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Evaluation of H_2S Sorption Capacity by Geopolymers Produced in Heterogeneous Medium

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Abstract: Geopolymers are composed of aluminosilicates that, upon activation by alkaline solution, form repeated units, and are classified as inorganic polymers. Geopolymers have gained great prominence due to the obtainment of the raw material, which can be natural or residual, the ease of production and low cost. These materials are widely used in civil construction to replace Portland cement and also in the environmental area for the remediation of toxic compounds. However, there is still little in the literature about the applications of these materials. Thus, this work aimed to use geopolymers for hydrogen sulfide gas sorption and it was possible to verify that they are able to adsorb twice its mass in gas.

Keywords: Geopolymer, remediation, hydrogen sulfide gas, cancrinite, safety

Adherence to the BJEDIS' scope: The article presented here has relevant results regarding the use and application of ANOVA statistical analysis and Tukey's method, which made it possible to identify the sorption capacity of the geopolymer during the test period. And the results showed that after 15 minutes there was no increase in the sorption capacity.

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1. INTRODUCTION

In the last decades the concern with the environment and human health has increased. This occurs mainly because of the release of toxic gases into the atmosphere, as well as environmental accidents that have caused the death of many people. These gases are known as greenhouse gases, namely nitrous oxide (NO_x), sulfur oxides (SO_x), carbon dioxide (CO_2), methane (CH_4), and chlorofluorocarbons (CFCs). Among these hazardous gases, SO_x have gained the most attention; they are produced from the burning of sulfur and its release by fossil fuel exploitation, for example, in the form of hydrogen sulfide (H_2S). Due to the danger of this gas, it is necessary to search for new materials that are able to capture it, avoiding damage to the environment and human health.(1).

Some authors have already shown some applications for the removal of hydrogen sulfide from the activities of the Oil and Gas industries. Nassan and collaborators in 2016, proposed the use of nanocomposites of vinyl acetate, acrylamide and Cadmium oxide in order to trap H_2S by means of fixed bed reactor. Moon and collaborators in 2019, meanwhile, produced a complex-structured crystal of Y-type zeolites loaded with manganese to perform a substitution reaction with hydrogen sulfide. Also in 2019 Bak and collaborators verified the sorption capacity of H_2S using commercial adsorbents such as, activated carbon, silica gels, iron oxide and iron oxide hydroxide (2- 3-4).

In this sense, it is possible to observe that there is the possibility of exploring new materials for H_2S removal. A new class of materials that has gained prominence in the application for environmental remediation are the geopolymers. Currently, they are used for the sorption of heavy metals (5).

These geopolymers are inorganic polymers with repeated units of alumino-silicates that form a three-dimensional structure with covalent bonds. The reaction occurs from the mixture of alumino-silicate with an alkaline solution (sodium hydroxide and/or sodium silicate) responsible for the activation of the reaction (6). Due to the structural configuration of geopolymers, mechanical properties such as flame resistance, acid resistance, high compressive strength, durability, low thermal conductivity, and low solubility are obtained, making them desirable for numerous applications. Moreover, the production of geopolymers is low cost, since they can be made from residual raw material rich in alumino-silicates, such as: fly ash, ash obtained from burning rice husk, red mud, glass powders, sedimentary rocks, clays and metakaolin (7-8).

Given these properties and structural configuration the geopolymers become promising, in the case of this work, its use consisted in the removal of hydrogen sulfide gas. To this end, activated geopolymers were produced in a basic medium and, verified the sorption capacity of hydrogen sulfide gas. The results obtained showed that the geopolymers were able to sorb 2g of gas per gram of geopolymer in 15 minutes of exposure.

2. MATERIALS AND METHOD

2.1. Geopolymer production

The geopolymers were produced from the use of a 12 M alkaline solution that was left to rest for 24 hours. After this period, 9 g of metakaolin was mixed in 20 mL of the alkaline solution and left to react for 10 minutes at 300 rpm. Next, the porosity agent (hydrogen peroxide) at 0.5% m/m was added and left reacting for 2 minutes at 300 rpm. Finally, the obtained paste was poured into a polypropylene pot and taken to the oven to cure for 2 days at 80°C.

2.2. Hydrogen Sulfide gas production (H_2S)

The production of hydrogen sulfide gas was done using 5 g of iron II sulfide and 10 mL of HCl. The reaction was done for 5 minutes in an erleymayer attached to a Kipp pipette. 0.5 g of geopolymer was inserted into a polypropylene tube, and the gas was piped into the tube for sorption. All tests were performed in triplicate.

2.3. Characterization

The samples were characterized by the following techniques:

X-ray Diffraction: The X-ray diffraction (XRD) tests were performed in a Rigaku X-ray diffractometer, Miniflex model. The method used was FT, at an angular step of 0.05°, in the 2θ range between 10° and 80°, with an acquisition time at each point of 1.0s.

