Thermal and Chemical Treatments to Rice Husk Valorization

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Abstract

Rice husk (RH) is a residue generated during the rice production. The main problem related with this residue it’s that exists in large quantities leading to management problems, as well as its high volume. After incineration, it is obtained only 20 wt% of rice husk ash (RHA) but has a high silica content. This high silica content makes the residue very interesting for a variety of different applications. The understanding of the influence that the thermal and chemical treatments have in the properties and silica content of the RHA is crucial. In this work, different thermal and chemical treatments were performed, characterization of RH and RHA was also carried out to understand how the different treatments can influence the properties of RHA. An adsorption study regarding the capacity of RHA to adsorb heavy metals was also carried out. In this study, solutions containing Cu, Pb, Zn, Ni and Cd were used. It was conclude that different thermal and chemical treatments influence the properties of the rice husk ashes obtained, like silica degree of crystallinity and morphology of the ash. The presence of certain elements in the husk, like potassium, can promote the carbon fixation in the ashes obtained. By studding the adsorption capacity of the different ashes was observed that some ashes were able to adsorb the 20ppm of heavy metal initially present in the solution.

Keywords: Rice Husk, Rice Husk Ash, RH incineration, Adsorption

1 Introduction

Rice is a staple food for over half the world’s population. World rice production is around 715 million tons annually (2013 data) while Asian countries account for 90% of the world production, with China and India accounting alone 50%[1].

Rice husk (RH) is generated during the rice production which makes it an agriculture waste. Due to its high volume it creates a management problem being the most common solutions landfills or incineration in an open field [2]. Nevertheless, other options must have to be taken into account.

The major constituents in RH are cellulose (35wt%), hemicellulose (24wt%), lignin (19wt%) and ash (19wt%) [3]. Chemically has a high concentration in carbon (37wt%), and presents H 8.80wt%, N 11.06wt%, Si 9,01wt% and O 33.03wt%. This values can vary according with location, atmospheric conditions and fertilizes used [4]–[8].

With the combustion of RH obtains rice husk ash (RHA) which has high silica content, 80-95% [5], 87-97% [8], [9], [10], 92-97% [11], with an amorphous structure. The understanding of combustion can help obtaining RHA with properties desired for specific applications.
According to the literature, different studies had been done regarding the thermal treatments performed to the RH. Studies involving the comprehension of the thermal degradation of the husk and the influence that different parameters can have in the properties of the RHA are of great importance. For example, the temperature employed in the thermal treatment can influence the structure of silica [3].

The use of chemical treatments before the incineration is common and takes place mostly to remove impurities of the rice husk [6]. The usual treatments are water wash and leaching using HCl or H₂SO₄. The impurity that has more influence on the properties of the RHA is potassium because causes fixation of carbon residues leading to silica crystallization at lower temperatures [12].

Characteristics and properties of RH and RHA allow a wide range of possible applications. RH is used as fuel in the production of energy [13] and its ash in the cement industry due to its pozzolanic properties [3], as a filler in polymers and rubbers [3], ceramic industry [14] and as a source of amorphous silica.

Other applications are treatment of wastewater by the use of RHA as an adsorbent of heavy metals [15]. The common technologies used on the treatment of wastewaters have high costs which makes this natural material, which exists in large quantity, a better economical option [16].

Recent studies on the adsorption capacity of RHA have been made in solution with individual heavy metals like Cu, Ni, Cr, Zn, Cd and Pb [17], [18].

The present study aims to understand the impact of different treatments, thermal and chemical, in the properties of the RH and RHA using characterization methods (XRD, SEM, TGA, AAS and a stereoscopic magnifying glass). An adsorption study regarding the capacity of RHA to adsorb heavy metals (Pb, Cu, Ni, Zn and Cd) was carried out using RHA obtain by different treatments to understand how it would influence its adsorption capacity efficiency.

2 Experimental

The rice husk was supplied by the combustion laboratory of Instituto Superior Técnico and was originated from Alcácer do Sal. The chemical analyses were supplied by Centro de Valorização de Resíduos (CVR) in Minho.

2.1 Chemical treatments

Chemical treatments carried out were water wash and leaching. The water wash was carried out using demineralized water to wash during 15 min with stirring in a 10L recipient. Afterword's was dried in an oven at 100°C for two days.

