Water Hyacinth–Cement Composites as Pollutant Element Fixers

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ABSTRACT:

Water hyacinth (WH) or *Eichhornia crassipes* is one of the 100 most dangerous invasive species in the world. Currently, WH has enormous negative impacts on various ecosystems, and its eradication poses a seemingly impossible challenge. Physical extraction has been found to be an adequate process for controlling the spread of WH, but sustainable waste management of WH has not been achieved due to its ability to absorb pollutants. In this study, preliminary research on the possibility of using water hyacinth root ash (WHRA) as an alternative to pozzolans in cement matrices in order to fix these pollutants is presented. Characterization of the samples was carried out by XRF, SEM, BSE, EDX, ICP-OES, XRD and FTIR. A complete study of the pozzolanic activity and hydrated products of WHRA was conducted. Mechanical characterization of 25% replacement mortars was evaluated, and a pollutant fixed/leaching characterization was made. The results indicate that WHRA reacts with calcium ions and other pollutants. Thus, WHRA–cement mortars can be utilized as a green method of fixing the pollutants present in WHRA. The incorporation of WHRA is suitable as a cement addition for non-structural constructive elements, such as pavements or precast products. WHRA–cement composite is a low-cost, greener material, which promotes the reuse of waste and pollutant elimination.

STATEMENT OF NOVELTY

This research confirms that WH biomass is a pollutant waste, and its condition as such has not been sufficiently considered in previous investigations. WH roots have a great capacity to absorb pollutants from surrounding water; however, previously proposed uses of WH have not taken this issue into consideration. Therefore, our proposed use of WHRA as an alternative addition to cement matrix is

novel. Moreover, our proposal reduces the environmental impact of WH and promotes the valorization of a pest biomass.

WH roots accumulate silicon and other pollutants. Nevertheless, previous studies have not focused on the pozzolanic utilization of ashes composed of WH roots. In fact, minor component interactions in such pozzolanic reactions have not been analyzed.

In this paper, we present a complete analysis of the hydration components of WH–cement composites during pozzolanic reactions, as well as an analysis of fixed/leaching elements in these composites.

KEYWORDS: water hyacinth root ash; invasive species; pollutant ash; pozzolanic activity; waste valorization; sustainable construction.

1. Introduction

Water hyacinth (WH) or *Eichhornia crassipes* grows in many different regions of the world [1]. It has been identified as one of the 100 most dangerous invasive species on Earth [2]. Over the last decade, several different studies have focused on its eradication; however, it seems to be a nearly impossible challenge to achieve [1–3]. The most effective solution is the physical removal of the plant [2, 4]; however, such measures are extremely expensive. Furthermore, the huge amount of WH biomass generates challenging waste management problems [1, 2, 4–6]. Several studies have investigated different uses of WH as animal feed [7], fertilizer [7–9], a component in bioethanol production [10–12], an energy producer via combustion [13, 14], or briquettes [15–17]. Nevertheless, these uses fail to consider the tendency of WH to fix heavy metals and other pollutants into its structure [18, 19]. Hence, WH promotes the accumulation of toxic elements in the food chain [20], and its sustainable valorization is difficult to achieve. The immobilization of pollutants in cement matrices is a common sustainable practice [21–23]. Thus, this research proposes the use of WH ashes as an alternative pozzolanic additive in cement matrices in order to immobilize the pollutants accumulated in WH biomass.

Countless investigations have been conducted over the last few years to identify new alternative pozzolanic additives based on wastes or biomass sub-products of the industrial field [23–31] or on agroindustrial waste [24, 27, 32–39]. Pozzolanic additions are generally characterized by their high silicon content. WH is rich in SiO₂ [40–42], and it accumulates silica in its roots [40]. However, there

are few investigations exploring the use of WH as a pozzolanic addition in cement matrices [41–43]. In addition, the part of the plant used in the few existing studies involving WH was not always clearly defined [41, 42]. To our knowledge, the case of [43] is the only instance in which WH petiole ash has been evaluated as a pozzolanic addition, and low pozzolanic behavior was found. Consequently, we hypothesize that WH roots are the most efficient part of the plant for use as a pozzolanic addition. In this paper, we conducted an evaluation of water hyacinth root ash (WHRA) as a pozzolanic addition in order to confirm our hypothesis.

As mentioned above, WH is an excellent water purifier [1], because it is able to fix pollutants in the surrounding water in its roots. Nevertheless, no previous studies have analyzed the interferences of minor components in hydration reactions involving WH. In addition, no chemical analysis of the hydration products of cement–WH composites has been presented in the literature. Therefore, an in-depth analysis of the pozzolanic activity of WH is needed in order to determine its main hydrate phases and to establish the nature of its pollutant fixation.

In the same way, WH fixes alkaline oxide and sulfates from the surrounding water. Therefore, WHRA typically has higher amount of alkali content [41–43]. Solubility in water is one of the common procedures to reduce alkali content. This technique diminishes the K_2O , NaO , and Cl^- contents [39, 44], and its effect can be improved by raising the temperature of the water [39]. In addition, pre-treatments with 0.01 N HCl remove alkaline compounds [39, 44]. Alkaline oxides and sulfates interfere in hydration reactions, and they reduce the long-term durability of mortars [27, 45, 46]. Nonetheless, previous studies did not investigate the effect of such a reduction on the durability of WHRA-based mortars. Therefore, optimized use of WH ashes in cement has not been developed. Thus, here, two pre-treatments were tested in order to reduce the alkali content of WHRA. The pre-treatments were water-based, because 0.01 N HCl pre-treatments were rejected because of their corrosive power and the environmental risk caused by their use. Different water temperatures were evaluated to determine their effects on the pozzolanic reactions.

This research investigated the viability of WHRA as alternative pozzolan addition in cement matrices in order to fix the pollutants contained in the ashes. In addition, two pre-treatments were evaluated to analyze their effects on the pozzolanic activity. To achieve this goal, a chemical characterization of the samples, a pozzolanic activity analysis, and a chemical characterization of the hydration products were

developed. An analysis of pollutant fixation in the cement–WHRA composite was also conducted. All the tests were designed to identify a low-cost green application that valorizes WHRA and, thus, to avoid the harmful environmental impacts of WH biomass.

