

## HYDROTHERMAL SYNTHESIS BY ALKALINE FUSION OF ZEOLITE NA-P1 OF KAOLIN TAILINGS FROM AMAZON AND ITS APPLICATION IN METHYLENE BLUE RETENTION

G. A. LIMA<sup>1</sup>, B. A. M. FIGUEIRA<sup>2</sup>, C. S. S. ARAUJO<sup>3</sup>, A. M. S. SOARES<sup>4</sup>

Universidade Federal do Oeste do Pará<sup>1</sup>

ORCID ID: <https://orcid.org/0000-0002-0328-0509><sup>1</sup>

gisele.lima@ufv.br<sup>1</sup>

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### ABSTRACT

The use of waste from the mineral industry to obtain materials of technological importance has intensified in the last two decades, with the aim of reducing the environmental impact generated by them and adding value to an unwanted product. In the case of kaolin tailings from the Amazon, it is already being used for the production of zeolites. In this study, the results of the synthesis and characterization of P1-type zeolite and its application as an adsorbent for methylene blue dye are

presented. Obtaining zeolite P1 was monitored by X-ray diffractometry, infrared and Raman spectroscopy, thermal analysis and scanning electron microscopy. The results showed that the zeolite was obtained without impurities, high degree of crystallinity, thermal stability above 300° C and very distinct and defined morphology. It was able to adsorb up to 90% dye. Showing that kaolin waste can be transformed into utility products..

**KEYWORDS:** Zeolite P1, Amazon, Kaolin tailings, Adsorption.

## SÍNTESE HIDROTHERMAL POR FUSÃO ALCALINA DE ZEÓLITA NA-P1 DE REJEITOS DE CAULIM DA AMAZÔNIA E SUA APLICAÇÃO NA RETENÇÃO DE AZUL DE METILENO

### RESUMO

O uso de rejeitos da indústria mineral para obtenção de materiais de importância tecnológica vem se intensificando nas últimas duas décadas, com a finalidade de se reduzir o impacto ambiental gerado por eles e agregar valor a um produto indesejado. No caso dos rejeitos de caulim da Amazônia, já se observa seu emprego para produção de zeólitas. Neste estudo, apresentam-se os resultados de síntese e caracterização de zeólita do tipo P1, e sua aplicação como adsorvente de corante azul de metileno. A obtenção da zeólita P1 foi monitorada por difratometria de raios-X, espectroscopia de infravermelho e Raman, análise térmica e microscopia eletrônica de varredura. Os resultados mostraram que a zeólita foi obtida sem impurezas, alto grau de cristalinidade, estabilidade térmica acima de 300° C e morfologia bem distinta e definida. Ela conseguiu adsorver até 90% corante. Mostrando que os rejeitos de caulim podem ser transformados em produtos de utilidade.

**Palavras chave:** Zeólita P1, Amazônia, Rejeito de caulim, Adsorção.

## 1. INTRODUCTION

The Brazilian economy significantly relies on the mining industry. According to the Mineral Summary from the National Department of Mineral Production in 2018, Brazil is among the top 10 producers of Kaolin globally. Its domestic production is mainly concentrated in the northern region of the country, and there is a possibility that this production has increased in subsequent years due to the growing demand for Kaolin. Kaolin is used in various industries, including catalysts, paints, cement, general plastics, cosmetics, ceramics, animal feed, and primarily in paper production (DNPM, 2018).

Alongside the substantial ore production, the beneficiation process results in the generation of rejects—materials not useful for industrial production—that are deposited in extensive reservoirs. Today, they are a major concern, especially after the ruptures of large ore tailings dams, such as the Samarco mining dam in Mariana/MG (2015) and the recent disaster at the tailings dam in Brumadinho/MG (2019), both causing alarming environmental and social catastrophes. Therefore, it is necessary for these rejects to serve a purpose to reduce the creation of large reservoirs and thus mitigate risks such as soil and water contamination, biodiversity compromise, and social issues resulting from their rupture.

In the beneficiation of Kaolin, two types of rejects are generated: the first composed of quartz (10% of gross production), and the second composed of kaolinite (26% of gross production), typically deposited in settling ponds (Maia et al., 2008). The second type allows for the production of low-cost synthetic zeolites because they are rich in Si and Al (Santana et al., 2012). Zeolites are hydrated aluminosilicates of alkaline earth metals or alkali metals, composed of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (Wasem et al., 2015). Their structure features cavities and channels of molecular dimensions, providing them with a large internal surface area relative to their mass (Wasem et al., 2015).

Zeolites are widely used in the market due to their unique adsorption capacity, ion exchange, molecular sieving, and other properties, and they can be commercially found in natural or synthetic forms (Polat et al., 2004). In the environmental field, synthetic zeolites have attracted attention as low-cost adsorbents, especially when synthesized from by-products (Bertolini, 2019). The literature shows several studies on the application of zeolites in environmental recovery and depollution, such as heavy metal adsorption (Dal-Bosco et al., 2004; Oliveira, 2011; Ferreira, 2018; Andrades, 2018) and pesticide adsorption (Bajuk-Bogdanović et al., 2017; Jevremović et al., 2019; Mojiri et al., 2020).

This study aims to provide a sustainable use for kaolin rejects, aiming to contribute to the fulfillment of objectives established by the 2030 Sustainable Development Agenda, such as goal 9 – "Industry, Innovation, and Infrastructure," in building resilient, inclusive, and sustainable infrastructure and fostering innovation; goal 11 – "Sustainable Cities and Communities," in making cities and communities inclusive, safe, and sustainable; goal 12 – "Responsible Consumption and Production," ensuring sustainable production and consumption patterns; and goal 15 – "Life on Land," protecting, restoring, and promoting the sustainable use of terrestrial ecosystems, using forests sustainably, combating desertification, and halting biodiversity loss.

Therefore, this study aimed to synthesize and characterize zeolite P1 using kaolin rejects from the Amazon region. Additionally, an investigation was conducted on the application of this

zeolite as an adsorbent for methylene blue dye, with the purpose of mitigating the risks associated with socio-environmental issues resulting from polluting dyes.

