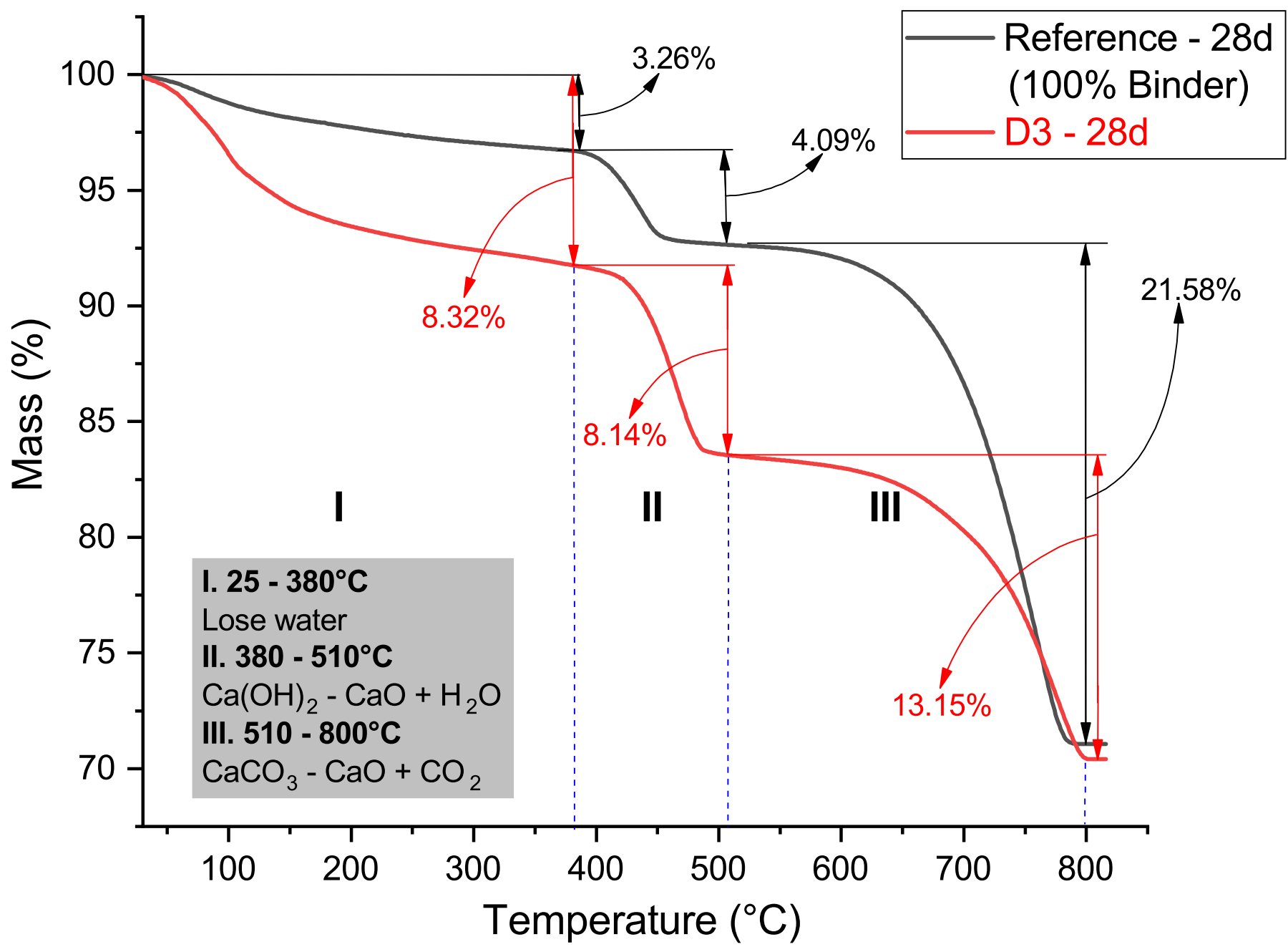
C1

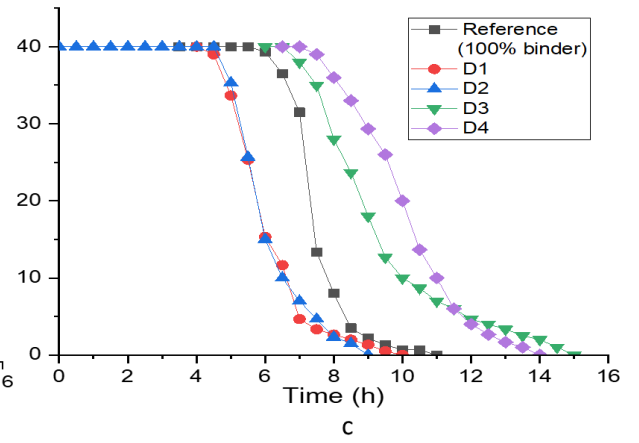
