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Byproduct-based zeolite type A as absorbent material for decontamination of simulated radioactive wastewater

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1. Introduction

One of the foremost concerns associated with nuclear energy is the generation of radioactive waste and its secure disposal, which ranks among its significant drawbacks. Radioactive wastewater, a byproduct of nuclear operations, contains hazardous radionuclides like cesium, uranium, plutonium, and iodine, presenting grave health risks, including cancer[1].

Cesium, as a significant fission product of uranium, stands out among the produced radionuclides due to its emission of potent beta-gamma and beta rays, coupled with its relatively lengthy half-life of 30,4 years[2]. Moreover, it poses a significant challenge for wastewater treatment due to widespread presence and unique chemical properties.

Efforts to address cesium contamination have intensified in the past decade due to radioactive contamination incident placed in Fukushima Daiichi. However, challenges persist due to cesium's properties, emphasizing the need for efficient removal methods to manage radioactive wastewater effectively. Its similarity to other alkali metals complicates selective separation methods, necessitating innovative approaches to safeguard ecosystems and human health[1,3].

Zeolites, versatile materials, find extensive use in water and wastewater. They play key roles in filtration, ion exchange, adsorption, and membrane separation technologies due to their inherent high ion exchange capacity, large specific surface area and high thermal stability all from their three-dimensional porous crystalline structure. The potential to obtain zeolites from agro-industrial residues abundant in silicon and/or aluminum offers a cost effective and sustainable alternative to enable all the aforementioned applications[4].

Finally, after the efficient removal, the selection of the most suitable method to immobilize the loaded zeolite depends on factors such as the type of contaminants, site-specific conditions, and regulatory requirements.

In the present study, the adsorption of cesium from simulated radioactive wastewater was tested using a zeolite type A synthesized from sugarcane bagasse ash. The samples were characterized by different techniques to evaluate their chemical composition and thermal stability. The results confirmed the obtention of high purity zeolites with adequate adsorption capacity and thermal integrity after the ionic exchange.

2. Methodology

The synthesis was carried by conventional hydrothermal according to previous works [5,6] using the sugar cane bagasse ash (SCBA) from a plant located in Franca, São Paulo/Brazil as source of silica. Simulated nuclear effluent containing Cs^+ ions were adapted from the procedure studied by Tian and Sasaki [7] and loaded zeolites were produced by mixing 5 g of zeolite with the simulated nuclear effluent. The suspension was stirred for 24 h followed by filtering and drying for overnight at 105 °C. The obtained samples were marked as Loaded-Z. Fig. 1 shows a schematic representation of the conducted process and the obtained materials.

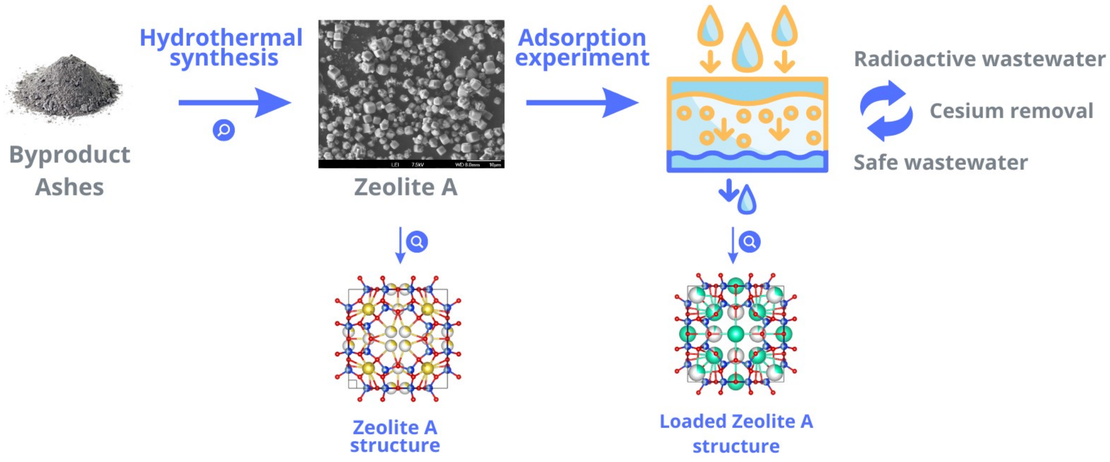

Figure 1: Schematic representation of the conducted process and the obtained materials.