2. Materials and Methods

2.1. Materials

WH, ordinary Portland cement (OPC), and standard siliceous sand were used in this research. WH from the Guadiana River in Extremadura (Spain) was used. The plant specimens were identified as *Eichhornia crassipes* in the Botany Area of the University of Extremadura (Badajoz). Vouchers of permission for scientific research (General Directorate of Environment Reference Number CN35/15/ACA) are conserved at the Herbarium of the University of Extremadura. The roots were separated from the petioles and leaves. They were washed rigorously with cool water in order to remove undesirable materials. Then, the roots were cut into approximately 5-cm pieces, and they were kept under sunlight for 15 days at 30 °C to achieve an 80 wt.% loss. Based on the literature [41], the roots were burned in open air at 650 °C (20 °C/min) for 45 min. The ashes were allowed to cool, and then, they were milled and sieved under 90 µm. According to previous studies [39], the ashes were subjected to two different pre-treatments (Table 1) in order to reduce the alkali content of the samples. A detailed description of the procedure is described below.

Table 1. Pre-treatments performed.

Name	Conditions		
	Water Temperature	Stirring Time	Water Change
WHRA	----	----	-----
P1	80 °C	4 h	No
P2	23 °C	24 h	Every 8 h
WHRA: water hyacinth root ash without pre-treatment			
P1: Pre-treatment 1			
P2: Pre-treatment 2			

WHRA and distilled water were introduced into a glass container in a 1:16 ratio (WHRA/water) and mechanically stirred [47] for 24 h. Afterward, the mix was separated into a solid from a liquid using a vacuum filter. The solid was dried at 105 °C for 24 h, and then, it was analyzed by X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectrometry (ICP-OES). The effects of the

pre-treatments were evaluated by comparing the chemical composition of the samples before and after the pre-treatments.

Finally, a type of commercial OPC, CEM I 42.5R [48], supplied by Portland Valderribas (Spain), was used in order to avoid the influence of additions into the studied properties. According to the manufacturer, this cement has 64.06 wt.% of CaO, 19.82 wt.% of SiO₂, 5.81 wt.% of Al₂O₃, 4.90 wt.% of CaCO₃, and 2.37 wt.% of Fe₂O₃. The minor detectable components are mainly Na₂O with 0.06 wt.% and K₂O with 1.05 wt.%. The Blaine fineness is 4002 cm²/g.

Mortars were prepared with standard siliceous sand [49] with a silica content of up to 98% and with a particle size of less than 2 mm.

2.2. Methods

2.2.1. *Chemical characterization of samples*

The major components of the samples were chemically characterized on a S8 Tiger Bruker (Karlsruhe, Germany) X-ray fluorescence (XRF) spectrometer fitted with a 4-kW rhodium anticathode tube.

Analyses were carried out in fused bead. In addition, chloride and SO₃ content, loss of ignition, and the active silica were analyzed under the instructions of European Standard EN 196-2 [50]. Moreover, minor components were measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), on a Varian 725-ES (Melbourne, Australia).

The mineralogical phases of samples were identified by a BRUKER AXS D8 GmbH (Karlsruhe, Germany) X-ray powder diffractor (XRD) fitted with a 3-kW (Cu K α 1.2) copper anode and wolfram cathode X-ray generator. Scans were taken between 2 Θ , angles of 5–60° at a rate of 2°/minute. The standard operating conditions for the voltage generator tube were 40 kV and 30 mA.

Finally, a Scanning Electron Microscopy (SEM) HITACHI S4800 equipped with a BRUKER nano XFlash Detector 5030 energy dispersive X-ray (EDX) analyzer was used. The ashes were fixed in the sample carrier with a bi-adhesive graphite sheet and then metallized with graphite.

2.2.2. *Evaluation of pozzolanic activity*

Different experimental methodologies were utilized in order to evaluate the pozzolanic activity in terms of qualitative and quantitative factors. Therefore, Lime Saturated Solution (LSS) and Strength Activity Index (SAI) tests were developed.

LSS is an accelerated method described above [51], which involves placing 1 g of sample in 75 mL of a saturated lime solution at 40 °C for a pre-established test time (1 day, 3 days, 7 days, 28 days, and 90 days). Two flasks and two blank tests per period were utilized. After the reaction time lapsed, the solutions were filtered, and the CaO concentration in the liquid was evaluated. Then, 0.02 M Ethylenediaminetetraacetic acid (EDTA) was used to determine the CaO concentration. The fixed lime (mmol/L) by the WHRA was then calculated as the difference between the reference CaO concentration (17.68 mmol/L) and the concentration in the test solution. The lower the CaO content in the liquid, the greater CaO amount fixed by the WHRA. For clarity, the result is given as a percentage of the mean lime fixed by the WHRA per period.

Subsequently, the obtained solid residue (WHRA with the fixed CaO) was analyzed by XRD, SEM, and EDX in order to identify the hydration products and the interactions produced. The procedures used here were the same as those described in Section 2.2.1.

In addition, a Thermo Scientific Nicolet 600 Fourier transform infrared spectrometer (FTIR) (Waltham, USA) was used in order to make a qualitative characterization of the possible amorphous material in the samples. A spectral resolution of 4 cm⁻¹ across a range of 4000–500 cm⁻¹ was featured. The samples were milled with KBr in a 1:3 ratio (sample/KBr). Then, the samples were introduced into a mold where they were subjected to vacuuming and pressure of 34.47 MPa, and tablets were obtained to identify the spectrum.

