ROLE OF SOME TREATMENTS ON ENHANCING THE ECO-
FRIENDLY UTILIZATION OF LIGNOCELLULOSIC WASTES IN
PRODUCTION OF CEMENT-FIBER BRICKS

Altaf H. Basta,* Magdy Z. Sefain, and Iman El-Rewainy

Rice straw (RS) and sawdust (SD) were evaluated for the manufacturing of fiber-cement bricks. The utilization of these bio-wastes will contribute to the reduction of the environmental impact of waste disposal. Pretreating the fiber wastes, mechanically and/or chemically, was carried out before mixing them with cement and the appropriate amount of water. This approach was done for trials to reduce the tendency of fibers to absorb water, and consequently overcome the side effects of exposing the fiber-bricks to humidity. Different chemical treating agents, based on organic and inorganic materials, were used, e.g., gelatin-hexamine mixture, sodium silicate, and linseed oil. The results obtained show that the investigated organic treatments, especially linseed oil, were effective to reduce the water retention value (WRV) of RS and SD by 60% and 65%, respectively. The treatment provided bricks with compressive strengths of 4.9 MPa and 5.4 MPa, respectively. According to the Engineering Encyclopedia of Building standards, these values are suitable for construction purposes. The bricks manufactured from linseed oil-treated fibers with cement and Nitobond AR may be suited for load-bearing walls, since the compressive strength reached is 7.8 to 8.6 MPa.

Keywords: Biowastes; Lignocellulosic wastes utilization; Rice straw; Sawdust; Cemented lignocellulosic composite; Fiber-cement bricks; Building materials.

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INTRODUCTION

In Egypt, agricultural waste accumulates in huge quantities ranging from 22 to 26 million dry tonnes per year (Agriculture ministry report 2009). Part of this amount is used as food for cattle and as fuel to produce energy. Another large amount of this waste remains unused. Therefore, the waste is burned in the open atmosphere, causing environmental pollution. Among this waste is rice straw, which is difficult to handle and store. Rice straw has been evaluated for its mechanical properties in straw-clay composites (Haygreen 1989). Unfortunately, the material produced possesses unacceptable waterproof properties. Rice straw has also been used to bind clay in built-up walls, as well as in the manufacturing of bricks for firing. Firing of straw-clay composites results in biomass loss, which can result in a lighter-weight product and improved insulation properties (Sera et al. 1990a; Beagle 1981). Wood sawdust waste also is accumulated in countries all over the world and causes certain serious environmental problems and health hazards.
In preparing for the present work, a decision was made to study the possibility of producing cemented fiber bricks by using some of these wastes and exploring the usability of the material in this kind of application. Different treatments were applied to reduce the tendency of these wastes to absorb water, and consequently to improve the dimensional stability of building materials produced. On the subject of utilizing lignocellulosic waste in the production of building elements, Udoeyo and Dashibil (2002) used sawdust ash as a replacement for ordinary Portland cement. In addition, Esmeralda et al. (2004) added CaCl₂ to wood-Portland cement-water systems to enhance its compatibility. Brown (2006) added alkoxysilanes and calcium salts, such as acidic phosphate or silicon containing alkoxide, to reduce hydroxyl content in fresh, setting, or hardened concrete. Cao et al. (2006) enhanced the flexural properties of bagasse-cement composites via pretreatment of bagasse with 1% NaOH solution, and after the alkali treatment, fibrillation occurred and the surface of the treated fibers became finer. Aamr et al. (2008) investigated the potential utilization of flax by-products in cement-containing matrices, as aggregate additives, to develop lightweight construction materials that could be used for load-bearing walls. A material containing different amounts of flax particles, ranging from 0% to 10% as partial replacement of cement, was aerated by artificially entrapping air voids by means of a protein air-entraining agent. They found that the use of calcium chloride reduced the inhibitory effect on cement hydration, resulting in a “low inhibition” classification. Results also showed that attractive properties, such as improvements in workability and air-entrainment, were achieved with increasing amounts of flax particles. Subjecting the samples to hardening led to the production of composites with compressive strengths compatible with the basic requirement of lightweight construction materials, corresponding to RILEM “class III” recommendations. The production of cement-bonded composite building products using arhar stalks was reported by Aggarwal et al. (2008). They found that the extractives adversely affected the cement hydration and strength development processes. Compressive strength for 28-day composite was reduced by 13% to 20% at 1 to 2% concentration of extractive powder. The strength properties of arhar stalks-cement composites were found to satisfy the minimum requirements of International Standard, (ISO:8335, 1987).

