

## Article

# Comparative Study of Two Organic Wastes as Adsorbents in the Treatment of Water Rich in Nitrogen Compounds

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**Citation:** Neulls, T.F.; Gouveia, P.L.S.; da Silva Pereira, C.D.; Souza, C.S.D.; Chaves, F.N.S.; Souza, I.N.; Tavares, R.R.d.J.; Aliança, A.S.d.S.; Gonçalves, M.C.; Gomes, W.C.; et al.

Comparative Study of Two Organic Wastes as Adsorbents in the Treatment of Water Rich in Nitrogen Compounds. *Water* **2023**, *15*, 876. <https://doi.org/10.3390/w15050876>

Academic Editors: Dibyendu Sarkar, Rupali Datta, Prafulla Kumar Sahoo and Mohammad Mahmudur Rahman

Received: 30 December 2022

Revised: 2 February 2023

Accepted: 7 February 2023

Published: 24 February 2023



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**Abstract:** Background: The objective of this work was to propose the treatment of the wastewater from Laguna da Jansen using adsorptive processes of residues of pineapple crown and shrimp chitosan. Methods: Residual substrates were distributed in 11 Erlenmeyers, and 250 mL of residual pond water were added; the solution was incubated under agitation at the times and amounts established by the Experimental Design (DCCR). After this period, analyses of pH, electrical conductivity, turbidity, nitrate, and nitrite, morphological analyses by SEM, and structural analyses by FTIR and XRD were performed. Results: The FTIR and SEM results showed that the biomass presented active chemical groups and a morphology rich in pores. The experimental design showed that the substrate content was the variable that influenced the lagoon effluent treatments for both tested biomasses; however, when observing the specific values of the response variables, the vegetable adsorbent was more efficient with the conditions of 15g of substrate and 30 days of process. Conclusion: Plant biomass is more efficient in the treatment of effluents rich in organic materials. It can be used in treatment plants as an alternative for the removal of toxic compounds present in wastewater and effluents.

**Keywords:** adsorption biomass; pineapple crown; chitosan; treatment

## 1. Introduction

Problems related to the burning of fossil fuels, automotive vehicle use, habitat destruction, natural landscapes, inconsistencies between energy resource limitations, adoption of urban transport models, and growing housing demands originate from human activities [1,2], which reflect a lack of adequate sanitation [3].

The importance of sanitation to the quality of life of a population is evident. However, water and effluent treatments do not cover the entire Brazilian population. In 2016, only 51.9% of the Brazilian population had a sewage system; only 44.9% of the sewage produced in the country received treatment. The remaining waste was inappropriately disposed of in

rivers, lakes, and lagoons [4]. Nutrient transport from terrestrial sources to surface water bodies is a natural phenomenon; however, increases in the human population and the expansion of urban areas without urban planning promote increases in the discharge loads of solid waste and sewage, accelerating the natural eutrophication process of these environments [5]. Globally, several countries have documented high levels of eutrophication in coastal lagoons due to anthropogenic activity, causing effects that can lead to toxic algal blooms, a decrease in or an absence of oxygen, fish mortality, reductions in biodiversity, and the loss of fish stocks, which can harm inhabitants on the margins of these ecosystems [5].

In this scenario of pollution generated by the urban environment, the Ecological Park of Lagoa da Jansen is an example initially implemented as an ecological and tourist reserve; however, since its formation, this park has suffered from severe environmental degradation, due to pollution generated on-site (i.e., degradation of both esthetic and landscape aspects, resulting in an imbalance in the local ecosystem) [6]. The park was built in a mangrove region and now constitutes a body of water reduced to a lagoon with marine characteristics, due to the interaction with the sea through a drainage channel [6]. The lagoon is characterized by nutrient concentrations (such as phosphate, nitrite, and sulfide) above the limits established by CONAMA Resolution No. 357 on 17 March 2005, which characterizes it as a eutrophic environment. Most material found in the lagoon is allochthonous, reaffirming its state of contamination resulting from human activity [6].

Eutrophication produces cloudy water in an ecosystem, yielding an unpleasant odor that often causes organism mortality. These processes negatively affect tourism and fishing activities, harming the local economy while also affecting public health, owing to the possible release of toxins harmful to human health, such as cyanobacteria and red, green, and brown algae, as well as the consumption of contaminated seafood that can generate severe human intoxication [7]. Therefore, we must recognize the vulnerability of aquatic systems and formulate remediation strategies. The selection of an appropriate treatment depends on economic, social, and geographic factors, as well as the physical, chemical, and microbiological quality of the water that requires treatment. Alternative treatments that are low-cost and effective are, therefore, the priority [7].

As a low-cost process for different types of effluents, adsorption using biomass as an adsorbent has generated significant interest [8]. Plant and animal biomasses have been used to decontaminate water via organic substances and have advantages over mineral coal due to their low costs [9]. Adsorption is a term generally used to describe the physical and chemical phenomena that occur when there are differences between the concentrations present in the fluid phase and the compounds that have a porous, solid form [10]. We examined pineapple crown, popularly known as pineapple, as the plant biomass and chitosan extracted from shrimp as the animal biomass.

