Immobilization of heavy metals adsorbed on rice husk in clayey matrix

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Introduction

Heavy metals, such as lead, copper, cadmium, zinc, chromium, among others, are toxic even at low concentrations and because they are not biodegradable, their impact in the environment is multiplied by their accumulation through the food chain. Most industrial activities lose and/or discharge large amounts of heavy metals. The removal of these metals from wastewater is an urgent environmental need. The ability of certain types of biomass to remove and concentrate heavy metals from solutions provides the basis for a cost-effective technology for their removal from industrial effluents. On the other hand, rice husks constitute a biomass waste that has found multiple applications in different fields, such as the removal of heavy metals. After this process, a biomass-contaminant waste is generated, which currently does not have viable and low cost alternatives for its final disposal. The objective of this work is to evaluate the feasibility of incorporating the rice-hush-contaminant residue in clayey ceramic matrices to immobilize the heavy metals cadmium and lead contained in these materials. For this purpose, rice husks were first studied in a series of adsorption experiments, ensuring that they retain a certain proportion of the contaminants.

Experimental

The rice husks (RH) used in this study were obtained from an agricultural cooperative in the province of Entre Ríos, after the husking of the rice grain, and without any physical modification before the chemical treatments. Two classes of adsorbent materials were obtained from these husks: RH activated with potassium hydroxide and RH activated with phosphoric acid. Sorption tests were performed under batch conditions. RH activated with H_3PO_4 were put in contact with a solution of Cd, and those activated with KOH were put in contact with a solution of Pb, the time necessary to guarantee the balance of sorption. At the end of the sorption tests, the samples were filtered and the husks loaded with the different contaminants were dried in an oven and reserved for later use in ceramic pieces. These biosorption processes have been exhaustively studied and their particular analyses have allowed to establish that the contaminants have been retained in the rice husk used in the present work.

The ceramic pieces were obtained by uniaxial pressure at 25MPa from mixtures of commercial clay-rice husks with and without adsorbed metal, added in 10% in volume, thermally treated at 1000°C following firing curves similar to those used by the ceramic industry. For comparative purposes, a sample of clay without added residue was prepared.

The rice husks were characterized by optical microscopy and scanning electron microscopy (SEM). The electronic microscopy images were obtained with an FEI Inspect S50.

The ceramic products obtained were characterized with different techniques: porosity (P), modulus of rupture (MOR), permanent volumetric variation (PVV) and loss of ignition (LOI), among others, tending to determine their properties. The porosity of the samples was determined according to ASTM C20-00. The modulus of rupture was obtained in an Instron Model 1125 machine, with a maximum capacity of 10000 kg. The test speed was 0.5 mm/minute.

In order to determine the immobilization of the heavy metals in the clay matrix, the ecotoxicity test was performed on the samples, according to IRAM 29114.

Results

Figure 1 shows the microstructure of natural rice husks, rice husks activated with H_3PO_4 + Cd and rice husks activated with KOH + Pb, obtained by SEM. As can be seen, the microstructure of the natural rice husk is globular, showing a cellular pattern of the pericarp or outermost layer, well organized, of homogeneous structure. In addition, there are elongated, acicular structures that resemble "hairs", typical of the fibrous structures of certain cereals. The samples of CA + H_3PO_4 + Cd show some superficial cracks and cut "hairs". In the case of CA + KOH + Pb a detachment of these from their root is observed .

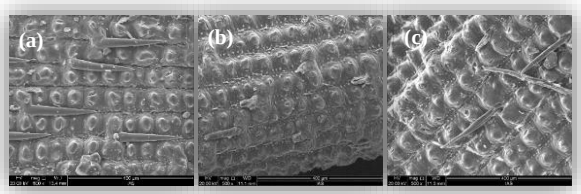

Figure 1: SEM images (a) natural rice husk, (b) RH activated with H_3PO_4 + Cd, (c) RH activated with KOH + Pb. Magnification: 500X

The ceramic products obtained present a homogeneous colour and a well-defined structure without shelling. The properties analysed in the bricks: porosity, water absorption, modulus of rupture, PVV and LOI, are summarised in Table 1.

It is observed that the incorporation of rice husk decreases the PVV of the pieces, which also present a greater porosity. Although the MOR is reduced, the values obtained are within the market requirement.

Table 1. Properties of the obtained products

	0% RH	10% RH	10% RH + H_3PO_4 + Cd	10% RH + KOH + Pb
LOI [%]	5.2	7.2	7.2	6.7
PVV [%]	- 9.9	-9.4	-8.8	-9.5
Porosity [%]	21.9	27.3	26.5	25.5
MOR [MPa]	8.7	6.3	6.2	7.3

In the ecotoxicity test, the evaluation of the effect on the radicle elongation of the seedlings allows to consider the toxic effect of soluble compounds present at so low levels concentration that they are not sufficient to inhibit germination, but which may delay or completely inhibit the process of radicle elongation. This test has been performed primarily for untreated rice husks, and for treated husks and with adsorbed metals. After obtaining the ceramic bricks, this same test was carried out with ground samples of the bricks.

Rice husk alone has a very important inhibitory effect, which increases significantly with subsequent treatment and adsorption in both cases (Pb and Cd). The ground bricks follow a similar behaviour in the case of RH alone aggregate, whereas when the metals are present, the observed effects are diminished, which is interpreted as the immobilisation of the metals by the brick structure after sintering.

Conclusion.

From the general results, it can be concluded that the obtained ceramic pieces have immobilized within their structure the heavy metals contained in the added rice husks, and the obtained products present homogeneous colour, defined edges, good degree of sintering and properties suitable to its use in service.