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Synthesis and Characterization of Bioadsorbent from *Spondias mombin L.* for Methylene Blue Removal using $ClZn_2$, NaOH and $Al_2(SO_4)_3 14H2O$

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Síntese e Caracterização de Bioadsorvente de *Spondias mombin L.* para Remoção de Azul de Metileno utilizando $ClZn_2$, NaOH e $Al_2(SO_4)_3$.14H2O

RESUMO

Objetivo – O objetivo deste estudo foi sintetizar e caracterizar um bioadsorvente produzido a partir do endocarpo da *Spondias mombin L.*, utilizando os ativadores químicos $ClZn_2$, NaOH e $Al_2(SO_4)_3{\cdot}14H_2O$, e avaliar sua eficiência na remoção do corante azul de metileno em soluções aquosas.

Metodologia - A pesquisa foi estruturada em três etapas: preparação e ativação do carvão ativado em diferentes temperaturas e tempos de pirólise; caracterização do material quanto ao teor de cinzas, teor de umidade, rendimento e pH; e realização de ensaios de adsorção para determinar a eficiência na remoção do corante.

Originalidade/relevância - Este estudo aborda a lacuna teórica relacionada ao reaproveitamento de resíduos agrícolas para produção de materiais adsorventes, promovendo alternativas sustentáveis ao uso de adsorventes convencionais e destacando sua relevância para o tratamento de efluentes.

Resultados - Os adsorventes ativados com NaOH e $ClZn_2$ demonstraram maior eficiência, com destaque para os materiais NA250-3, ZN300-2 e ZN300-4, que apresentaram capacidades de adsorção de 1,40 $mg{\cdot}g^{-1}$, 1,39 $mg{\cdot}g^{-1}$ e 1,37 $mg{\cdot}g^{-1}$, removendo 93,23%, 93,02% e 91,69% do corante, respectivamente. O material ZN250-4 destacou-se pelo equilíbrio entre desempenho (1,33 $mg{\cdot}g^{-1}$, remoção de 88,78%) e custo-benefício, devido ao elevado rendimento (64,27%) em relação aos demais.

Contribuições teóricas/metodológicas: A pesquisa amplia o conhecimento sobre condições ideais de ativação e uso de ativadores químicos, fornecendo subsídios para a aplicação de bioadsorventes.

Contribuições sociais e ambientais - A pesquisa promove a sustentabilidade ao propor a reutilização de resíduos agrícolas como matérias-primas para produção de bioadsorventes, reduzindo a poluição ambiental e oferecendo soluções para o tratamento de efluentes.

PALAVRAS-CHAVE: Bioadsorventes. Carvão Ativado. *Spondias mombin L.* Adsorção.

Synthesis and Characterization of Bioadsorbent from *Spondias mombin L.* for Methylene Blue Removal using $ClZn_2$, NaOH and $Al_2(SO_4)_3 14H_2O$

ABSTRACT

Objective – The objective of this study was to synthesize and characterize a bioadsorbent produced from *Spondias mombin L.*'s endocarp, using the chemical activators $ClZn_2$, NaOH and $Al_2(SO_4)_3{\cdot}14H_2O$, and evaluate its efficiency in removing methylene blue dye from aqueous solutions.

Methodology - The research was structured in three stages: preparation and activation of activated charcoal at different temperatures and pyrolysis times; material characterization regarding ash content, moisture content, yield and pH; and carrying out adsorption tests to determine the efficiency of dye removal.

Originality/relevance - This study addresses the theoretical gap related to the reuse of agricultural waste to produce adsorbent materials, promoting sustainable alternatives to the use of conventional adsorbents and highlighting their relevance for the treatment of effluents.

Results - The adsorbents activated with NaOH and $ClZn_2$ demonstrated greater efficiency, with emphasis on the materials NA250-3, ZN300-2 and ZN300-4, which presented adsorption capacities of 1.40 $mg{\cdot}g^{-1}$, 1.39 $mg{\cdot}g^{-1}$ and 1.37 $mg{\cdot}g^{-1}$, removing 93.23%, 93.02% and 91.69% of the dye, respectively. The ZN250-4 material stood out for its balance between performance (1.33 $mg{\cdot}g^{-1}$, 88.78% removal) and cost-benefit, due to its high yield (64.27%) compared to the others.

Theoretical/methodological contributions: The research expands knowledge about ideal activation conditions and use of chemical activators, providing support for bioadsorbents applications.

Social and environmental contributions: The research promotes sustainability by proposing the reuse of agricultural waste as raw materials for the production of biosorbents, reducing environmental pollution and offering solutions for the treatment of effluents.

KEYWORDS: Bioadsorbents. Activated Charcoal. *Spondias mombin L.* Adsorption.

Síntesis y Caracterización de Bioadsorbente de *Spondias mombin L.* para la Eliminación de Azul de Metileno utilizando $ClZn_2$, NaOH y $Al_2(SO_4)_3 \cdot 14H_2O$

RESUMEN

Objetivo – El objetivo de este estudio fue sintetizar y caracterizar un bioadsorbente producido a partir del endocarpio de *Spondias mombin L.*, utilizando los activadores químicos $ClZn_2$, NaOH y $Al_2(SO_4)_3 \cdot 14H_2O$, y evaluar su eficiencia en la remoción del colorante azul de metileno de soluciones acuosas.

