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MAGNETIC GEOPOLYMER BASED ON RICE HUSK ASH FOR THE REMOVAL OF METALS FROM AQUEOUS SOLUTIONS

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Abstract

In this work, a study of the removal efficiency for lead(II), copper(II), zinc(II), niquel(II), and cadmium(II) from aqueous solutions using modified geopolymer with magnetite, through an adsorption process is presented. Various pretreatments and calcination steps at different temperatures were applied to rice husks to obtain a silica-rich ash, which is the raw material in the synthesis of geopolymers. Their mineralogical composition and microstructural property were determined by XRF and XRD, respectively. The major functional groups on the surface were identified by spectrometry FT-IR. The major functional groups on the surface were also identified as well. SEM micrographs were taken to acknowledge the ashes morphology. The results indicate that the geopolymer modified with magnetite and obtained from rice husk ash with a Si/Al ratio of 0.5, solid/liquid ratio of 1.5 and 10% of magnetite showed the best metals adsorption capacity than same metals taken by the iron-free geopolymer and the rice husks.

These results indicate that the magnetic geopolymer from rice husk ash is an efficient and low-cost alternative adsorbent to remove Pb, Cu, and Zn from aqueous solutions.

Key words: geopolymers, magnetite, rice husks, metals adsorption.

Introduction

Geopolymers consist of tetrahedral AlO_4 and SiO_4 units polycondensed at ambient temperature under highly alkaline conditions into three-dimensional structures (like amorphous zeolites) with electric charge stabilization provided by alkaline earth ions. Geopolymers are used to immobilize and stabilize radioactive low-level waste materials, or metals as well (1-2). The use of low cost reagents for their production, such as ashes with high SiO_2 content from rice husk, is an attractive option to utilize them for geopolymer synthesis ending in low cost adsorbents. The polysilicates empirical formula can be described as $Mn\text{-}(SiO_2)z\text{-}AlO_2)nH_2O$, where z can take values between 1, 2 or 3, M corresponds to a monovalent cation (K^+ or Na^+) and n is the degree of polycondensation. Some geopolymers contain alkaline cations, particularly Ca^{2+} due to the used primary source (3). The commercial potential of the geopolymers using as raw ash resource, is growing due to its dependency on cheap materials and easy availability (4-5).

Rice husks contain about 75% of volatile organic matter where 25% of its weight is converted into ash during the incineration process, the waste is known as rice-husk ash. During the conversion of the rice husks in ash at 100 °C occurs weight loss associated with evaporation of the absorbed water, at 350 °C volatile compounds cause a heavy weight loss, the husks begin a burn out step between 400-500 °C, the residual carbon oxidizes and a maximum weight loss is observed during this step, while the silica remains amorphous; when the temperature increases to near 800 °C, it starts the silica crystallization process (6). Therefore, the rice husks are a potential source for raw material in the production of silicon compounds and the basis for the production of new materials such as geopolymers as well, which can be efficient for metals removal from aqueous solutions.

Thus, the objective of this work is the synthesis and characterization of magnetite geopolymer based on SiO_2 from rice-husk ash and its metal adsorption capacity evaluation.

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Methodology

Rice husks treatment

The rice husks were obtained from a rice 2009 harvest in the city of Nagaoka, Niigata, Japan. The husks were sieved and washed several times with distilled water and HCl 3 M to eliminate debris, as showed in Figure 1.

Fig.1. Rice husks treatment.

After the washing step, the material was dried at 25 °C during 1 h and then at 80 °C for 12 h. Figure 2 shows the washed dried rice husks with acid (left) or water (right). Later on, this material was calcined at 600 °C for 4 h to get a silica-rich (SiO_2) ash.

Fig. 2. Rice husks treated with acid (left) and water (right).

