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Abstract

Three types of treatments of miscanthus were performed, alkali, silanization and the combination of both. There is a direct inverse relation between the amount of sugar-containing molecules extracted from miscanthus and the mechanical strength of the concrete blocks. The use of alkali treated stems as fillers increased remarkably the strength of the blocks, and this was even higher when the alkali treated fibers were coated with silica, with a compression strength of 11 MPa compared with an initial 2.2 MPa. The use of alkali-treated stems result in a faster cement hydration, compared to untreated ones suggesting that specific sugars or other components released from the alkali-treated plant may favor cement hydration. A remarkable decrease of the cellulose and xylose content is observed for the miscanthus pieces after being soaked in a cement-water-sand mixture, these two molecules being adsorbed on cement particles.

Key-words

Concrete; Fibers; Miscanthus; Chemical treatment; Polysaccharide, Sugar

1 Introduction

In the building and construction sector, plant parts can be used as fillers in concrete to reduce the use of non-renewable natural resources such as sand or gravel. In addition, plant-based fillers have a positive CO_2 balance and good thermal and acoustic insulation properties [1] as well as reducing the weight of concrete materials. However, the use of plant-based fillers has several drawbacks. Besides their unfavorable economics [2], such concretes show a lack of affinity between the organic phase (plant) and the inorganic concrete matrix. This results in a non-effective stress transfer at the interface between both materials, weakening the mechanical properties of the concrete composite and leading to a poor compressive strength. Long-term durability is also an open question since plant material may decompose over time. Another difficulty is to limit the amount of water absorbed by the plant material at the expense of the water content needed for cement setting and hardening. Finally, the alkalinity of water in concrete pores has a strong degradation effect on natural fibers [3,4]. This is well known in the pulp and paper industry where soda treatments are used to extract various components from wood or lignocellulosics, in particular hemicelluloses [5]. The extraction of hemicelluloses and their possible degradation in various lower molar mass sugars and sugar derivatives are strongly affecting the setting of concrete. Some sugars, among other components, released from the plants in the presence of water and cement are resulting in a delay of the cement hydration [6] and affecting the setting and hardening process of cement

[7]. In the latter study, the authors used three different hemp shiv samples to prepare Portland cement concrete. They concluded that molecules extracted from shiv in contact with the water-cement mixtures had a strong influence on the setting and hardening of cement, acting as strong retarders. They also showed that these extractives are decreasing the amount of Calcium-Silicate-Hydrate (C-S-H) and portlandite in the final product. When extracted in water, the three shivs showed a variation of the total amount of extracted sugar-based molecules, correlated with the retardation and decrease of C-S-H and portlandite in the final products, the highest amount of sugars leading to the strongest effects. The type of sugars could also have an influence in the concrete setting since glucose was not related to any variation of its properties while the shiv having the strongest deleterious effect has a much higher proportion of xylose-based molecules. The effect of sugars on the setting of concrete is a rather complex matter, extensively studied over years, but with very ambiguous and puzzling results. Sugars have been shown to behave as retarders or accelerators, mostly depending on concentration, but in some cases these two effects are observed in an overlapped concentration range or with very small concentration differences [8]. This probably evidences that the mechanisms at stake, adsorption and poisoning, complexation or formation of barriers around cement grains [9–12] are not well understood. Using different types of fibers, it was shown that increasing the percentage of fibers as filler decreased the workability of concrete [13]. One way to overcome some of these difficulties is to treat the lignocellulosic fibers to reduce the water absorption capacity, protect the lignocellulose fraction from the cement alkalinity and improve the affinity between the plant and the inorganic matrix [14]. Another important piece of information is that the behavior of lignocellulosics is different when using cement-water or pure water extracts, rendering the task of understanding the role of theses extractives more difficult [15].

Lignocellulosic fibers are composed of cellulose, hemicellulose, lignin, pectin, inorganics and waxy components with small amounts of other organic molecules [16]. Cellulose is the main constituent contributing to the strength and stiffness of the biomass, forming intra- and intermolecular hydrogen and Van der Waals bonding between cellulose chains and with hemicellulose constituents. The percentage of each component varies depending on the plant species and tissue types, where fibers with higher cellulose contents are generally stronger [17]. When applying chemical treatments to the plant fibers many different effects can be seen. For example, partial removal of superficial layers of the plant material exposes a rougher surface with many accessible hydroxyl groups, resulting in a better interaction between the fiber and the matrix, as in the case of polymer composites [16,18]. Among the treatments tested, two of them will be examined in more detail in this work: alkali and silane treatments. Treatment with alkali is a very common strategy to remove hemicelluloses, pectins and other minor components [17,19], to change the morphology of the surface of lignocellulosic objects, increasing interface strength [20] and removing surface debris [21,22]. This is expected to lead to an improvement of fiber strength and fiber-matrix adhesion [4,23]. Alkali treatments induce a fibrillation of cell wall cellulose fibers due to the removal of their hemicellulose binder thereby improving matrix-cellulose binding by increasing the biomass - cement contact interface. Many conditions can be applied for alkali treatments such as varying concentrations, usually in the range 0.5-10% as tested with hemp [23], coconut [21,24] and jute [25]. Silane treatment have been shown to reduce the hydrophilic character of natural fillers [4,26–28], to act as compatibilization agents and to increase the mechanical performances of concrete. For example, silanization of bagasse fibers resulted in a decrease in water absorption by the fiber, improved its affinity with the cement matrix and the durability of the fibers within the concrete matrix, and shortened the setting time of the composite [29]. A correlation between the concentration of silane and the strength of Kraft fiber-cement composite was shown [30]. In another study, Eucalyptus Kraft pulp surfaces were modified with several silanes [26] and methacryloxypropyltrimethoxysilane had a positive effect. It reduced the hydrophilicity of the biomass, leading to improved mechanical properties, dimensional stability and durability of the concrete, and decreased the final water/cement ratio, with the cellulose fibers being free from cement hydration products. Aminopropyltriethoxysilane had an adverse effect on concrete properties (increased hydrophilicity, reduced strength and durability, accelerated mineralization and higher embrittlement).