## 2. LITERATURE REVIEW

### 2.1. Kaolin as a Starting Material for Green Zeolite Production

Seeking methods for synthesizing zeolites in a more sustainable and eco-friendly manner has become a concern for scientists. Meng, Wang, and Xiao are examples of researchers who have sought to synthesize zeolites in a more environmentally friendly way by eliminating the use of solvents, reducing organic synthesis models, and employing non-toxic models. Stemming from the concept of sustainable production, some materials can serve as cheaper and more ecological raw materials for zeolite synthesis, such as clay minerals, coal ashes, solid waste incineration ashes from municipal areas, and industrial slags (Meng et al., 2016). These alternatives contribute not only to the efficiency of synthesis but also to the reduction of environmental impact, aligning with the pursuit of more sustainable practices in scientific research.

Kaolin, a type of clay composed essentially of minerals from the kaolinite group (Ribeiro, Egreja Filho, Fabris, Mussel & Novais, 2007), is one of the most widely used natural resources as a raw material for synthesizing zeolites. This is because it has a layered structure, mainly composed of silica and alumina (Luz, 1995; Hartati et al., 2020). The waste generated in kaolin mining poses significant environmental impacts, requiring large areas for disposal (Longhi, Rodrigues, Bernal, Provis, & Kirchheim, 2016). Tendo como matéria prima os rejeitos de caulim, por exemplo, podem ser sintetizadas zeólitas do tipo faujasita, sodalita, zeólita A, analcima, chabazita e outras, que são usadas com diferentes finalidades, como: uso em produtos cosméticos, medicamentos, detergentes, adsorção de materiais pesados e agricultura (Moraes, 2014). Portanto é notável que os rejeitos de caulim podem ser promissores na indústria de síntese de diversos tipos de zeólitas, contribuindo para uma síntese mais verde e sustentável, buscando atender as três demandas da sustentabilidade.

The production of zeolites from kaolin rejects not only adheres to sustainability principles but also contributes to achieving various goals of the Agenda 2030. In this context, goals 9, 11, 12, and 15 stand out. Goal 9, "Industry, Innovation, and Infrastructure," benefits from the contribution to the development of new, more sustainable synthesis methods. Goal 11, "Sustainable Cities and Communities," is promoted by the responsible use of local resources. Goal 12, "Responsible Consumption and Production," is directly addressed by using rejects for zeolite production. Finally, Goal 15, "Life on Land," is favored by promoting environmentally friendly practices in the industry, reducing negative impacts on the ecosystem. This integrated approach not only contributes to sustainability but also aligns with global efforts to achieve broader sustainable development goals.

### 2.2. Zeolites

#### 2.2.1. Structure and Composition

The term zeolite comes from the Greek words "zeo" and "lithos," meaning boiling stone. Zeolites are hydrated aluminosilicates with a precise crystalline composition and uniform-sized pores that form molecular-sized channels. They are composed of tetrahedra TO<sub>4</sub>, structured into three-dimensional crystal networks, where T can be a silicon (Si) or aluminum (Al) atom, bonded to oxygen atoms (Abdullahi, Harun & Othman, 2017; Ilić & Wettstein, 2017; Luz, 1995; Payra & Dutta, 2003; Weitkamp, 2000), as illustrated in Figure 1. Their structure features open cavities resembling channels and cages, which are often occupied by water molecules or cations (Hartati et al., 2020).

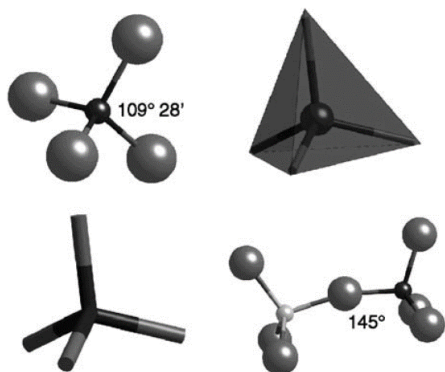


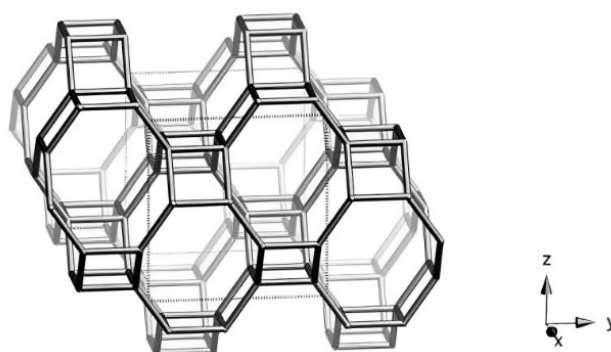
Figura 1: Basic unit of a zeolite. Source: Lobo, 2003.

A zeolite is composed of three components: a structural component (framework), an extrastructural component (extraframework), and an adsorbed component (water molecule) (Lobo, 2003). The extrastructural cationic part is exchangeable by ions, allowing for the zeolites' property of rich cation exchange (Payra; Dutta, 2003). This is because the bonds between ions and pore molecules are weak, enabling them to be easily broken without compromising the zeolitic material's structure (Jha & Singh, 2011; Yoldi, Fuentes-Ordoñez, & Korili, 2019).

Complex composite building units or secondary building units can be formed by linking basic building units (Baerlocher, Mccusker & Olson, 2007; Lobo, 2003). These secondary units can contain up to 16 atoms, forming single or double rings of four, six, or eight tetrahedra (Luz, 1995; Braga and Morgon, 2007). Subunits can be grouped in different combinations, allowing the construction of tertiary units, encompassing units with diverse chains and facilitating the formation of various zeolites such as zeolite A, X, Y, sodalite, and others (Braga and Morgon, 2007).

### 2.2.2. Zeolite P1

Zeolites P1 have an orthorhombic crystal system and share a structure similar to Gismondine-type zeolites. Topologically, they are related to the natural zeolite gobbinsite (Hansen, Håkansson, and Fälvh, 1990), as illustrated in Figure 2.



**Figure 2: Gismondine-type zeolite, similar to P1. Source: Baerlocher et al., 2007.**

There is widespread application of P-type zeolites in various studies. However, studies involving the application of P1-type zeolites are less common when compared to P-type zeolites. Examples of applications of P1-type zeolites include their use as adsorbents for dyes (Tsai, Hsien & Hsu, 2009) and heavy metals (Barkat, Nibou, Amokrane, Chegrouche, & Mellah, 2015), as removers of ammonia from water (Liu et al., 2018), and as soil stabilizers (Fungaro & Silva, 2004).

