

## Characterization of synthesized geopolymer and commercial zeolite 13X for application CO<sub>2</sub> adsorption

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### Abstract

The capture, storage, and utilization of greenhouse gases play a key role in combating global warming. It is estimated that around 90% of CO<sub>2</sub> emissions can be captured and stored, after a separation process. Therefore, increasing efficiency and reducing the costs of CO<sub>2</sub> capture and use processes need to be studied. Some authors have reported that zeolitic and geopolymeric adsorbents are efficient in controlling CO<sub>2</sub> emissions since they can be used in CO<sub>2</sub> separation processes from exhaust gases. Moreover, desorbed CO<sub>2</sub> can be utilized in different processes, such as electrochemical reduction, photocatalytic reduction, and catalytic methanation. This study presents a critical analysis and experimental data for the adsorption of CO<sub>2</sub> on commercial zeolite 13X and a phosphate waste based-geopolymer using phosphate at different temperatures. All solid adsorbents were deeply characterized using XRF, XRD, FTIR, SEM, EDS, XPS, DLS, NMR, real density, BET area, and porosity. Although the crystallinity of the adsorbents used in this work are different, the materials showed similar BET area and porosity. Furthermore, no difference in the crystallinity of the materials was observed during the CO<sub>2</sub> adsorption, as confirmed by XRD in situ measurements, which confirms that no carbonation or chemisorption of CO<sub>2</sub> occurs. Finally, both commercial zeolite and phosphate waste based-geopolymer showed similar CO<sub>2</sub> adsorption capacity in the temperature range 30-100°C, indicating that cost-effective adsorbent produced from phosphate waste can be produced to replace the most common adsorbent – commercial zeolite 13X – for CO<sub>2</sub> capture purposes.

**Keywords:** zeolite 13X; geopolymer; synthesis; characterization; CO<sub>2</sub> adsorption.

### 1. Introduction

Fossil fuels have been the world's primary energy source and are expected to remain for several decades [1]. Their combustion is one of the factors responsible for the emissions of greenhouse gases, like methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>), that produce permanent and irreversible damage to the climate system [2]. However, it is estimated that up to 90% of the CO<sub>2</sub> emission can be captured and stored after a separation process. Though, the high capital cost and limited storage have demanded utilization processes for the sequestered carbon dioxide [3]. Thus, CO<sub>2</sub> capture, and utilization need to be improved since they have an essential role in converting CO<sub>2</sub> into usable materials, such as methane, methanol, dimethyl ether, etc. [4]. Zeolites have been extensively studied in CO<sub>2</sub> separation due to their crystalline and microporous structures, high surface area, thermal stability, and adsorption selectivity. Moreover, zeolites can be synthesized using aluminosilicates or industrial solid waste, like fly

ash, rice husk ash, and coal ash [5]. In addition, geopolymer has gained a relevant research interest in recent years, mainly due to its low-cost and eco-friendly synthesis. The geopolymer matrix is predominantly amorphous and formed by a 3D network of aluminosilicates, overall activated by an alkaline solution [4,6]. Through the adsorption equilibrium isotherms carried out in three different temperatures, 30°C, 50°C, and 100°C, with pressure from 0 to 760 mmHg of the synthesized geopolymer and commercial zeolite 13X type.

### 2. Methodology

The process used to synthesize the geopolymer samples was based on [7,8], where low-cost geopolymers were developed by partial replacement of metakaolin by phosphate mining tailing, and a mix of sodium hydroxide and sodium silicate as alkaline activator. The molar ratios for the geopolymer's synthesis are SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> = 3.30; Na<sub>2</sub>O:SiO<sub>2</sub> = 0.30; Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub> = 0.99; and H<sub>2</sub>O:Na<sub>2</sub>O = 12.00, based on a study developed by

Davidovits [6]. The geopolymer was prepared by following steps: i) the metakaolin and phosphate waste were mixed; ii) the alkaline activator was prepared by mixing sodium hydroxide, sodium silicate, and deionized water; iii) the alkaline activator was mixed with solid mix materials; iv) the geopolymeric slurry was molded in a cylindrical shape, using silicon molds, and ; v) the material was submitted to the cure process, at 65°C for 48h in an oven, and then was submersed in deionized water at room temperature (20°C ± 2 °C) for 30 days, to remove the unreacted sodium ions. The geopolymer and zeolite 13X pellets (purchased from TradeShinli, China) were powdered using a high energy ball mill.

### 3. Results and Discussion

#### 3.1. Surface area, Porosity and Density

The density, surface area and pore volume and size are important factors for the selection of an adsorbent, and these characteristics are shown in Table 1. The desorption pore size of the Z13X is twice the GP, and they also showed a significant difference in the adsorption size, in the Langmuir surface area, the total pore volume is very alike, however, in the zeolite is also a little higher. The density of the GP sample is higher than the Z13X sample, with is expected, since the total pore volume is lower.