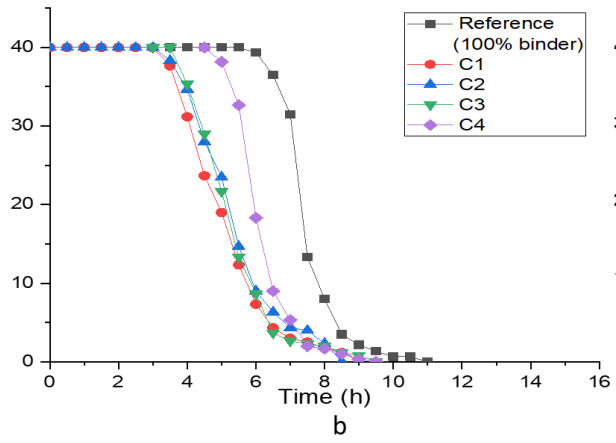
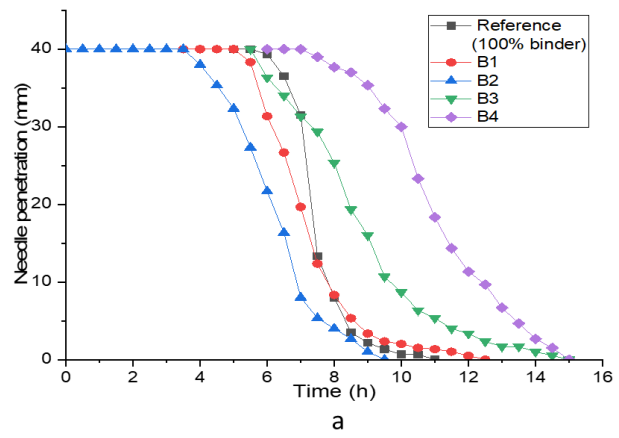
C2