For semi-quantitative determination of the chemical compounds present in the residue and zeolites, chemical analyzes were carried out on an energy dispersive X-ray fluorescence spectrometer (ED-XRF) SHIMADZU EDX 720. The fundamental parameters (FP) method was used in powder samples. X-ray diffraction analyzes to identify the crystalline phases present in the materials obtained were carried out on a Rigaku SmartLab diffractometer in the theta-2theta configuration, using CuKα radiation ($\lambda = 1.5406$ Å). The X-ray diffraction data was recorded having a step of 0.05°/second. The evaluation of the thermal behavior of the zeolites during their heating was carried out by differential thermal analysis (ATD) and by thermogravimetry (TGA), using synthetic air, heating rate of 10 °C/min up to a temperature of 1300 and 950 °C respectively.

3. Results and Discussion

The chemical composition of sugarcane bagasse ash (SCBA) obtained by X-ray fluorescence spectroscopy is shown in Table I. As expected, SiO_2 is the main component corresponding to 83.7 wt.%[6,8]. Despite the presence of silica, alumina, iron oxide and small amounts of other metal oxides were detected. The loss of ignition was 2 wt.%.

The chemical compositions of synthetized zeolite obtained was adequate in comparison to other byproduct based in literature and the proportion of $SiO_2Al_2O_3$ was 1.06, in agreement with expected for Na zeolite-A, 1. The sodium content is related to its incorporation into the zeolitic material by hydrothermal synthesis, in which NaOH was used as an activating agent. Iron oxide was observed in an amount of 1.6 wt.% and other impurities below 1 wt.%. After the adsorption experiment, the retention of Cs_2O was up to 28.3 wt.%.

Table I: Chemical composition all materials studied (weight%) obtained by X-ray fluorescence.

	SiO_2	Al_2O_3	Fe_2O_3		Na_2O	Cs_2O	Other	L.O.I.*	SiO_2/Al_2O_3
By-product									
SCBA	83.7	4.8	5.8	-	-	-	3.5	2.0	17.43
Zeolites									
Synthesized	33.2	31.3	1.6		17.4	-	0.7	15.8	1.06
Loaded-Z						28.3			

The diffractograms obtained by the X-ray diffraction technique of the synthesized and loaded zeolite are shown in Fig.2.

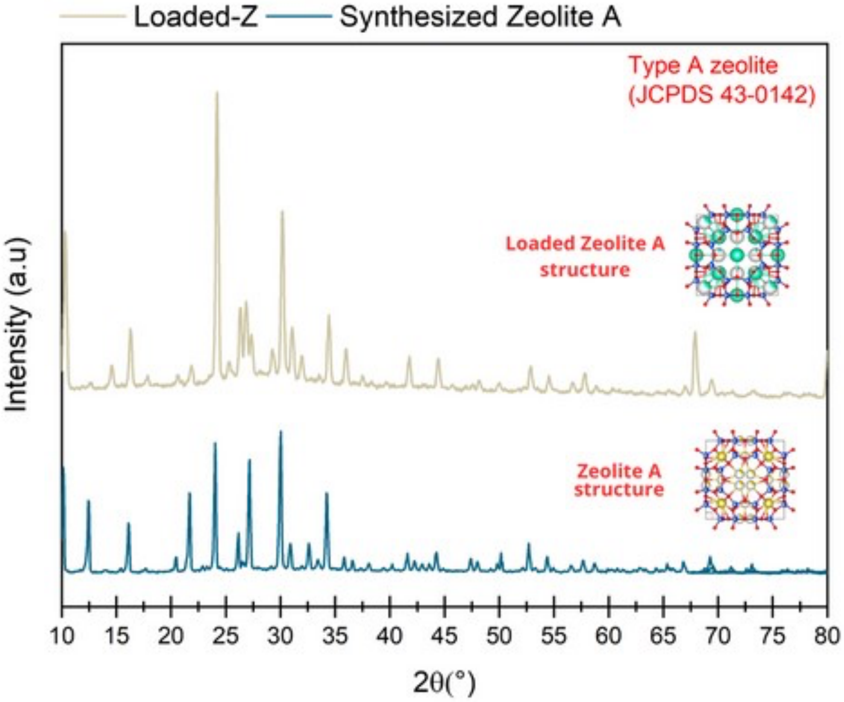

Figure 2: X-ray diffraction patterns of the zeolite before (as synthesized) and after (loaded) the adsorption experiment.

