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PRODUCTION AND CHARACTERISATION OF AMORPHOUS SILICA FROM RICE HUSK WASTE

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Abstract

Rice covers about 1% of the earth's surface. Rice husk is the major by-product of the rice-processing industries which must be appropriately managed. On average 20% of the rice paddy is husk.

The major constituents of rice husk are cellulose, lignin and silica. During growth, rice plants absorb silica and other minerals from the soil and accumulate it into their structures. Its composition varies with the diversity, climate and geographic location of growth. The high grade of silica in the husk opens a possibility for its valorisation. Through thermal treatment by calcination, with or without energy recovery, the ash obtained is constituted by amorphous silica with high porosity having potential application as ligand in construction materials, catalyst support, metals adsorbent, insulation or ceramics, among others.

In the research developed, the rice husk was processed by washing, acid leaching and calcination in order to produce an ash, which was characterized aiming at assessing possible valorising solutions. The chemical treatment involved water washing for partial purification of the husk, and leaching with diluted sulphuric acid solution, allowing obtaining high metals removal efficiency, decreasing at least 90% of the initial content of contaminants (K, Fe and Mn). After calcination at 540ºC for organics decomposition, the final ash consisted in white colour amorphous silica as confirmed by XRPD analysis, being characterized by SEM to evaluate the microstructure. The results showed that after calcination the rice husk ash had a very porous, alveolar and even tracery morphology, which seems promising for applications requiring high reactivity, such as in construction materials and technical ceramics.

1- INTRODUCTION

Rice grows on every continent except Antarctica, covering about 1% of the earth's surface. Rice husk is the residue generated on the processing of rice. In this process, called rice milling, the paddy or rough rice is treated to remove the husk and the bran layers, producing a white rice kernel free of impurities. On average, it is estimated that about 20% of the rice paddy is husk, the internal bran layer constitutes about 11% and the finished rice is therefore 69% of the initial product. Since rice is the most produced cereal all over the world, totalising about 720 million tons of paddy annually (equivalent to 482 million tons of milled rice) [1], the resulting husk constitutes a high volume waste material with costs for the companies.

Several components of the rice husk are interesting concerning its potential valorisation, namely energetic for the organics (about 75-80wt%, essentially cellulose, hemicellulose and lignin) and materials valorisation for minerals (about 15-20wt%, mainly silica).

The rice husk has no commercial value due to its hardness, fibrousness and abrasive nature, being an underused biomass resource. However, it is normally used because of its high caloric content (about 16 720 kJ/kg), as an alternative source of heat to generate hot gases for the drying of the cereal itself. This corresponds to 50% of the thermal capacity of a good quality bituminous coal and about 33% of the thermal capacity of the oil [2].

Besides thermal valorisation above referred, there are several options of materials valorisation to produce a silica-rich ash by calcination (rice husk ash, RHA) for use in construction materials, insulation or ceramics [3]. Other applications include catalyst support, fillers (e.g. in paper, paint, rubber, polymers) and other several types of additives, abrasives, insulators and pollutant absorbers/adsorbents. Silica ash, with amorphous nature, has high value as cement replacement or additive [4-6], in the zeolites production [7] and other ceramic applications [8]. Under appropriate conditions, an ash containing porous/activated carbon can also be produced [9-11].

Although various research studies concerning the production and application of RHA have already been made, there are still gaps regarding the optimization of treatment conditions and its relationship with the properties of the final RHA. In this sense, for producing high reactive and pure silica, some conditions are crucial in order to obtain an amorphous structure and the absence of unreacted carbon.

In this paper, laboratory studies on the chemical and thermal treatment of rice husk for producing amorphous silica are presented, aiming at contributing for a better knowledge about the appropriate conditions to achieve a good quality product.

2- MATERIALS AND METHODS

Rice husk was collected in a rice processor. The process developed in this work involved three main steps: washing, leaching and calcination (or incineration). In the washing step, the rice husk was mixed with water, for 15 min at room temperature, using a liquid/solid (L/S) ratio of 20 L/kg. At the end the solids were separated by settling and filtration and were dried at 60ºC in an oven. In the second step, the leaching was carried out with sulphuric acid solutions, using a reflux boiling apparatus, for 2 hours and an L/S ratio of 10 L/kg. The solids, after separation by settling and filtration, were washed with water, to remove the acid retained, and therefore dried at 60ºC. The calcination at 540ºC for 2 hours using a muffle furnace (Carbolite AAF-1100) was the last step where a final ash was obtained.