The present work is revisiting the use of alkali and silane treatments for improving the properties of plant-based concrete. Its objective is to understand the effect of these treatments on miscanthus stem fragments in the context of the preparation of concrete, in particular considering the effect of polysaccharide release from stems on the compressive mechanical properties of the produced concrete.

2 Experimental

2.1 Materials

Miscanthus X giganteus stems were harvested from Seine-et-Marne region (France) on March 2014 by the Biomass Environment System company and ground by SD Tech (Alès, France). For the preparation of the concrete mixture, Portland cement (CEM I 52.5R Couvrot) was provided by Calcia Ciments (Guerville, France) and sand of grain side 0/4 mm was purchased in Castorama (Sophia Antipolis, France). All experiments were performed with distilled water.

The general polysaccharide composition of miscanthus pieces used is given in Chupin *et al.,* 2017 [31]. The two major sugars are cellulose and xylose from hemicellulose.

2.2 Treated miscanthus stem fragments

Miscanthus stem fragments were alkali treated and silica coated, as detailed in Boix *et al.,* 2016 [32]. Briefly, miscanthus stem fragments of an average length and width of 1.2 ± 0.6 mm and 0.2 ± 0.1 mm, respectively, were soaked and stirred in a 5% NaOH solution for 30 minutes, then rinsed with diluted acetic acid and abundant water until the rinsing water reached neutral pH. The silane treatment was applied to both the as-received miscanthus stem pieces and to the alkali treated stem pieces using a 2.6 % v/v aqueous tetraethyl orthosilicate (TEOS) emulsions at pH 4, pH 6 and pH 10 during 2 hours. Table 1 summarizes the treatments and properties of miscanthus stem fragments used in this study, including their water absorption and ash content values [32]. These samples were chosen in order to study the effect of silane media conditions in water (noted Sw), acid (noted Sa) and basic (noted Sb) conditions. Samples with only the alkali treatment (no silane) are noted as A and samples with a silica coating in acid conditions on alkali pretreated stem fragments are noted as A-Sa. Untreated stem fragments are noted as U.

Table 1. Characteristics of miscanthus samples previously prepared [32] and used in this study. U: untreated miscanthus pieces, A: with only the alkali treatment , Sw: silanization in water, Sa: silanization in acid conditions, Sb: silanization in basic conditions, A-Sa: silica coating in acid conditions on alkali pretreated pieces.

Sample name	Media silane treatment	Alkali pre-treated	Water absorption (Weight %)	Ash content (Weight %)
U	No silane	No	80 ± 3	1.4 ± 0.2
Sw	Aqueous (pH 6)	No	64 ± 5	1.5 ± 0.1
Sa	Acid (pH 4)	No	62 ± 5	4.3 ± 0.1
Sb	Basic (pH 10)	No	62 ± 3	4.9 ± 0.1
A	No silane	Yes	91 ± 3	1.0 ± 0.1
A-Sa	Acid (pH 4)	Yes	84 ± 4	3.2 ± 0.1

As the size of natural pieces used as fillers for concrete may have a crucial effect on the composite strength, untreated and treated miscanthus fragments were previously sieved at an amplitude of 40 Hz with a Retsch AS200 Digit shaker (Retsch, Germany) operating at 40mm amplitude (2mm/g) in order to use the same length of miscanthus stem fragments for all composites. The sieves applied were 1 mm, 600 µm, 400 µm, 200 µm, 100 µm. However due to their relative abundance, only the most populated and bigger fragments were chosen and population was set as: 26% of ≥ 600 µm, 37% ≥ 400 µm and 37% of ≥200 µm.

2.3 Concrete blocks preparation and compression test

The biomass-based concrete blocks contained a mixture of cement, sand, miscanthus stem fragments and water. The density of untreated miscanthus stem fragments was considered the same for all samples and was measured in ethanol using a 10 ml pycnometer, giving the value of 0.31 ± 0.01 g/cm^3 obtained from the average of four measurements. The mixture of cement, sand and miscanthus pieces had the following composition: 40% dry weight of cement (density 3.09 g/cm^3), 57% dry weight of sand (density 2.60 g/cm^3) and 3% dry weight of miscanthus (corresponding to 22% miscanthus by volume). The water to cement ratio (w/c) was set to 0.4, which allowed an easy manipulation and a fast demolding of the concrete blocks. The quantity of water was readjusted for each mixture by measuring the moisture contents (Mettler Toledo HX204) of the sand and miscanthus used and subtracting this amount of water from the quantity required for the concrete mixture. A total of 1.5 kg of dry mixture was used per batch, which allowed the production of nine concrete cubes of 5x5x5 cm^3.

The wet concrete mixing was performed in a metallic flat-bottom recipient using a trowel. The mixing process was based on the ASTM C192/C192M-07 standard methodology when using a mixing machine. Nonetheless, the manual mixing was found to be more reliable for the preparation of such low quantities. The methodology for the preparation of the bulk mixture was done in six steps: mix sand and miscanthus, add some of the water to wet the stem fragments, add the cement, mix during three minutes, cover the mixture and let it rest for three minutes and mix during two more minutes while adding the remaining water. The wet mixture was then transferred into a metallic mold of 15x15 cm^2 surface over 5 cm thickness fitted with partitions to obtain cubic structures of 5x5x5 cm^3, and then placed on a vibration table (Netter Vibration NV, Germany). After pouring the mixture into the mold, a vibration of 50 Hz during 20s was applied in order to enhance compaction and removal of air bubbles. Concrete samples were then removed from the 15x15 cm mold and kept with the partitions for two days at 21 ˚C and 99 % relative humidity by covering the specimens with a non-absorbing plastic foil, in a temperature-controlled room. Samples were then removed from the partition mold and kept for a further five days under the same conditions. The compression strength of the concrete cubes (four replicates) were tested after seven days from preparation by a hydraulic Dartec HA 250 (Zwick, Germany) compression test machine. The instrument imposed a displacement of the specimen at a deformation rate of 0.1 mm/sec and a displacement limit of 4 mm. The compression strength was measured before the rupture of the test sample. The density of the concrete blocks was measured from the cube dimensions and weights just prior to the compression test.