From the data obtained it was possible to identify the crystalline phases present in the samples. As expected, the peaks identified in the synthesized sample correspond to the crystalline phase of zeolite 4A (JCPDS 43-0142). The absence of peaks related to quartz (SiO_2) indicates that this compound present in the ash has completely reacted with sodium hydroxide during the formation of the zeolite, resulting in a high purity zeolitic material. The diffractogram of the loaded-Z mainly showed changes in intensity, due to the scattering properties and the high X-ray absorption coefficient of the Cs^+ ions, a behavior already reported in the literature[7,9]. The observed changes are indicative of the high selectivity of the Cs^+ ions for, with Na^+ ions being replaced by Cs^+, which perform the same function of stabilizing residual charges in the zeolite crystalline structure. The identified crystalline phase corresponds to dehydrated zeolite A, partially or completely replaced by cesium containing five crystalline structures[10], a result in agreement with data obtained by XRF.

To ensure the proper disposal of loaded or contaminated zeolites and considering the temperature range of this procedure, it's crucial to comprehend their thermal stability thresholds. The comparative results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of loaded Z are shown in Fig.3.

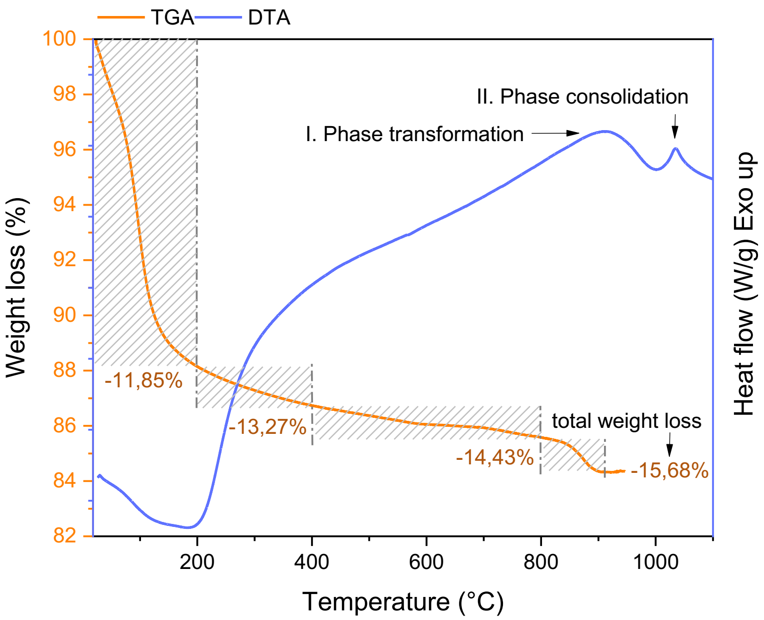

Figure 3: Differential thermal (DTA) and thermogravimetric (TGA) analysis of Loaded-Z.

Amorphization is the conversion of a crystalline state into an amorphous state without going through a melting or vitrification process. This phase transformation occurs gradually due to chemical, thermal, or pressure-induced alterations in the crystalline structure [11]. In general, zeolite A is characterized by having an exothermic around 900°C related to this phase transformation[12] and an exothermic peak at 1035°C to its consolidation[13,14].

From the graph of heat flow as a function of temperature it is possible to observe that at 400 °C the dehydration was complete, associated with a weight loss of approximately 13%. As the temperature rises, the material demonstrates stability until reaching around 800°C, at which point a notable exothermic shift commences and stabilizes at 913°C. At 1035°C, an exothermic event occurs, characterized by a peak. The cumulative weight loss observed was 15.68 %. The results are in accordance with the reported in literature supporting the thermal stability maintenance after the ionic exchange.

The allusion to amorphization process is evident when observing SEM images of Loaded-Z before and after heating treating, as shown in Fig. 4. The original cubic structure of the zeolite changes into globular shapes after being heated at 913°C for 2 hours.

