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Study on the synthesis of bionanocomposite materials based on pectin and clays for CO_2 adsorption.

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Abstract

The increase in carbon dioxide (CO_2) emissions has generated a growing demand for effective capture and storage technologies for this gas. This study investigates the potential of pectin-based bionanocomposites to enhance CO_2 adsorption. Pectin, a biodegradable biopolymer extracted from renewable sources, was combined with both pillared and non-pillared clays to form the composites. Pillaring of the clays, a process that replaces interlayer cations with larger polycations, increases interlayer spacing and surface area, improving adsorption capacity and the thermal stability of the clays. The materials were characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Thermogravimetry (TG), and Fourier Transform Infrared Spectroscopy (FTIR). The results showed that the composites with natural pillared clays exhibited more stable structures with smaller pores compared to composites using commercial clays, which displayed more irregular pores. These findings suggest that the bionanocomposites developed with natural pillared clays offer greater strength and efficiency in CO_2 capture, although further analysis is necessary to fully validate their properties and performance.

Keywords: Carbon dioxide (CO_2); Pillared clays; Bionanocomposites; CO_2 adsorption.

1. Introduction

The growing need to reduce CO_2 emissions has driven the search for materials capable of effectively capturing and storing this gas. Clays stand out in this context due to their natural adsorption ability, although they present limitations in their natural form, which has led to the development of methods to enhance this capacity [1]. Pillaring, a technique that replaces interlayer cations with larger polycations such as Al13, increases the interlayer spacing and surface area of clays, improving their adsorption capacity and thermal stability [2].

In this study, pectin, a biodegradable biopolymer obtained from renewable sources, was chosen as the polymeric matrix to synthesize bionanocomposites. The combination of pectin with both pillared and non-pillared clays aims to increase the efficiency of these materials in CO_2 adsorption, as well as to improve their mechanical, thermal, and morphological properties [3].

These bionanocomposites have the potential to combine the high CO_2 adsorption capacity of clays with the biodegradability of pectin, creating an innovative and sustainable solution for carbon dioxide capture. This approach not only improves CO_2 capture efficiency but also promotes a positive impact by reducing greenhouse gas emissions. By integrating natural and technologically advanced materials, this development offers a promising alternative that could significantly contribute to climate change mitigation and long-term environmental preservation.

2. Methodology

2.1 Synthesis

In this research, bionanocomposites were developed using pectin, supplied by Sigma-Aldrich with a galacturonic acid content ≥ 74%, as the polymeric matrix. Pectin was chosen due to its biodegradable and renewable properties. To enhance structural reinforcement and improve CO_2 adsorption capacity, five different clays were

incorporated. These clays were selected based on their specific characteristics and are detailed in Table 1 below.

Table 1. Clays used in the synthesis of the bionanocomposites.

Clays	Nomenclature
Natural White Pillared Clay	FCA
Natural Gray Pillared Clay	FCI
Commercial Pillared Bentonite	BENT P
Natural Bentonite	BENT
Natural Kaolinite	CAUL

The synthesis process involved dissolving 1 g of pectin in 50 mL of distilled water using a magnetic stirrer (IKA C-MAG HS 7) until a homogeneous solution was obtained. Simultaneously, 0.05 g of each clay were weighed and dissolved in 30 mL of distilled water, also under magnetic stirring, until complete dissolution. After complete dissolution, the solutions were mixed and kept under magnetic stirring for 30 minutes. The mixture was then transferred to an orbital shaker model SL-180/DT, where it was stirred for 48 hours to ensure complete incorporation of the materials and homogenization of the solution.

After stirring, the solutions were poured into cylindrical molds and placed in a freezer, where they were maintained at -20°C for 24 hours to allow complete solidification. The frozen samples were then subjected to the freeze-drying process in a lyophilizer (Christ alpha 2-4 LD plus) for 72 hours at -20°C.

2.2 Characterization

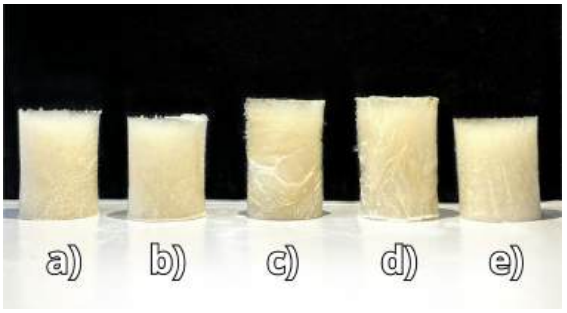
To evaluate the formation of the bionanocomposites and analyze the influence of each type of clay on the morphology of the foams, Scanning Electron Microscopy (SEM) was used. SEM was crucial for detailed analysis of the surfaces and internal structures of the bionanocomposites, allowing visualization of the interactions between pectin and the clays.