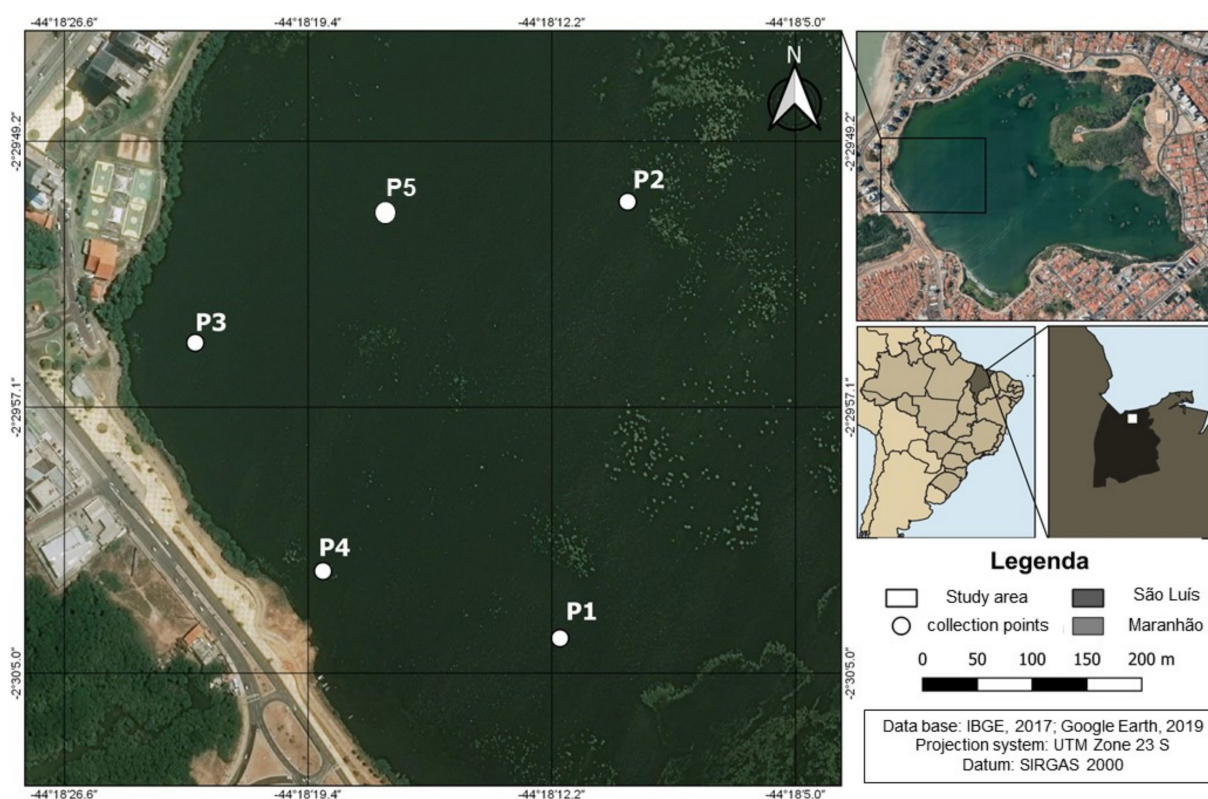
Brazil is the second-largest producer of pineapple [*Ananas comosus* var. *comosus* (L.) Merrill], accounting for 15% of global production, equivalent to 1,617,684 thousand tons and a planted area of 60,016 ha in 2019 [11]. Maranhão ranks fourth in terms of pineapple production and area in northeastern Brazil, with 1218 ha representing 5.4% of the area, which accounts for 37.2% of the cultivated area of Brazil [11]. Several by-products can be obtained from the pineapple-processing residue and discarded biological material during the pineapple production chain. Reducing the environmental damage caused by inadequate waste management can add value to these materials and yield new products of biotechnological interest [12]. Chitosan was obtained from shrimp waste; its national production, in greater quantities in the northeast region, was approximately 69,385 thousand tons in 2015 [11]. Shrimp fishing is a primary activity in marine, estuarine, or freshwater ecosystems. Large amounts of solid waste are generated during shrimp processing, particularly during the shelling process, which corresponds to approximately 40% of the total industrialized mass [13]. This residue is often discarded in the sea and in rivers, causing environmental problems. Considering this residue consists of chitin [14], significant interest centers on its reuse to develop products with high added values.

Despite these possibilities, Jansen Lagoon has suffered from significant environmental degradation, mainly due to the dumping of untreated domestic sewage. The release of untreated sewage into the lagoon intensifies the eutrophication process, which seriously affects the structure of the ecosystem, generating imbalances and potentially causing toxic algal blooms. The objective of this study was to compare two biomasses used as substrates for the treatment of water from Laguna da Jansen via an adsorptive process.

## 2. Materials and Methods

### 2.1. Study Area

The absorbate used in this study was water from Laguna da Jansen, located in São Luís, Maranhão between latitudes  $2^{\circ}30'$  and  $8^{\circ}38''$  S and longitudes  $44^{\circ}18'$  and  $35^{\circ}26'$  W. The ecosystem is characterized as a lagoon because it has a direct connection with the sea, which yields brackish water. Figure 1 shows the locations of the sample collection at five different points. These points were selected because they were near sewage spill pipes.



**Figure 1.** Location map of Laguna da Jansen indicating the collection points of water requiring treatment.

Five liters of the absorbate was then collected in gallons. After collection, the samples were transported to the Environmental Science Laboratory (LACAM) at Ceuma University (UNI-CEUMA) to prepare a composite sample.

### 2.2. Physicochemical Characterization of Lagoon Water (Adsorbate)

Physical and chemical analyses of the lagoon water were performed, including nitrate, nitrite, electrical conductivity, hydrogen potential (pH), and turbidity. A benchtop photometer was used to measure the nitrate and nitrite concentrations. The electrical conductivity was measured using a bench meter. To measure the pH, instrumental measurements were performed using a portable digital pH meter. The turbidity analyses were performed using a bench turbidimeter. All readings were performed in quintuplicate, and the analytical procedures were based on standard methods for water and wastewater. AWWA APHA WEF [15].