2.4 Chemical analysis

Miscanthus-concrete mixture aqueous extracts were obtained after one hour of the preparation of the wet concrete mixture (cement, sand, miscanthus and water), 26 g of the mixture were diluted in 25 ml of water, mixed and filtered (300 µm pore filter) to obtain aqueous extracts for further carbohydrate analysis. Miscanthus-water soak extracts were prepared as follows: miscanthus samples (2 g) were soaked in 400 ml of water for 24 hours. A longer period of soaking was allowed for water extracts (24 h), in comparison to soaks in concrete (1 h), to allow a sufficient amount of sugar to be detected as water extraction was less efficient than the concrete one. The soaking water was then extracted by filtration. 200 ml of the soaks were freeze-dried for further carbohydrate analysis. The other 200 ml were used for the cement hydration and setting conductivity studies. The neutral monosaccharide composition was obtained from 100 µL of aqueous extract, which was dried under vacuum and hydrolyzed. This process followed the protocol described by Harholt *et al.*(2006) with slight modifications in the hydrolysis reaction, using 100 µL of 2.5 M trifluoroacetic acid (TFA) for 2 h at 115 °C instead of 2 M TFA for 1 h at 120 °C. The hydrolyzed sample was diluted 15 times and the released monosaccharides of hemicellulose were measured using an HPAEC-PAD chromatography [33].

2.5 Cement hydration and setting studies

2.5.1 Conductivity measurements

The water soaks of untreated and treated miscanthus samples (1g / 200 ml) were used to hydrate 1 g of cement (cement: water ratio, 1:200). Hydration was followed by an electric conductimeter (SCHOTT instruments, ProLab 4000) during approximately 30 hours at 25 ˚C under stirring. Two independent tests were performed for each case.

2.5.2 Attenuated total reflectance-Fourier transform spectroscopy

Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR, Bruker Tensor 27) was used to analyze cement setting in concrete samples. Samples were freeze-dried at 7 days in order to stop the hydration/curing process and allow comparison between samples. Dry cementitious samples were ground and filtered through a mesh of 0.1 x 0.1 mm prior to analysis to avoid the presence of most of the lignocellulosic fragments. The instrument was operated from 4000 to 600 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

3 Results and discussion

3.1 Influence of chemical treatments on compression properties of concrete

The chemically treated miscanthus pieces were used for evaluating their effect on the compression strength of concrete blocks. Figure 1 gives a typical example of the stress-strain curves obtained with samples Sa. As can be seen, there is a clear agreement between the four different test blocks. There is no plastic plateau and rupture is occurring quickly after loading.

Figure 2 shows that silica treatments on the untreated stem fragments had a slight positive influence on the compression strength of the composite with no significant differences between treatments at different pH values (Sw, Sa, Sb). The small differences could also be attributed to a variation in the density due to the compaction process. The use of alkali treated stems (Sa) as fillers increased remarkably the strength of the blocks, and this was even higher when the alkali treated fibers were coated with silica (A-Sa). The A-Sa concrete composite had a compression strength of 11 MPa compared with 2.2 MPa for untreated miscanthus stem pieces. The greater compression strength of A-Sa was uniquely attributed to the filler treatment since the densities of the blocks were comparable (see A versus A-Sa specimens in Figure 2). Since the A-Sa treatment (alkali plus silane) showed such a large improvement in mechanical properties, we looked at the influence of the water content for this specific concrete mixture. The amount of water that the A-Sa miscanthus fragments were able to absorb (Table 1) was additionally included in the wet concrete mixture, increasing the w/c ratio from 0.4 to 0.46. Consequently, a higher compression strength (13 MPa) was measured, but the material showed cracks after the compression test. Under compression, the concrete block is compacting until failure, which may or not lead to its disintegration into several pieces. Instabilities were observed for concrete blocks in the absence of miscanthus (blank) even at the low w/c ratio of 0.4 (image not shown). In contrast, miscanthus concrete with w/c ratio of 0.4 had the advantage of keeping its structure after the compression test. There exists thus a range of water/cement ratio for preventing the collapse of the concrete composite under compression by adding flexibility to the material.

3.2 Sugar-based molecules present in free water of the concrete mixture and cement curing

After one hour of contact between cement, sand, miscanthus and water, the available water was collected and the presence of sugar-based molecules was measured. The effect of the plant treatments on the release of sugar-containing molecules when mixed to cement was measured and related to the mechanical properties of the concrete blocks at seven days, as shown on Figure 3.

There is a very clear correlation between the presence of sugar-based molecules in the free water of concrete and the compression strength. The higher the amount of sugar-based molecules is, the lower is the compression strength. We conclude that the better performance of the concrete obtained with alkali (A) and alkali-silane (A-Sa)-treated stem fragments may be mainly due to two factors: Firstly, the alkali treatment is eliminating parts of pectin, hemicellulose and waxes leading to a higher roughness of the plant stem surface [32], as well as increasing the number of cellulose molecules exposed to the surface, available to react with the cement matrix [16,34]. Secondly, it is known that polysaccharides and sugars released from the lignocellulosic plants are in most cases delaying cement hydration and setting [35] and in many cases impairing strongly the mechanical properties of concrete [36]. The alkali pretreatment (A and A-Sa samples) greatly reduced the amount of sugars in the cement-water mixture and increased the compression strength of the blocks (Figure 3). Thus the presence of extractable sugars could be seen as one of the main factors determining the strength of the composite. Similar observations were reported by Diquélou *et al.*, 2015 [7]. By comparing untreated miscanthus to the silane treated samples (Sw, Sa and Sb), one can observe that the silica coating also decreases the amount of sugar present in the water. A similar trend is observed between A and A-Sa samples. The silica coating seems to act as a protection of the lignocellulosic fragments against cement alkalinity. A more detailed analysis of the type of sugars present in concrete water after one hour of contact between the miscanthus stems and cement-water is shown in Figure 4. For both, treated or untreated stems, glucose was the main sugar constituent, followed by xylose for (non-alkali-treated stems) and fucose (for alkali-treated stems).