### 2.2.3. Application of Zeolites

Zeolites are minerals used in various applications due to their specific characteristics, such as a high degree of hydration, low density, large void volume when dehydrated, stability of the crystalline structure, cation exchange property, electrical conductivity, gas and vapor adsorption, and catalytic properties (Luz, 1995). Their large internal surface area makes them useful in different areas of application, ranging from use in the petrochemical industry to the adsorption of heavy metals.

In agriculture, zeolites are used as soil conditioners, nutrient carriers, as substrates in seedling production (GRUGIKI, 2007), and as natural fertilizers (Aainaa, Ahmed & Majid, 2018). With growing environmental concerns, these porous materials have gained significant importance in applications in this field as well. Zeolites are widely known for their adsorption capacity for various materials. They are used in the separation of pollutants and recovery of useful species (Ng et al., 2013), such as adsorbents for pesticides (Barbosa, Moura & Aouada, 2018) and heavy metals (Mgbemere, Ekpe, Lawal &, 2017).

### 2.3. Methylene Blue Dye

Methylene blue is a common, hazardous, and widely used dye (Muniyandi, Govindara & Bharath, 2021), primarily employed for dyeing silk, cotton, and wood (Zamel & Khan, 2021). It is a cationic thiazine used in various applications, from dyeing to medicinal uses (Subaihi & Naglah, 2022), and its structure is depicted in Figure 3.

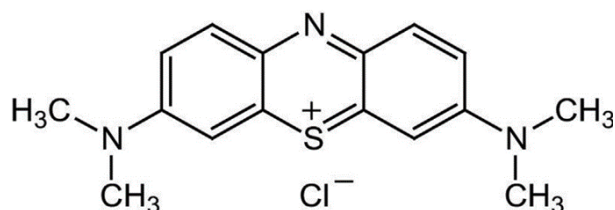


Figura 2: Estrutura do corante azul de metileno

Excessive exposure to this dye has harmful effects, such as nausea, diarrhea, necrosis, vomiting, diarrhea, and eye problems (Subaihi & Naglah, 2022). Inhalation of this substance can lead to short periods of rapid heartbeats or difficulty breathing (Zamel; Khan, 2021).

### 3. METHODOLOGY

#### 3.1. Study area

The kaolin rejects used in this study were collected from the kaolin mine waste basin located in the city of Vitória do Jari, in the far south of the state of Amapá. Kaolin extraction in this region has been taking place since 1976 by the company CADAM S/A (Costa, 2019). The kaolin collection in this area happened without specific quantification, with only the necessary portions for the experiment being extracted for this study.

#### 3.2. Synthesis Route of Zeolite P1

The initial material underwent a calcination process at 700°C for a period of 2 hours, resulting in the formation of an amorphous phase called metakaolin. For the synthesis of zeolite P1, metakaolin was used through an alkaline fusion method, following a hydrothermal treatment with adaptations based on Ma et al.'s methodology (2014). The process began with the production of a molten material, resulting from the combination of 4 grams of NaOH with 1 gram of reject, subjected to a temperature of 200°C in a muffle furnace over 4 hours. The generated product was cooled, pulverized, and mixed with 50 mL of H<sub>2</sub>O to obtain a white gel that was stirred and hydrothermally treated for 48 hours at 90°C in an oven. The final product was washed with deionized water, dried at 70°C, and pulverized for mineral characterization. The synthesis route can be illustrated in Figure 4.

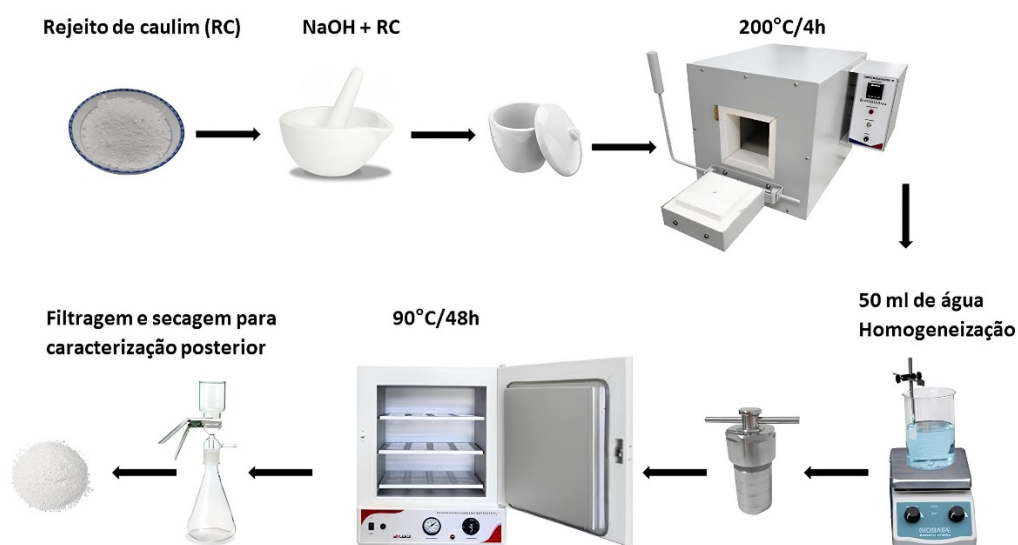


Figura 4. Rota de síntese da zeólita P1. Fonte: autora.

### 3.3. Material Characterization

To perform the characterization of zeolites, several techniques are required, such as X-ray diffraction (XRD), infrared spectroscopy, Scanning Electron Microscopy (SEM), and thermal analysis, which are described below:

#### 3.3.1. X-ray Diffraction

In this work, the X-ray diffraction (XRD) technique, powder method, was employed for the identification of mineral phases in rejects and synthetic products. Thus, a benchtop diffractometer D2Phaser (Bruker) available at the Laboratory for the Synthesis and Characterization of New Materials (LSCNM) at the Institute of Engineering and Geosciences (UFOPA) was utilized. This equipment features a vertical scanning goniometer and a copper tube ( $\text{CuK}\alpha = 1.5406 \text{ \AA}$ ) with a power of 400 W, adopting a Bragg-Brentano geometry in continuous mode, a scan speed of  $0.25^\circ/\text{min}$ , and a fast LynxEye model detector as the detection system. The voltage and current were set at 30 kV and 10 mA, respectively.