SAI was calculated in accordance with European Standard EN 450-1 [52]. It is based on the mechanical performance evaluation of a control mortar with 100% OPC compared with a sample with 25 wt.% ash replacement. In both cases, a dosage ratio of 1:3 by mass (blinder/sand) was used with a water/blinder ratio (w/b) of 0.5 following the standard [49]. The mixture was cast immediately into the molds (4 x 4 x 16) cm³ and allowed to set for 24 h. Thereafter, the samples were demolded and then allowed to cure in water for 28 and 90 days in ambient temperatures. After the desired period of curing,

the samples were removed from the curing chamber, surface dried, and allowed to characterize. Compressive strength was measured with an Ibertest Autotest 200/10-SW test frame, following EN 196-1 [49]. Complementary to the mechanical performance analysis, water absorption by immersion test was performed after 28 and 90 days of curing time, according to the American Society Test Materials Standard C642 [53]. Specimens were placed in an oven at 103 ± 2 °C until constant weight (M_d) was reached. Afterward, they were introduced into the water at 25 °C for 24 h. After soaking, the samples were drained on paper towels to remove excess water, and their weights were recorded (M_{sat}). An electronic balance with a precision of 0.01 g was used. At least four specimens per each sample were tested to obtain reliable average coefficient and standard deviations. The water absorption coefficient (WA) was determined using Equation (1).

$$WA (\%) = \frac{M_{sat} - M_d}{M_d} \times 100 \quad (1)$$

where M_{sat} is the weight of the samples registered after 24 h of water immersion and M_d is the oven dry mass of the samples.

In order to identify the samples, a designation of 25 was assigned, indicating 25% replacement of cement with WHRA (25-WHRA), 25% replacement of cement with ash with pre-treatment 1 (25-P1), or 25% replacement of cement with pre-treatment 2 (25-P2) compared with the control sample (OPC).

2.2.3. *Evaluation of the fixed pollutants*

The fixed pollutants were evaluated by a leaching test based on that of the North American Environmental Protection Agency [47]. Thus, pH modifiers were not incorporated in order to replicate real conditions. The test consisted of continuous agitation (for 24 h) of the solid waste in deionized water (lixiviant) in a 1:16 ratio (WHRA/water). Later, the sample was filtered with a vacuum filter, and the lixiviants were analyzed by ICP-OES.

Based on previous results, fixed analysis was only conducted in WHRA. Therefore, tests were performed with WHRA, 25-WHRA, and OPC. In order to identify the samples, the designation L was assigned, indicating the lixiviant collected from WHRA (L-WHRA), from 25-WHRA (L-25-WHRA) and from OPC (L-OPC).

At the same time, OPC and 25-WHRA were observed by Backscattered Electron Microscopy (BSE) using a HITACHI S4800 equipped with a BRUKER nano XFlash Detector 5030 EDX, and an elemental mapping of the mineral composition was generated. The samples were embedded in an epoxy resin and then cut and polished, thus ensuring a perfectly flat surface.

3. Results and Discussion

3.1. Chemical characterization and pre-treatment effect evaluation

The WHRA's silica content was high (24.31 wt.%; Table 2), but it was not as high as in previous studies [41, 42]. Different content was detected because of the environmental context, as stated previously [54]. In this context, WHRA was rich in K_2O , SO_3 , MgO , and P_2O_5 due to the agricultural activity in the areas close to the Guadiana river [1]. All these components were fixed in the WH roots because of its macrophyte properties [2, 14, 18]. Therefore, as expected, the need for pre-treatments was confirmed [45, 55].

Table 2: Chemical composition of the studied ash via X-ray fluorescence (XRF) (wt. %).

Samples	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	SO ₃	Cl	Na ₂ O	MgO	P ₂ O ₅	MnO	TiO ₂	LOI
WHRA	24.31	7.84	7.94	3.06	16.92	6.04	3.84	3.26	6.34	4.88	2.29	0.39	11.15
P1	33.52	11.46	9.30	3.75	6.83	1.78	0.34	1.54	8.83	5.28	2.45	0.34	13.81
P2	33.56	12.03	10.14	4.13	5.31	0.74	0.07	1.37	9.69	6.03	2.71	0.41	13.12

LOI= Loss on ignition

WHRA: water hyacinth root ash without pre-treatment

P1: WHRA washing with water at 80 °C for 4 h

P2: WHRA washing with water at 23 °C for 24 h. The water was replaced every 8 h.

In terms of the reduction in alkaline content, both pre-treatments were efficient. However, P2 was the most effective, because K_2O , SO_3 , and Cl were reduced by 68.61%, 87.75%, and 98.17%, respectively (Table 2). Pre-treatment efficiency was corroborated by XRD (Fig. 1). As Fig. 1 displays, potassium, chromium, and sulfates could be identified in the WHRA by XRD (Fig. 1) as sylvite (KCl) and anhydrite ($CaSO_4$) phases. However, in P1 and P2, they disappeared, because they were dissolved in the pre-treatment water. Microscopic observation by SEM-EDX (Fig. 2 and Table 3) corroborated the lower alkali contents in both the pre-treatment samples (Fig. 2c,d) compared with WHRA (Fig. 2a,b). High alkali content causes long-term durability problems [45]. For this reason, European Standards [52] limit the total alkali content of such materials to 5.0% by weight of total mass. Therefore, only P2

met these requirements, but it was just within the limit. Hence, prismatic crystals of CaO (Fig. 2d) were found due to its precipitation in the alkaline medium. Thus, a potential risk of delayed expansion due to the hydration of CaO exists [56].

Fig. 1 XRD patterns for WHRA, P1, and P2. S=KCl, C=CaCO₃, Q=SiO₂, P=MgO, A=CaSO₄, Ap=Ca₅(PO₄)₃(OH).

On the other hand, pre-treatment did not reduce the magnesium and phosphate content of the samples (Table 2), and both contents were higher than the standard requirements [52]. In fact, traces of periclase (MgO) and hydroxyapatite (Ca₅(PO₄)₃(OH)) were seen by XDR (Fig. 1), as well as by SEM-EDX (Fig. 2b). Thus, they could interfere in the hydration cement reaction, and long-term durability problems related to periclase hydration could appear [45, 55]. A detailed study of the interactions between these components is discussed in Section 3.2.

Fig. 2 SEM microphotography of WHRA (a,b), P1 (c), and P2 (d). Chemical analysis by EDX is displayed in Table 3.

Table 3: Chemical compounds of WHRA without treatment by EDX (Fig. 2) (wt.%).