Leaching of rice husk was accomplished using 6 g of solid and 100 ml of different acid solutions, hydrochloric acid (0.6M and 1M) and sulfuric acid (0.3M and 0.5M). The test lasted 2 h and temperatures used were 25 and 80°C. Then, the solutions were filtered, the rice husk washed with distilled water to remove the excess of acid and dried in an oven at 50°C for 24 h.

2.2 Thermal treatments

The calcination of rice husk occurred at 400, 500, 600, 700 and 800°C. The rice husk was introduced in the oven at room temperature,
heated until it reached the desire temperature, remain there for a certain amount of time and then removed to cool outside. The amount of time the rice husk was maintained at a certain temperature varied according to the type of chemical treatment done: the natural RH and the washed RH were 2h, 4h and 6h; leached RH was 2h.

2.3 Adsorption study

For the adsorption study, 0.3g of RHA obtained from different thermal treatments were placed in erlenmeyes with 30ml of solution with 20ppm of Pb, Cu Zn, Ni and Cd for 2h at room temperature with stirring at 120 rpm. During the test, samples of about 3ml were taken at a specific time to be diluted in order to be analyzed through atomic absorption spectrometry. The pH was measured at the end of the test and the RHA was filtered and dried in an oven for 24h.

2.4 Characterization

The solutions from the water wash and leaching steps were analyzed by atomic absorption spectroscopy to determine the potassium content. The solutions used in the adsorption study were also analyzed in order to find out the heavy metals content after the adoption test.

It was used a spectrometer with double beam ThermoElemental Solar969AA. To determine the composition of potassium in the natural and washed RH, 0.5g was used and digested at high temperature with 100ml of aqua regia (HCl:HNO3 = 3:1 v/v) during 2h. The solid was filtered and washed and the solution analyzed.

To identify the phases present in RH and RHA was used X-ray diffraction (XRD). A diffractometer Philips PW 1830 using Cu \( \lambda = 1.5418 \ \text{Å} \), voltage 40kV, current 30mA and scan speed of 1.2°/min in a range of 5° to 50° of 2θ.

The morphologic characterization of RH and RHA was accomplished with a stereoscopic magnifying glass Nikon SMZ645 and a scanning electron microscope (SEM) JEOL JSM7001F coupled with an energy-dispersive X-ray spectroscopy (EDS) Bruker.

A thermogravimetric analyzes (TGA) of treated and untreated RH was performed using a thermobalance NETZSCH STA 409 PC in alumina crucibles. The samples used had 40-70mg under air flux (2l/h) and were heated from room temperature until 1100°C.

3 Results and Discussion

3.1 Rice husk characterization

The chemical characterization was supplied by Centro de Valorização de Resíduos (CVR) and allowed to determine the silica content in the ash. It was also possible to verify that exist high concentrations of potassium and calcium. The XRD performed to the RH allowed to confirm the presence of amorphous silica and identified also the presence of calcite.

The morphology characterization was carried out by stereoscopic magnifying glass allowing to differentiate the external and interior shape of the husk. The SEM analyzes allow to observe that the external shape of the husk was covered with protuberances and hairs. The internal shape was smooth and with some porosities (Fig. 1). Using EDS was possible to conclude that the silica present in the rice husk is mainly present in the external husk.
3.2 Chemical treatments

Chemical treatments performed were water wash and leaching with hydrochloric and sulfuric acid. This treatment aims to understand how some parameters variation could influence the potassium removal. The water wash during 15 minutes removed 56% of the potassium present in the natural RH. Leaching results are presented in Fig. 2. The removal efficiency of potassium is superior with H$_2$SO$_4$, however different concentrations of both acids used didn’t have any influence. The leaching temperature also doesn’t have any influence on the removal efficiency of potassium.

The effect of washing prior to leaching doesn’t have any significant effect on the potassium removal relative to the results for the leaching of RH without any previous treatment.

It’s possible to conclude that the leaching step is effective on the removal of potassium from RH.

3.3 Rice husk ash characterization

Phase identification with XRD identified two main phases: Amorphous silica and Cristobalite (depending on calcination temperature) and Calcite. The formation of cristobalite varies with calcination temperature, holding time, washing and/or leaching.