Geopolymers synthesis

Geopolymers were synthesized from SiO_2 and $NaAlO_2$ in different proportions (1, 1.5, 2, 2.5 and 3), they were previously mixed, then distilled water was added while shaking the synthesis blend with a glass rod for 10 min, until a homogeneous paste is attained which was poured applying extrusion when needed into a ceramic mold that was then heated in an oven at 80 °C for 24 h. The obtained geopolymers were powdered and sieved with a mesh set No. 100 for particles smaller than 0.1 mm in diameter. For the magnetite geopolymers, Fe_4O_3 was added at different proportions.

Geopolymers characterization

The mineralogical composition and crystalline structure of the rice husks ashes were determined by X-ray Fluorescence (XRF) and X-ray Diffraction (XRD). FT-IR spectrometry was used to identify the main functional groups on the rice husk ash and geopolymer surface; SEM micrographs were taken to get the geopolymers morphology.

Metals adsorption on magnetite geopolymer

In all of the experiments for metals adsorption, the geopolymer synthesized with a ratio of 0.5, solid/liquid, 1.5 and 10% magnetite, identified as 0.5(1.5)10% was utilized.

The metals adsorption experiment in the magnetite geopolymer was determined in constant agitation of 120 rpm and 25 °C. Several tubes with 15 mL of a solution of 100 ppm of lead, copper, zinc, niquel, and cadmium adjusted to pH 4 were in contact with the 1 mg by 12 h, respectively. For copper and zinc 5 mg of the magnetite geopolymer were used.

After the adsorption process ended, the geopolymer were removed magnetically and the metals in solution were analyzed by Atomic Absorption Spectrophotometry (EAA). It was assumed that the difference between the metal concentration in the supernatant subtracting the metals concentration in the controls was the metal adsorbed on the geopolymer and this value was related to the material adsorption capacity.

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Results and discussion

Geopolymers characterization

XRF analyses of ashes from rice husks ash (RHA) treated with H_2O and HCl show that the SiO_2 is the most abundant component, followed by the K_2O. These results are presented in Table 1.

Table 1. XRF of rice husks ash.

% mass	RHA (H_2O)	RHA (HCl)
SiO_2	*97.137*	*99.4994*
K_2O	1.739237	0.138445
CaO	0.385708	0.110627
P_2O_5	0.282774	0.080997
MgO	0.276858	0.070775
SO_3	0.13488	0.050332
Al_2O_3	0.04354	0.049426

XRD analyses obtained from the 2 types of ashes are shown in Figure 3.

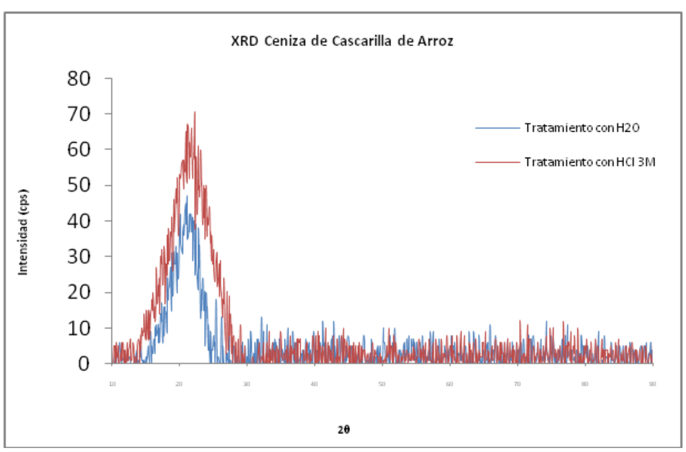

Fig. 3. XRD of RHS.

The peak in the period (15 to 25) 2θ is characteristic of amorphous materials and short-range atomic order, which indicates that both ashes are amorphous with an incipient crystallization of silica to quartz. The presence of carbon in ash water treatment is confirmed by the peak in the region (25-26) 2θ.

The FT-IR spectroscopy analyses were made to the rice husks ashes, and to the synthesized geopolymers as well; those are shown in figures 4 and 5, respectively.