Metodología – La investigación se estructuró en tres etapas: preparación y activación del carbón activado a diferentes temperaturas y tiempos de pirólisis; caracterización del material en términos de contenido de cenizas, contenido de humedad, rendimiento y pH; y ensayos de adsorción para determinar su eficiencia en la remoción del colorante.

Originalidad/Relevancia – Este estudio aborda la brecha teórica relacionada con la reutilización de residuos agrícolas para la producción de materiales adsorbentes, promoviendo alternativas sostenibles a los adsorbentes convencionales y destacando su relevancia en el tratamiento de efluentes.

Resultados – Los adsorbentes activados con NaOH y ClZn2 demostraron mayor eficiencia, destacándose los materiales NA250-3, ZN300-2 y ZN300-4, que alcanzaron capacidades de adsorción de 1,40 $mg \cdot g^{-1}$, 1,39 $mg \cdot g^{-1}$ y 1,37 $mg \cdot g^{-1}$, removiendo el 93,23%, 93,02% y 91,69% del colorante, respectivamente. El material ZN250-4 sobresalió por su equilibrio entre rendimiento (1,33 $mg \cdot g^{-1}$, remoción del 88,78%) y rentabilidad, debido a su alto rendimiento (64.27%) en comparación con los demás.

Contribuciones Teóricas/Metodológicas – La investigación amplía el conocimiento sobre las condiciones óptimas de activación y el uso de activadores químicos, proporcionando bases para la aplicación de bioadsorbentes.

Contribuciones Sociales y Ambientales – La investigación promueve la sostenibilidad al proponer la reutilización de residuos agrícolas como materias primas para la producción de bioadsorbentes, reduciendo la contaminación ambiental y ofreciendo soluciones para el tratamiento de efluentes.

PALABRAS CLAVE: Bioadsorbentes. Carbón activado. *Spondias mombin L.* Adsorción.

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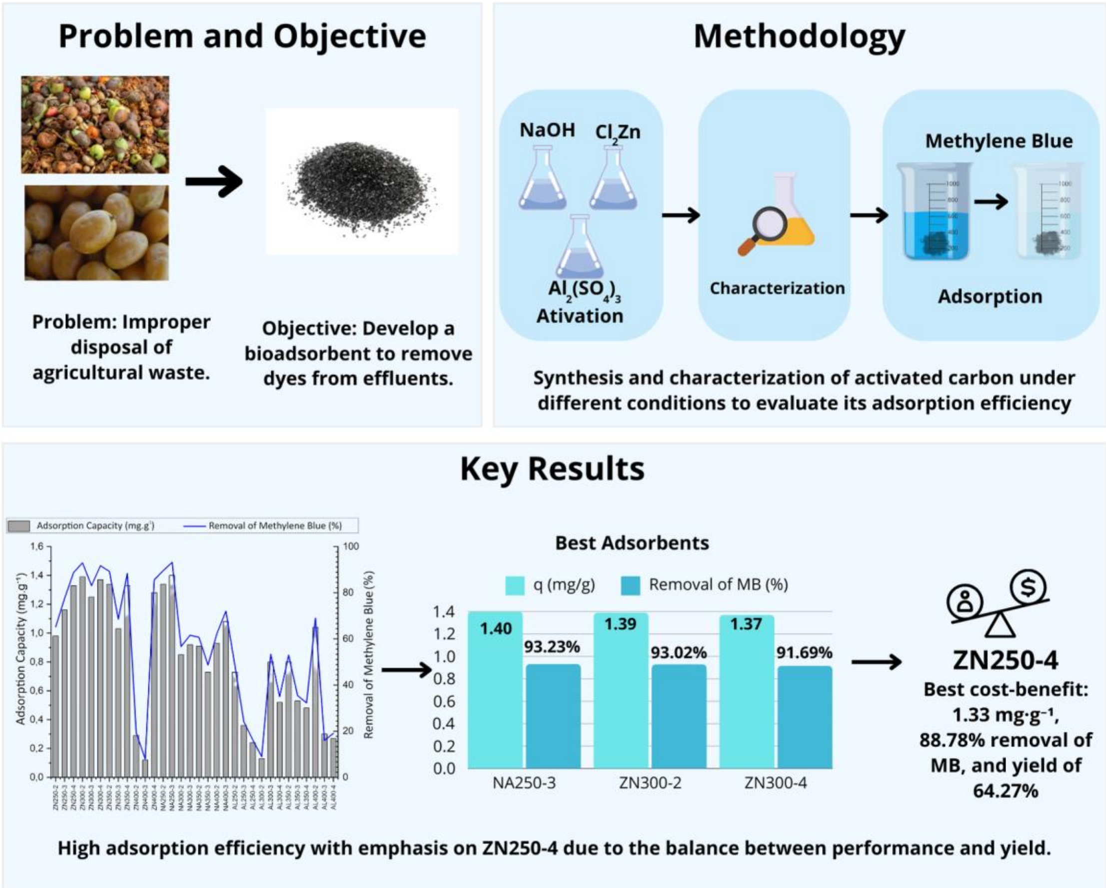
GRAPHICAL ABSTRACT