The analysis was conducted using the TESCAN MIRA 4 Scanning Electron Microscope, with a secondary electron (SE) detector at 5 KeV energy. This technique was employed due to its capability to provide high-resolution images of the surface and interior of the materials, allowing detailed visualization of the foam morphology and interaction between the polymer and nanoparticles.

3. Results and Discussion

Ongoing tests include a detailed evaluation of the CO_2 adsorption capacity of the composites, stability tests, and comprehensive characterization of the physical and chemical properties of the materials. These tests are crucial for understanding the actual performance of the foams under varied conditions and for validating the hypotheses formulated during the study. Figure 1 shows the bionanocomposites produced in the research.

Figure 1. Bionanocomposites produced in the research



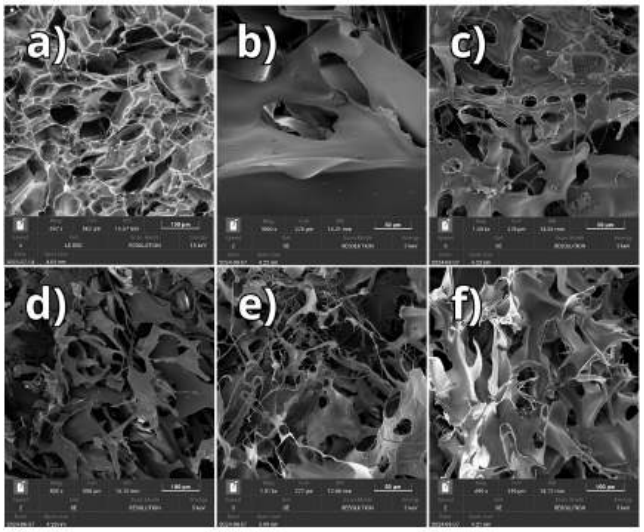
Based on the described synthesis process, all the clays used formed foams. These foams exhibit different structures and pore organizations due to the varying types of clays used. Figure 1.a shows the foam produced from the incorporation of FCI clay, Figure 1.b displays the foam produced with FCA, while Figure 1.c shows the bionanocomposite made with BENT clay, and Figures 1.d and 1.e present the foams produced with CAULI and BENT P clays, respectively. These differences in porous structure directly influence mechanical strength, structural stability, and CO_2 adsorption efficiency, as well as impacting the thermal and mechanical properties of the materials. These characteristics are crucial for optimizing the performance of the bionanocomposites.

3.1 Scanning Electron Microscopy

The micrographs presented in Figure 2 show the structure of the different materials: Figure 2.a

presents the foam produced with pectin without clay incorporation. Figure 2.b displays the foam produced with FCI clay, Figure 2.c illustrates the foam obtained with FCA clay, Figure 2.d shows the bionanocomposite incorporated with BENT clay, Figure 2.e refers to the bionanocomposite produced with CAULI clay, and Figure 2.f shows the bionanocomposite formed with BENT P clay.

Figure 2. Scanning Electron Micrographs of the synthesized foams



As illustrated in Figure 2, it can be observed that the foam produced with only the polymer has thin walls and large voids, making it less resistant compared to the others. In the foams produced from the polymer with clays, pores were formed in all samples, presenting thicker walls and smaller voids, thus confirming the formation of the bionanocomposites. Notably, foams produced from natural pillared clays, as evidenced in Figure 2.b for FCI clay and Figure 2.c for FCA clay, exhibit a distinct morphology compared to foams obtained from commercial clays. These natural clays display smaller pores and thicker walls, contributing to greater structural strength of the materials.

In contrast, foams formulated with commercial clays, as shown in Figure 2.d, Figure 2.e, and Figure 2.f, have a morphology with a greater number of voids and irregular pores. The presence of these voids can lead to reduced mechanical strength of the bionanocomposites, as the irregular distribution of pores compromises structural uniformity. The influence of pore size and distribution on material strength is well documented in the literature. Studies have shown that smaller pore dimensions and more uniform distribution are associated with greater mechanical strength and better structural performance of porous materials (Kumar et al., 2018).