At the end of each above referred processing steps, rice husk samples were collected for analysis of the contained metals. The method used was acid digestion in a microwave furnace

(CEM MDS 2000) followed by determination of elements by atomic absorption spectrometry (Thermo Elemental Solaar 969).

The final rice ash obtained was also characterized by X-ray powder diffraction (XRPD, Philips PW 1830) in order to evaluate its chemical and structural characteristics, and by scanning electron microscopy (SEM, Hitachi S-2400) to assess its morphology.

3- RESULTS AND DISCUSSION

The flowsheet of the process developed for producing RHA is illustrated in Figure 1. In the initial washing step, several impurities present in the waste are removed, namely dust and small stones, which are sinking in the settling vessel. The removal of such impurities is important since they can contaminate the final ash product. At the same time, the washing can provide the dissolution of some soluble substances, including metal salts, allowing a preliminary chemical purification. However, some contaminants are still present in the rice husk after water washing, and a further treatment with hot diluted acid is therefore required, in order to obtain a final purified husk ready for thermal treatment. The calcination (or incineration) allows the removal of the organics from the husk and a final white ash rich in silica can be afterwards produced.

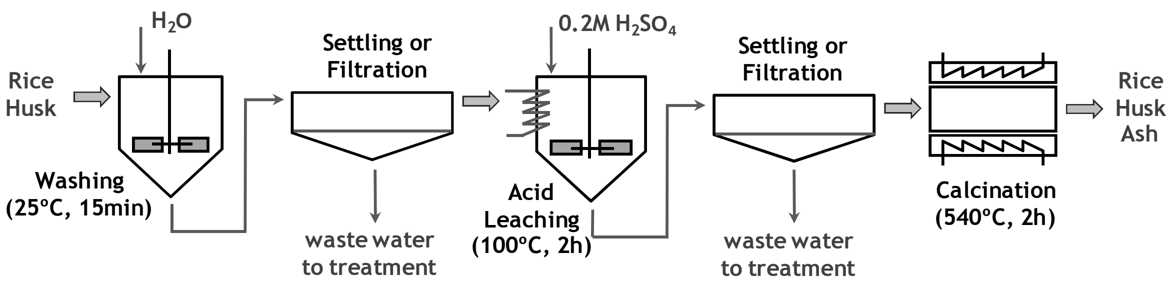

Figure 1: Flowsheet of the process for producing rice husk ash.

During the process, a significant weight loss occurred (Figure 2a). In the washing and leaching steps, near 30% of the husk weight was lost. The main weight loss, however, occurred in the calcination, where the weight of the husk was reduced about 80%. The overall value referred to the initial weight was 86%.

The main metallic contaminants identified in the husk were potassium, iron, manganese and zinc, with concentrations 0.54%, 0.13%, 0.04% e 0.003%, respectively. The washing and acid leaching were used to remove these metals from the product (Figure 2b). It was found that the washing step was very efficient in the removal of zinc (85%), while the remaining zinc practically stays in the husk after acid leaching (overall removal was 92%). Concerning the other metals, the water also allowed the dissolution of near 45-65%, which seemed a good result regarding the possibility of obtaining a reasonable ash with minimum costs. To achieve metal removal yields higher than 90% the acid leaching step is necessary. The cumulative leaching yields attained were 99.5%, 92% and 98%, respectively for K, Fe and Mn.

The evolution of the concentration of metals in the husk in the successive steps of the treatment process is presented in Figure 3a. After chemical treatment (washing and leaching) the concentrations were reduced to 37 ppm K, 150 ppm Fe, 10 ppm Mn and 3 ppm Zn, which can be considered very promising taking into account the production of a very pure silica in the calcination. Normally, these values were increased during the thermal treatment (195 ppm

K, 790 ppm Fe, 53 ppm Mn and 16 ppm Zn) due to the decomposition of organics and the subsequent weight loss.

The ratios between initial and final concentrations, presented in Figure 3b, illustrate these findings. After chemical purification, the ratios are so high like 150 for K, 40 for Mn, and about 10 for Fe and Zn. In the final ash product the ratios were 28 for K, 8 for Mn and about 2 for Fe and Zn, which are the final purification factors achieved. The most important aspect to be stressed is that, without the chemical purification, the contaminants will be concentrated in the ash in proportion to the weight loss found in the process, and the foreseen concentrations in these conditions would be 2.7% K, 0.7% Fe, 0.2% Mn and 0.015% Zn.