1 INTRODUCTION

The consumerist model and population growth have caused increased pressure on the environment, whether due to the exploitation of raw materials or the release of effluents. This phenomenon has caused environmental degradation and pollution (Arora and Gagneja, 2020; Clark *et al.*, 2019). Dyes, metals and nutrients, such as phosphorus, are considered potential polluters, as they contribute to the pollution of rivers and lakes, affecting aquatic fauna and flora (Gao *et al.*, 2023; Yaqoob *et al.*, 2020).

Technological innovation in water treatment for human consumption is necessary to remove contaminants, even in low concentrations, ensuring compliance with potability standards (Ghosh and Webster, 2021; Roque *et al.*, 2023). Water treatment techniques, based on coagulation, flotation or sedimentation processes, are efficient in removing particulate matter. However, for the removal of color, nutrients and dissolved organic compounds, adsorption processes are more effective in the post-treatment of these effluents (Pivokonsky *et al.*, 2021; Sher *et al.*, 2021).

According to Popa and Visa (2017), activated charcoal is characterized by having a high specific surface area and pore volume, good chemical stability and functional groups on the surface, resulting in high adsorption capacity and reactivity. It is widely used in water remediation due to its adsorption potential, which is one of the reasons why it has attracted worldwide attention (Yagub, Sen and Ang, 2012). Activated charcoal has been applied in several areas, such as control and purification of atmospheric air, industrial systems, separation of impurities from drinking water and treatment of industrial effluents (Chouhan, 2022; Jiao *et al.*, 2020).

Research by Geçgel, Kocablylk and Üner (2015) and Mahamad, Zaini and Zakaria (2015) verified the adsorption potential of activated charcoals in removing dyes (methylene blue) and analyzed its effectiveness. The production of activated charcoal from biomass is sustainable and has potential for industrial wastewater treatment and bioremediation of contaminated areas (Deniz and Kepekci, 2017).

The quality and applicability of activated charcoal generated from biomass depend on the specific characteristics of the precursor material and the production method, including chemical activation agent, activator/precursor material ratio, activation time, heating rate and carbonization temperature (Vukčević *et al.*, 2015). In the last decade, interest in using biomass to produce activated charcoal has grown due to the low cost, renewability and high availability of materials such as agro-industrial waste (Popa and Visa, 2017).

In Brazil, agriculture and agroindustry generated approximately R$533 billion in the economy (Brazil, 2017), representing 43% of the country's exports in 2021 (Grytz and Guero, 2023), and generating various waste. The reuse of this biomass mitigates the environmental impact and reduces the producing cost of activated charcoal. One example is the endocarp ("pit") of Taperebá/Cajá (*Spondias mombin L.*), a common fruit in the Amazon region and the Northeast known for its exotic charactheristcs of flavor and aroma (Yahia, 2011).

Although the production of *Spondias mombin L.* is still mostly extractive, its agro-industrial exploitation is viable due to fresh consumption and in derivatives such as juices, ice creams and creams (Infante *et al.*, 2023). The high production generates waste that can be reused to create adsorbent materials (Brito *et al.*, 2022; Sebastião *et al.*, 2018; Sousa *et al.*, 2023).

Thus, this research addresses the need for new applications for agricultural waste and the removal of dyes from effluents. The research combines the synthesis of the adsorbent material and its use to remove methylene blue.

2 OBJECTIVES

Synthesize and characterize a bioadsorbent produced from the pit of *Spondias mombin L.* using three different activators ($ClZn_2$, NaOH and $Al_2(SO_4)_314H_2O$) and evaluate its efficiency in removing the methylene blue dye in aqueous solutions.

3 METHODOLOGY

The methodology was divided into three stages: charcoal preparation and activation, characterization of the activated charcoal, Methylene Blue adsorption tests.

The precursor material comes from a family fruit pulping production in Tomé-Açu, in the interior of the state of Pará. The production uses Taperebá/Cajá as raw material and the pits were donated to the Multi-User Water Treatability Laboratory at the Federal University of Pará. Next, the pits were washed in running water, to remove unwanted materials adhered to the surface, and dried in an oven for 24 hours at 105ºC.

To activate the precursor material, three different activating agents were used, Zinc Chloride ($ClZn_2$), Sodium Hydroxide (NaOH) and Aluminum Sulfate ($Al_2(SO_4)_314H_2O$), varying the temperature and pyrolysis time for later characterization.

Activations were carried out at temperatures of 250ºC, 300ºC, 350ºC and 400ºC, at a concentration of 0.1 M NaOH, in a 1:1 mass ratio (activator/precursor material) of $ClZn_2$, and 2:1 of ($Al_2(SO_4)_314H_2O$). The exposure time to the pyrolysis temperature was varied, using 2, 3 and 4 hours. In all activations, the precursor material was in contact with the activator solution for 24 hours and was subsequently dried for 3 hours at 130 ºC in an oven. Subsequently, the particle size of the material was standardized to range from 1.2 to 2.0 mm.