### 2.3. Preparation of Adsorptive Material

#### 2.3.1. Pineapple Crown

To prepare the adsorptives, 12 pineapple (*Ananas comosus*) crowns were detached from the leaves, washed, cut, and dried in an oven at 80 °C for 12 h. After drying, they were ground in an industrial processor (ULTRA) and sieved (ABRONZINOX) to obtain a granulometry of 0.32 to 0.6 mesh, resulting in a total substrate of 189.6 g [16].

#### 2.3.2. Chitin and Chitosan Preparation

Chitin was obtained in stages according to the methodology recommended by Moura et al. [17]: pretreatment, demineralization, deproteinization, deodorization, and drying. Therefore, 5 kg of shrimp shells were used for laboratory and pilot tests. Chitosan was produced by chitin deacetylation, followed by reaction with 45% NaOH solution (42.3%) under stirring and heating. The reactor was maintained at 130 °C for 2 h. At the end of the reaction, excess reagent was removed [18]. Chitosan was obtained after deacetylation and was then purified, precipitated, and neutralized [18].

### 2.4. Characterization of Adsorbent Support

#### 2.4.1. Morphological Characterization

Photomicrographs of the treated biomass samples were obtained using scanning electron microscopy (SEM; JEOL model JSM5310, Tokio, Japan), based on the secondary detection of electrodes after depositing the sample on a gold substrate. The particle sizes and surface visualizations were obtained at magnifications of up to 5000×. The analyses were performed at the Federal Institute of Bahia (IFBA).

#### 2.4.2. Structural Characterization

The amorphous and crystalline regions of the samples were characterized by energy-dispersive X-ray diffraction spectroscopy (XRD; Shimadzu Corp., model XRD-6000), with a CuK radiation source radiamo-delo XRD-6000 fraction from Eram caramA. Scans were completed over a range of 2 values from 10 to 90, with a scan speed of 0.05° min<sup>-1</sup> [14] at the Instituto Federal da Bahia (IFBA). Characterization, in terms of identifying and/or determining the structural characteristics, mainly with regard to the functional groups and bonds present in the samples, was carried out using Fourier-transform infrared spectroscopy (FTIR) (Nicolet 6700-FTIR) [19]. These analyses were conducted at the Institute of Technology and Research (ITP).

### 2.5. Treatment Conditions

To obtain the treatment conditions, the methodology of the fractional factorial experimental design matrix was used, which consisted of two levels (−1, +1), two axial points (−1.41, +1.41), and three central points for 11 experiments, where time and amount of substrate content were the independent variables (Table 1). The pH, conductivity, and turbidity parameters, in addition to the contents of nitrogen compounds, ammonia, nitrate, and nitrite, were dependent variables and analyzed according to APHA (American Public Health Association) (APHA, 2012) [15]. The experimental matrix, as well as the analysis of the results, were processed with the Statistic software, Version 8.0.

Eleven Erlenmeyer flasks (250 mL) were used; 200 mL of the sample was added to each Erlenmeyer flask. The samples were placed in a rotating incubator at 70 °C and incubated according to the times stipulated in the matrix. To avoid loss, the containers were covered during the entire process.

Subsequently, all samples were filtered. The solid portion was dried in an oven at 80 °C for approximately 5 h and morphology analyzed in SEM. In the liquid phase, 1 mL of the sample was removed and diluted in 100 mL of distilled water to determine the pollutant concentrations. All measurements were performed in triplicate.

**Table 1.** Experimental matrix containing coded and real values of the independent variables of the experimental design Central Compost Rotational (CCR).

| Runs | Independent Parameters |          |               |          |
|------|------------------------|----------|---------------|----------|
|      | Codes Values           |          | Reals Values  |          |
|      | Substrate (g)          | Time (d) | Substrate (g) | Time (d) |
| 1    | −1                     | −1       | 8             | 4        |
| 2    | +1                     | −1       | 22            | 4        |
| 3    | −1                     | +1       | 8             | 26       |
| 4    | +1                     | +1       | 22            | 26       |
| 5    | −1.41                  | 0        | 5             | 15       |
| 6    | +1.41                  | 0        | 25            | 15       |
| 7    | 0                      | −1.41    | 15            | 0        |
| 8    | 0                      | +1.41    | 15            | 30       |
| 9    | 0                      | 0        | 15            | 15       |
| 10   | 0                      | 0        | 15            | 15       |
| 11   | 0                      | 0        | 15            | 15       |

## 2.6. Toxicity Assessment

The acute toxicities of the liquid, solid, and treated wastes were evaluated using an in vivo model (*Tenebrio molitor* larva), which allowed for a comparison with the immune system and may provide some indication of the toxicity in this area. Ten microliters of the phosphate buffer solution (PBS) control buffer and lagoon water samples were inoculated with 10 larvae and properly packed into the identified plates. The larvae were maintained at 30 °C for 10 d; dead or non-stimulation-responding larvae were quantified at 24 h intervals.

## 2.7. Statistical Analysis

For physicochemical analyses, the results were expressed as the mean  $\pm$  standard deviation (SD) using Microsoft Excel Professional Plus 2019. Significant variables in the form process were evaluated using the ANOVA methodology, considering a confidence level of 95% ( $p < 0.05$ ) in the Grand Prism 8 software.

The data generated in the toxicity test using the *T. molitor* larvae were analyzed using the GraphPad Prism version 5.0 software, with a significance level of  $p < 0.05$ . The survival curve was plotted based on the Kaplan–Meier analysis; the results were analyzed using the log-rank test.