4. Conclusions

The main expectation is that the composites developed from natural pillared clays would exhibit superior adsorption capacity and greater strength compared to commercial clays, leveraging the properties of the combined materials.

SEM results suggest that the composites produced from these clays may indeed offer advantages in terms of adsorption compared to commercial clays. Detailed analyses are currently underway to confirm and quantify these advantages. Additional tests are being conducted to assess the stability and durability of the materials at high temperatures. These analyses are crucial to validate the obtained results and determine the potential of the composites for practical applications.

With the SEM results alone, it is already possible to conclude that the composites were formed and that all clays were incorporated into the polymer. It is hoped that these studies will deepen our understanding of the composites' performance and contribute to the development of more effective solutions for CO_2 capture and storage.

References

[1] Nascimento, V. F. Study on the CO_2 adsorption capacity of pillared clays. *Journal of Environmental Management*, v. 160, p. 1-8, 2015.

[2] Oliveira, R. L. de. Pillared clays for CO_2 adsorption. 2024. [Undergraduate Research Report] – Federal University of Rio Grande do Norte, Natal, 2024.

[3] Guinesi, V.; Gomes, J.; Oliveira, L. M.; Silva, C. The role of pectin in the development of advanced materials. *Polymer Science Series B*, v. 44, n. 6, p. 563-572, 2006.

[4] Almeida, J. A. de. Low-density bionanocomposites based on rice starch, pectin, and palygorskite. 2017. 61 p. [Undergraduate Thesis

(Petroleum Chemistry)] - Institute of Chemistry, Federal University of Rio Grande do Norte, Natal, 2017. Available at: https://repositorio.ufrn.br/handle/123456789/38335. Accessed on: 15 Jul. 2024.

[5] Cardoso, A. L. Pectin: Characteristics and applications in the food industry. *Journal of Food Science*, v. 79, n. 12, p. 2805-2812, 2014.

[6] Corradini, E.; Carrillo, C.; Carvalho, J. M.; Coelho, P. Applications of pectin in pharmaceuticals. *International Journal of Pharmaceutics*, v. 330, n. 1-2, p. 15-21, 2007.

[7] Darder, M.; Matos, C.; Aranda, P.; Gouveia, R.; Ruiz-Hitzky, R. Bionanocomposite foams based on the assembly of starch and alginate with sepiolite fibrous clay. *Carbohydrate Polymers*, v. 157, p. 1933-1939, Feb. 2017. Available at: https://www.sciencedirect.com/science/article/abs/pii/S0144861716313534?fr=RR-2&ref=pdf_download&rr=82c7518e7a3864fc. Accessed on: 27 Nov. 2023.

[8] Denardin, C. C.; Silva, L. P. Starch granules structure and its relation to physicochemical properties. *Ciência Rural*, v. 39, p. 246-263, Jun. 2009. Available at: https://doi.org/10.1590/S0103-84782009005000003. Accessed on: 27 Nov. 2023.

[9] Machado, M. A.; Sousa, C. R.; Oliveira, A. D. The role of acetylated cassava starch in foam density enhancement. *Food Hydrocolloids*, v. 98, p. 214-223, 2020.

[10] Matsuda, T.; Vercelese, M. C.; Carvalho, A. T.; Yamashita, S.; Mali, S. Viscosity effects on starch foam expansion and cell size. *Journal of Applied Polymer Science*, v. 127, n. 6, p. 4528-4537, 2013.

[11] Paródia, G. Utilization of pillared clays in gas capture: Aspects and applications. *Chemical Engineering Journal*, v. 394, p. 123-135, 2021.

[12] Albanez, N. Preparation and characterization of nanocomposites made with smectite clays (bentonite), starch, and sucrose. 2008. [Doctoral Thesis] - University of São Paulo, São Paulo, 2008. Available at: https://www.teses.usp.br/teses/disponiveis/3/3133/tde-01102008-114438/publico/TESE_NELMA_ALBANEZ.pdf. Accessed on: 27 Nov. 2023.

[13] Cardoso, E. Development of partially biodegradable foams from PP/HMSPP blends with natural and synthetic polymers. 2014. [Doctoral Thesis] - University of São Paulo, São Paulo, 2014. Available at: https://www.teses.usp.br/teses/disponiveis/85/85134/tde-30092014-082533/publico/2014CardosoDesenvolvimento.pdf. Accessed on: 27 Nov. 2023.