The characterization of the adsorbent material activation was carried out by determining the ash content, moisture content, yield and pH. All characterizations were performed in triplicates. Table 1 summarizes the methods that were used in each of the characterizations, as well as the reference used.

Table 1 - Methodologies that were used to determine bioadsorbent parameters

Characterization	Methodologies
Ash content	D2866-11 (ASTM International, 2018)
Moisture content	D2867-17 (ASTM International, 2023)
Yield	(Vargas, 2010)
pH	(Medeiros, 2008)

Source: Autors (2024).

For the adsorption test, 150 mL of methylene blue solution at 20 $mg.L^{-1}$ was used, in contact with 2 g of the adsorbent material under constant stirring (250 rpm) on a magnetic stirring platform, at 24ºC, for 24 hours.

To evaluate the ability to remove methylene blue by activated carbon, we used the measurement of the methylene blue concentration after contact with the material, by measuring the absorbance at 665 nm in the UV-visible spectrophotometer.

Initially, the methylene blue calibration curve was determined, which relates the absorbance of the substance to its concentration. To draw the calibration line, seven standard solutions of different concentrations were prepared. Through linear regression techniques it was possible to arrive at the equation that relates absorbance and concentration.

The adsorptive capacity was calculated using Equation 1, derived from the laws of mass conservation and chemical equilibrium (Atkins and Paula, 2021).

$$q = \frac{(C_0 - C_e)V}{m} \qquad \text{Equation 1}$$

Where q is the adsorption capacity in $mg.g^{-1}$, Co is the initial concentration of the adsorbate in mg, Ce is the concentration of the adsorbate at equilibrium in mg, V is the volume of the solution in liters, and m is the mass of the adsorbent in grams.

With the data obtained, the best adsorbent was determined in relation to methylene blue removal capacity and also the material characterization (ash content, moisture content, yield and pH), providing a comprehensive view on the performance and quality of the bioadsorbent.

4 RESULTS

To facilitate the nomenclature of the various adsorbents, the following naming logic was established: the first two letters refer to the activating agent (ZN = Zinc Chloride, AL = Aluminum Sulfate, and NA = Sodium Hydroxide), followed by the temperature pyrolysis and temperature exposure time. Therefore, the adsorbent ZN250-2 was produced with Zinc Chloride, subjected to 250 ºC for 2 hours.

4.1 Characterization of the adsorbent activated with $ClZn_2$

In Table 2 below are the average values for the characterization of activated carbon with ClZn2.

Table 2 - Average values of the characterization parameters from the adsorbents activated with Zinc Chlorid

Charcoal	Yield (%)	pH	Ash content (%)	Moisture content (%)
ZN250-2	73.65 ± 2.72	6.11 ± 0.12	4.60 ± 0.56	10.67 ± 1.95
ZN250-3	59.89 ± 3.95	5.96 ± 0.16	6.55 ± 0.43	8.27 ± 0.76
ZN250-4	64.27 ± 1.68	6.14 ± 0.18	8.39 ± 1.06	9.85 ± 0.60
ZN300-2	47.61 ± 2.85	5.90 ± 0.09	6.51 ± 0.49	12.28 ± 4.52
ZN300-3	47.53 ± 0.48	6.12 ± 0.18	7.60 ± 0.36	11.79 ± 1.26
ZN300-4	48.31 ± 4.47	6.06 ± 0.14	8.68 ± 0.98	7.57 ± 7.57
ZN350-2	39.46 ± 0.40	5.82 ± 0.07	6.55 ± 0.10	10.71 ± 0.76
ZN350-3	33.29 ± 1.61	6.13 ± 0.08	7.05 ± 0.52	9.17 ± 0.24
ZN350-4	39.16 ± 3.47	6.00 ± 0.25	8.83 ± 0.17	10.88 ± 1.20
ZN400-2	28.01 ± 1.29	6.03 ± 0.17	6.33 ± 1.94	5.54 ± 0.40
ZN400-3	26.04 ± 0.80	6.00 ± 0.22	5.94 ± 0.31	8.25 ± 0.21
ZN400-4	34.91 ± 0.32	5.43 ± 0.30	8.48 ± 0.42	5.44 ± 0.19

Source: Autors (2024).

It is observed that the charcoal yield varies significantly, with values between 28.00% (ZN400-2) and 73.65% (ZN250-2). In general, charcoals produced at lower temperatures (250°C) showed higher yields than those produced at higher temperatures (400°C).

Lower temperatures result in a reduced degree of carbonization, which implies that the organic matter does not volatilize completely, increasing the final activated charcoal yield. Consequently, less intense pore formation occurs, limiting the development of the material's porous structure (Jones *et al.*, 2021).

As for pH, all charcoals have values close to 6, which indicates a slightly acidic characteristic.

Regarding ash content, it is noted that charcoals produced at higher temperatures have higher ash contents, with values between 5.94% (ZN400-3) and 8.83% (ZN350-4). On the other hand, charcoals produced at lower temperatures have lower ash contents, with values between 4.60% (ZN250-2) and 6.55% (ZN250-3).