#### 3.3.2. Espectroscopia de infrav Infrared Spectroscopy

The mid-infrared spectra ( $4000 \text{ to } 400 \text{ cm}^{-1}$ ) were obtained using vacuum-pressed pellets containing 0.200 g of KBr and 0.0013 g of powdered sample, and a Fourier-transform infrared molecular absorption spectrometer from Bruker, model Vertex 70, available at the Mineral Characterization Laboratory (LCM) of the Institute of Geosciences (UFPA).

#### 3.3.3. Scanning Electron Microscopy

For SEM studies, the samples were pulverized, dispersed onto graphite-coated supports, and gold-coated. The instrument used was a LEO-Zeiss 430 Vp microscope, under analysis conditions



with secondary images obtained at 20 kV, and a working distance of 11 mm, at the Federal University of Pará (UFPA).

#### 3.3.4. Thermal Analysis

The TG and DTA curves were obtained using a Stanton Redcroft thermal analyzer, equipped with a vertical cylindrical furnace and a digital converter linked to a microcomputer. The analyses were performed in a platinum crucible, with a heating rate of 20°C/min, and the initial and final temperatures varied from 20°C to 1100°C, respectively, conducted at the LCM of UFPA.

#### 3.4. Determination of the Zero Point of Charge

The pH<sub>zpc</sub> of NaP1 zeolite was measured using the pH change method reported by Liu, Li, and Zhou (2021). The specific measurement steps are as follows: A NaCl solution (0.01 mol/L) was prepared, and its pH was adjusted to 3.0-11.0 using 0.1 mol/L NaCl and 0.1 mol/L HCl. Subsequently, 20mg of the adsorbent (NaP1 zeolite) was added to 20ml of NaCl solutions with different pH values and stirred using a thermostatic oscillator at 250 rpm and 25°C for 48 hours. The final pH of the samples was measured and recorded.

#### 3.5. Adsorption Test

For the adsorption tests, this study was based on the methodology described by Liu et al. (2018), with adaptations. Firstly, a stock solution was prepared with a concentration of 250 mg/L. From this solution, a calibration curve was constructed with the following concentrations: 1 mg/L, 3 mg/L, 5 mg/L, 7 mg/L, 7.5 mg/L, 10 mg/L, and 15 mg/L, following the dilution law. After preparing these solutions at different concentrations, readings were taken using UV-visible spectroscopy, and absorbance values were recorded and plotted in an Excel spreadsheet.

Three concentrations were created from the mother solution for the study of time vs. contact with zeolite P1. To assess the effect of time, three time points (1, 2, and 3 hours) were studied at three concentrations (3 mg/L, 5 mg/L, and 15 mg/L). In Falcon tubes, 0.05g of zeolite P1 was added to 25 ml solutions of methylene blue, and the mixtures were stirred at 200 rpm at room temperature for a specified time. At each hour, a solution was withdrawn, filtered, and its absorbance was measured using UV-visible spectroscopy for subsequent data analysis. The test can be illustrated in Figure 5.



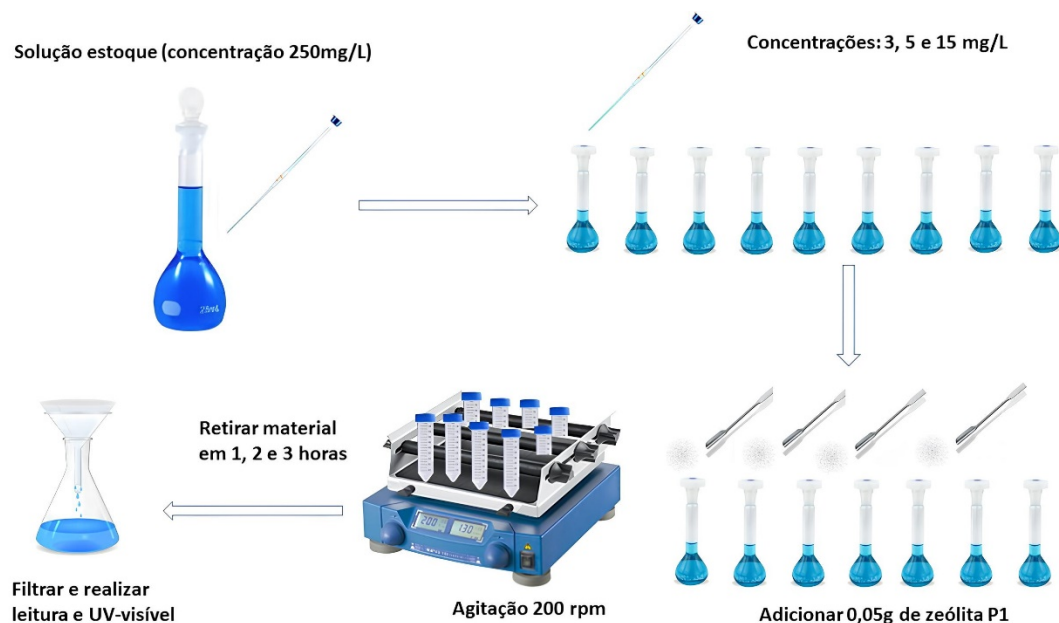


Figure 5. Path of Methylene Blue Adsorption Test.

The efficiency of methylene blue removal and the amount of adsorbed methylene blue by the zeolite were estimated by equations 1 and 2, respectively:

**Equation 1. Methylene Blue Removal Efficiency**

$$R = \frac{(C_0 - C)}{C_0} \times 100\%$$

**Equation 2. Amount of Adsorbed Methylene Blue:**

$$qe = \frac{V(C_0 - C)}{m}$$

Where R is the removal efficiency,  $qe$ : is the amount of adsorbed methylene blue,  $C_0$  represents the initial concentration, C is the final concentration; V: is the volume in liters, and m: s the mass in grams.