EXPERIMENTAL

Materials and Analyses

Lignocellulosic wastes

The rice straw that was collected from Egyptian farms, and the sawdust was obtained from Egyptian factory waste. These materials, which can be described as available agricultural and industrial wastes, were subjected to chemical and physical analyses, and the data obtained from standard reported methods are shown in Table 1.

Cement material

Normal Portland cement, with the following specifications, was supplied from Suez Company for Cement.

Silica: 18 to 25%,
Alumina: 3 to 10%,
Iron oxide: 2 to 5%,
Lime: 60 to 66%,
Magnesia: 0.5 to 4%,
Sulfuric anhydride: 0.5 to 2.75%, and
Water and carbonic anhydride to 1- 3%

Chemicals
- Commercial gelatin, hexamine and linseed oil,
- Sodium silicate and aluminum sulphate were purchased from Adwic Chemical Co., Egypt, and
- Nitobond acrylic (AR) was delivered from Fosroc Co., Egypt. The manufacturer describes this product as non-flammable and non-toxic, providing excellent bond to concrete, masonry, stone work, plaster and block board, improving tensile and compressive properties.

<table>
<thead>
<tr>
<th>Table 1. Chemicals and Physical Analyses of used Lignocellulosic Wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Analysis</td>
</tr>
<tr>
<td>Chemical Analysis:</td>
</tr>
<tr>
<td>- α- cellulose, % (IV/29 to Merkblatt Zellcheming)</td>
</tr>
<tr>
<td>- Pentosans, % (Jayme and Sarten 1940)</td>
</tr>
<tr>
<td>- Lignin as Klason lignin (TAPPI Method T222 05 – 54)</td>
</tr>
<tr>
<td>- Ash, % (Doree method)</td>
</tr>
<tr>
<td>- MeOH-Benzene extractives, %</td>
</tr>
<tr>
<td>Physical Analysis:</td>
</tr>
<tr>
<td>- Water Retention Value (Jayme et al. 1958)</td>
</tr>
<tr>
<td>- X- ray Analysis (scanning was carried out between 5 to 35º (2θ) at 38 Kv and 16 mA.</td>
</tr>
<tr>
<td>- The degree of order</td>
</tr>
<tr>
<td>- d- spacing</td>
</tr>
<tr>
<td>- Crystallite size</td>
</tr>
</tbody>
</table>

Treatments of the Lignocellulosic Wastes
Different treatments were carried out to improve the water resistance properties of RS and SD wastes. In this respect, the prepared samples were mechanically as well as chemically treated with different organic and inorganic materials. To evaluate the success of these treatments, water retention values (WRV) were determined (Jayme et al. 1958).

Grinding and screening
To study the effect of fiber length and size on the properties of the cemented lignocellulosic bricks, samples were ground and screened to different mesh sizes using an electric mill. Sieving under vibration was carried out in order to separate the fibers into three categories according to their size. The first coarse size was with fiber length less than 2.5 mm and bigger than 1.25 mm, the second was a medium size with fiber length less than 1.25 mm and bigger than 0.8 mm, and the third was a fine size, with length less than 0.8 mm. The percentages of coarse, medium and fine fibers in “100 gm” rice straw and sawdust samples are recorded in Table 2.
### Table 2. Weight Percentages of Coarse, Medium, and Fine Particle Size in Rice Straw and Sawdust

<table>
<thead>
<tr>
<th>Lignocellulosic wastes</th>
<th>Coarse</th>
<th>Medium</th>
<th>Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw</td>
<td>13</td>
<td>30</td>
<td>57</td>
</tr>
<tr>
<td>Sawdust</td>
<td>5</td>
<td>49</td>
<td>47</td>
</tr>
</tbody>
</table>

*Chemical treatments with organic substances*

The prepared samples with different mesh sizes were treated with a gelatin-hexamine mixture and linseed oil in different ratios, and then their water retention values were measured.

**Treatment with gelatin-hexamine mixture:**

Two concentrations of gelatin-hexamine solutions were prepared by mixing 0.5% (w/w) of gelatin with 0.5% (w/w) hexamine; and 0.5% gelatin with 1% solution of hexamine. This was followed by treating the wastes in a ratio of 20/1. The treated fibers were split into four portions (a-d), in order to study the effect of concentration together with contact time between the waste and the mixture on the waste’s WRV.