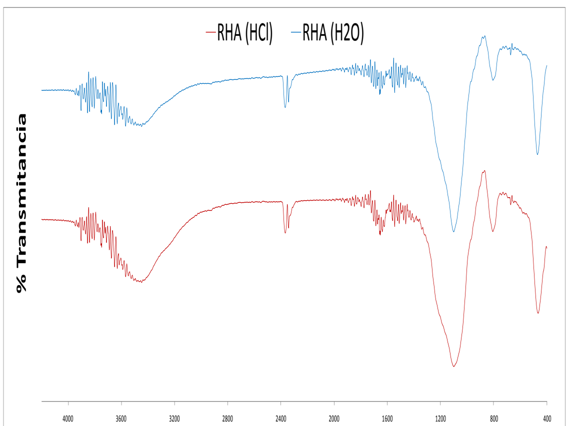

Fig. 4. FT-IR of rice husks ash.

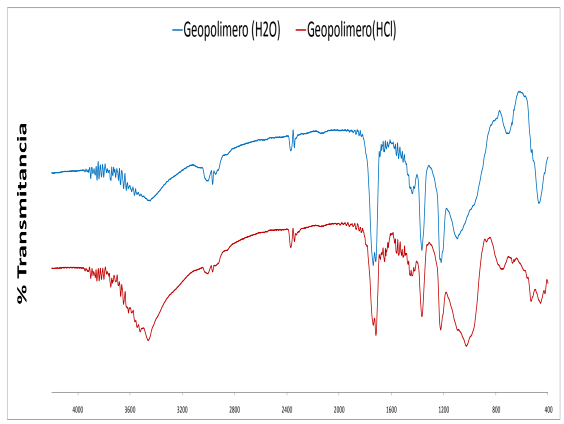

Fig. 5. FT-IR of geopolymers.

The bands located at 1088 and 1094 cm^{-1} are evidence of the presence of a geopolymer from ash and are assigned to asymmetric tension of the bonds from each tetrahedron or are present in the geopolymeric matrix of quartz Al-O and Si-O.

SEM micrographs of synthesized magnetite geopolymer were taken to assess the morphology of materials as shown in Figure 6.

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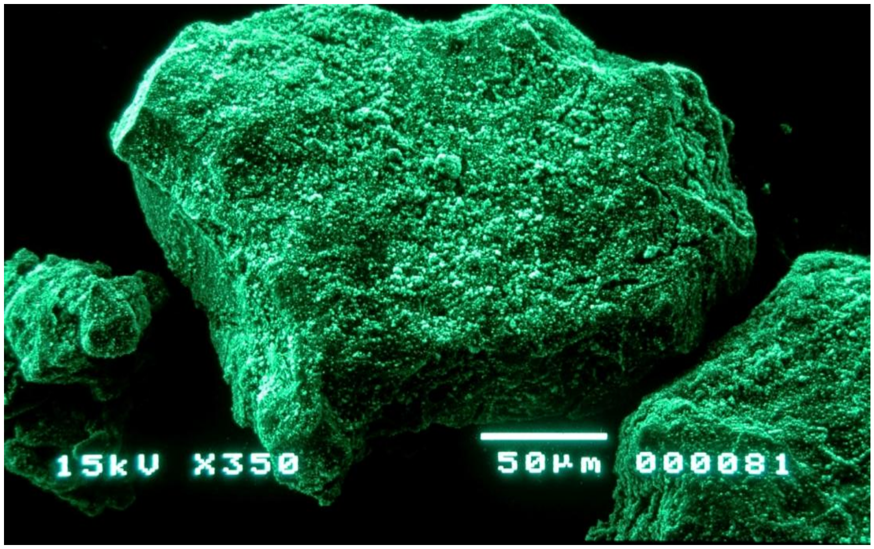

Fig. 6. SEM of synthesized magnetite geopolymer.

The geopolymer particles in micrographs present uniform morphology averaging 50 µm in length, formed by the small porous surface agglomeration.