Fourier Transform Infrared Spectroscopy: The samples' spectra were obtained in FTIR equipment - Nicolet iN10, using the attenuated total reflection (ATR) accessory equipped with a zinc selenide crystal. The parameters used

were resolution of 4 cm-1, with background reflection (run without sample) collected before each sample, in the range 4000 to 400 cm-1 and the samples analyzed in powder form.

Gravimetry: The geopolymers were weighed before and after sorption, so that it was possible to evaluate the increase in mass as a function of exposure time to gas. Every 15 minutes the material was weighed, and the test time was 1 hour. The calculation of the mass difference was performed by the following formula:

$$S = mf15\,\min(g) - mi(g) \quad (1)$$

S= increase of the weight after sorption (g)

mf15min(g)= final weight after 15 minutes of the exposition (g)

mi(g)= massa inicial.

Statistical Analyses: A mean comparison test was performed for the gravimetry test. The means were compared by the ANOVA and Tukey's method to observe the different values in the sorption capability.

3. RESULTS AND DISCUSSION

X-ray diffraction analysis was performed to investigate the crystalline structure of the geopolymers and its modification after sorption. The results obtained allowed us to identify peaks at angles of 14°, 25°, 36°, 44° and 50° for sodalite, and 31° for quartz (9), the main crystalline structures that indicate the formation of geopolymers, shown in Figure 1 (a). In Figure b, which shows the geopolymers after sorption, it was possible to identify crystalline peaks at 9° and 33° referring to the production of a new structure, known as cancrinite (Figure 1 (c)) with the following chemical composition: ((Na, Ca,) 8 (Al_6Si_6) O 24 (CO_3 , SO_4)$_2$ 2H_2O) (10), it was observed in this case, that the presence of sulfur modified the geopolymer favoring the formation of this new mineral.

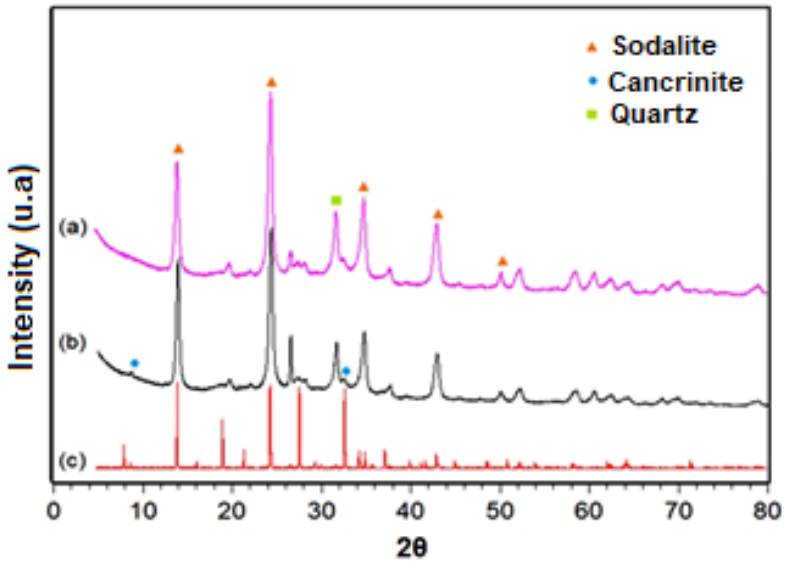

Figure 1. X-ray diffraction of (a) geopolymer before sorption; (b) geopolymer after sorption and (c) crystal structure of Cancrinite.

The Fourier Transform Infrared Spectroscopy was done in order to verify the chemical composition of geopolymers. It was possible to observe characteristic bands of the components present in geopolymers, being those at 665 and 732 cm^{-1} that refer to the vibrations of Al-O-Si bonds. The bands at 945 cm^{-1} are attributed to the asymmetric stretching vibrations of Si-O-T bonds (T=Si or Al) and the bands 1626 cm^{-1} and 3328 cm^{-1} refer to the stretching of hydroxyls in water, Figure 2 (curve b) (11). For the analysis of the presence of hydrogen sulfide gas, it was possible to evaluate the increase in intensity of the bands at 3328 cm^{-1}, which refers to the hydroxyls, indicating that the hydrogens of hydrogen sulfide gas bind to the oxygen of the geopolymer, thus increasing the band referring to the

hydroxyls. At 1123 cm^{-1} it was possible to identify the presence of S-O bonds, indicating that there was the absorption of gas molecules in the geopolymer structure (Figure 2 (b)) (12).