## 3. Results

### 3.1. Physicochemical Characterization of Crude Adsorbate

Samples were collected from Laguna da Jansen. The analyses were carried out to characterize the liquid residue in terms of the nitrogen compound contents, conductivity, turbidity, and pH. Table 2 presents the pH as approximately neutral, the only parameter that conformed to the values stipulated by the CONAMA/2005 legislation [20]. The turbidity parameter was 153NU, fourfold higher than that in the legislation, similar to the nitrogen compounds, where ammonia was 13.57mg/NL<sup>−1</sup>, nitrate was 4.95 mg/L, and nitrite was 0.23 mg/L.

The Ministry of Health, in its Consolidation Ordinance No. 5, does not stipulate values for the electrical conductivity, nor do these values appear in the CONAMA resolution 357/2005 [20,21]; however, for natural water, conductivity values range from 10 to 100  $\mu$ S/cm. In environments polluted by domestic sewage, these values can reach 1000  $\mu$ S/cm [20].

**Table 2.** Physicochemical characterization of the crude adsorbate used for the treatment of water from Laguna da Jansen.

| Physicochemical Parameters | Unit                           | CONAMA 357/2005 | Gross Adsorbate |
|----------------------------|--------------------------------|-----------------|-----------------|
| pH                         |                                | 6.5–8.5         | 6.65 ± 0.89     |
| Conductivity               | ( $\mu\text{S}/\text{cm}$ )    | ***             | 845.5 ± 2.61    |
| Turbidity                  | (UNT)                          | 40              | 153 ± 2.24 **   |
| Ammonia                    | ( $\text{mg}/\text{NL}^{-1}$ ) | 5               | 13.57 ± 1.86    |
| Nitrate                    | ( $\text{mg}/\text{L}$ )       | 0.4             | 4.95 ± 0.15 **  |
| Nitrite                    | ( $\text{mg}/\text{L}$ )       | 0.07            | 0.23 ± 0.00 **  |

\*\*  $p < 0.01$ . \*\*\* no reference value.

When performing statistical data analysis and comparisons with the values provided in the CONAMA/357 resolution [20], we observed a significant statistical difference in the turbidity, nitrate, and nitrite parameters ( $p < 0.01$ ). This demonstrates the value above that is determined as acceptable by law.

### 3.2. Characterization of Adsorptive Supports

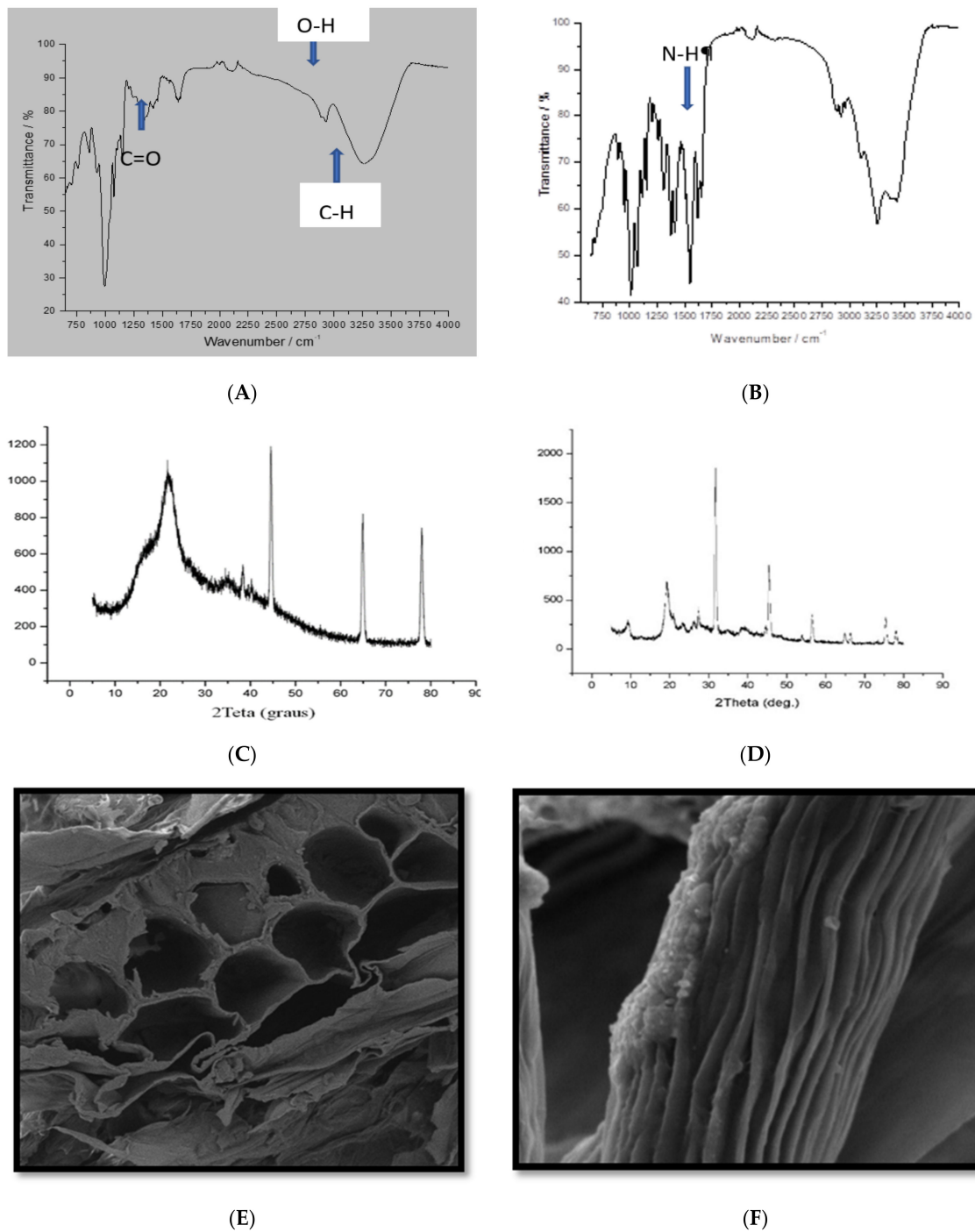
Figure 2 shows the morphological and structural characterizations of the residues used as adsorptive supports. In the FTIR characterization, typical adsorptive spectra were observed (Figure 2A). In the spectrum, we observed a broad band in the range of  $3400\text{--}3500\text{ cm}^{-1}$ , characterizing O-H bond stretching of the phenolic groups or carboxylic acids [22]. The band at  $1634\text{ cm}^{-1}$  was attributed to the C=O vibrations of carboxylates originating from organic matter [23]. The region between  $2850$  and  $3000\text{ cm}^{-1}$  was attributed to C-H bonds in alkanes, between  $1620$  and  $1680\text{ cm}^{-1}$  to C=C bonds in alkenes, and between  $1000$  and  $1400\text{ cm}^{-1}$  to C-F bonds in alkyl halide.