	EDX	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl	TiO ₂	MnO
(a)	Si	97.479	0.557	0.489	0.320	0.001	0.212	0.615	0.003	ND	0.001	0.002	0.320
	δ (+/-)	1.875	0.080	0.054	0.051	ND	0.050	0.080	ND	0.001	ND	ND	0.127
	K-Ca	0.504	56.391	0.513	0.626	0.236	6.530	31.691	2.585	0.208	0.712	0.002	0.001
	δ (+/-)	0.052	1.090	0.052	0.060	0.110	0.276	0.722	0.084	0.048	ND	ND	0.075
	Si-Al	38.213	5.604	22.858	5.073	4.350	1.997	14.382	3.910	0.778	2.597	0.002	0.236
	δ (+/-)	0.660	0.222	0.498	0.185	0.440	0.129	0.427	0.108	0.078	0.146	ND	0.103
	K-S	0.501	2.913	0.503	3.451	0.002	4.007	48.629	0.304	0.619	38.212	0.196	0.664
	δ (+/-)	0.054	0.170	0.055	0.155	ND	0.224	1.284	0.044	0.073	1.224	0.062	0.174
	K-S	0.588	2.354	0.209	1.324	0.465	2.532	48.695	33.197	0.108	10.526	0.002	0.001
	δ (+/-)	0.054	0.139	0.041	0.083	0.144	0.150	1.167	0.448	0.041	ND	ND	0.371
(b)	K-Cl	0.003	2.714	0.003	5.628	1.845	7.352	41.738	0.607	0.001	39.682	0.002	0.425
	δ (+/-)	ND	0.140	ND	0.185	0.256	0.299	0.936	0.048	ND	1.057	ND	0.123
	S	0.451	20.542	0.512	25.573	1.318	6.019	15.723	20.094	6.148	0.737	0.474	2.410
	δ (+/-)	0.051	0.527	0.053	0.673	0.239	0.275	0.451	0.303	0.254	0.079	0.079	0.307
	S	0.451	20.542	0.512	25.573	1.318	6.019	15.723	20.094	6.148	0.737	0.474	2.410
(c)	Ca	40.513	18.663	13.066	7.091	9.587	0.631	3.723	0.029	0.434	0.001	2.327	3.934
	δ (+/-)	0.713	0.497	0.320	0.241	0.682	0.071	0.171	0.005	0.062	ND	0.150	0.388
	1	30.416	40.006	8.453	10.845	0.149	1.381	1.324	1.207	4.874	0.401	0.367	0.577
	δ (+/-)	0.503	0.840	0.211	0.307	0.088	0.099	0.096	0.062	0.206	0.060	0.069	0.144
	2	45.437	10.716	21.422	12.566	2.569	0.716	4.749	0.236	0.934	0.043	0.002	0.610
	δ (+/-)	0.736	0.314	0.451	0.354	0.307	0.071	0.188	0.040	0.081	0.010	ND	0.144
	3	30.416	40.006	8.453	10.845	0.149	1.381	1.324	1.207	4.874	0.401	0.367	0.577
	δ (+/-)	0.503	0.840	0.211	0.307	0.088	0.099	0.096	0.062	0.206	0.060	0.069	0.144

3	52.535	9.424	10.560	7.055	5.974	2.569	8.031	0.653	0.482	0.500	0.471	1.746
$\bar{\sigma}$ (+/-)	0.923	0.313	0.276	0.245	0.528	0.156	0.288	0.053	0.065	0.068	0.078	0.257
(d) Ca	1.484	84.234	1.618	6.487	0.021	2.004	1.442	1.152	0.961	0.594	0.003	0.002
$\bar{\sigma}$ (+/-)	0.054	1.180	0.065	0.185	0.005	0.112	0.060	0.045	0.061	0.048	ND	ND
4	4.028	50.025	2.143	14.040	0.002	3.334	4.905	6.185	12.875	2.457	0.002	0.003
$\bar{\sigma}$ (+/-)	0.095	0.804	0.078	0.381	ND	0.165	0.130	0.103	0.402	0.099	ND	0.002
5	2.994	44.896	1.748	16.936	0.002	3.677	7.521	4.803	13.886	3.493	0.002	0.042
$\bar{\sigma}$ (+/-)	0.077	0.682	0.068	0.424	ND	0.169	0.170	0.085	0.405	0.120	ND	0.007

$\bar{\sigma}$ (+/-) Standard deviation

ND: not detected

In the pozzolanic reaction, amorphous silica reacts with calcium from the cement to generate calcium silicate. Therefore, a higher amount of reactive silica is related to better pozzolanic performance. The reactive silica (amorphous) content detected was 14.11 wt.% (WHRA), 18.27 wt.% (P1), and 19.11 wt.% (P2). However, none of the results complied with the standard requirements for pozzolanic additions, because the reactive silica contents were lower than 25 wt.% [48]. Similarly, the sum of SiO₂, Al₂O₃, and Fe₂O₃ (35.31 wt.% for WHRA, 46.57 wt.% for P1, and 47.83 wt.% for P2) did not exceed 70 wt.% [57]. To the contrary, some authors claim that pozzolanic activity is not necessarily related to the sum of "pozzolanic oxides" [58]. Therefore, in-depth study of the pozzolanic activity of the samples is justified.

The presence of amorphous material, which is characteristic of pozzolanic materials [41], was confirmed in all the cases (Fig. 1) due to the small elevation of the baseline of the diffractograms between 25 and 60° (2theta) [26, 28, 54, 59–61]. It can be stated that pre-treatment did not affect the amorphous material. In fact, in contrast with previous research [39], high temperature did not increase the amorphous material in the ash, because there was no differences in the elevation of the baseline (Fig. 1). In addition, P2 caused an increase of SiO₂ (38.05%), Al₂O₃ (27.70%), and Fe₂O₃ (34.95%) (Table 2), which are important oxides in term of pozzolanic activity [48, 57] as mentioned above.