- a - The first portion was dipped in the first concentration of gelatin-hexamine mixture (0.5%) for 5 minutes at room temperature followed by heating at 60 °C for 30 minutes.
- b- The same previous experiment was carried out by dipping the second portion for 30 minutes in the previous gelatin-hexamine concentration at room temperature, and then heating at 60 °C for 30 minutes in an electric oven.
- c- In another experiment, samples were dipped in 0.5:1 gelatin-hexamine mixture for 5 minutes at room temperature, followed by heating at 60 °C for 30 minutes.
- d- The fourth portion was dipped in 0.5:1 gelatin-hexamine mixture for 30 minutes at room temperature (28 to 30 °C) followed by heating at 60 °C for 30 minutes.

**Treatment with linseed oil:**

Linseed oil was added to the lignocellulosic wastes of different mesh sizes in different ratios (20, 40, and 60% w/w based on the dry weight of the raw material) at room temperature. Oil was homogeneously distributed by manual stirring. Then, the samples were left to dry in air (28 to 30 °C), followed by subjecting them to a thermal treatment for 2 hr. at 120 °C.

**Treatment with inorganic substances**

The selected lignocellulosic wastes were treated with different concentrations of sodium silicate solutions (5 to 25 wt% /based on the dry weight of the wastes), followed by treatments with the same concentrations of each of aluminum sulphate, calcium chloride, magnesium chloride, or calcium oxide solution. The latter solution in the form of Ca(OH)₂ was prepared from fresh conversion of calcium carbonate to calcium oxide in a muffle furnace at 800 °C and cooled in desiccator, to prevent the reverse formation of...
calcium carbonate, followed by dissolution in water and cooled again, forming a turbid solution, with pH-value 12.9. Each treatment was carried out in a closed system for 10 minutes, left to dry in air, and then at 100 °C for three hours. The effect of adding other inorganic compounds, such as magnesium chloride, calcium chloride, and calcium oxide on WRV was also studied.

Manufacturing of Bricks

The traditional method for the preparation of bricks from cement was carried out by gradually adding, with mixing, the water to Portland cement, in a ratio of 1:3, for 3 minutes (Weatherwax 1964). The prepared mixture was poured into 5 cm dimensional cubic moulds under manual compaction, ensuring that air bubbles were not trapped in the fresh mixture. The filled moulds were kept in air for 15.5 hours, and then in a controlled room temperature of 20 °C in order to attain the final setting of the sample. The brick samples were subjected to ageing in desiccators at a temperature of 20 °C and 65% relative humidity for 28 days hydration period (Egyptian Standards 1975).

In case of the preparation of bricks from lignocellulosic waste and cement, the method was carried out by mixing 10% of untreated and treated wastes with 90% cement in the same previous manner but with a calculated amount of water, using the following empirical relationship (Simatupang 1979),

Water (liters) = \[0.35 \times C + (0.3 - MC)\] / \(F\)  

(1)

where \(C\) is the cement weight (g), \(MC\) is the fiber moisture content, and \(F\) is the oven-dried fiber aggregates (g).

Properties of Bricks

The compressive strength of bricks was tested to determine the field of application of the building product, according to standard specifications of building elements recorded in the Egyptian Engineering Encyclopedia (1975). The brick density \(D\) was calculated from the relation: \(D = W/V\) gm/cm\(^3\), while the water resistance was determined by immersing the produced cemented-lignocellulosic bricks in water (at 20-22 °C) for 24 hours after determination of its volume \(V_1\) and its weight \(W_1\). The water level was maintained 5 cm higher than the upper surface of the immersed bricks. The excess water was wiped off with a damp cloth; then for each sample, the volume \(V_2\) and weight \(W_2\) after immersion were determined. The change in volume of the brick is a good pointer to its dimension stability. Therefore, it can be measured from the difference between the volume before and after immersion. In the same manner, the change in weight is calculated, which indicates the water absorbance of the bricks.

Compressive strength of the prepared bricks was measured by using an Instron Universal Testing machine. The specimens were tested after a hydration period of 28 days and after heating the samples at a temperature of 105 °C in an electric oven for 6 hours. The specimens were exposed to the load until fracture occurred. The fracture load was determined as \(N\), and the compressive strength of the exposed surface of brick as MPa.
Each reading of the foregoing properties, as reported below, was the mean of three measurements.

RESULTS AND DISCUSSION

Effect of Treatment Process on Water Retention Value (WRV)

For the case of mechanical treatment, Table 3 shows that coarse fibers of sawdust exhibited relatively lower WRV than other screened fibers, whereas the WRV was reduced from 80 to 63%. However, for rice straw there was no significant or only a slight difference in WRV noticed between the different mesh sizes (140 to 136%). Therefore, for economic considerations, a decision was reached to use the whole ground sample for further studies.