## 4. RESULTS AND DISCUSSIONS

### 4.1. Material Characterization

#### 4.1.1. X-ray Diffraction

The X-ray diffractograms obtained for the kaolin rejects samples (RCJar) and the synthesized zeolite (Gizeo-P) are presented in Figure 6.

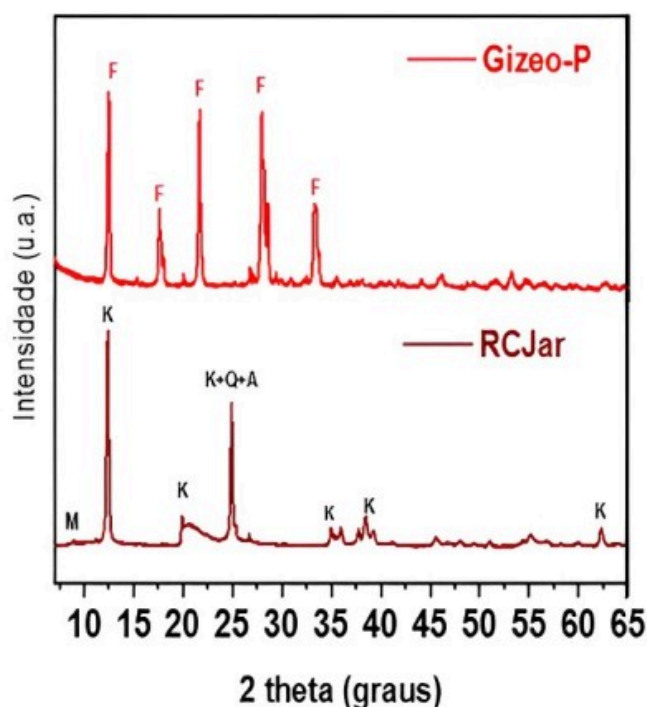


Figure 6. X-ray diffractogram of kaolin reject and Na-P1 zeolite. Where: F: Zeolite P1, K: Kaolinite, M: Muscovite, Q: Quartz, A: Anatase. Source: Author.

The XRD pattern of the RCJar sample showed peaks around 12° and 24° (theta), which are indicative of the mineral kaolinite, being the main phase in the sample. Additional peaks of minerals such as quartz (according to the PDF materials designation 01-082-0511), anatase (PDF 01-086-1157), and muscovite (PDF 00-007-0042) were identified at 25.3°, 26.67°, and 8.8° (2 theta), respectively. These results align with the mineralogy of these Amazonian kaolin rejects, as described by Maia, Angélica, & Neves (2008), who reported that the kaolin rejects are primarily composed of kaolinite, with major peaks on the (001) and (002) planes, and also mentioned a mineralogy composed of quartz, anatase, and muscovite in small quantities. The peaks found in this study also corroborate the results found by Silva, Cancio, Couto, Lima, Marinho & Figueira (2019) in the characterization of kaolin rejects from the Jari region.

In the XRD pattern of the Gizeo-P1 sample, more intense peaks were observed at positions 12.3°, 17.5°, 21.6°, 27.9°, 28.5°, and 33.2° (theta), corresponding respectively to the planes: (011), (002), (112), (031), (301), and (123), representing the structure of P-type zeolite.

#### 4.1.2. Average Chemical Composition of Kaolin

The average chemical composition of the rejects is presented in Table 1. As observed, there is a predominance of SiO<sub>2</sub> with an average around 44.85%, which can be related to the mineral phases belonging to the silicate group, such as kaolinite and quartz. Another element that stands out is Al<sub>2</sub>O<sub>3</sub> with a percentage of 36.91% on average, referring to the minerals kaolinite and muscovite. Fe<sub>2</sub>O<sub>3</sub> is at 2.02%. Finally, TiO<sub>2</sub> with an average of 1.89%, corresponding to the mineral anatase, constitutes contaminants in Amazonian kaolin (Sabadot et al., 2013). These values are

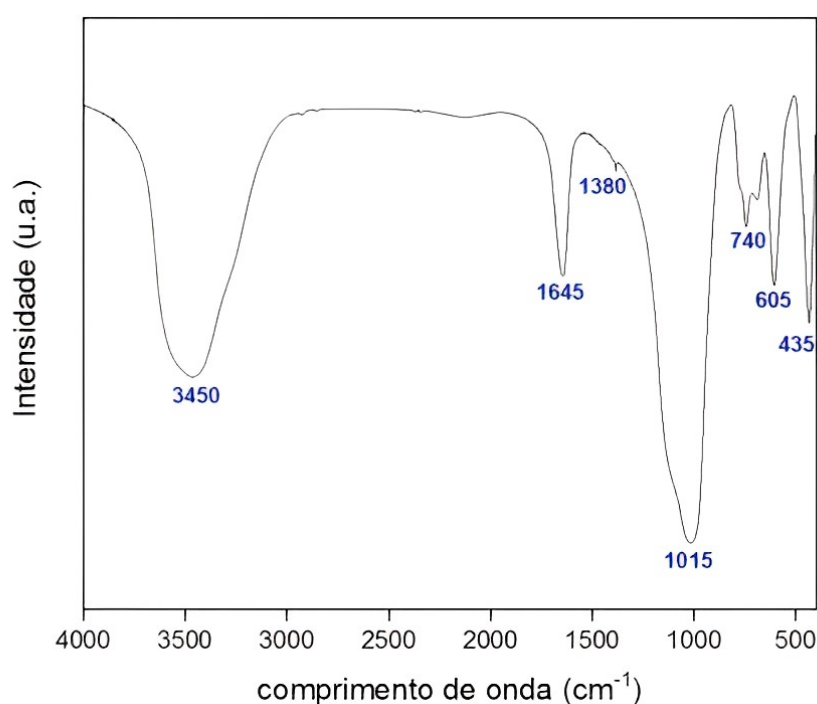
similar to those found in the study by Santana, Saraiva, Neves & Silva (2012), where higher percentages of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were found, being the main components of Amazonian kaolin rejects.