The results confirmed that largest amount of amorphous material in WH was in the roots (Table 2). A prior study found differences in silica content depending on the part of the plant used LARA. However, previous WH pozzolanic studies did not clearly state which part of the plant was used [41, 42]. To our knowledge, only water hyacinth petiole ash (WHPA) has been evaluated separately from other parts of the plant, and low amorphous material was detected [43]. Calcite and potassium oxide were present as major constituents in WHPA, while silica content was low (4.4 wt.%), and it was mainly in the form of

quartz [43]. Therefore, it can be concluded that the roots are more suited for the pozzolanic activity proposed here due to their higher silica content and lower crystallinity. As in other plants [62], the higher silica content in the roots is related to the genetic and life cycle of WH. WH roots can survive underwater for more than a year, whereas petioles and leaves die in less than a year. Therefore, roots are more likely to have higher silica accumulation than petioles and leaves.

On the other hand, an analysis of minor components by ICP-OES was performed (Table 4) in order to identify pollutants fixed in the samples. As stated above, WH is a successful biosorbent of pollutants in water [2, 14, 18, 19] and is capable of eliminating 70% of toxic elements [63]. The results were interesting, because the roots captured 10 times more heavy metal elements than any other part of the plant [63]. Those contents can increase in waters without environmental regulation, such as in developing countries [64].

Table 4. Minor components of the studied ashes by ICP-OES (ppm).

Samples	B	Ba	Cr	Cu	V	Zn	Zr	Co	As	Cd	Hg	Ni	Pb	Sr	Ru	Mo
WHRA	6410	540	100	110	80	440	111	10	ND	ND	200	130	ND	550	140	180
P1	4320	509	105	111	81	448	115	15	ND	ND	217	138	ND	553	150	160
P2	4155	527	108	116	77	452	115	16	ND	ND	230	142	ND	567	107	178

ND: not detected

WHRA: water hyacinth root ash without pre-treatment

P1: WHRA washing with water at 80 °C for 4 h

P2: WHRA washing with water at 23 °C for 24 h. The water was replaced every 8 h.

As a result, all the samples presented undesirable elements as minor components (Table 4). This confirmed that previous proposed uses of WH [7, 8, 10, 13–16] represent unsustainable practices, because they promote the bioaccumulation of toxic elements in food chains. This will cause long-term health problems as well as harmful environmental impacts [65]. Therefore, immobilization of those contaminants in WHRA by fixing them in cement matrices could be a new alternative solution in order to promote WHRA valorization. Therefore, pozzolanic activity analyses are needed. The effects of the minor components on cement hydration are discussed in Section 3.2.

3.2. Evaluation of the pozzolanic activity

3.2.1. Lime Saturation Solution

Quantitatively, WHRA, P1, and P2 could fix more than 90% of the available calcium ions after 90 days of exposure (Fig. 3). P2 showed the best performance with 95.6% fixed lime, while WHRA and P1 demonstrated similar behavior, achieving 93% fixed lime at 90 days. The reaction was fast, and during the first 7 days, around 80% of the total lime was fixed. Thus, if amorphous silicon reacts with calcium ions, these results suppose that mechanical resistances will reach values close to the maximum in the first 7 days. Compared with the literature, the samples showed pozzolanic activity similar to other agrowaste from elephant grass [59], sugarcane bagasse [60], or bamboo leaf [54, 61]. However, its pozzolanic activity was poor compared with alternative pozzolanic materials coming from industrial waste, such as ceramic casts [28] or wasted catalysts of catalytic cracking [26].

Once it was confirmed that there was material coming from the samples that was able to fix lime from LSS, it was necessary to develop a qualitative pozzolanic analysis. This required a hydration product characterization in order to determine if C-S-H gel had been forming. Solid products of all the samples (WHRA, P1, and P2) obtained after the LSS test at 7, 28, and 90 days were analyzed by XRD (Fig. 4 (WHRA) and 7 (P1 and P2)), SEM-EDX (Fig. 6 (WHRA) and 9 (P1 and P2)), and FTIR (Fig. 5 (WHRA) and 8 (P1 and P2)).

Fig. 3 Lime fixed by the studied ashes over time.

Similar to pozzolans coming from other agrowaste [33, 37, 54, 59], the elevation of the baseline after the LSS test indicated the presence of amorphous C-S-H gel. It has a non-crystalline nature, so this hydrated phase was not identified by XRD patterns (Fig. 4). However, its presence was confirmed by SEM/EDX analysis (Fig. 6 and Table 5), as well as by FTIR spectra (Fig. 5). The characteristic band at 950 cm^{-1} [66, 67] of C-S-H gel increased over time (Fig. 5). In addition, its amorphous character was confirmed by the non-sharp bands, which implied that the gel does not have a structural order [67]. All the samples presented absorption bands at 1082 , 460 , and 600 cm^{-1} (Fig. 5). Those bands indicated the existence of crystalline traces of mineralogical phases, such as quartz, cristobalite, or amorphous silicon [26]. C-S-H gel indicates that pozzolanic reactions were occurring, and it confers the mechanical resistance of the final product.

Fig. 4 XRD patterns of WHRA at different points in the pozzolanic reaction. S=KCl; C=CaCO₃; Q=SiO₂; P=MgO; A=CaSO₄; Ap=Ca₅(PO₄)₃(OH); T= CH₂₄Al₂Mg₆O₂₃; E=Ca₃Al₂(SO₄)₃(OH)26H₂O.

Fig. 5 FTIR of WHRA over time after the lime saturated solution (LSS) test.

As the hydrated product in the case of WHRA (Fig. 4), ettringite was detected as a result of the reaction between the anhydrite in the ashes and the LSS (Fig. 6c). Primary ettringite is a normal product of early Portland cement hydration [45, 55]. Its initial formation does not lead to expansion [68]. The ettringite content increased with the reaction time (Fig. 4), but not all the anhydrite dissolved in the LSS. This was confirmed due to the band at 1100 cm^{-1} showing after 90 days of reaction (Fig. 5). Therefore, this band established the presence of other hydration products combined with sulfur with a low-crystallinity nature. Such components could interfere in the long-term durability of the mortars.

Fig. 6 SEM/EDX test of WHRA after 28 days in contact with LSS: General appearance (a) and ettringite formation (b). $\text{Ap}=\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. $\text{E}=\text{Ca}_3\text{Al}_2(\text{SO}_4)_3(\text{OH})26\text{H}_2\text{O}$.