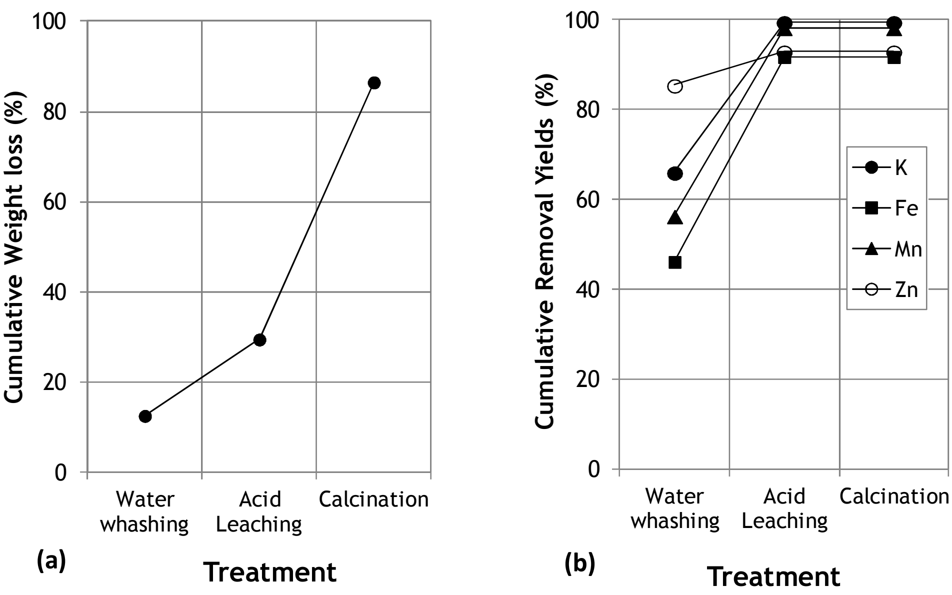

Figure 2: Weight loss and metal removal yields achieved in the successive steps of the process.

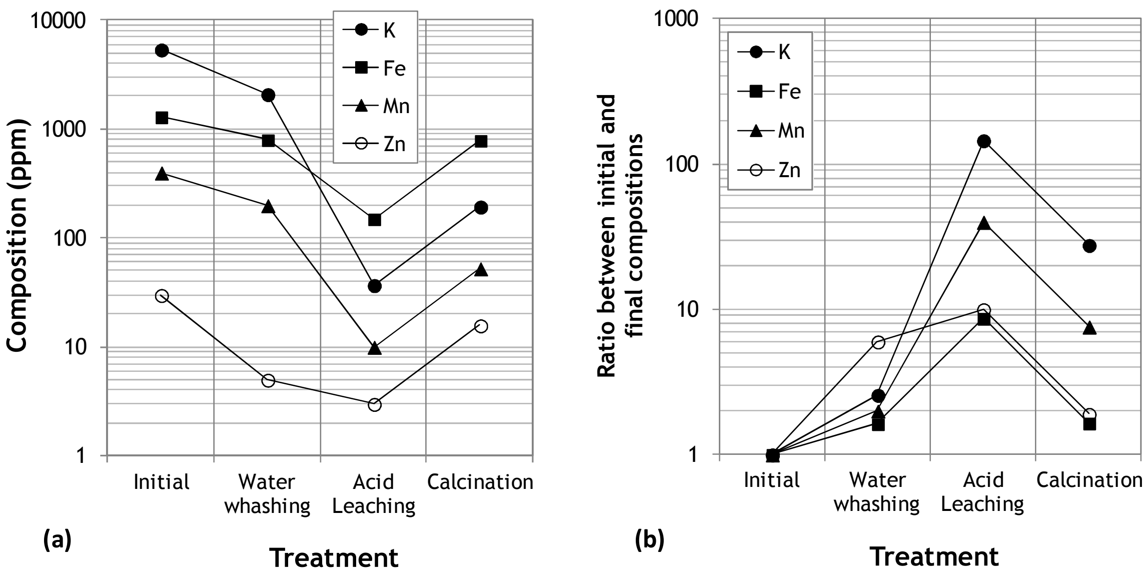

Figure 3: Chemical composition and purification ratios in the successive steps of the process.

The final ash obtained was very white, which indicates a low carbon grade and therefore a high efficiency of decomposition. This fact is related with the absence of alkaline metals during calcination, which avoids the formation of black carbon particles due to incomplete decomposition.

Figure 4 shows a SEM micrograph of a sample of rice ash obtained, showing a very porous tracery surface morphology, with a high surface area. This seems adequate for specific applications such as special ceramics material, catalyst support or construction material.

The phase identification in the RHA was assessed by XRPD (Figure 5). The pattern show a very broad line and no defined peaks due to crystallinity were encountered. On the Figure are also represented the theoretical positions of the main reflexions of the phases cristobalite (SiO_2) and graphite (C) and no peaks were found in these positions. The results obtained allowed to conclude that the ash produced has an amorphous structure.