The cement curing can also be evaluated by infrared spectroscopy [7,37]. The hydration process of the concrete samples was stopped at seven days by freeze-drying and then analyzed by FT-IR. The hydrated form of cement is characteristic by the Si-O related peaks for C-S-H at 970 cm^{-1} whereas the 920 cm^{-1} peak is related to the tricalcium silicate (C_3S), which is the non-hydrated phase (see dotted lines in Figure 5). Therefore the hydration of the cement can be estimated from the measurement of the relative abundance of these two Si-related peaks. The lower the 970/920 cm^{-1} ratio, the lower is the amount of hydrates [7]. The 970 cm^{-1} peak was not noticed in the untreated and Sw samples. On the contrary, A-Sa had the largest 970/920 cm^{-1} ratio, meaning that this sample had the lowest inhibition of C-S-H formation. This is expected since these samples had the highest mechanical resistance, coming from a more complete C-S-H formation. However, it should be noted that despite the $SiO4^{4-}$ content within the cement matrix, samples may contain a few additional SiO_2 from the miscanthus coating, although most fibers were filtered out before analysis. These silica bands would appear at a similar wavelength in the infrared spectra. $CaCO_3$ is one of the components bringing hardness to concrete. It is originally present in cement as well as due to the reaction of portlandite and atmospheric CO_2 and it has associated peaks at 713, 870 and 1421 cm^{-1} [37]. These IR bands are more intense for A, Sa, Sb and specially A-Sa than for U or Sw, which is in full agreement with the mechanical property ranking of these samples.

3.3 Soaking miscanthus in water and use of soaked water

Extracting molecules from lignocellulosic materials by water soaking and using this water to wet cement has been used previously as a way to explore the influence of extractable molecules on the setting and hardening of cement. Results have shown that these extracts are increasing the latency period, increasing the total time for complete setting, decreasing the amount of hydrates and decreasing the mechanical properties compared with pure water [7,15]. It is worth looking if there is a correlation between sugars extracted in water and in cement-water mixtures. Figure 6 is showing the amount and the composition of sugars present in the water from soaking untreated, alkali treated or alkali plus silane-treated stems. There is a factor of five between the amount of sugars extracted by pure water between untreated (158 µg/mL) and alkali-treated stems (32 µg/mL). It shows the expected decrease in the total amount of sugars released in water after a mild alkali treatment of miscanthus (U and A). The relative proportion of sugars is changed before and after an alkali treatment. It shows that while glucose and xylose are the most important released sugars, considering their predominance in miscanthus stems, xylose is the most abundant sugar extracted after an alkali treatment. The difference between A and A-Sa where much less sugars are soluble in water after alkali followed by silanization treatments suggests that the silica coating acts as a barrier protecting miscanthus pieces against water penetration (the relative proportion of sugars between A and A-Sa is considered as similar).

A very striking result is that the total amount of sugars extracted from untreated miscanthus in contact with concrete is about 11 µg/mL of fluid (Figure 4), compared to 158 µg/mL of sugars extracted in pure water (Figure 6). The possible explanations are (i) cement is not extracting sugars, a very unlikely result considering the high pH, (ii) these extracted sugars are so degraded that they cannot be detected, not probable considering the sugar detection methods used, or (iii) sugars are extracted and they bind to the cement particles, and are thus not present in the free water present between sand and cement particles. Being the last hypothesis the most probable. There is thus the need to better understand which sugars are released and where they sit.

3.4 Comparison of sugar composition between miscanthus and the soaks in water and in cement mixture for untreated miscanthus

Table 2 gives the composition of untreated miscanthus pieces and of the supernatant after soaking 24 h in water and one hour in cement-sand-water. The results show that water is not extracting cellulose but it does extract a small amount of hemicellulose, which is detected in the supernatant. There is a huge decrease of the cellulose and xylose content of the miscanthus pieces after being soaked in cement-water-sand mixture. The very interesting result is that these two molecules which have been extracted from the miscanthus pieces due to the presence of cement are not found in the water extracts between cement particles and sand grains. They are thus potentially adsorbed on cement particles. This confirms several previous studies in which the effect of extracted molecules on cement is a mechanism associated with the adsorption of sugar-based compounds [9].

Table 2. Composition of the untreated miscanthus pieces and of the supernatant after soaking 24 h in water and one hour in cement-sand-water. The three minor sugars (fucose, rhamnose, mannose) were not measured.

Miscanthus pieces (in µg/mg of used miscanthus)						
	Hemicellulose				**Cellulose**	
	Arabinose	Galactose	Glucose	Xylose	Cellulose	Xylose
24h in water	24.5	5.2	12.5	181.9	418.7	27.3
1 h in cement	22.7	3.9	12.6	140.6	311.3	31.0

Supernatant				
Hemicellulose (in µg/mg of used miscanthus)				
	Arabinose	Galactose	Glucose	Xylose
24h in water	0.13	0.4	0.9	0.83
1 h in cement	Nd	nd	0.57	0.13