Table 5. EDX test of WHRA after 28 days in contact with LSS (Fig. 6) (wt.%).

EDX	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl	TiO ₂	MnO
CSH (1)	47.279	28.200	9.731	2.152	2.828	0.274	5.142	1.119	0.439	0.001	0.962	1.873
$\bar{\sigma}$ (+/-)	0.811	0.685	0.251	0.107	0.339	0.051	0.207	0.062	0.061	ND	0.101	0.259
CSH (2)	37.362	34.593	7.903	7.462	3.666	0.002	4.213	1.412	1.039	0.342	0.611	1.395
$\bar{\sigma}$ (+/-)	0.591	0.735	0.198	0.228	0.375	ND	0.172	0.065	0.084	0.057	0.082	0.216
CSH (3)	34.488	44.498	4.955	4.219	2.702	0.002	3.228	2.976	1.431	0.030	0.007	1.464
$\bar{\sigma}$ (+/-)	0.543	0.883	0.138	0.146	0.282	ND	0.136	0.083	0.091	0.007	0.005	0.196
CSH (4)	32.725	43.644	6.555	4.304	1.756	0.021	2.836	6.269	0.365	0.076	0.002	1.447
$\bar{\sigma}$ (+/-)	0.601	1.008	0.189	0.168	0.255	0.006	0.142	0.138	0.056	0.039	ND	0.219
(5)	37.381	9.639	16.293	9.577	18.071	0.002	6.723	0.489	0.321	0.123	0.129	1.253
$\bar{\sigma}$ (+/-)	0.657	0.315	0.381	0.304	1.047	ND	0.252	0.049	0.057	0.045	0.052	0.220
(6)	20.575	20.609	15.383	31.099	0.738	0.780	2.017	1.434	4.856	1.642	0.002	0.864
$\bar{\sigma}$ (+/-)	0.426	0.607	0.383	0.813	0.239	0.090	0.154	0.083	0.248	0.330	ND	0.103

ND: not detected

$\bar{\sigma}$ (+/-) Standard deviation

Hence, it can be stated that the amount of fixed lime was not only caused by the samples' pozzolanic reaction, but also by the formation of other compounds with calcium. In this sense, the phosphates of WHRA reacted with calcium ions, and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) was found by XRD (Fig. 4) and microscopy (Fig. 6a).

On the other hand, as it was shown before [38], sylvite was dissolved in the water of the LSS. It was confirmed by a decrease of its peaks in the solid product after the test (Fig. 4), as well as the characteristic band of sulfate around 1100 cm^{-1} (Fig. 5) [69]. The dissolution of sylvite causes an increase in the alkalinity of the water of the LSS. Therefore, the lime precipitates, causing an interference with the results of the LSS test. In addition, the amount of calcite increased over time due to contact with the atmosphere and the carbonation process [31]. The presence of carbonates was confirmed also by common absorption bands of C–O bonds at 1420 , 875 , and 720 cm^{-1} [26], which is related to calcite (CaCO_3) (Fig. 5). Therefore, pre-treatments in order to reduce the alkali content were necessary. An in-depth study of the hydration products of the P1 and P2 samples is displayed below.

Regarding P1 and P2 (Fig. 7), as well as in the case of WHRA (Fig. 4), the elevation of the baseline in the diffractograms between 15 and 60° (2theta) indicated the presence of amorphous C-S-H gel [33, 37, 54, 59], which was confirmed by SEM-EDX (Fig. 9). Moreover, the FTIR spectra of both samples (P1

(Fig. 8a) and P2 (Fig. 8b)) confirmed the presence of amorphous C-S-H gel with an increasing band over time at 950 cm^{-1} [69]. In these cases (P1 and P2), it was more evident, because there were no interferences with the sulfate bands (Fig. 8). Even so, in terms of the amount of amorphous material, no relevant differences were found between the pre-treatment ashes (P1 and P2) and WHRA. Hence, pre-treatments were not required in order to increase the pozzolanic reaction; nevertheless, the reduction of the alkali content will reduce the expansion risk in the long term.

Fig. 7 XRD patterns for P1(a) and P2 (b). S=KCl; C=CaCO₃; Q=SiO₂; P=MgO; Ap=Ca₅(PO₄)₃(OH); T= CH₂₄Al₂Mg₆O₂₃.

Fig. 8 Infrared absorption spectrum after the LSS test of P1(a) and P2 (b).

In general terms, the composition of the C-S-H gels is commonly defined by its calcium/silicon ratio (Ca/Si), with 1.75 having been established as the optimum value for the Ca/Si ratio [55]. However, pozzolanic additions decrease the Ca/Si ratio values to less than 1, as was shown previously [59]. Table 6 shows the average of 25 EDX tests performed on all the samples (WHRA, P1, and P2). The mean

Ca/Si values of the C-S-H gels of WHRA and P2 were 1.47 and 0.65, respectively (Table 6). In both cases, these values correspond to a C-S-H type I gel ($\text{Ca/Si} < 1.5$) according to the Taylor classification [55]. Ca/Si ratios lower than 1 tend to incorporate higher amounts of aluminum, creating a C-A-S-H gel instead of a C-S-H gel [27], as occurred in P2. This phenomenon is broadly accepted [19,59,70], especially when incorporating aluminum pozzolanic materials, and no interactions in the mechanical requirements were stated.

Table 6. Average values of chemical components by EDX after 28 days of reaction with LSS (wt.%).

	SiO ₂	CaO	Al ₂ O ₃	MgO	FeO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Cl	TiO ₂	MnO	Ca/Si
WHRA	30.004	33.549	8.854	10.727	4.156	0.310	3.244	3.333	2.390	0.821	0.491	2.121	1.473
∂ (+/-)	0.520	0.747	0.229	0.315	0.420	0.041	0.153	0.089	0.137	0.084	0.066	0.283	
P1	26.465	33.683	13.017	10.872	5.375	1.565	3.063	1.016	2.352	0.221	0.330	2.041	1.902
∂ (+/-)	0.395	0.467	0.259	0.279	0.107	0.083	0.078	0.028	0.093	0.020	0.015	0.067	
P2	33.707	16.951	17.126	15.502	4.507	2.271	3.768	0.555	2.582	0.121	0.114	2.795	0.658
∂ (+/-)	0.508	0.273	0.337	0.389	0.104	0.112	0.100	0.022	0.098	0.015	0.015	0.085	

∂ (+/-) Standard deviation

WHRA: water hyacinth root Ash without pre-treatment

P1: WHRA washing with water at 80 °C for 4 h

P2: WHRA washing with water at 23 °C for 24 h. The water was replaced every 8 h.