Figure 7 shows the synthesized magnetite geopolymer and particles, respectively.

Fig. 7. Synthesized magnetite geopolymer (left); magnetite particles (right).

Metals adsorption on magnetite geopolymer

Figure 8 shows the metal adsorption on Zn, Cd, Ni, Cu, and Pb.

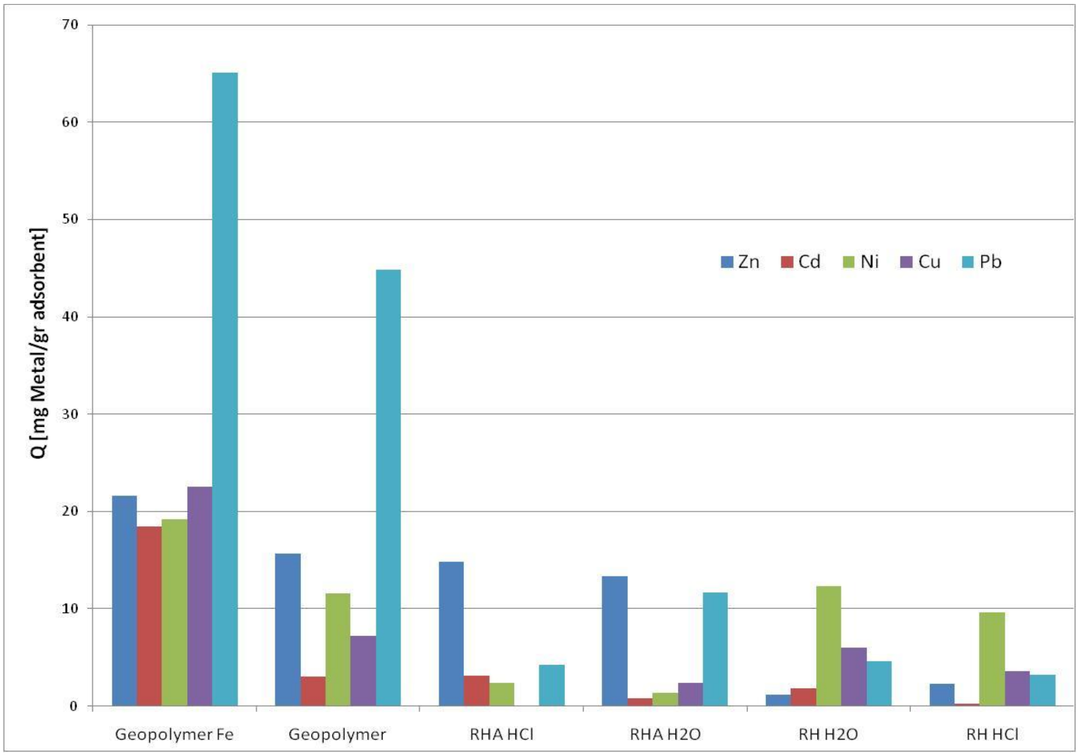

Fig. 8. Metals adsorption on magnetite geopolymer

This Figure shows that Pb, Cu, and Zn were adsorbed by magnetized geopolymers in higher amounts than same metals taken by the iron-free geopolymer and the rice husks ashes.

Conclusions

The synthesized geopolymer from rice husks, subjected to two treatments, showed differences in morphology and chemical structure. Acid treatment removed impurities from the husk resulting in bright and white ash with a high SiO_2 content. Washing with distilled water managed to get ash with small carbon residues and an acceptable SiO_2 purity. The FT-IR spectra showed that both ashes have silica characteristic groups, the ash of the acid treatment as opposed to water treatment, presents aldehyde and ketone groups as a possible consequence for the cellulose and lignine chain breaking. Geopolymer modified with magnetite, obtained from rice husk ash synthesized with a Si/Al ratio of 0.5, solid/liquid ratio 1.5 and 10% magnetite showed the best metals adsorption capacity than same metals taken by the iron-free geopolymer and the rice husks.

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