3.5 Hydration kinetics

The hardness of a cement-based material is tightly related to the physicochemical environment in which the mixture is performed. This is due to hydration and setting being the result of interfacial and solid-state reactions between water and powdered minerals [9]. This includes the degree of hydration, water to cement ratio, the humidity and temperature during curing but also the amount and nature of components released from lignocellulosic fragments. Portland cements are multi-phasic inorganic materials consisting of several oxides with one of the main components being tricalcium silicate (Ca_3SiO_5 or C_3S), which can be used as a tracer to monitor the effect of admixtures in cement hydration by measuring electrical conductivity. During hydration, C_3S is dissolved, followed by the formation of a hydrated mineral (C-S-H) and finally precipitates as portlandite ($Ca(OH)_2$) [38]. Since the presence of plant sugars is known to have a strong effect on the strength of the concrete blocks, the following analysis aimed to investigate at which stage the plant extracts affected the curing process of the concrete: hydration, setting or hardening, keeping in mind that extraction was conducted by soaking miscanthus in pure water. For this, the cement hydration was monitored by conductimetry measurements with water having been previously soaked in untreated (U), alkali treated (A) and alkali-silane (A-Sa) treated miscanthus fragments. The water to cement ratio (w/c) was set to 200 for all samples. Dilution grades of $0.5 < w/c < 300$ have been previously validated by Nonat *et al.*, 1997 [38], although it should be noted that the higher the w/c ratio is, the longer is the induction period and the later the precipitation of portlandite takes place [38]. As the miscanthus fragments were simply soaked in water, the amount of sugars released is much lower and different in composition than under the alkali conditions to which miscanthus is exposed during the whole concrete formation. However, soaking allows a comparison between the different plant treatments and may bring some clues regarding the effects of miscanthus fillers in concrete formation. To increase the amount of sugars released into the water and allow observing an effect on the cement hydration, the weight ratio of cement over miscanthus was set to 1:1, higher than for the concrete mixture used to prepare the concrete blocks (1: 0.075). The interpretation of the conductivity curves was performed according to previous cement hydration studies by Comparet *et al.*, 2000 and Govin *et al.*, 2005 [6,39]. The curves in Figure 7 show a first fast increase in the conductivity due to the C_3S dissolution and formation of Ca^{2+} ions, followed by a slow increase related to the C-S-H nucleation and a more rapid conductivity rate increase due to the crystal growth. The maximum conductivity peak corresponds to the highest concentration of portlandite before its precipitation, detected by the decrease of the curve due to the conversion of Ca^{2+} ions into $Ca(OH)_2$.

Results show that cement dissolution differs when, instead of pure water, miscanthus soaks were added. In this latter case, a lower conductivity is recorded from the first hours of the measurement (Pure water> Alkali and silane treated (A-Sa) >Alkali (A) >Untreated (U)) which suggests a complexation effect of calcium ions by the released polysaccharides, sugars or other released miscanthus organic admixtures [9]. The hydrate nucleation step was delayed for around two hours for the untreated miscanthus soaks compared to pure water, whereas for A and A-Sa, hydration was two hours shorter than the pure water. In previous studies, the delay in the hydrate nucleation was related to a reduced number of hydrate nuclei which are precipitating [39]. This delay in the hydrate nucleation consequently postpones the portlandite precipitation as it is the case for untreated samples relative to the pure water. Therefore, high concentrations of sugar or other extracts released by the untreated plant produce a delay in the hydration of cement. However, the contrary is observed when using soaks from alkali or alkali plus silanization stem fragments which give a faster hydration. It is well known that the effects of sugars are complex and often concentration dependent. For example, adding a small amount sucrose in cement caused a delay in hydration of tricalcium silicate [40] while adding sucrose in large quantities had a positive effect on concrete prepared with flax shaves, increasing the mechanical properties of concrete, decreasing setting time and improving concrete behavior in water. The results found here contradict previous results that suggested that extracts coming from lime or cement-water were detrimental to the setting of cement, concluding that degradation products created in high alkaline environments (mainly carboxylic acids) have a negative effect [6]. The effects of sugars, extracted or added, are not easily predictable. Precipitation of portlandite starts nearly 20 h earlier when using alkali treated miscanthus soaks when compared to untreated stem soaks and even sooner than for pure water. This confirms that some sugars or other components released from the alkali-treated plant favors cement hydration. A closer look at Figure 7 shows that despite the similar hydration time for A and A-Sa, the plateau of nuclei growth is longer for A-Sa and precipitation takes place at the same time as the untreated miscanthus composite (U).

4 Conclusions

The use of miscanthus stem pieces for preparing concrete is giving blocks with a very moderate compressive strength. Using different treatments, it is shown that there is a relation between the amount of sugar-containing molecules able to be extracted from the miscanthus stem fragments and the mechanical strength of the blocks. The lower the amount of such molecules is extracted, the higher the mechanical strength is obtained. When the miscanthus stem pieces were previously treated with an alkali solution able to extract some of the hemicelluloses present in the cell walls, the extraction of sugar-containing molecules by cement-water-sand mixtures is decreased. Such a treatment is highly efficient for improving the mechanical performances of miscanthus-based concrete. Silanization is moderately efficient as it is also slightly decreasing the sugar-containing molecule released probably due to a barrier effect, and thus improving compression strength. The addition of the two treatments is giving very good results, increasing the compression strength by more than five times compared to untreated miscanthus. The analysis of the sugars present at the beginning of the cement hydration process shows that two sugar-based molecules play a main inhibition role, glucose and xylose. The effect of the amount of sugar released is showing a contrasted image. High amounts of sugar or other extracts released by the untreated plant produce a delay in the hydration of cement. In contrast, a lower concentration of the sugar extracts or a specific composition results in a faster cement hydration, as obtained for the A and A2 samples results. Precipitation of portlandite starts nearly 20 h earlier when using alkali treated miscanthus soaks when compared to untreated soaks, even sooner than for pure water. This suggests that some sugars or other components released from the alkali-treated plant may favor cement hydration. When analyzing untreated miscanthus stem pieces and the supernatant after 24 h soaking in water and one hour in cement-sand-water, results show that there is a huge decrease in the cellulose and xylose content of the miscanthus pieces after being soaked in cement-water-sand mixture. These extracted molecules are not sitting in the water present between cement particles and sand grains. They are thus adsorbed on cement particles, probably polluting their surfaces and inhibiting their hydration.