Compared with WHRA, in P1 and P2, the ettringite phase disappeared as a reaction product, as well as sylvite (Fig. 7), because sulfates and potassium were dissolved during the pre-treatment, as was stated in Section 3.1. On the other hand, P1 and P2 were rich in magnesium (Table 2), which was identified as a periclase (MgO) phase by XDR (Fig. 7). When the P1 and P2 ashes were in contact with LSS, hydrotalcite ($\text{CH}_{24}\text{Al}_2\text{Mg}_6\text{O}_{23}$) was identified as the hydration reaction phase by XDR (Fig. 7) and by SEM (Fig. 9b) due to the reaction of magnesium as replacement for calcium. Therefore, as can be seen in Fig. 9, aluminum and magnesium were incorporated into the hydrated products.

Fig. 9 SEM/EDX test of P1 (a) and P2 (b) after 28 days in contact with LSS. * = C-S-H gel within

aluminum and magnesium; # = C-S-H gel within calcium aluminum and magnesium; T=
 $\text{CH}_{24}\text{Al}_2\text{Mg}_6\text{O}_{23}$; Ca= CaO.

As it was shown previously in WHRA, the potassium fixed the calcium ions in the hydration process, and as a result, hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ was kept in the final reaction (Fig. 7). This was also confirmed by FTIR spectra (Fig. 8). The characteristic hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) bands occur at 1100, 1080, 1040, 850, 600, and 575 cm^{-1} [70], but they overlapped with the detected bands. However, the existence of the phosphate is evident due to the presence of its characteristic band located around 567 cm^{-1} [30].

Thus, it was concluded that the samples could react with calcium ions in order to give both C-S-H gel with different element interferences and other compounds with calcium. These incorporations into C-S-H gel, as well as the calcium compounds, could affect the mechanical properties of the final product.

3.2.2. *Strength Activity Index*

Contrary to expectations, the addition of the ash did not improve the mechanical performance of the mortars (Table 7). After 90 days of curing time, the compressive strength was 48% (25-WHRA), 46% (25-P1), and 44% (25-P2) lower than that of the control OPC sample. This implies that the 25% replacement percentage is not suitable for structural purposes [52]. Furthermore, the loss of strength was similar to that in previous studies developed with WHPA [43], but in the case of WHPA, the silica content was lower and amorphous material was not detected by XRD, as discussed previously in Section 3.2.1. These two parameters suggest that better mechanical behavior should be displayed in the root ashes than in the petiole ashes, but this expectation was not realized.

On the other hand, the results were in agreement to the water absorption by the blends not only at 28 days of curing time but also at 90 days. Indeed, the mechanical strength values increased at 90 days, which could be due to the slowdown of the hydration product reactions due to the pozzolanic behavior of the ashes [45]. The WHRA addition increased the porosity of the sample (Fig. 10), which could be due not only to the hydration products, but also to the increase of water content to achieve the same workability. Water absorption at 90 days of curing in the samples was lower than the values at 28 days

due to the fact that new hydration product were formed because of the pozzolanic reaction. Therefore, the porous structure was refined.

Table 7. Compressive strengths of mortars (MPa) and water absorption coefficient (%) with 25% ash addition.

Samples	Mechanical strength (MPa)				Water absorption (%)			
	28d	∂	90 d	∂	28d	∂	90d	∂
OPC	59.61	± 0.77	66.11	± 1.50	5.20	± 0.079	5.36	± 0.064
25-WHRA	29.22	± 0.99	34.15	± 0.67	6.24	± 0.079	5.73	± 0.046
25-P1	30.72	± 1.30	35.44	± 0.68	6.14	± 0.060	5.71	± 0.029
25-P2	27.74	± 0.88	37.13	± 0.85	6.37	± 0.075	6.18	± 0.061

∂ : Standard deviation

On the other hand, the 25% replacement was fixed because of the fly ash standard [52]. However, previous studies of alternative pozzolans have stated that the optimum percentages of replacement are 5%–10%. This was the case for waste ashes of bamboo leaf [35], wheat [34], corncob [71, 72], banana leaf [36]; the optimum percentage was 20% for elephant grass [37] and the combustion of biomass [58, 73, 74], among other materials. This implies that a lower percentage of replacement could vary the performance of the blends.

Furthermore, the results were influenced by different factors apart from the replacement percentage. In fact, the LSS test supposes that fixed lime is caused by the sample due to the amorphous silicon reaction (pozzolanic reaction). However, the hydration product analysis stated that just part of the fixed lime reacted with silicon to produce C-S-H gel. In fact, the presence of other elements, such as magnesium or phosphate (Table 2), coming from the samples reacts given other products without mechanical performance. This was the case with the hydrotalcite phase ($\text{CH}_{24}\text{Al}_2\text{Mg}_6\text{O}_{23}$) and the hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), which were detected in all of the samples as a reaction product (Figs 4 and 6).

All the samples studied (WHRA, P1, and P2) showed high levels of magnesium (Table 2). As it was

reported before [75], magnesium inhibits C-S-H nucleation and high magnesium concentration could produce interchange reactions between Mg^{2+} and Ca^{2+} ions. Under these circumstances, calcium silicates and calcium aluminates were replaced by magnesium silicate [76, 77]. Higher amounts of magnesium were also found previously in WHPA [43], as well as in other alternative pozzolans from waste [73, 78], and the loss of mechanical properties was similar.

Moreover, WH ash present pollutants in its chemical composition, such as heavy metals, because of WH's ability to fix them in its chemical structure (Table 4). Heavy metals could be incorporated into C-S-H gel formed by pozzolanic reactions [22, 79], but the interaction was difficult to identify because of the low crystallinity [21]. It has been stated that their interaction reduces the compressive strength at earlier times [58, 80].