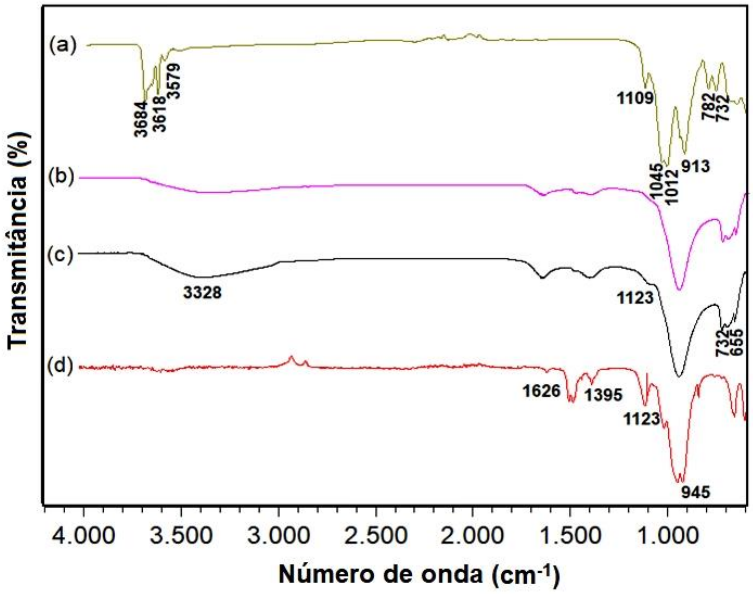

Figure 2. Fourier Transform Infrared Spectroscopy (a) Kaolin; (b) geopolymer before sorption; (c) geopolymer after sorption and (d) cancrinite.

The results of the gravimetry test showed that every 15 minutes of exposure of the geopolymer to the gas there was sorption of the gas by the material, which can be observed by the increase in mass. However, after 30 minutes of exposure, the mass remained constant, evidencing the saturation of the material. This effect can be more clearly observed in Figure 3, whereas the exposure time increases there is a stabilization of the mass of the material, but the results obtained were efficient; for each 0.5 g of geopolymer 1 g of gas was sorbed. According to reports in the literature, the sorption capacity of materials composed of zeolites is 10 mg of gas in 1 g of zeolite (13), thus, the geopolymer proved to be more efficient than these composites, because in a short exposure time the material can sorb twice its initial mass, which is of great importance, because the exposure time that can lead a human being to death in high concentrations of gas is 10 minutes (14). In addition, the statistical evaluation also proved the efficiency of the geopolymers in absorbing the hydrogen sulfide gas, applying the ANOVA and Tukey methods, it was possible to identify the equal and different values at 5% probability. Thus, the letters a and b indicate the difference in values, showing that after 15 minutes the material was able to sorb the gas.

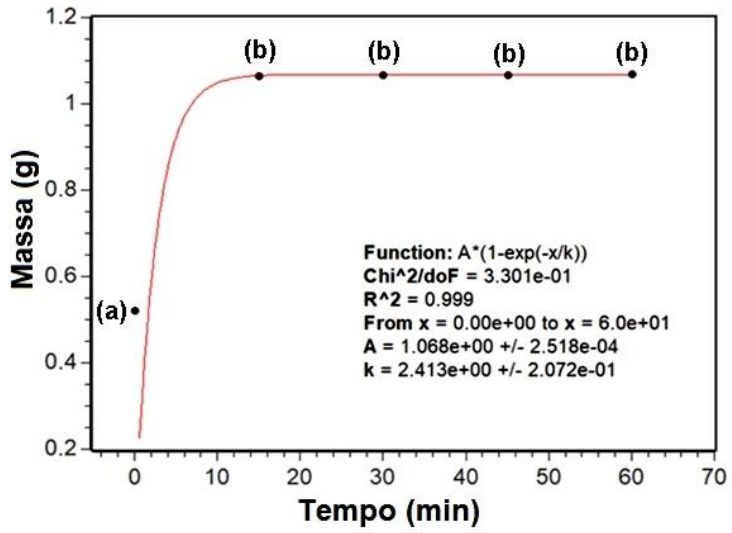

Figure 3. Increase of the weight of geopolymers when exposure hydrogen sulfide gas.

4. CONCLUSION

Through the results obtained it was possible to conclude that, the XRD and FTIR techniques showed the formation of geopolymers, as well as the modification of the crystalline structure and chemical composition after the sorption of hydrogen sulfide gas. The presence of sulfur and increased hydroxyl bands in the FTIR spectra evidenced chemical bonds between H_2S and the geopolymer, thus confirming the gas absorption. In addition, the gravimetry results showed an increase in mass as a function of the exposure time of the geopolymer to the gas, showing that the geopolymer was able to retain in its structure 2 g of gas per gram of geopolymer. These results are satisfactory, since they indicate that the use of a low-cost and environmentally harmless material can be a great mitigator of environmental impacts involving accidents with hydrogen sulfide gas.

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Sample CRediT author statement

Fabíola da Silveira Maranhão: Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation. **Fernando G. de Souza Junior:** Conceptualization, Supervision, Reviewing and Editing. **Sérgio Thode Filho:** Conceptualization, Supervision, Reviewing and Editing. **Daniela Batista de O. Gaspar:** Reviewing. **Arícia G.B. da Motta:** Reviewing. **Diganta B.Das:** Data analysis and Reviewing.

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