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7 Caption for the figures

Figure 1. Stress-strain curves for four different tests of sample Sa.

Figure 2. Compression strength results and density of the blocks (5x5x5 cm3) prepared with differently treated miscanthus.

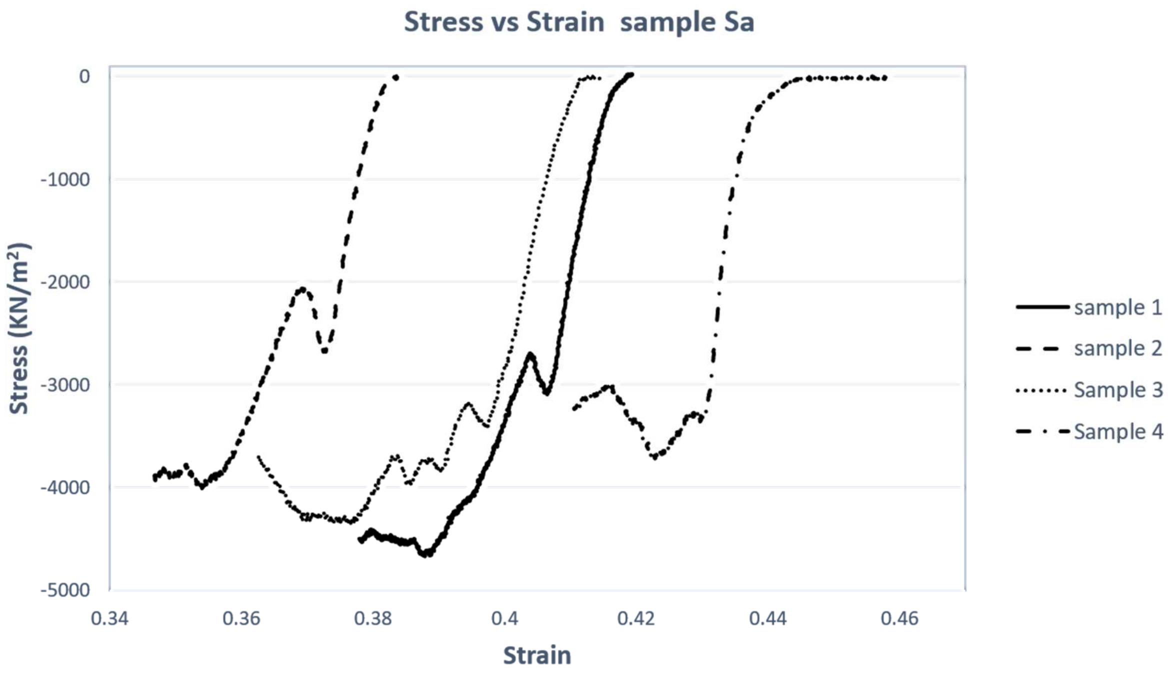
Figure 3. Crossed data of concrete compression strength versus the total amount of sugar released from miscanthus fragments and present in the free water during the concrete preparation with water and sand, after one hour of contact.

Figure 4. Distribution of sugars in the free water from the cement-sand water-miscanthus slurry extract mixture after one hour of the mixing.

Figure 5. Infrared spectra of concrete samples after seven days of curing in presence of the miscanthus stems.

Figure 6. Sugar content of the extracts used for hydrating cement after a 24 hour soak in water with U: untreated miscanthus stem fragments, A: alkali treated and A-Sa: silica coating on alkali treated.

Figure 7. Electric conductimetry monitoring of cement hydration (w/c= 200) in pure water, in water soaks of untreated miscanthus (untreated U), in water soaks of alkali treated miscanthus (A) and of alkali followed by silanization (A-Sa).



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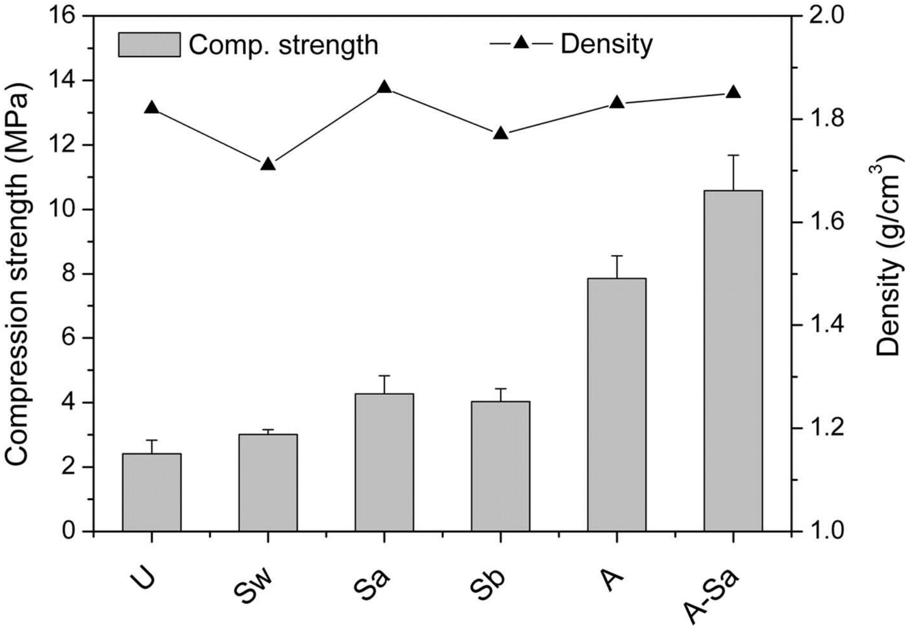