**Table 1. Average Chemical Composition of the Kaolin Sample by XRF Analysis. LOI: Loss on Ignition. Source: Author.**

FRX da amostra de rejeito de caulim – Jari												
Elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	P.F	Soma
Weight (%)	44,85	36,91	2,02	0,02	<0,01	0,04	0,04	1,89	<0,01	0,18	13,98	99,92

#### 4.1.3. Infrared

To complement the characterization of zeolitic materials, an infrared spectroscopy analysis was conducted, as illustrated in Figure 7.



**Infrared Spectra of Zeolite P1. Source: Author.**

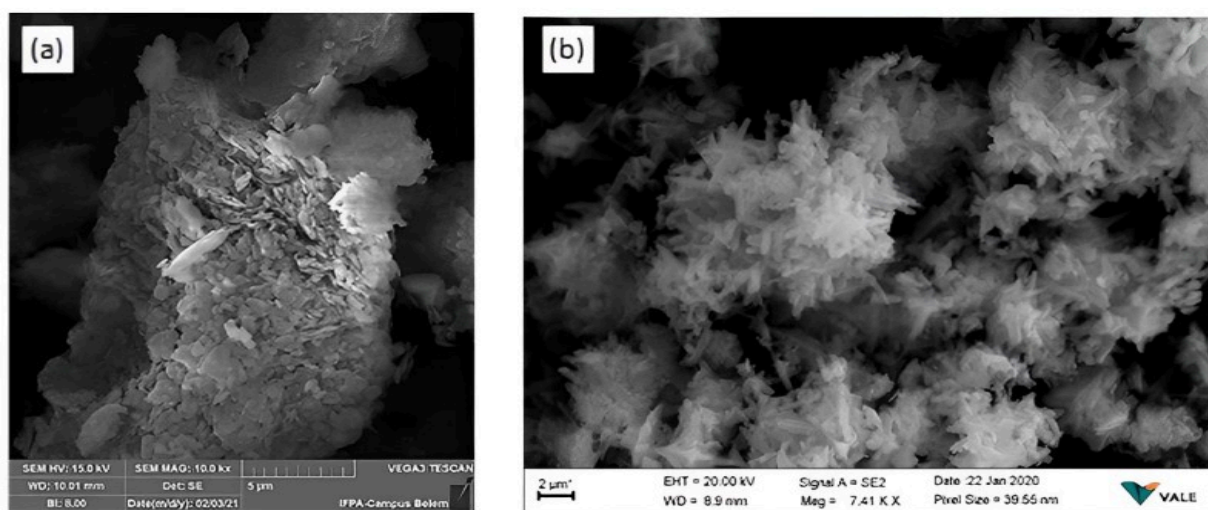
In the infrared spectroscopy, 7 bands were observed in zeolite P1. The first peak is found at approximately 3450 cm<sup>-1</sup>. In zeolites, bands around 4000 to 3000 cm<sup>-1</sup> correspond to the stretching vibration of OH groups and water molecules that may be present in the zeolite pores (Byrappa; Kumar, 2007).

Peaks around 1600 cm<sup>-1</sup> may indicate water absorption peaks (YUZAY et al., 2010). Infrared spectra around 1500 to 400 cm<sup>-1</sup> indicate structural characteristics of each zeolite, serving as a "fingerprint" for each one (Byrappa; Kumar, 2007). As observed in this study, from the 1600 cm<sup>-1</sup> peak onward, the peaks of each sample show notable differences. Peaks around 1000 are characteristic of zeolitic materials, as seen in the three samples (975, 980, and 1015 cm<sup>-1</sup>), associated with the asymmetric stretching mode of the tetrahedron.

Na zeólita P1 o pico em torno de  $740\text{ cm}^{-1}$ , corresponde a vibrações de alongamento simétrico relacionado a ligações externas à zeólita, a banda em  $605\text{ cm}^{-1}$  corresponde ao anel duplo presente na estrutura da zeólitas P1 e a vibração do tetraedro é encontrada no pico  $435\text{ cm}^{-1}$  (Sharma, Song, Han & Cho, 2016 In zeolite P1, the peak around  $740\text{ cm}^{-1}$  corresponds to symmetric stretching vibrations related to bonds external to the zeolite. The band at  $605\text{ cm}^{-1}$  corresponds to the double ring present in the structure of P1 zeolites, and the tetrahedron vibration is found at the peak  $435\text{ cm}^{-1}$  (Sharma, Song, Han & Cho, 2016).

#### 4.1.4. Scanning Electron Microscopy

Scanning electron microscopy images of the kaolin reject samples (RCJar) and the obtained zeolites are presented in Figure 9.



**Scanning Electron Microscopy Images of Kaolin Reject (a) and Zeolite P1 (b).**

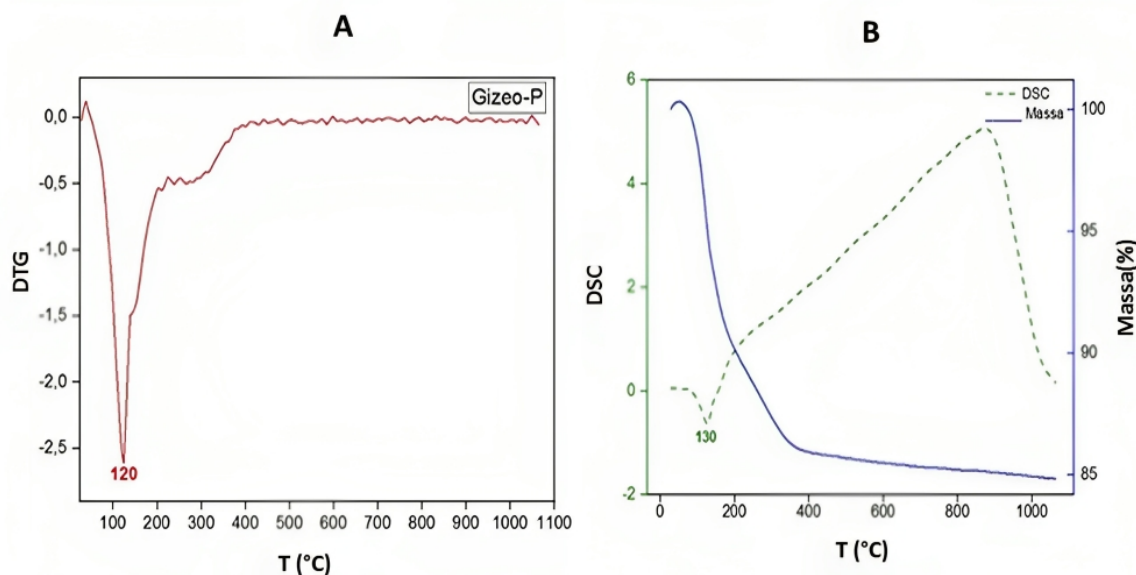
Scanning Electron Microscopy (SEM) is crucial for zeolite characterization, as it morphologically highlights differences between its raw material and the formed product (Bessa, 2016). The SEM analysis results of the RCJar sample show structures resembling stacked plates, confirming the X-ray diffraction results, primarily composed of kaolinite. Kaolinite, in turn, has a pseudo-hexagonal plate-like structure that can occur stacked or not, as in the structures of Amazonian kaolin described by Santos, Rocha Junior, Silva, Angélica & Neves (2013). These findings are similar to the SEM results found by Bertolino et al. (2013) in kaolin from Bahia, Brazil.