Table 3. Water Retention Value Percentages (WRV) of Different Mesh Sizes of Rice Straw and Sawdust

<table>
<thead>
<tr>
<th>Lignocellulosic wastes Type</th>
<th>Water Retention Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coarse</td>
</tr>
<tr>
<td>Rice straw</td>
<td>136 ± 5.5</td>
</tr>
<tr>
<td>Sawdust</td>
<td>63 ± 1.7</td>
</tr>
</tbody>
</table>

For the chemical treatments with organic substances, Fig. 1 shows that increasing the percentage of hexamine from 0.5% to 1%, and the contact time of the fibers with gelatin-hexamine mixture, led to improvement of the water resistance of the fiber wastes. Reductions of WRV were 38% and 36% in the case of RS and SD, respectively. As can be seen from Fig. 1, the sawdust samples treated with gelatin-hexamine mixture (method d, page 4) showed the lowest WRV. This observation is ascribed to the conversion of the soluble form of gelatin into an insoluble form due to the reaction with formaldehyde, producing a layer around the fibers, and consequently reducing their accessibility to water. The proposed mechanisms for cross-linking are as follows:

1- Degradation of hexamine occurs in the presence of water during the drying process with the liberation of formaldehyde, which acts as a cross-linking agent. Here, the liberated formaldehyde reacts with the gelatin as in Eq. (1) (Sydney 1985). The reaction then continues as the resulting product acts as a cross-linking agent with cellulose according to the mechanism given in Eq. (2).

\[
\begin{align*}
\text{O} & \quad \text{O} \\
-\text{C-NH-} + \text{CH}_2 \text{O} & \quad \leftrightarrow \quad -\text{C-NCH}_2 \text{OH} \\
\end{align*}
\]
The second mechanism can be elucidated by the presence of a lone pair of electrons on the nitrogen atom of the hexamine molecule, which can form a hydrogen bond with the cellulose, and hence it acts as a cross-linking agent with the cellulose molecule.

In the case of treatment with linseed oil, Fig. 2 shows that increasing the percentage of linseed oil decreased the value of WRV of rice straw and sawdust fibers. The lowest WRV was observed after treatment with 60% linseed oil, followed by thermal treatment for 3 hours at 120 °C. The WRV values were reduced from 140% to 85% and from 80% to 30% in the case of RS and SD, respectively. The role of linseed oil in improving the WRV is based on the fact that linseed oil forms a layer around the fibers, blocking its pores, which reduces the amount of water absorbed.

In the case of treatment with sodium silicate solution, one solution of the following salts (aluminum sulphate, calcium chloride, magnesium chloride, or calcium oxide) was used, followed by thermal treatment for 3 hours at 100 °C. Figure 3 shows that the best results were obtained after treatment with (15%) sodium silicate together with aluminum sulphate. The percentages of reduction (improvement) in WRV reached ca. 46% in both RS (from 140% to 75%) and SD fibers (from 80% to 43%). This is ascribed also to the formation of an insoluble film around the fibrous wastes.

\[ \text{O} \quad \hat{\mid} \quad \text{C-NCH}_2 \text{OH} + \text{Rcell OH} \quad \leftrightarrow \quad \text{O} \quad \hat{\mid} \quad \text{C-NCH}_2 \text{ORcell} + \text{H}_2 \text{O} \]
In comparison with the previous investigated treatments, under conditions that provide high reduction in WRV, Fig. 4 shows that chemical treatments were more successful in reducing WRV than mechanical treatments. Therefore, rice straw and sawdust fibers treated by chemical agents (gelatin hexamine, linseed oil, and sodium silicate-alumium sulphate), were used for further studies of the effect of the type of treatment on the properties of the final bricks.

**Effect of the Type of the Chemical Treatment on Bricks Properties**

The effects of the selected chemical treatments on the brick properties were studied. The results are tabulated in Table 4 and illustrated in Figs. 5 and 6.

It is noticed that (Table 4) untreated and treated rice straw yielded bricks with lower density than sawdust. However, cemented-sawdust bricks had higher values of compressive strength, dimensional stability, and water resistance. As shown, the best chemical treatment, producing bricks with good mechanical and physical properties, was that made by treating the fiber wastes with 60% linseed oil, followed by hardening for 2 hrs at 120°C. The compressive strengths of bricks obtained from treated RS and saw dust were 4.9 MPa and 5.4 MPa, respectively. These types of bricks are suitable for construction applications.