The diffractogram in Figure 2C shows that the adsorptive material had crystalline and amorphous regions. In the SEM images (Figure 2E) at  $5000\times$  magnification, “pits” or a surface area could be observed, where the material attracted to the surface of the adsorptive was lodged.

Typical chitin and chitosan spectra were observed based on the FTIR analyses (Figure 2B). Differences between these materials were observed in the region from  $3000$  to  $3600\text{ cm}^{-1}$ , in which the OH and NH elongation bands overlapped. In the chitin spectrum, two bands were observed at  $3200$  and  $3450\text{ cm}^{-1}$ , which could be attributed to NH bonds and hydrogen in the amide groups, respectively. These bands were absent in the chitosan spectrum. The region from  $1500\text{--}1700\text{ cm}^{-1}$  presented angular deformation bands of C=O ( $1650\text{ cm}^{-1}$ ) and N-H ( $1550\text{ cm}^{-1}$ ). In the chitin spectrum, the intensities of these bands were essentially identical, whereas the intensity of the C=O band significantly decreased in chitosan, indicative of chitin deacetylation.

The diffractogram (Figure 2D) shows that chitosan had a structure with crystalline and amorphous regions. Crystalline regions were observed at angles of  $20^\circ$ ,  $32^\circ$ ,  $45^\circ$ , and  $78^\circ$ . “Pits” were observed in the microphotographs of chitosan (Figure 2F) at  $5000\times$  magnification, i.e., small holes where materials attracted to the chitosan surface were lodged. Based on these characteristics, chitosan can be used as an adsorptive, owing to its structure and morphology [24].

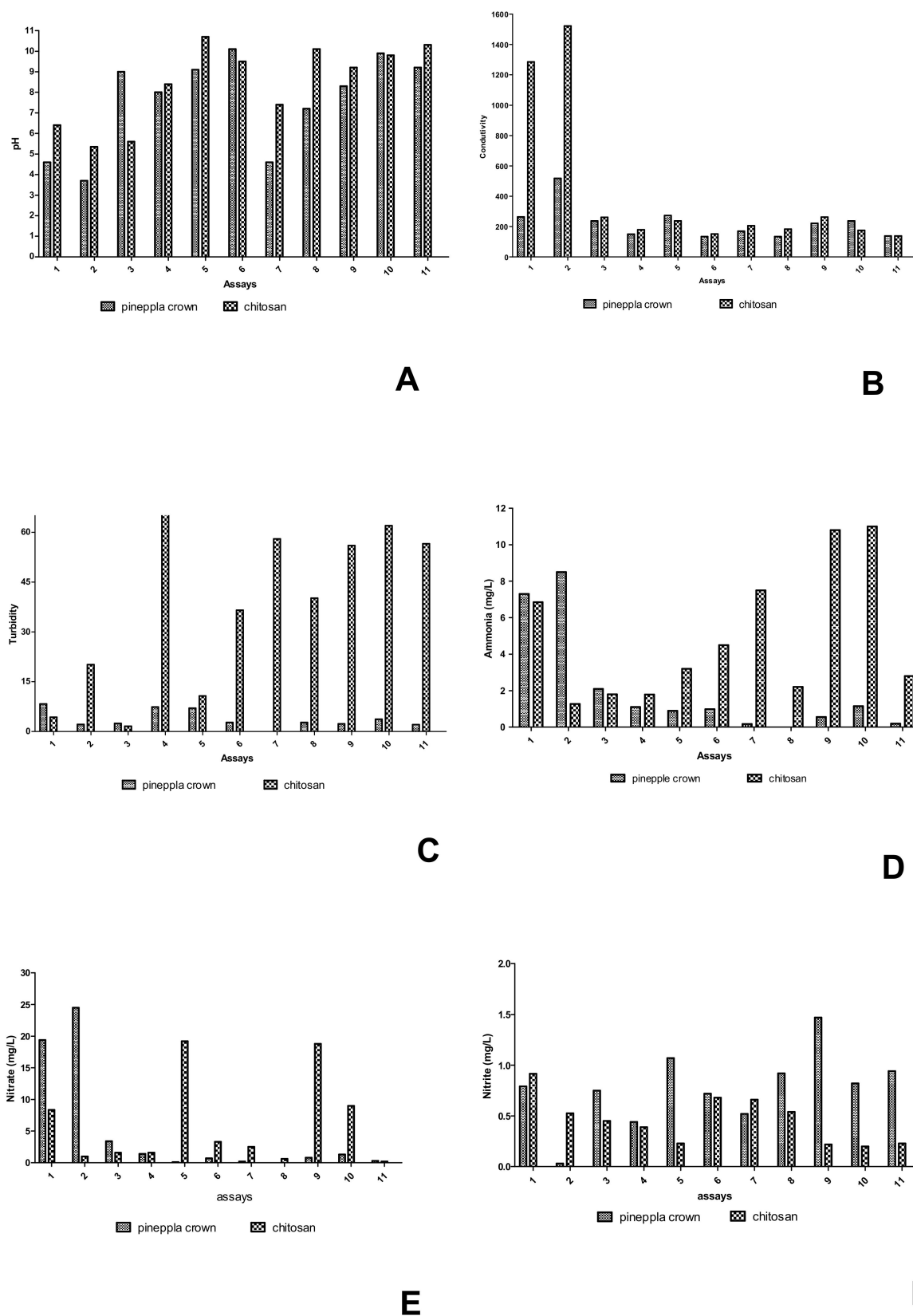
Each of these methods (photographic and diffractometric) have advantages and disadvantages. The photographic technique instantaneously records the entire diffraction pattern and is excellent for initially locating diffraction maxima; however, it does not excel at producing quantitative data, owing to problems with the photometric reading of the data. In contrast, the diffraction counter directly provides quantitative results; however, there may be loss of diffraction points, which provides adequate conditions for obtaining the diffractogram [25].