In spite of the loss of mechanical properties, it was found that WHRA could react with calcium ions, and it could incorporate magnesium and phosphate into its hydration products. It was supposed that pollutants were also incorporate in them. Therefore, a fixed element analysis was developed to confirm this assumption. Because no significant differences were found in terms of mechanical properties and pozzolanic reactions, pre-treatment ashes were not include in the fixed element analysis.

3.3. Leaching/fixed pollutants in blended cements

As mentioned above, interferences during hydration reactions provoke contaminant element fixation. Therefore, a fixed element study was developed with respect to 25-WHRA in order to confirm the pollutant fixation in the WH–cement composites.

Table 8 shows the pollutants detected in the different lixiviant samples. First of all, there are no heavy metal listed, excepted for vanadium in the ashes, which was fixed in 25-WHRA. Therefore, heavy metals are part of hydration compounds. Instead of heavy metals, there are other leaching elements, such as boron or barium, which are also fixed in the cement. On the other hand, the incorporation of WHRA in the cement matrix (25-WHRA) improved the fixed potassium, as well as sodium, sulfur, and chloride. The fixation percentages, compared with the theoretical values, were 73.78%, 55.28%, 92.81%, and 59.08%, respectively. As mentioned above, pollutants are present in WHRA (Table 4), but

they were not found in the leaching study. Thus, they were fixed successfully in the WHRA–cement matrix.

Table 8. Detected leaching elements by ICP-OES (mg/L),

Elements	Leaching (mg/L)				LD
	L-WHRA	L-OPC	L-25WHRA	Theoretical Value (*)	
Al	0.277	0.452	0.310	0.015	0.006
B	1.952	-	0.075	0.107	0.005
Ba	0.142	2.643	0.791	0.008	0.001
Ca	95.034	679.595	275.726	5.227	0.001
K	6227.630	85.446	89.782	342.520	0.001
Mg	0.749	0.018	0.005	0.041	0.001
Na	724.273	15.393	17.814	39.835	0.035
S	1154.230	2.802	4.561	63.483	0.120
Si	14.106	0.345	1.354	0.776	0.013
V	0.035	-	-	-	0.002
Cl	5724.903	25.904	128.831	314.870	0.500

(*) Theoretical leaching value (by %) is the percentage which corresponds to the WHRA content in the mass of the mortar. The mortar consists of 1350 g of sand, 337.5 g of cement, 112.5 g of WHRA, and 25 g of water. Therefore, WHRA content in the total mass of mortar would correspond to 5.5 wt.%.
LD: limit detected.

In order to confirm this result, pollutant mapping of 25-WHRA mortar by BSE-EDX was performed (Fig. 10). Each element was represented by one color, and an increase in saturation indicates a higher concentration of the element. In this way, the elements displayed in Fig. 11 are Cr, Zn, Ti, Hg, Cu, Ni, and Zr. All of them are minor components present in WHRA (Table 3), and their presence in OPC (Fig. 11) was lower compared with that in 25-WHRA. Therefore, it can be concluded that they are fixed in cement matrix.

Finally, there are no toxic elements in L25-WHRA (Table 9), so bioaccumulation in food chains does not occur. This would not be the case such elements were available as in the proposals of previous studies [7, 8, 10, 13–16]. Hence, this study confirmed the viability of the use of WHRA as an addition in cement matrices for pollutant immobilization.

Fig. 10 Pollutant mapping by BSE/EDX of 25-WHRA

Fig. 11 Pollutant mapping by BSE/EDX of OPC.

4. Conclusion

The huge biomass generated by WH and its great capacity to fix pollutants in its roots makes the sustainable valorization of WH biomass difficult to achieve, because it promotes the accumulation of toxic elements in food chains. Despite the fact that the immobilization of pollutants in cement matrices is a common sustainable practice, none of the previous WH–cement composite studies analyzed the effect of minor components in WH in pozzolanic reactions. Moreover, it was not clearly stated in the literature which part of the plant could be most efficiently used for the proposed pozzolanic additions. Therefore, in this research, we proposed the use of WH root ash as an alternative addition to cement matrices in order to immobilize the pollutants in WH biomass. Two water-based pre-treatments were tested as well. Chemical characterization and pozzolanic analysis of the samples were conducted. In addition, a pollutant fixed analysis was developed.

According to the results, WHRA–cement composites can fix pollutants from WHRA due to their amorphous materials. Contaminant substances are incorporated into hydration products thanks to WHRA’s ability to react with calcium ions. Hence, contaminant substances, such as Hg, Zr, Ti, and V, among others, are immobilized in WHRA–cement composites.

In addition, it could be concluded that WHRA are the most efficient part of the plant to use as the proposed addition. Amorphous material coming from WHRA react with calcium oxide, producing C-S-H gel, which is characteristic of pozzolanic additions. However, the interference of elements such as magnesium and phosphate in the C-S-H gels provoked the reduction of the compressive strength of the samples with 25% of cement replacement. The reduction of the compressive strength was 48% (25-WHRA), 46% (25-P1), and 44% (25-P2) after 90 days of curing. Finally, pre-treatments were not efficient in terms of increasing pozzolanic reactions and mechanical requirements. Thus, a low percentage of WHRA can be used as a pozzolan addition in non-structural applications.

We consider this paper to be a preliminary study. It is clear that the previously proposed applications of WH generate pollutant waste. In addition, physical extraction and open-air combustion continue to be the most effective solutions for managing this pest in low-income countries. Both cases, WH waste could be used as an alternative addition in order to create a new material for non-structural elements.

This application promotes reuse of pollutant waste, and therefore, it is a low-cost material and an eco-friendly composite. In fact, the cost reduction of such composites will be directly proportional to the amount of ashes added, because the raw material is waste. In addition, especially in low-income countries, WH biomass valorization promotes the eradication of the WH pest, because the extraction and combustion of WH are more profitable than the extraction of raw material from quarries and cement fabrication. Therefore, the proposed applications of this material are street furniture, paving, or precast products. However, future research regarding durability should be conducted.

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