Regarding moisture content, it is observed that the charcoals present relatively low values, varying between 5.44% (ZN400-4) and 11.79% (ZN300-3). However, between the twelve adsorbents, nine presented moisture content values greater than 8%, the limit recommended by AWWA (2012).

In summary, according to data in Table 2, the production of $ClZn_2$ activated charcoals at different temperatures can significantly influence the properties of the charcoals, such as yield, pH, ash content and moisture content. Furthermore, the results suggest that the burning temperature is an important factor to be considered in the production of activated charcoals with Zinc Chloride, as it directly affects the product characteristics.

4.2 Characterization of the adsorbent activated with NaOH

Likewise, in Table 3 are the average values for the characterization of adsorbents produced with NaOH.

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Table 3 - Average values of the characterization parameters from adsorbents activated with Sodium Hydroxide

Charcoal	Yield (%)	pH	Ash content (%)	Moisture content (%)
NA250-2	61.37 ± 2.43	6.69 ± 0.77	3.53 ± 0.00	9.09 ± 1.22
NA250-3	36.70 ± 5.06	7.35 ± 0.31	4.65 ± 0.23	8.75 ± 5.19
NA300-2	44.39 ± 4.11	6.57 ± 0.32	3.88 ± 0.28	9.77 ± 2.10
NA300-3	36.42 ± 2.11	6.64 ± 2.42	5.13 ± 0.65	8.85 ± 1.71
NA350-2	30.05 ± 7.81	7.81 ± 1.74	4.75 ± 0.27	12.90 ± 2.58
NA350-3	26.99 ± 5.72	7.36 ± 0.34	5.46 ± 0.27	5.95 ± 1.45
NA400-2	25.28 ± 0.42	7.95 ± 0.89	4.52 ± 1.56	17.85 ± 6.18
NA400-3	25.25 ± 3.86	8.14 ± 1.06	5.69 ± 0.64	6.65 ± 0.42

Source: Autors (2024).

Despite the low NaOH concentration, it was not possible to carry out the tests for 4 hours due to the significantly low yield, which resulted in a product with an extremely fragile structure that was difficult to manipulate.

It can be seen, in Table 3, that the NA250-2 and NA300-2 charcoals present the highest yields, with values of 61.37% and 44.39%, respectively. Charcoals produced at higher temperatures, such as NA350-2 and NA400-2, have lower yields, with values around 25-30%.

Regarding pH, it is observed that most coals have alkaline values, with variations between 6.57 and 8.14. Coals produced at higher temperatures, such as NA350-2 and NA400-2, have higher pH.

This phenomenon can be attributed to the more efficient incorporation of NaOH into the surface structure of the charcoals during the activation process at high temperatures. The integration of NaOH facilitates the formation of carboxylic functional groups on the charcoal surface. Carboxylic groups (-COOH) can lose a proton (H^+) in aqueous solution, transforming into carboxylate groups ($-COO^-$). This deprotonation contributes to the alkalinity of the solution, as it increases the ability of carboxylates to bind to cations, such as metal ions, which can lead to the removal of H^+ ions from the medium (Sun *et al.*, 2017).

Regarding the ash content, it is noted that the charcoals produced from sodium hydroxide have low ash contents, with values between 3.53 and 5.69%, with the exception of CA-NA-350-3 which had a higher ash content (5.46%).

Studies suggest that NaOH can react with minerals and other inorganic substances, forming soluble compounds that, when washed, result in lower ash content in the final activated charcoal. Yuan *et al.* (2017), for example, demonstrate that NaOH can serve as a homogeneous catalyst in the aerobic selective oxidation of alcohols in water, indicating its ability to interact with and modify inorganic substances. Similarly, Siriphannon *et al.* (1999) illustrate that NaOH can be used as a precipitant in the preparation of inorganic compounds.

For moisture content, it is observed that most charcoals present values within the limit recommended by AWWA (2012), which is a maximum of 8%, with the exception of NA350-2 which presented a higher moisture content (12 .90%).

In general, it can be observed that charcoals produced with sodium hydroxide have low ash contents and alkaline pH values, and that the highest yields are obtained at lower temperatures. However, it is important to highlight that some charcoals had moisture levels above the recommended level, which could affect their quality as adsorbents.

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4.3 Characterization of the adsorbent activated with $Al_2(SO_4)_3 14H_2O$

The characterization results of the adsorbents produced with $Al_2(SO_4)_3 14H_2O$ are presented in Table 4.

Table 4 - Average values of characterization parameters from adsorbents activated with Aluminum Sulfate.