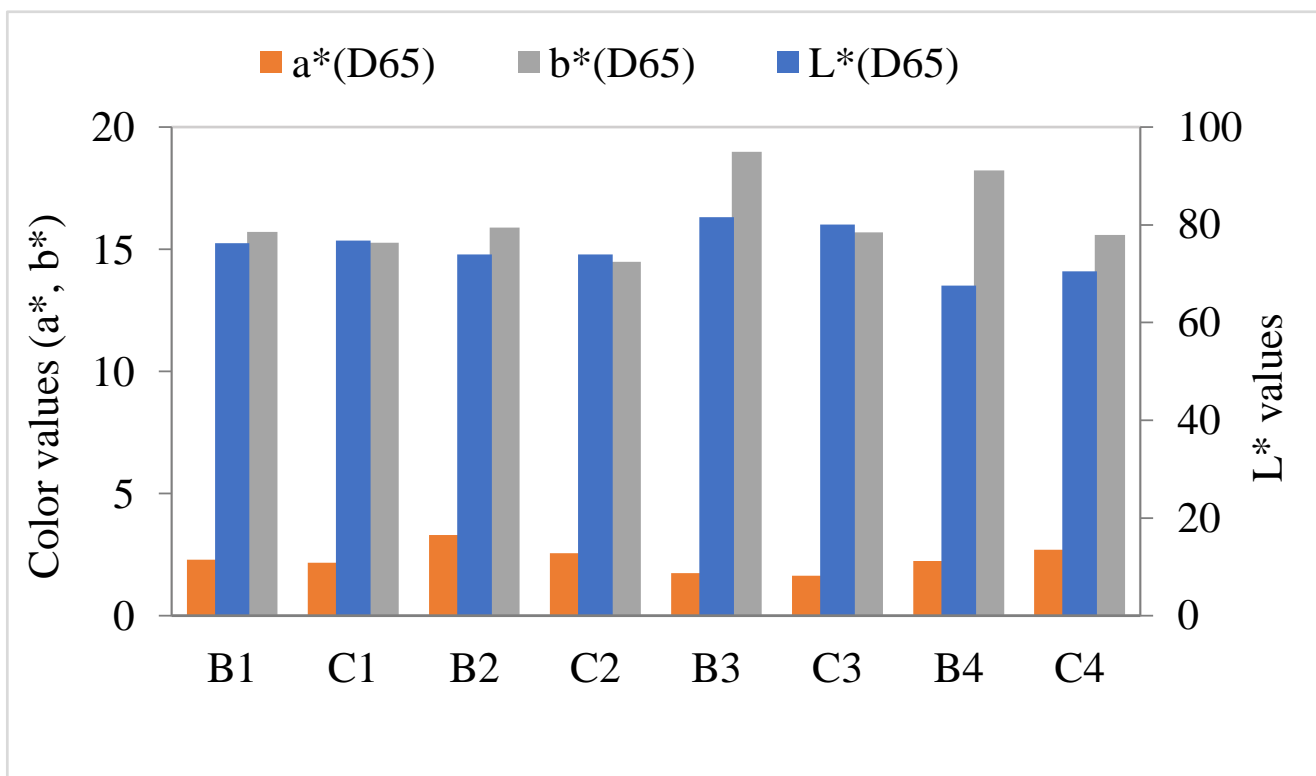
C3

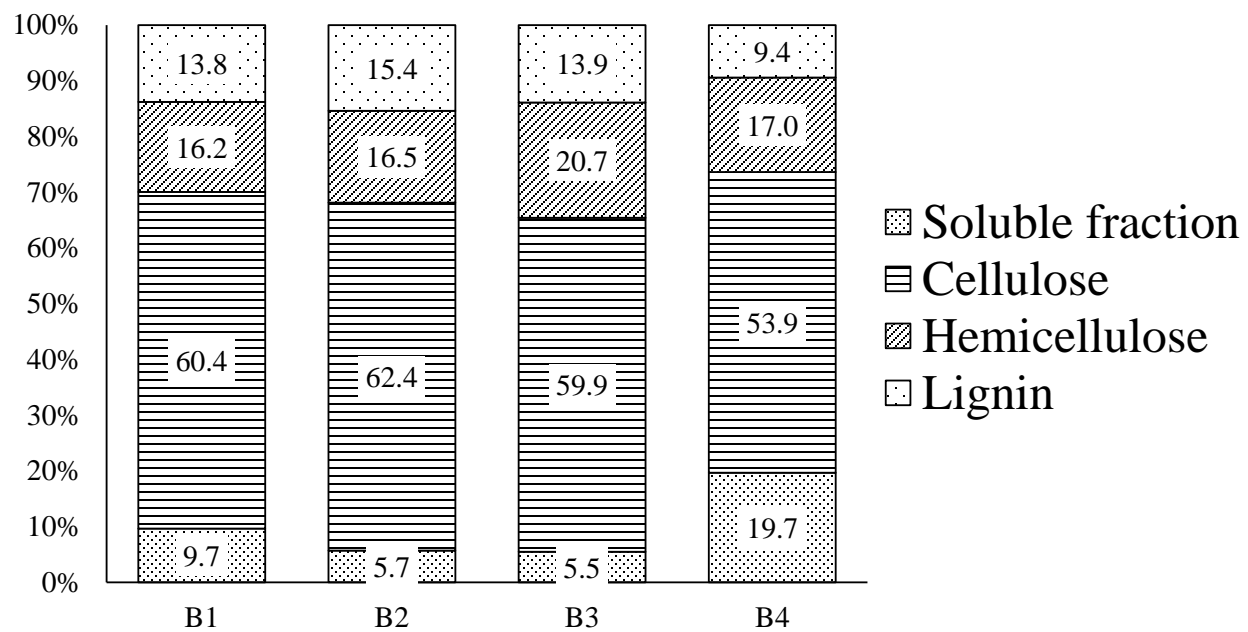
C4











D1

D2

D3

D4

H<sub>2</sub>O