Table 1. Surface area, pore volume and size, and density of the Z13X and GPW samples.

	Z13X	GP
<b>Surface area (m<sup>2</sup>/g)</b>	628.56	573.85
<b>Total pore volume (cm<sup>3</sup>/g)</b>	0.20710	0.17345
<b>Adsorption pore size (Å)</b>	78.933	42.603
<b>Density (g/cm<sup>3</sup>)</b>	2.0999	2.2125

#### 3.2. Mineralogical Composition and Crystallinity

The XRD pattern of the Z13X and geopolymer samples before and after being subjected to a CO<sub>2</sub> adsorption process at different temperatures (30°C, 50°C, and 100°C) are presented in Figure 1 and 2. In this study both samples presented two crystalline phases, Faujasite (Na<sub>2</sub>Al<sub>2</sub>Si<sub>12</sub>.4O<sub>8</sub>.8·6.7H<sub>2</sub>O – ICDD 00-012-0246) as the main phase, and Quartz (SiO<sub>2</sub> ICDD 01-086-1628), however, as the Z13X sample have sharp and intense indicating a high degree of crystallinity [9], the geopolymer presented peaks at a very lower intensity. The presence of mineralogical crystalline phases in geopolymer especially when there is thermal cure in the synthesis process, is reported in many studies in literature [6,10,11]. Through the Figures 1 and 2

is possible to notice that there was no significant modification in the patterns of the Z13X and GP samples, only a slight difference in the intensity, discarding the presence of carbonate and confirming that there was no chemisorption.

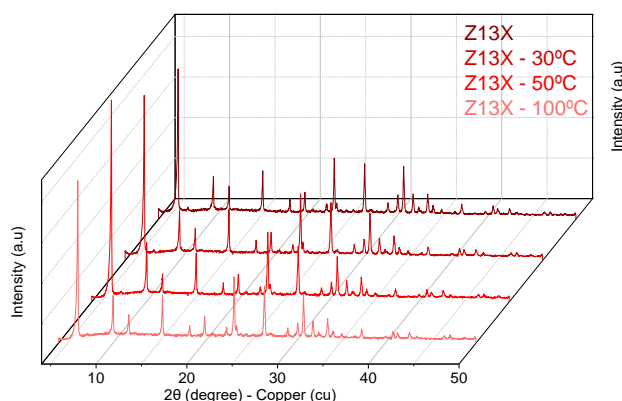


Fig. 1. XRD pattern of the Z13X sample before and after CO<sub>2</sub> adsorption

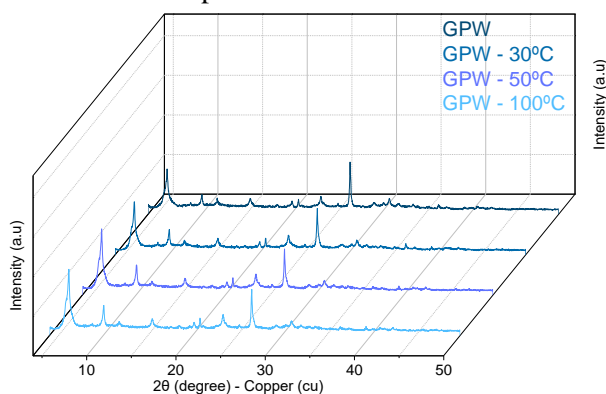


Fig 2. XRD pattern of the GP sample before and after CO<sub>2</sub> adsorption

#### 3.3. Morphology

The morphology of the microstructure of the samples are shown in Figure 3. The octahedral crystalline of the zeolite 13X particles can be observed in the images, some conglomerates also can be seen, also, despite the high crystallinity of the sample, it is possible to notice an amount of amorphous material in the sample. And it is possible to notice its dense and homogeneous structure of the GP sample, confirming the large amount of oligomers (Si-Al) in the reaction medium, which increases degree of geopolymerization of the material [12].

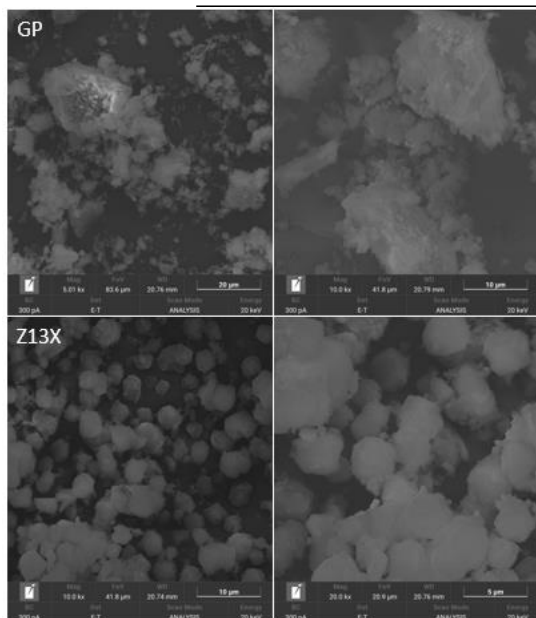


Fig 3. SEM images of the Z13X and GP samples.