Charcoal	Yield (%)	pH	Ash content (%)	Moisture content (%)
AL250-2	79.50 ± 2.22	3.88 ± 0.09	3.82 ± 0.66	8.11 ± 1.32
AL250-3	55.82 ± 2.59	3.69 ± 0.04	3.05 ± 0.00	7.11 ± 0.57
AL250-4	50.05 ± 1.11	4.02 ± 0.10	5.36 ± 0.90	4.12 ± 0.08
AL300-2	41.48 ± 0.86	3.86 ± 0.13	3.97 ± 0.90	7.48 ± 1.34
AL300-3	34.34 ± 0.69	3.91 ± 0.04	4.31 ± 0.41	6.41 ± 0.67
AL300-4	33.67 ± 2.07	4.17 ± 0.00	4.46 ± 0.44	6.90 ± 1.05
AL350-2	26.91 ± 1.23	4.45 ± 0.40	4.40 ± 0.34	8.19 ± 0.11
AL350-3	27.62 ± 0.39	3.88 ± 0.11	3.98 ± 1.43	5.50 ± 0.19
AL350-4	26.14 ± 7.84	5.01 ± 0.24	6.05 ± 0.73	6.72 ± 0.63
AL400-2	21.79 ± 4.01	5.15 ± 0.49	4.66 ± 1.48	6.43 ± 0.31
AL400-3	24.71 ± 0.69	4.87 ± 0.25	5.91 ± 0.31	4.93 ± 0.27
AL400-4	25.13 ± 1.41	4.97 ± 0.25	7.09 ± 2.51	6.46 ± 0.46

Source: Autors (2024).

It can be seen in Table 4 that the AL250-2 charcoal obtained the highest yield (79.5%), followed by AL250-3 (55.82%) and AL250-4 (50.05%). Charcoals produced at higher temperatures, such as AL400-2, AL400-3 and AL400-4, showed lower yields, with values around 21 to 25%. Furthermore, there is a relationship between burning temperature and ash and moisture content, where charcoals produced at higher temperatures have higher ash contents and lower moisture contents.

The activation temperature has a significant influence on the final characteristics of activated carbon, particularly in relation to ash and moisture content. Raising the temperature during the activation process can lead to a reduction in moisture content through more intense dehydration, while it can also contribute to a decrease in volatile organic mass. This thermal decomposition process not only removes moisture, but can also result in the concentration of mineral components, reflected in an increase in the product ash content (Jones *et al.*, 2021).

All charcoals have slightly acidic pH values, with relatively small variations between them. When comparing the adsorbents produced with different activators, it was observed that the highest yield was obtained by AL250-2 (79.5%), followed by ZN250-2 (73.65% and ZN250-4 (64.27%). The adsorbents activated with NaOH obtained the lowest yields, with the highest yield obtained by NA250-2 (61.37%) and the lowest obtained by NA400-3 (25.25%), indicating that it is necessary to use more precursor material in activation using NaOH compared to other agents.

Regarding pH, the adsorbents activated with $Al_2(SO_4)_3 14H_2O$ and $ClZn_2$ presented slightly acidic values (3.69 to 6.14), while those activated with NaOH had a more alkaline pH (6.57 to 8.14). Analyzing the ash content, the adsorbents activated with NaOH presented the lowest values in relation to the others.

With regard to moisture content, activated charcoals with $Al_2(SO_4)_3 14H_2O$ presented contents ranging from 4.12% to 8.11%, within the recommended limit. The $ClZn_2$ and NaOH adsorbents presented higher levels, ranging from 5.44% to 12.28% and from 5.95% to 17.85%, respectively, with values above the limit indicated by AWWA.

4.4 Methylene blue adsorption tests

Table 5 presents the results obtained for adsorption capacity and percentage of Methylene Blue removal from adsorbents produced with $ClZn_2$.

Table 5 - Adsorption capacity (q) of activated charcoals produced with Zinc Chloride and their respective percentage of methylene blue removal.

Adsorbent	Adsorption Capacity q ($mg.g^{-1}$)	Methylene Blue Removal (%)
ZN250-2	0.98 ± 0.09	65.24 ± 6.05
ZN250-3	1.16 ± 0.01	77.55 ± 0.46
ZN250-4	1.33 ± 0.02	88.78 ± 1.30
ZN300-2	1.39 ± 0.00	93.02 ± 0.07
ZN300-3	1.25 ± 0.00	83.05 ± 0.41
ZN300-4	1.37 ± 0.03	91.69 ± 2.18
ZN350-2	1.34 ± 0.03	89.27 ± 1.96
ZN350-3	1.03 ± 0.02	68.51 ± 1.48
ZN350-4	1.33 ± 0.00	88.44 ± 0.29
ZN400-2	0.29 ± 0.02	19.31 ± 1.15
ZN400-3	0.12 ± 0.06	7.89 ± 4.20
ZN400-4	1.28 ± 0.01	85.59 ± 0.61

Source: Autors (2024).

Among the adsorbents investigated, ZN300-2 and ZN300-4 stand out as the most efficient in dye removal. ZN300-2 demonstrated a remarkable adsorption capacity of 1.39 $mg.g^{-1}$ and a removal rate of approximately 93.02%. Similarly, ZN300-4 exhibited an adsorption capacity of 1.37 $mg.g^{-1}$ and an efficiency in removing Methylene Blue reaching around 91.69%.