On manufacturing of bricks by the same previous treated fibers with cement, but with adding 10% Nitobond AR, Figs. 5 and 6 show that further improvement was achieved on adding Nitobond AR., especially in the case of linseed oil-treated RS and SD fibers (6.7 and 7.8 MPa). These types of bricks are suitable for applications as load-bearing walls. These results nearly in agreement with those previously obtained by Kasai et al. (1998), on using wood particles of construction wastes (compressive strength 5 to 8 MPa).
Fig. 3. Effect of the concentration of sodium silicate and additives on WRV percentage of rice straw (upper) and sawdust (lower)
Correlating the properties of the foregoing bricks (Figs. 5 & 6), and based on the values of $R^2$, it is obvious that, for bricks made from treated RS, there were good linear relationships between compressive strength and density, against water absorption (Figs. 5a & 5b). This indicates that the change in any property of a brick as a result of treating the RS, significantly affects other properties. This trend was however not observed in the case of bricks made from treated SD (Figs. 6a & 6b). This may be ascribed to the relatively higher degree of order and lignin content of saw dust substrate compared to RS (Table 1). This leads to restricting the crosslinking of the hydroxyl groups of cellulose with the methylol groups of gelatin (equation 2, section 3.1). Consequently the change (improvement) in water resistance of bricks does not follow the trend of other properties. This view is emphasized from the increasing of the $R^2$ values of these relations to 1.0, after omitting the water absorption values of bricks related to gelatin-hexamine treated fibers, as shown in the following polynomial equations;

For compressive strength against water absorption $(R^2 = 1.0)$,

$$Y_1 = 655 + 345.04X + 68.83X^2 - 6.435X^3 + 0.2842X^4 - 0.0048X^5$$  \hspace{1cm} (3)

For Density against water absorption $(R^2 = 1.0)$,

$$Y_2 = 59617 - 31173X + 6267.8X^2 - 588.63X^3 + 26.05X^4 - 0.439X^5$$  \hspace{1cm} (4)

where, $Y_1$ and $Y_2$ are compressive strength and density of bricks, respectively; while $X$ is the water absorption.
Fig. 5-a. Effect of treatment with different investigated treatments on strength and density of bricks produced from rice straw and their relation.

Fig. 5-b. Effect of treatment with different investigated treatments on water resistance property of bricks produced from rice straw, and its relation with strength and density properties.
Fig. 6-a. Effect of treatment with different investigated treatments on strength and density of bricks produced from saw dust and their relation.
Fig. 6-b. Effect of treatment with different investigated treatments on water resistance property of bricks from saw dust and its relation with strength and density properties
Table 4. Effect of Untreated and Treated Rice Straw and Sawdust Fibers on Mechanical and Physical Properties of Bricks

<table>
<thead>
<tr>
<th>R.M. status</th>
<th>Compressive strength MPa</th>
<th>Density kg/m³</th>
<th>Dimensional change %</th>
<th>Water absorbance %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rice straw</td>
<td>Sawdust</td>
<td>Rice straw</td>
<td>Sawdust</td>
</tr>
<tr>
<td>Untreated samples</td>
<td>0.65±0.08</td>
<td>2.7±0.18</td>
<td>1360±9.08</td>
<td>1600±10.4</td>
</tr>
<tr>
<td>Treated with gelatin-hexamine mixture</td>
<td>3.1±0.58</td>
<td>4.7±0.72</td>
<td>1320±11</td>
<td>1560±8.0</td>
</tr>
<tr>
<td>Treated with linseed oil</td>
<td>4.9±0.53</td>
<td>5.4±0.64</td>
<td>1500±8.4</td>
<td>1614±14.1</td>
</tr>
<tr>
<td>Treated with sodium silicate+ aluminum sulphate</td>
<td>1.1±0.12</td>
<td>3.5±0.53</td>
<td>1038±5.7</td>
<td>1420±6.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

From all the foregoing results, the following conclusions can be drawn:

1. Mesh size of the lignocellulosic wastes, obtained by mechanical treatment, has a minor effect on its water retention value (WRV). The water resistance of screened sawdust was higher than that of rice straw.

2. It is possible to reduce the WRV of the lignocellulosic wastes by treating their fibers with different types of reagents. Using 60% linseed oil as treating agent, followed by hardening for 3 hours at 120 °C achieved the best improvement in water resistance, compared to other chemical treatments (gelatin-hexamine, and sodium silicate-aluminum sulfate). In this case the reduction was from 140 to 85%, and from 80 to 36%, for the cases of RS and SD, respectively.

3. The best quality fibers-cement bricks were produced by replacing 10% of the cement by 10% of pretreated RS or SD fibers with 60% linseed oil and adding 10% Nitobond AR during mixing. According to the Engineering Encyclopedia of Building Standards this type of fiber-cement bricks would be suitable for applications as load-bearing walls, since the compressive strength reached 7.8 to 8.6 MPa.
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