Utilization of the Paragominas mining tailings to obtain FAU zeolite: Synthesis optimization using a factorial DOE and Response Surface Methodology

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Abstract

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The bauxite processed in the Mineração Paragominas SA has its content of reactive silica reduced by disaggregation/washing and classification stages. This process generates a significant amount of fine fraction rich in kaolinite, which is currently discarded in tailings dams. Considering the environmental liability regarding this disposal, this work investigates the technical feasibility for using the tailings waste material to produce zeolite – a material that has several industrial applications due to its microstructural characteristics. A sequential methodology of factorial design of experiments (DOE) and response surface methodology (RSM) was used to evaluate experimental variables that influence the production of synthetic FAU-type zeolite. The experiments were carried out in hydrothermal system using NaOH solution and the products were analyzed by XRD where peak intensities of the zeolitic phases were used as the response variables. A crystalline FAU zeolite was successfully produced. Among all the variables considered in this study the alkaline concentration, SiO_2 / Al_2O_3 molar ratio and time of reaction showed to be the most important factors for the FAU synthesis. In conclusion, the tailings proved to be a feasible resource to produce zeolitic materials and most influential parameters for this process were determined. The transformation of kaolinite rich tailings into a useful product could represent benefits in economic and environmental terms. Further studies should be done to evaluate the product's performance and potential market demands.

Keywords: Bauxite tailings, DOE, FAU-type Zeolite.

1. Introduction

The mining industry plays an important role in the Brazilian economy, and the Amazon region is a major center of mining of bauxite. According to the Mineral Summary 2016, the state of Pará - Northern Brazil - was responsible for 93.1 % of the national production of bauxite [1]. Despite its importance, the production bauxite generates a significant amount of tailings during ore processing. Currently, the tailings represent an environmental liability to the mining industry, especially in the Amazon region, where areas are deforested for their disposal, and because of its very fine particle size (< 4 µm), it hampers vegetation recovery [2, 3].

Most recently a quite similar clay material – kaolin tailings – have been widely studied on zeolite synthesis using it as cheap and environmentally friendly raw material. The results showed that it is technically feasible to produce several types of zeolites, such as NaA, NaP, Faujasite (FAU), chabazite and basic sodalite [4, 5, 6, 7, 8, 9]. Previous studies shown that the tailings generated by bauxite washing process (Mineração Paragominas - Norsk Hydro) is mainly composed of gibbsite (chemically represented as $Al_2O_3 \cdot 3H_2O$) and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). This fact brings a glimpse to explore both kaolinite and gibbsite present in this waste as a source of SiO_2 and Al_2O_3 to produce zeolites. The concept to use of industrial tailings as raw material for the production of new materials with potential economic application can represent a sustainable approach with financial and environmental returns for the industries and society, in this case, inserted in the Amazon region.

Several variables, such as metakaolinization [10], the SiO_2 / Al_2O_3 molar ratio [11, 12], the reaction medium alkalinity [13], temperature and time of synthesis, have been reported to be influencing factors for the zeolitization process, both in relation to the type of zeolite to be formed and its microstructural characteristics [14, 15, 16]. However, it is difficult to estimate what experimental conditions are adequate to synthesize only a specific phase for the following reasons: a) The number of possibly significant controllable variables in the reaction system is very large; in addition to the factors mentioned above (which are examined in this study), several others have been reported, such as the kaolin calcination conditions [17, 18, 19], aging conditions [20, 21, 22], and the presence of impurity minerals [23]; b) The factors are usually studied separately and at different levels, which makes it impossible to correlate reported results or to identify interactions between the factors [24]; and c) Some data cannot be reproduced under similar conditions, which makes it difficult to confirm the conclusions of other authors [23, 25].

For this reason, the present study aimed to investigate the best synthesis conditions for producing not only a zeolitic material (composed by several zeolite phases) but a FAU-type zeolite as the only synthesized material. Therefore, the factorial design of experiments (DOE) and response surface methodology (RSM) with the desirability tool were applied to determine an optimized experimental region and a regression model of FAU-type zeolite synthesis considering the most influential experimental factors. Such study appears to be a novel approach, both for transforming this tailings into something of economic value and for bringing together a large number of factors in the hydrothermal syntheses of FAU-type zeolites and analyzing their influence and interactions, which could be helpful for futures studies on FAU-type zeolite synthesis from clay minerals.