**Figure 2.** Characterization of the (A) pineapple crown and (B) chitosan in terms of the Fourier-transform infrared spectroscopy (FTIR) analyses. X-ray diffraction analyses of the (C) pineapple crown and (D) chitosan. Scanning electron microscopy (SEM) analyses of the (E) pineapple crown and (F) chitosan (500 $\times$ ).

### 3.3. Lagoon Water Treatment Conditions

Optimal water treatment conditions were established using the factorial planning methodology with the response surface graph in the Statistic software (version 8.0) (Figure 3A–F).



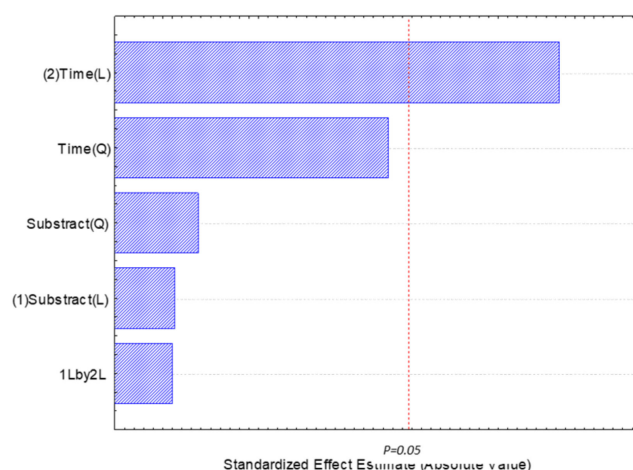
**Figure 3.** pH (A), conductivity (B), turbidity (C), ammonia (D), nitrate (E), and nitrite (F) values obtained in the tests using the conditions established in the rotational composite central experimental design (DCCR).

After the experiment, we observed that the lowest values in relation to the parameters tested in the adsorbate occurred at 15 g of adsorption during the period of 30 days of Experiment 8 when the pineapple crown was used as the adsorbent, based on the central rotational composite experimental design (DCCR).

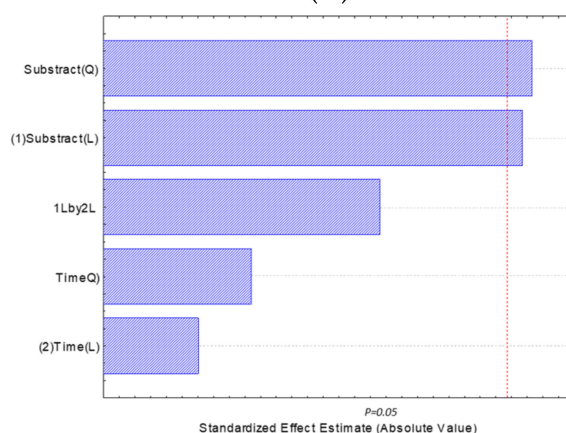
The pH, conductivity, and turbidity values in the absorbate were 6.65, 845.5  $\mu\text{S}/\text{cm}$ , and 153NU. After the treatment of wastewater using the adsorptive pineapple crown, a decrease in pH value to 7.2 was observed, which remained around neutral, as well as an increase in conductivity to 135  $\mu\text{S}/\text{cm}$  and a decrease in turbidity to 3.70NU.

The ammonia, nitrate, and nitrite contents in the crude absorbate were 13.57  $\text{mg}/\text{NL}^{-1}$ , 4.95  $\text{mg}/\text{L}$ , and 0.23  $\text{mg}/\text{L}$ , respectively. After the treatment using the pineapple crown as the adsorbent, according to the conditions previously established, a decrease in nitrogen compounds was observed, with 00  $\text{mg}/\text{L}$  of ammonia, 00  $\text{mg}/\text{L}$  of nitrate, and 0.92  $\text{mg}/\text{L}$  of nitrite. L was similar to the values provided in the CONAMA 357/2005 legislation. Although lower nitrite values were observed in the absorbate treated with chitosan, it was also observed that nitrite and ammonia values were found, which suggested that total conversion by the bacterial group did not occur.

After analyzing the variables, according to Pareto's graphs, we observed that when the substrate was pineapple crown, the time variable was the influencing variable in its linear form (Figure 4A). In contrast, when chitosan was used, the influencing variable was the substrate in linear and quadratic forms (Figure 4B).