However, it was also observed that the least efficient activated charcoals in removing Methylene Blue were ZN400-3 and ZN400-2. ZN400-3 achieved an adsorption capacity of 0.12 $mg.g^{-1}$, removing only 7.89% of the dye, while ZN400-2 achieved 0.29 $mg.g^{-1}$ adsorption capacity and 19.31% adsorbate removal.

It was observed that adsorbents activated at 400 ºC showed lower performance compared to those activated at 300 ºC. This phenomenon can be attributed to the degradation of the porous structure at higher temperatures, thus reducing its adsorption capacity. Xu *et al.* (2021), for example, tested different activation temperatures using phosphoric acid as an activating agent, and came to the conclusion that high temperatures, especially those above 500ºC, produced coals with lower adsorption capacities, due to the increase in the structure of aromatic and condensed rings, reducing the availability of active sites, the degree of graphitization, which makes the material more ordered and less porous, and the proportion of mesopores, as an excessive increase in this proportion to the detriment of micropores can lead to loss of total surface area.

Table 6 presents the results obtained for adsorption capacity and percentage of

Methylene Blue removal, from activated charcoals produced with Sodium Hydroxide

Table 6 - Adsorption capacity (q) of activated charcoals produced with Sodium Hydroxide and their respective percentage of methylene blue removal.

Adsorbent	Adsorption capacity q ($mg.g^{-1}$)	Methylene Blue removal (%)
NA250-2	1.34 ± 0.016	89.55 ± 1.10
NA250-3	1.40 ± 0.002	93.23 ± 0.14
NA300-2	0.85 ± 0.048	56.69 ± 3.20
NA300-3	0.92 ± 0.007	61.63 ± 0.52
NA350-2	0.91 ± 0.009	60.70 ± 0.61
NA350-3	0.73 ± 0.017	48.63 ± 1.20
NA400-2	0.93 ± 0.007	62.30 ± 0.41
NA400-3	1.08 ± 0.002	72.06 ± 0.01

Source: Autors (2024).

According to the data in Table 6, the most efficient adsorbents in removing Methylene Blue were NA250-3 and NA250-2, with adsorption capacity of 1.40 $mg.g^{-1}$ and 1.34 $mg.g^{-1}$, respectively. Dye removal was in the order of 93.23% for NA250-3, and 89.55% for NA250-2.

On the other hand, the two least efficient in removing Methylene Blue were NA350-3 and NA300-2. NA350-3, with an adsorption capacity of 0.73 $mg.g^{-1}$ and 0.85 $mg.g^{-1}$, respectively, representing removal of 48.63% and 56.69%.

In contrast to adsorbents prepared with $ClZn_2$, those activated with sodium hydroxide demonstrated superior performance at lower temperatures. This phenomenon can be attributed to the more aggressive nature of sodium hydroxide compared to the precursor material, which eliminates the need for elevated temperatures to promote the development of the desired porous structure. This observation is supported by the study by Xu *et al.* (2021) who investigated the effect of different activation temperatures (400°C, 500°C, 600°C, 700°C and 800°C) on the properties of adsorbents. They found that activation at 400°C resulted in the highest surface area and adsorption capacity.

Table 7 presents the results obtained for adsorption capacity and percentage of removal of Methylene Blue, from activated charcoals produced with Aluminum Sulfate

Table 7 - Adsorption capacity (q) of activated charcoals produced with Aluminum Sulfate and their respective percentage of methylene blue removal.

Adsorbent	Adsorption Capacity q ($mg.g^{-1}$)	Methylene Blue removal (%)
AL250-2	0.73 ± 0.02	48.69 ± 1.52
AL250-3	0.36 ± 0.06	24.14 ± 4.01
AL250-4	0.24 ± 0.06	16.18 ± 4.09
AL300-2	0.13 ± 0.03	8.96 ± 2.30
AL300-3	0.80 ± 0.00	53.34 ± 0.29
AL300-4	0.52 ± 0.07	34.92 ± 4.52
AL350-2	0.80 ± 0.02	53.01 ± 1.66
AL350-3	0.53 ± 0.05	35.46 ± 3.45
AL350-4	0.48 ± 0.04	32.25 ± 3.02
AL400-2	1.04 ± 0.00	69.04 ± 0.11
AL400-3	0.30 ± 0.05	15.97 ± 0.70
AL400-4	0.27 ± 0.03	19.09 ± 2.12

Source: Autors (2024).

AL400-2 was the most efficient, with an adsorption capacity of 1.04 $mg.g^{-1}$ and a removal of 69.04% of methylene blue. On the other hand, AL300-2 was the least efficient, with an adsorption capacity of just 0.13 $mg.g^{-1}$ and a methylene blue removal of just 8.93%. The result indicates that activation with aluminum sulfate at higher temperatures and for a shorter time was more efficient in developing the porous structure of the material, a result similar to that found by Xu *et al.* (2010), who obtained a greater surface area (1.547 $m^2.g^{-1}$) and greater pore volume (0.89 $cm^3.g^{-1}$) when using 400°C to activate sawdust (from trees of the Abies genus).