The Fig. 3 and Fig. 4 show that for lower calcination temperatures, the silica present has an amorphous structure. The lump that appears in the diffraction pattern is centered on the 20 values characteristics of cristobalite [19]. With the increasing of temperature, the silica appears to become more crystalline due to the narrowing of the peak.

The RHA obtained from washed RH before calcination show less crystalline structures for the same calcination conditions. Normally, silica doesn’t crystallize before reaching temperatures higher than 900°C, but due to the presence of impurities like potassium the crystallization happens at lower temperatures.
Fig. 3 - Diffraction patterns of natural RHA for different calcination temperature: a) 400°C; b) 500°C; c) 600°C; d) 700°C; e) 800°C

Fig. 4 - Diffraction patterns of washed RHA for different calcination temperature: a) 400°C; b) 500°C; c) 600°C; d) 700°C; e) 800°C

The Fig. 5 and Fig. 6 show that doesn’t appear to be an influence in the structure of RHA by applying different holding times during calcination of RHA obtained ether from natural RH and washed RHA.

Fig. 5 - Diffraction patterns of natural RHA for different holding times during calcination: a) 2h at 600°C; b) 4h at 600°C; c) 6h at 600°C; d) 2h at 700°C; e) 4h at 700°C; f) 6h at 800°C

Fig. 6 - Diffraction patterns of washed RHA for different holding times during calcination: a) 2h at 600°C; b) 4h at 600°C; c) 6h at 600°C; d) 2h at 700°C; e) 4h at 700°C; f) 6h at 800°C

In Fig. 7 is shown that leaching RH before calcination at 500°C doesn’t change the structure relatively to the structure of untreated RHA. However, when comparing RHA obtained at 800°C with or without leaching, the leaching allow the RHA to have an amorphous structure even after calcination at 800°C. It appears that the reason for this is that the leaching step removed some amount of potassium, which since it tend to decrease the crystallization temperature, its removal allowed to remain the structure amorphous.

Fig. 7 - Diffraction patterns of leached RHA with HCl 0.6M for different calcination temperatures: a) RHA 500°C; b) washed RHA 500°C; c) RHA 800°C; d) washed RHA 800°C

The morphology of rice husk ash heat treated at 800°C is shown in Fig. 8. It was observed that washed RHA has less black particles that the untreated, and that the leached RHA doesn’t have any. The difference between the
amount of black particles in washed and natural RHA was observed for all the temperatures executed. The carbon is formed during the decomposition of organic matter with the increase of temperature. Potassium oxide dissociates and happens fusion which traps the carbon in the melt.

Fig. 8 – samples of RHA after calcination at 800ºC: a) Natural RHA, b) washed RHA c) leached RHA

In Fig. 9 a) it's possible to observe that the morphology of the RHA is similar to the RH. In image b) the pores left by the volatilization are observed.

Fig. 9 - Samples of RHA after calcination at 800ºC: a) observed with a stereoscopic magnifying glass, b) SEM micrograph

The thermogravimetric analysis can be observed in Fig. 10. Until reaches 200ºC occurred weight loss due to water evaporation. Then, weight loss starts at 280-300ºC, characterize by a change of slope, which corresponds to the active zone of pyrolysis being is responsible for the decomposition of organic matter. At 360-380ºC a second change of slope happens, where oxidation of carbon occurs, until it reaches 850-880ºC where it stabilize.

The principal differences in thermal degradation of RH with distinct chemical treatments are better observed in the DTG curves. In the range of temperatures where the degradation of organic matter occurs, the DTG presents two curves representing hemicellulose (lower temperatures) and cellulose. The washing of RH leads to a displacement of the curves for higher temperatures.

The decomposition of lignin happens in a wide range of temperatures not being able to be identified in the graph.

The weight loss near 850ºC can be attributed to the decomposition of calcium carbonate, since the temperature at which normally occurs decomposition is near this range of temperatures [20].

Fig. 10 - TGA and DTG of natural RH (green), washed RH (violet) e leached RH (pink)

3.4 Adsorption study with Rice husk ash

In this study RHA obtain from different chemical and thermal treatments were studied
regarding the adsorption capacity of heavy metals.