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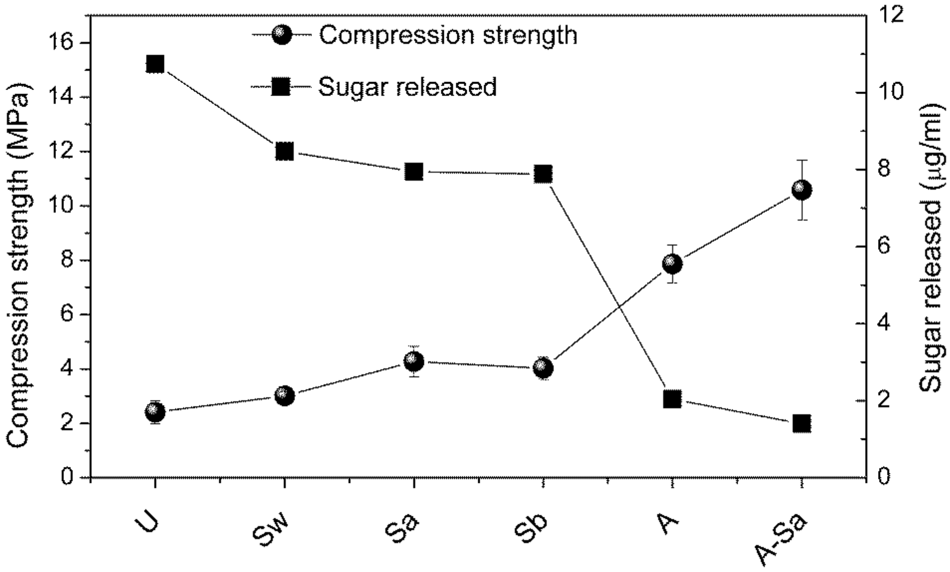

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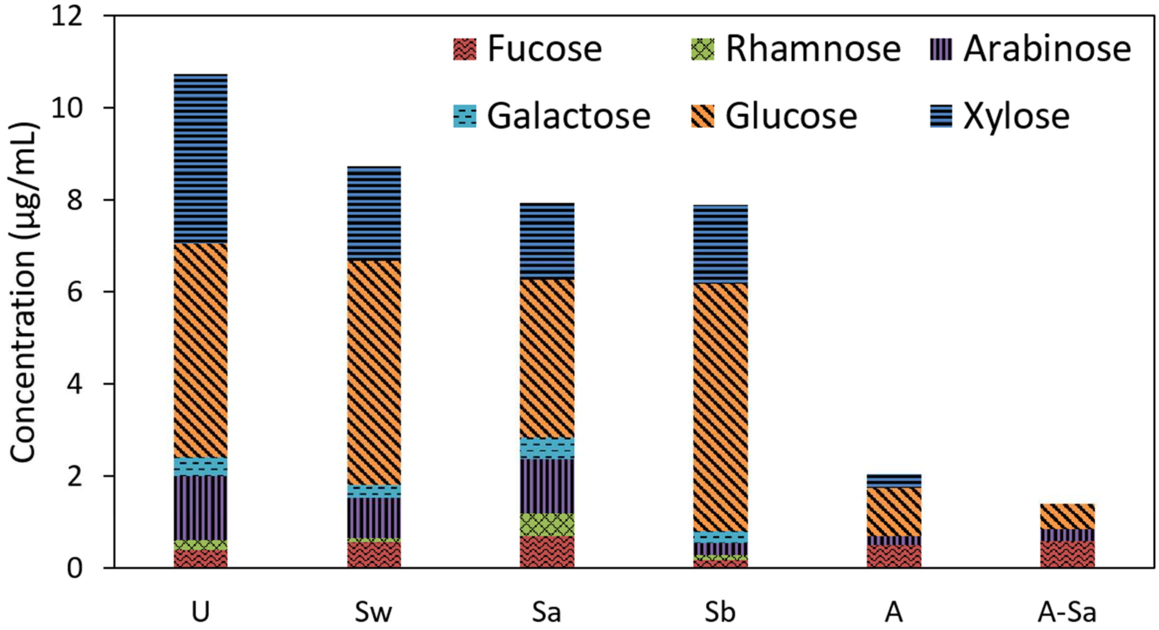

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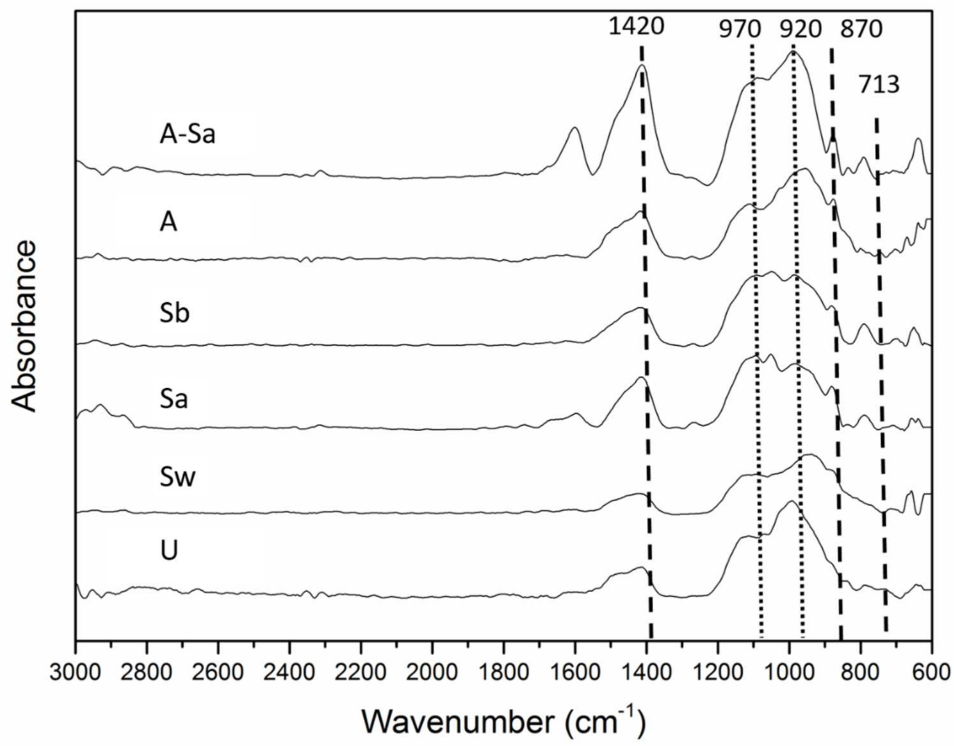