(A)



(B)

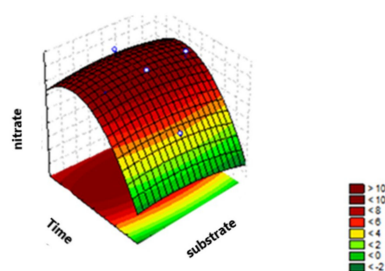
**Figure 4.** Pareto chart representing the variables that influenced the lagoon water treatment process using residues of (A) pineapple crown and (B) chitosan as the absorbates.

To generate the response surface from the Pareto graph, the predicted model of the pH variable was generated as follows:

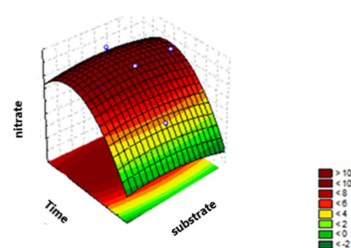
$$\text{Nitrate} = 9.30 + 4.47 x^2 \text{ and} \quad (1)$$

$$\text{Nitrite} = 57.16 + 31.90 x^1 - 38.81 x^2 \quad (2)$$

Based on the predicted model, we generated a surface response graph to determine the trends of the adsorbent values and the time for adsorbate treatment (Figure 5).



(A)



(B)

**Figure 5.** Response surface indicating the trend of the optimal values when treating the lagoon water with adsorbents of (A) vegetable and (B) animal origins.

When the adsorptive had a vegetable origin (pineapple crown), we observed a region with a higher concentration in relation to the nitrate parameter (i.e., the dark red areas in Figure 5A) and a lower concentration region (i.e., the red areas in Figure 5A). These regions showed a trend toward optimal time and substrate values for the nitrate variable. From this perspective, after the experimental period, we observed that 15 g of the adsorbent in the 30 d period, as established in Experiment 8 of the DCCR, presented the lowest nitrate values, compared with the other tested conditions.

When the evaluated applicator was of animal origin, the influence of the time and substrate on the nitrite variable was evident in the experimental planning. Figure 5B shows the trend of the nitrite response variable. There was a region with a higher concentration in relation to the nitrite parameter (i.e., dark red areas in Figure 5B) and a lower concentration region (i.e., light red areas in Figure 5A). Thus, we could verify the existence of an optimal region for low nitrite values, i.e., a ring-shaped band in the light-red color near 0. The optimal nitrite variable values in the experimental design were 8 g of adsorptive and 26 d of treatment.

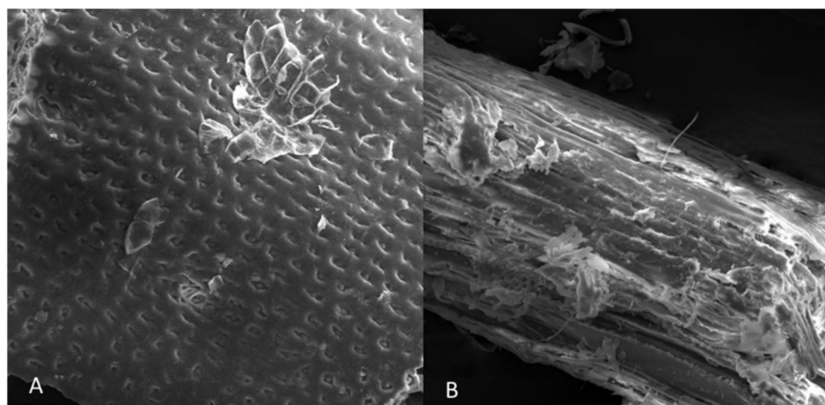
We noted that the nitrate and nitrite contents found in water constituted a preponderant factor for analyzing the physicochemical properties of water. For example, the higher the contents of these substances, the lower the water quality [26,27].

The response surface methodology consists of a collection of statistical and mathematical techniques useful for developing, improving, and optimizing treatment processes. It also has important applications in planning, developing, and formulating new products, as well as in improving existing projects and products [28,29]. In this work, the methodology was used to optimize the treatment process of water rich in nitrogen compounds, reducing treatment cost and time.

The microphotograph of the post-treatment substrate showed wear of the pits of both biomasses. However, the plant biomass was a little more preserved. It was possible to observe dirt particles adsorbed on the surface of both biomasses, showing their ability to adsorb particulates.

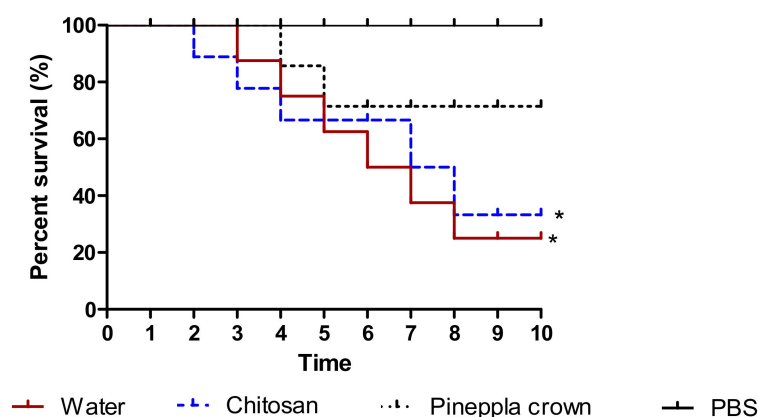
### 3.4. Toxicity Assessment

When evaluating the survival percentage (Figure 6), we observed that the value for larvae in pure water was 20%. When the water was treated with a vegetable adsorbent, there was a survival percentage of 70% for the larvae of *T. molitor*. In the treatment with an animal adsorbent (chitosan), the survival percentage decreased to 40%.