### 3.4. CO<sub>2</sub> adsorption equilibrium isotherms

The capacity of a material to be adsorbent depends on many factors, such as some properties like surface area, volume, density, pore size and volume, and connectivity between the pores [13]. Figure 4 shows the CO<sub>2</sub> adsorption equilibrium isotherms at 30°C. The Figure also shows Sips mathematical model for each isotherm, which best fitted the samples.

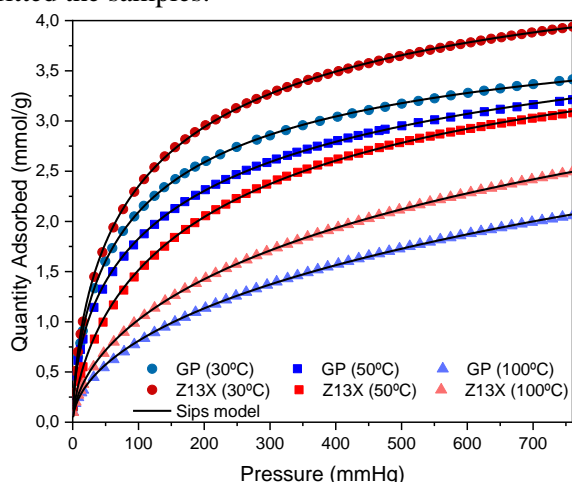


Fig 4. Adsorption isotherms and Sips mathematical isotherm model.

The fitted parameters are presented in Table 2, where we can see that  $n$  and  $K$  values decrease as the temperature increases, this decrease indicates that the adsorption phenomenon is exothermic.

The Z13X exhibited an adsorption capacity of 3.94 mmol/g and the GP 3.94 mmol/g at 30°C. At

50°C, the Z13X and GP adsorbed 3.21 and 3.08 mmol/g, respectively. As expected, the adsorption decreased at 100°C, which is consolidated in the literature for zeolites and geopolymers, so the zeolite adsorbed 2.50 mmol/g, while the geopolymer adsorbed 2.05 mmol/g. Comparatively, the adsorptive capacities of Z13X and GP are consistent with or slightly lower than those reported in relevant studies in the literature [7,8,14]. Furthermore, studies that investigated adsorptive capacity across multiple temperatures also observed a decline in adsorption with increasing temperature.

In both samples an increase in gas adsorption capacity is observed with increasing the gas pressure and temperature decreasing. This occurs because increasing the temperature, the internal energy and mobility of the adsorbed molecules in the pores of the samples also increase, resulting in a decrease in the interaction between adsorbate and surface [14].

Table 2. Z13X and GP parameters of Sips model.

Temp.	Sips model*	Z13X	GP
30°C	$K_S$	0.0076	<b>0.0088</b>
	$q_m$	6.84	<b>4.37</b>
	$n$	0.660	<b>0.662</b>
	$R^2$	0.999	<b>0.999</b>
50°C	$K_S$	0.0035	<b>0.0039</b>
	$q_m$	4.65	<b>4.97</b>
	$n$	0.699	<b>0.570</b>
	$R^2$	0.999	<b>0.999</b>
100°C	$K_S$	$5.84 \times 10^{-4}$	<b><math>1.19 \times 10^{-4}</math></b>
	$q_m$	6.84	<b>9.63</b>
	$n$	0.584	<b>0.539</b>
	$R^2$	0.999	<b>0.999</b>

\* $K_S = L \cdot \text{mg}^{-1}$ ;  $q_m = \text{mg} \cdot \text{g}^{-1}$ )

## 4. Conclusion

In this study a deep analysis of a synthesized metakaolin-phosphate mining tailing based geopolymer and a commercial zeolite 13X type for use in CO<sub>2</sub> capture was carried out. The XRD analysis was performed in the sample without adsorption and after being subjected to a CO<sub>2</sub> the adsorption process and through the results it was possible to confirm that there was no modification in the patterns, discarding the presence of carbonate and confirming that there was no chemisorption, just physisorption in the adsorption process, supporting the applicability of these materials for CO<sub>2</sub> adsorption. Also, the GP CO<sub>2</sub> adsorption capacity of 4.37 mg·g<sup>-1</sup> confirms that metakaolin-phosphate mining tailing as precursor for geopolymer synthesis results in a promisor material for capture and separation of CO<sub>2</sub>.

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