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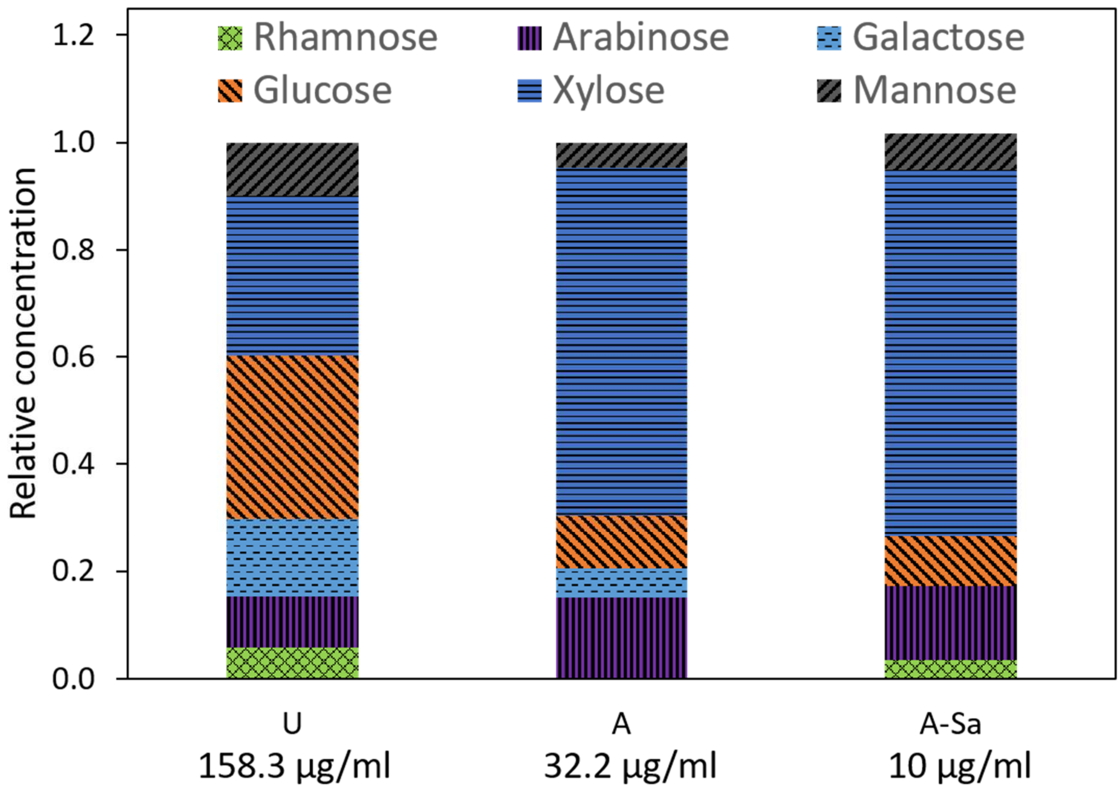

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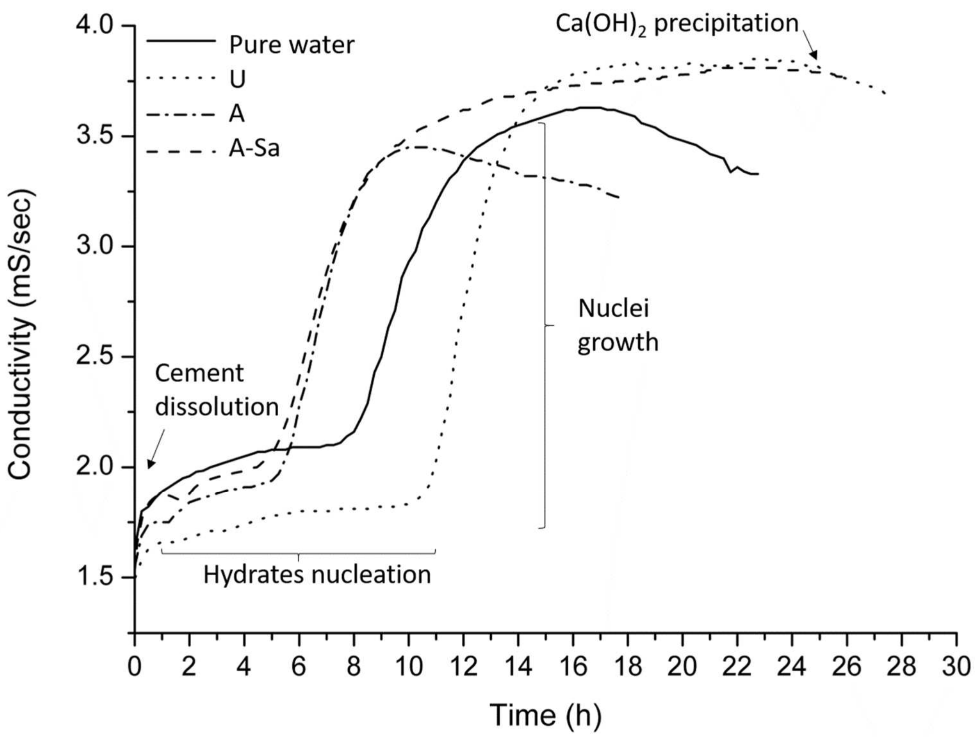

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