The Gizeo-P1 sample exhibited morphology similar to GIS-type zeolite structures, within which P1 zeolites are included. In the literature, it has been observed that there is difficulty in morphologically differentiating P1 and P2 zeolites due to their high visual similarity. Therefore, it emphasizes the importance of analyzing them through X-ray diffraction to differentiate them

accurately (Oleksiak et al., 2016). Zeolites of this type present different morphologies depending on the Si/Al ratio and synthetic conditions (Liu et al., 2018).

#### 4.1.5. Thermal Analysis

The heat flow results of the zeolites during heating are shown in Figure 9:



**Figure 9: A: DTG (Derivative Thermogravimetry) and B: TG (Thermogravimetry) and DSC (Differential Scanning Calorimetry) of Zeolite P1.**

The DSC of zeolite P1 showed a single sharp peak at 130°C, and the DTG at 120°C. This endothermic peak corresponds to the loss of water adsorbed by the zeolite structure (LIU et al., 2018). Regarding the mass loss, this sample exhibited a significant loss of 15% of its weight around 400°C. This loss around 400°C is due to the decomposition and removal of the OH group. The exothermic peak at approximately 900°C, unrelated to the mass loss of the structure, supports the studies of Xiao et al. (2015) and Liu et al. (2018), explaining that this peak is related to the transformation of the zeolite P1 structure and its decomposition. It can be concluded that its heat resistance occurs around this temperature.

#### 4.1.6. Zeolite as an Adsorbent

##### 4.1.6.1. Point of Zero Charge (pzc)

pH measurements were conducted to assess the pH influence on adsorption by determining the Point of Zero Charge (pzc) of zeolite P1. The pzc is defined as the pH of the solution where the charge of positive surface sites equals that of the negatives, resulting in a zero net surface charge for the adsorbent. Thus, the surface charge is negative if the pH is greater than the pH<sub>pzc</sub> and positive if the pH is lower than the pH<sub>pzc</sub> (Gulicovski, Čerović & Milonjić, 2008). Surface charge characteristics of adsorbents, such as zeolites, at different pH values influence the adsorption capacity, making it crucial to measure the pH<sub>pzc</sub> (Liu et al., 2021).

This study determined that the  $\text{pH}_{\text{pzc}}$  of zeolite P1 is 5.1, as observed in Figure 10. When the pH of the medium is below 5.1, the surface of zeolite P1 will be predominantly positively charged. This occurs because, under acidic conditions (low pH), functional groups on the surface of the zeolite accept protons ( $\text{H}^+$ ), resulting in a net positive charge. On the other hand, when the pH of the medium is higher than 5.1, the surface of zeolite P1 will be negatively charged.

This information is crucial in various applications, especially in adsorption processes, catalysis, and interactions with ions in solution. Knowledge of the point of zero charge helps understand how the zeolite interacts with different chemical species based on pH conditions, being essential for optimizing and controlling its performance in various applications.

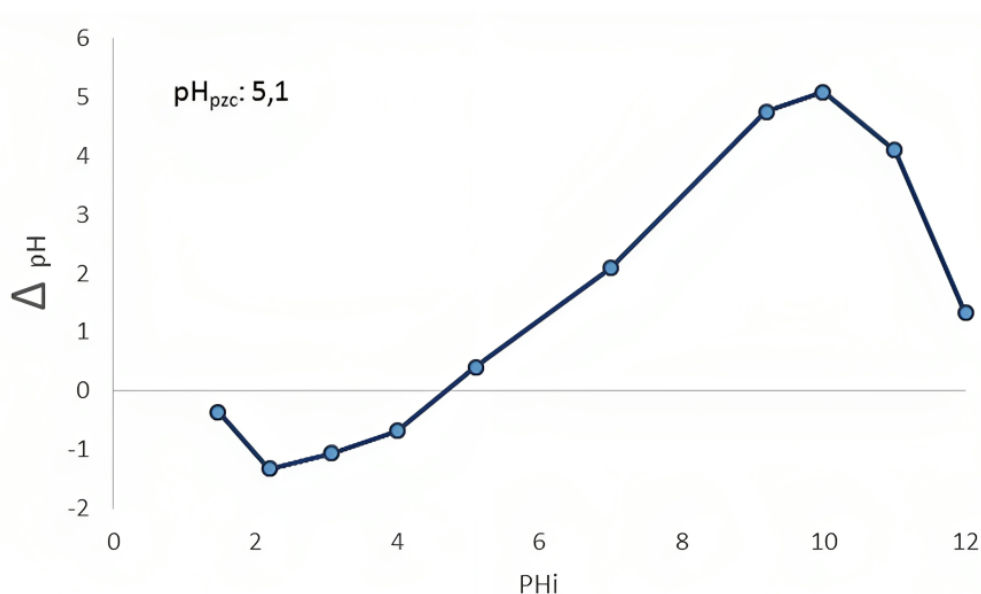
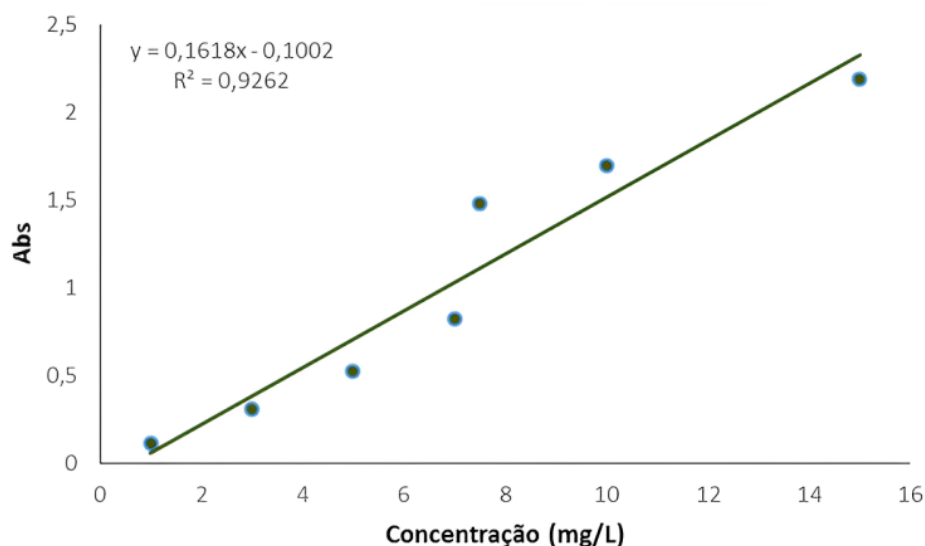