2. Experimental

All the experiments performed to obtain the zeolitic material were conducted in a hydrothermal system using Teflon lined stainless steel reactors (50 mL capacity), under autogenous pressure. It was used a fixed mass of the gibbsite-kaolinite waste (3 g) and volume of the NaOH solution (25 mL) varying the concentration of the alkaline solution. An amount of amorphous silica was added to ensure the SiO_2 / Al_2O_3 molar ratios desired – previously calculated from the content of SiO_2 and Al_2O_3 in the tailings. The reactors were placed in an oven for heating with the temperature and time varying. All the variable values were set according to the experimental design. After the syntheses, the products were filtered and washed using distilled water until pH ~7, dried in an oven at 105 °C for 6 hours, and analyzed by X-ray diffraction (XRD).

2.1. Materials

The raw materials used were the bauxite tailings (BT) from Mineração Paragominas SA - Norsk Hydro generated by ore washing/grading; an amorphous silica (commercially named SILMIX®) co-product from the silicon metal production by Dow Corning Metals of Pará. It is noteworthy that this amorphous silica was previously considered as an industrial mineral waste, however, due to its potential applications (mainly for the cement industry) it has become a co-product. Alkaline solution (NaOH) was used as the leaching agent and source of Na_2O for the zeolite.

2.2. Experimental Design

This whole study was based on a sequential experimental design methodology. In the first step, a fractional factorial design was conducted to determine the most significant variables. In the second step, after establishing the values of the less significant variables, a path of steepest ascent

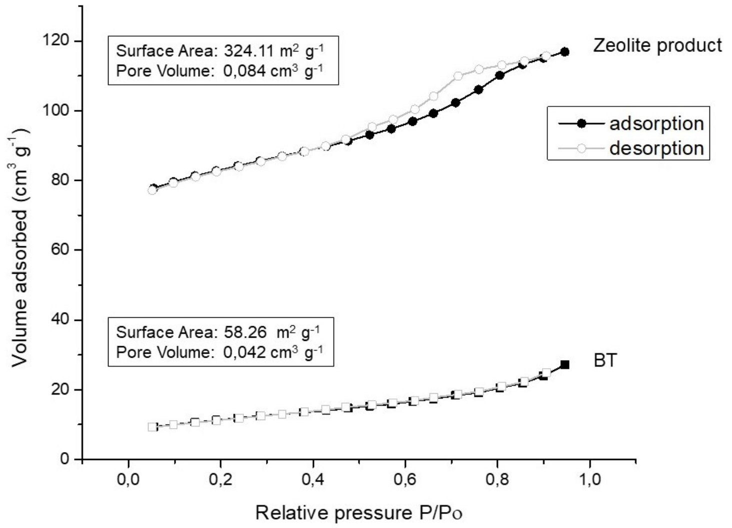

Figure 8. N_2 adsorption-desorption isotherms. a) raw material (BT); b) zeolite product (run n° 5).

4. Conclusion

The objective to produce FAU zeolite from the Mineração Paragominas SA bauxite tailings was successfully achieved. This approach can represent an economical proposal and environmentally friendly, using this abundant waste as a cheap material to produce zeolites. Of course, it is extremely necessary not only evaluate the technical feasibility, but also the performance, application, costs and marked demand for this product. This assessment is ongoing.

To produce FAU zeolite, the synthesis parameters were optimized using a sequential factorial design methodology. The results showed that the most influential factors in the hydrothermal synthesis process are the alkalinity, SiO_2 / Al_2O_3 ratio and time. Calcination of the Bauxite Tailings is needed in order to favor the FAU zeolite and avoid the formation of basic sodalite. In addition, higher temperatures strongly favor the formation of sodalite.

The regression model showed a satisfactory fit. The response surface had a saddle profile which indicates that there is more than one optimal condition for FAU zeolite synthesis. In this context, considering a low consumption of the raw material and time, the best condition proposed to produce FAU zeolite from the Bauxite Tailings are: alkaline concentration = 126 g/L, SiO_2 / Al_2O_3 ratio = 1.82, time = 74 h, temperature = 70 ºC and calcined material.

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