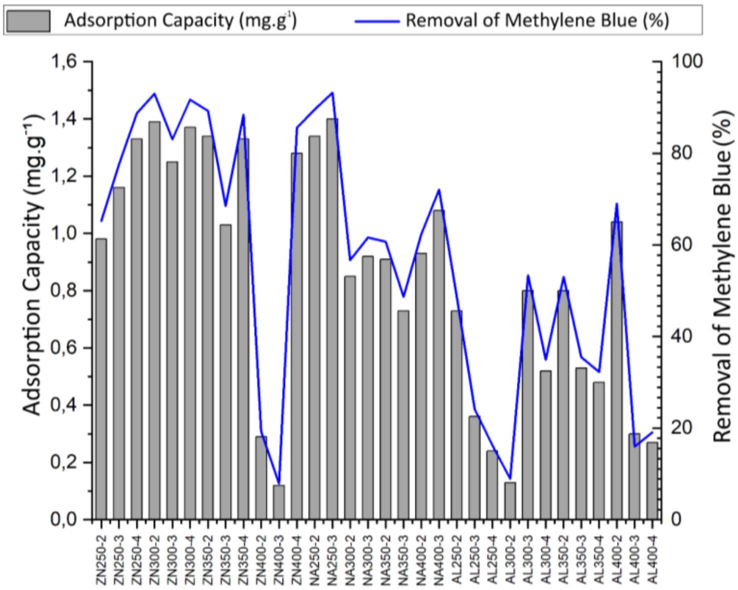
Still according to Xu *et al.* (2010), temperatures above or below 400°C presented lower values of the aforementioned parameters, indicating that each charcoal will have optimal parameters for its activation, which will depend on the precursor material, temperature, chemical activation agent, impregnation proportion, impregnation time, pH and others.

In Figure 1, the results are available graphically, highlighting the adsorption capacity and the removal rate of Methylene Blue for each adsorbent studied.

Among the adsorbents activated with $Al_2(SO_4)_3 14H_2O$, none showed methylene blue removal greater than 90%. On the other hand, materials produced with $ClZn_2$ showed results close to or above 90%. The three most efficient adsorbents in removing methylene blue were NA250-3, ZN300-2 and ZN300-4, which presented, respectively, 93.23% (1.40 $mg.g^{-1}$), 93.02 % (1.39 $mg.g^{-1}$) and 91.69% (1.37 $mg.g^{-1}$) of removal.

Although the NaOH-activated adsorbent showed the best removal, it had the lowest yield among the three best adsorbents, with a yield of 36.70%. In comparison, the ZN300-2 had a yield of 47.61%, and the ZN300-4, 48.31%. This means that for similar removal capabilities, ZN300-4 is more advantageous as its production process requires a smaller amount of precursor material, while still achieving the same removal range as other adsorbents.

Figure 1 – Adsorption and Removal Capacity of Methylene Blue by Different Adsorbents



Source: Autors (2024).

Another promising adsorbent was ZN250-4, as it achieved removal close to the three best, with 88.78% (1.33 $mg.g^{-1}$), with a much higher yield of 64.27%. Depending on the desired application, this adsorbent can offer the best value for money.

5 CONCLUSION

The study demonstrated that adsorbents produced from the endocarp of *Spondias mombin L.* and activated with different agents, showed significant variations in terms of yield, ash content, moisture content and pH. Adsorbents activated with $ClZn_2$ and NaOH were more efficient in removing methylene blue dye, with NA250-3, ZN300-2 and ZN300-4 achieving removals greater than 90%.

The activation temperature appeared to have a significant impact on the properties of the adsorbents. Materials activated at lower temperatures (250 °C to 300 °C) showed better yields and adsorption capabilities, while higher temperatures (400 °C) tended to degrade the porous structure of the precursor, decreasing adsorption efficiency.

NaOH as an activating agent produced adsorbents with alkaline pH and low ash content, but with lower yields. $Al_2(SO_4)_3 14H_2O$ produced adsorbents with higher yields, however with lower adsorption efficiency than those activated with $ClZn_2$ and NaOH.

Among the adsorbents analyzed, ZN250-4 stood out for combining a high yield, with 64.27%, and methylene blue dye removal, with 88.78% (1.33 $mg.g^{-1}$), offering a better balance between production cost and adsorptive performance, and can be an alternative in effluent treatment applications containing dyes.

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DECLARATIONS

CONTRIBUTION OF EACH AUTHOR

When describing each author's participation in the manuscript, use the following criteria:

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DECLARATION OF INTEREST CONFLICTS

We, Antônio Jorge Silva Araújo Junior, Marina Scarano Corrêa, Luiza Carla Girard Mendes Teixeira, Maurício Alves da Motta Sobrinho, declare that the manuscript entitled "Synthesis and Characterization of Bioadsorbent from *Spondias mombin L.* for Methylene Blue Removal using $ClZn_2$, NaOH and $Al_2(SO_4)_3 14H_2O$":

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2. **Professional Relationships:** Does not have professional relationships that could impact the results analysis, interpretation or presentation. No professional relationships relevant to the content of this manuscript have been established**.**
3. **Personal Conflicts:** No personal interest conflicts related to the content of the manuscript.