Figura 30: Ponto de carga zero da zeólita P1.

#### 4.1.6.2. Adsorption of Methylene Blue

The calibration curve was performed with data from different concentrations of methylene blue dye solution, concerning absorbance data. Through the graph, the equation formula and  $R^2$  were obtained to assess the effectiveness and reliability of the results, with an  $R^2$  value of 0.92 indicating high reliability, as this value is close to 1.



**Figure 11: Calibration Curve: Absorbance Data Error Parameter of Methylene Blue.**

The results of the adsorption tests yielded the following percentages: For tests with a concentration of 3 mg/L, the optimal percentage occurred with 3 hours of contact between zeolite P1 and the solution, resulting in an 87% adsorption of methylene blue, followed by 80% adsorption at 2 hours and 37% at 1 hour. In adsorption tests with concentrations of 5 mg/L, 2 and 3 hours showed similar results, with 90% dye adsorption, while 1 hour of contact resulted in 89% adsorption. At a concentration of 15 mg/L, the contact time of 3 hours stood out, achieving 90% adsorption, followed by 86% and 84% adsorption at 2 and 1 hour, respectively.

These results are also confirmed when observing the  $q_e$  values, which represent the amount of methylene blue adsorbed at equilibrium, as shown in Table 2. Regarding equilibrium values, this study observes that at a concentration of 3 mg/L, the best adsorption occurred at 3 hours. At a concentration of 5 mg/L, equilibrium values equalized at 2 and 3 hours. At a concentration of 15 mg/L, the highest equilibrium value occurred at 3 hours, with a higher adsorption percentage as well.

The  $q_e$  values are higher, indicating that the higher the initial concentration of methylene blue, the greater the adsorption quantity of the adsorbent needed to reach adsorption equilibrium (LIU; LI; ZHOU, 2021).

**Table 2: Influence of Contact Time on Zeolite P1 and Methylene Blue.abela 1: Influencia do tempo de contato da zeólita P1 e Azul de metileno.**

Conc. (mg/L)	T (h)	$q_e$ (mg/g)	% adsorption
3	1	0,57	37,87
3	2	1,20	80,07
3	3	1,31	87,04
5	1	2,25	89,85
5	2	2,27	90,63
5	3	2,27	90,83
15	1	6,30	84,04
15	2	6,45	86,00



15	3	6,75	90,02
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## 5. CONCLUSION

The kaolin waste from the Jari sedimentary basin is predominantly composed of kaolinite, with the presence of quartz, anatase, and muscovite. Chemically, they have high levels of SiO<sub>2</sub> (44.85%) and Al<sub>2</sub>O<sub>3</sub> (36.91%).

Zeolite P1 can be obtained through the alkaline fusion method, exhibiting purity and high crystallinity, along with thermal stability exceeding 300°C and thermal resistance up to 900°C.

Adsorption studies of methylene blue using zeolite P1 as an adsorbent demonstrated its efficacy, achieving up to 90% dye adsorption. The optimum adsorption time was found to be 3 hours of contact time.

Thus, the kaolin waste from Jari proves to be an interesting raw material for the cost-effective production of zeolite, contributing to a more sustainable production of materials and reducing the disposal of such waste into the environment.

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## ABOUT THE AUTHORS

### G. A. LIMA

Doctoral student in the Rural Extension Graduate Program at the Federal University of Viçosa. Holds a Master's degree in the Society, Environment, and Quality of Life Graduate Program from the Federal University of Western Pará. Graduated with a Bachelor's degree in Agrarian Sciences and a Bachelor's degree in Forestry Engineering from the Federal University of Western Pará (UFOPA).

E-mail: gisele.lima@ufv.br

ORCID ID: <https://orcid.org/0000-0002-0328-0509>

### B. A. M. FIGUEIRA

Works as a lecturer in the Materials Engineering Graduate Program (UFPA; IFPA). Holds a degree in Industrial Chemistry from the Federal University of Pará (2005) and completed a Sandwich Doctorate (Brazil-Germany) in Geochemical Sciences from the Federal University of Pará and Martin Luther University (2012).

E-mail: brunoufopa@hotmail.com

ORCID ID: <https://orcid.org/0000-0002-0507-8662>

### C. S. S. ARAÚJO

Master's degree in the Society, Environment, and Quality of Life Graduate Program from the Federal University of Western Pará. Graduated in Nursing.

E-mail: carlaaraujoenfermagemuepa@gmail.com

ORCID ID: <https://orcid.org/0000-0001-6844-4781>

### A. M. S. SOARES

Graduated in Industrial Chemistry from the Federal University of Pará (2012). Currently works as a laboratory technician and is a Master's student at the Federal University of Western Pará.

E-mail: adriele.soares@ufopa.edu.br

ORCID ID: <https://orcid.org/0000-0001-9763-6897>

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