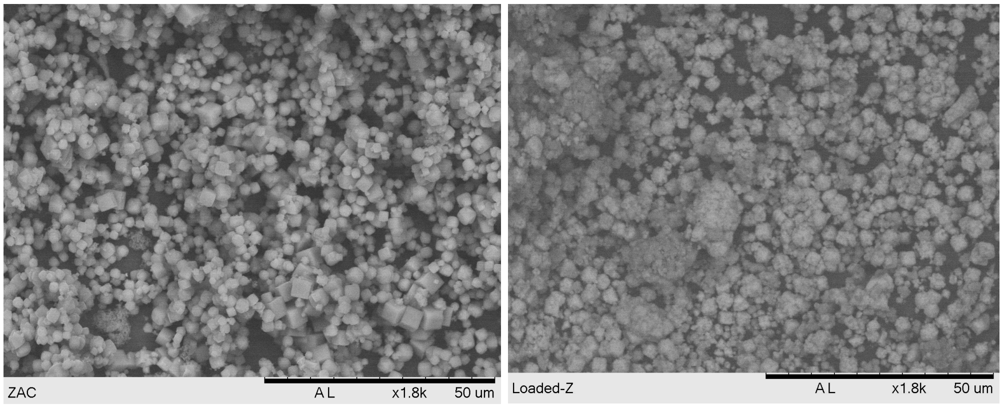

Figure 4: Scanning electronic micrographs obtained of Loaded-Z at room temperature (left) and after heat treated at 915°C for 2 hours (right).

To complement the results from thermogravimetric analysis reported above, XRD analysis was conducted to investigate whether any temperature-induced mineralogical transformations were occurring at 913 and 1035 °C and are presented in Fig.5.

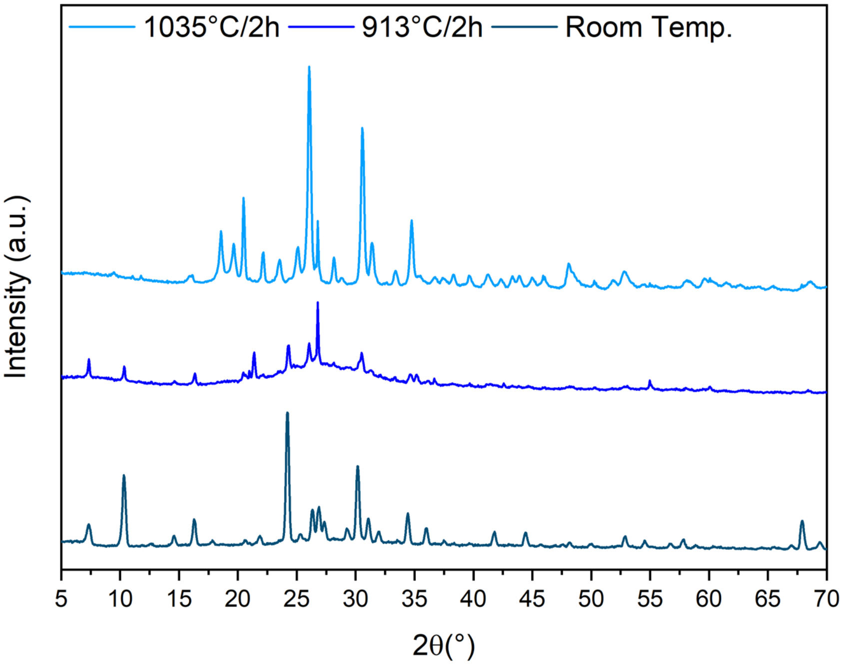

Figure 5: XRD powder diffraction profiles for Loaded-Z at Room temperature and after treatment at 913 and 1035 °C for 2 hours.

As previously discussed, and observed in Fig. 2, zeolite synthesized under pre-determined conditions from bagasse ashes sugar cane resulted in type A zeolite, corresponding to the crystalline phase 4A, also known as Na-A. According to diffractograms presented in Fig. 5, after heat treatment at 915 °C for 2 h, the formation of a new crystalline phase with different peaks, identified as carnegieite[15].

In conjunction with the results obtained from thermal analysis differential, the formation of carnegieite, polymorphic phase of nepheline, is associated with the well-defined exothermic peak observed at this temperature, which despite essentially being obtained at higher temperatures (around 1000 °C), in zeolites with higher sodium content, can be obtained at lower temperatures. At 1035 °C, new peaks can be observed with the formation and consolidation of the nepheline phase (4A)[15], the most stable phase.

As we have seen in this work the capacity for altering the composition of the starting zeolite by ion exchange, did not compromise its thermal stability required for the immobilization processes.

4. Conclusions

The results confirmed the obtention of high purity zeolites with adequate adsorption capacity. Moreover, most of the sodium content present in the zeolite was replaced by the ionic exchange of Na^+ ions for Cs^+ ions. Thermal gravimetric analysis and XRD analysis were successfully used to investigate the thermal stability of the zeolite type A synthesized from sugarcane bagasse ash. The ability of the synthesized material to retain structural integrity upon heating after the ionic exchange, make it a promising solution for the treatment and removal of cesium-137 content in radioactive wastewater.

Acknowledgements

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