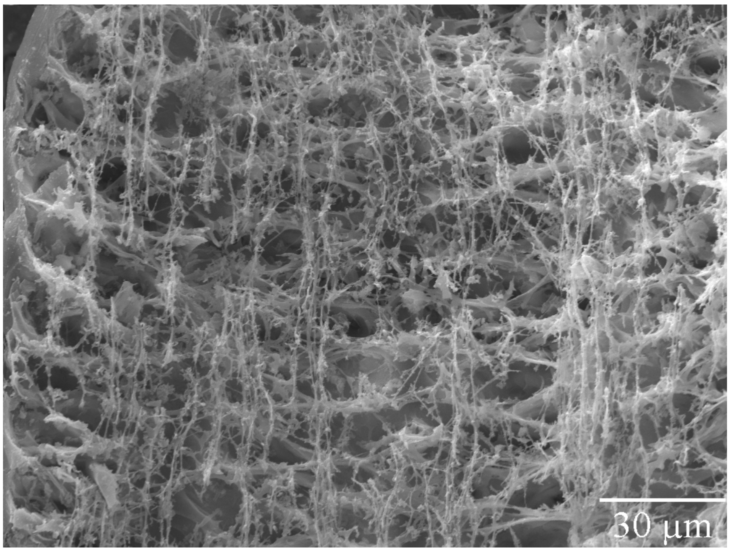

Figure 4: SEM micrograph of a sample of RHA obtained by the process.

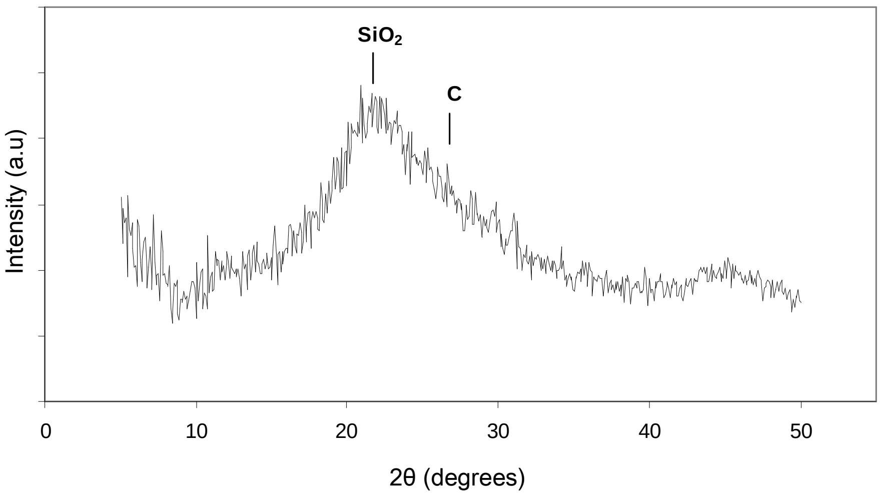

Figure 5: XRPD pattern of the RHA obtained by the process (radiation Cu-Kα).

4- CONCLUSIONS

A very pure, white-coloured, porous and amorphous silica ash was obtained from rice husk, by a valorisation process including water washing, acid leaching and calcination. The purification attained by washing and leaching allowed the removal of more than 90% of the metals K, Fe, Mn and Zn. By calcination under controlled conditions, the organics decomposition and liberation was efficiently achieved avoiding carbon fixation. Potential utilization of the ashes obtained by this process in applications requiring high reactivity, such as in construction materials and technical ceramics, can be envisaged.

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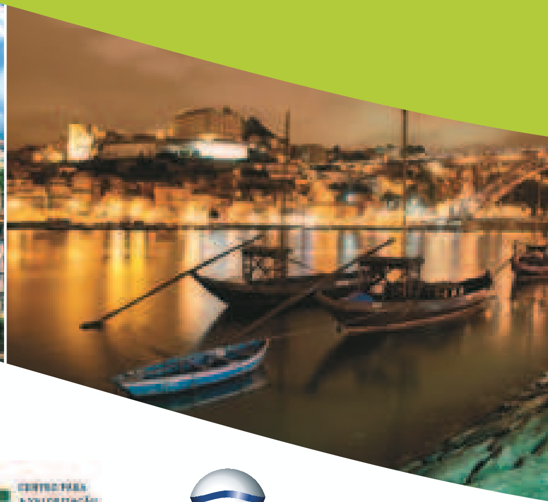

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