The adsorption capacity, $q$ (mg/g), was calculated based on the equation (1):

$$ q = \frac{(C_0 - C_t) \times V}{m} \quad (1) $$

where $C_0$ is the initial concentration of each metal in solution and $C_t$ the concentration of each metal after some time $t$, $V$ the volume of solution at the beginning of the test and $m$ the mass of RHA used.

The efficiency of adsorption of each metal after some contact time, $t$, was calculated using the equation (2):

$$ \eta(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2) $$

where $C_0$ is the initial concentration of each metal in solution and $C_t$ the concentration of each metal after some time $t$.

Comparing different efficiency values was concluded that a leaching step before the calcination would decrease the adsorption capacity of RHA and that washing the rice husk before calcination doesn’t have any effect comparing the results for untreated RHA.

Regarding the calcination temperatures, lower calcination temperatures increases the adsorption efficiency. Since carbon tends to be released at higher temperatures, maybe it has some contribution besides silica in the adsorption capacity of RHA.

The contact time has influence in the adsorption efficiency, Fig. 11. At the beginning, the surface has some number of free zones so the adsorption occurs fast. After a while, this zone start to be occupied leaving less free zones, which are becoming more and more difficult to occupy due to repulsive forces. So, after a while the adsorption stabilizes [17].

![Fig. 11 – Relation between efficiency and contact time in a solution at pH 5](image)

The effect of the pH of the solution was also studied in this work. It was observed that if the pH of the initial solution wasn’t adjusted to a certain value, the RHA would adsorb almost nothing. The increase of pH solution leads to increase of adsorption efficiency until it reaches a value where stabilizes. For lower pH the H$^+$ concentration is higher meaning a completion between these ions and heavy metal ions for places at the RHA surface.

Altering the liquid-solid ratio can lead to the understanding of the selectivity of the RHA to each heavy metal. In Fig. 12 is possible to observe that with the increase of L/S, the RHA adsorbs in a selective way indicating the following order: Pb > Cu > Zn > Cd > Ni. This order is related to the values for the equilibriums of hydrolysis of each metal.

![Fig. 12 - Ratio between efficiency and L/S](image)
There are very models of adsorption and the two most common are Langmuir and Freundlich. The Langmuir model is present in this equation (3):

\[ q = \frac{q_m * K_L * C}{1 + K_L * C} \]  

(3)

where \( q \), \( q_m \), \( C \), \( K_L \) are the adsorption capacity for a certain concentration, adsorption capacity at equilibrium, concentration and a constant. The linearize equation is used to apply this model. In Fig. 13 are represented the experimental values and curve for each element as well as the curves calculated using the Langmuir model since the other model couldn’t be applied.

By comparing both experimental and theoretical curves, it’s possible to consider that this model might explain the adsorption mechanism. According to the model, the RHA surface has specific places were solute molecules can be adsorbed being adsorbed as a monolayer.

![Isothermal curves: a) Pb; b) Cu; c) Ni; d) Zn; e) Cd](image)

**Fig. 13 – Isothermal curves: a) Pb; b) Cu; c) Ni; d) Zn; e) Cd**

### 4 Conclusion

The phases present in the RH, identified by XRD, are amorphous silica and calcite. The high silica content present in the RH is located in the external zone.

The water wash during 15 minutes removed 56% of the potassium present in the natural RH. The leaching step had higher efficiency regarding the removal of potassium having between 60 to 110% of efficient removal.

The phase identification of RHA, with XRD, identified Cristobalite and Calcite as the main
phases present. The higher the temperature the higher the crystallization of silica.

The washing and leaching steps had an influence on the morphology of RHA being responsible for reducing the amount of black particles.

The thermogravimetric analysis showed that washed RH leads to a displacement of the DTG curves for hemicellulose and cellulose for higher temperatures. The decomposition of calcium carbonate is observed in the graph and occurred around 850ºC.

Adsorption studies allowed to realize that lower calcination temperatures lead to RHA with better adsorption properties.

Different parameters can influence the adsorption capacity of RHA like contact time, pH of the solution and L/S ratio.

The Langmuir adoption model can possibly explain the adsorption mechanisms occurring in the surface of RHA.

References