**Figure 6.** Microphotography of the plant adsorptive from the pineapple crown (A) and chitosan (B) after the treatment of polluted pond water with nitrogenous compounds. 500× magnification.

In Figure 7 it can be observed the difference in the survival percentages was confirmed based on statistical analyses using the log-rank test, where a statistically significant difference was observed in the survival percentage of larvae subjected to untreated water and water treated with an adsorbent of animal origin, compared with the control group ( $p = 0.026$  and  $0.035$ , respectively).



**Figure 7.** Toxicity evaluation of the treatments using different adsorptives in *Tenebrio molitor* larvae under conditions established by the experimental design. \* Significant statistical difference in relation to the control.

#### 4. Discussion

The characterization of the lagoon water showed that, despite approximately neutral pH values, i.e., within the parameter values provided by the CONAMA 357 legislation, the turbidity, nitrate, and nitrite parameters were high when compared to those of the established values. According to da Silva et al. [30], changes in water quality parameters indicate a need for treatment, especially in urban waterbodies or those used by inhabitants for recreation. Some studies have demonstrated that urban lakes suffer from human interference, such as sewage discharge, boat traffic, and waste disposal. These activities interfere with the water quality, increasing the levels of organic compounds, such as nitrogen and phosphorus, which facilitate eutrophication processes [30,31]. All changes in water quality parameters indicate the need for treatment.

The characterization of the adsorptive support is important because it allows us to understand the nature of the morphology and the chemical compounds that form the adsorptive matrix. The biomasses used in this study showed adequate characteristics for optimal adsorptive support, with a low cost and ease of acquisition.

Several characterization methodologies can be used to identify the crystallinity, which is important for understanding the behavior of organic materials of a cellulosic nature, such as pineapple crowns and chitosan, as they have different crystalline and amorphous regions, as identified in the XRD-generated diffractogram. These regions demonstrate that the biomasses present have a potentially adsorptive area, owing to their purity, as reflected in the crystalline areas. Therefore, plant biomass (pineapple crown) was more suitable because it has more crystalline regions than that of chitosan, which has a semi-crystalline nature. Some studies have attributed this characteristic to strong interactions between the hydrogen bonds, which chemically compose the cellulose [16,32,33].

An adsorptive is commercially attractive when it has certain characteristics, such as an extensive internal surface area, which must be accessible through pores that are sufficiently large to allow the adsorption of the particles of interest [10]. The morphology of the pineapple crown, as identified by SEM, presented a surface with many openings, concavities, and exposed pores, known as “pits”, which provided a greater area for adsorbate deposition, thus ensuring a higher adsorption rate. These spaces were attributed to the fiber configuration of the carbohydrate cellulose. Meurer and Silva [33] and Miranda et al. [16] reported similar results; they analyzed the morphology of different materials of lignocellulosic origin. In contrast, the chitosan morphology presented a spiral shape, with limited openings and concavities, which yielded a surface area more limited by the absence of the “pits”.

The FTIR spectra of the pineapple crown showed a large number of peaks, indicating a highly complex material. Machado et al. [34] used activated carbon for the adsorption of phenol and bisphenol A. Miranda et al. [16] characterized the adsorptive in terms of its chemical characteristics, identifying substances such as cellulose, hemicellulose, lignin, extractives, and ash. Vaz Junior [35] stated that such compounds are characteristic of lignified plant biomass. The spectrum of chitosan revealed polysaccharides (carbohydrates); when these materials experience hydrolysis (contact with water), they transform into natural polymers.

The characterization carried out after the treatment proposed in the experimental design showed that, in terms of the chemical analyses, the adsorptive method was efficient in improving the quality of most parameters in the adsorbate.

We observed the influence of a pH value of 7.0 on the reduction of nitrogenous compounds; in neutrality, the residue surface was characterized by enhanced interactions with cations. This is a common behavior for lignocellulosic materials, such as pineapple crowns, whose surface agglomerates have not been charred. The decrease in conductivity and turbidity values also influence bacterial activity, as they favor cation exchange and allow the incidence of sunlight, favoring the activity of chlorophyll organisms and thus keeping dissolved O<sub>2</sub> available for the metabolic activity of aerobic bacteria. Albina et al. [36] reported that absorptivity, as it contains substances of basic character, such as glucose and lignin, increases the pH, as observed during treatment. This is a factor that influences

bacterial activity, as it favors growth and metabolic activity, which consequently reduces nitrate to nitrite. Nitrogen compounds, such as nitrate, nitrite, and ammonia, are the main forms of nitrogen associated with water contamination [36].

The accumulation of these compounds favors eutrophication processes; thus, previous studies have already reported increasing levels of pollution, which can even compromise human health. High levels of nitrite in the blood induce the formation of metal hemoglobin, causing several neurological dysfunctions [37,38]. Although both treatments showed a decrease in the values obtained for the nitrogen compounds, we found that when the adsorptive substrate was pineapple crown, the reduction was more significant than that when using chitosan. (The basic pH favors the growth of denitrifying bacteria.) This group of bacteria participates in the conversion of nitrite to nitrate, followed by the formation of free nitrogen [38].

According to Peng et al. [39], the adsorption technique has been used for a long time, predominantly with mineral adsorptive (activated carbon); however, more recent studies have demonstrated the efficiency of natural substrates or bio-sorbents, as they are renewable, available in large quantities, and cheaper when compared to other materials, making the process economically viable [40]. In this context, several researchers have investigated the removal of various pollutants using natural materials, such as chicken feathers [41], banana skins [42], potato skins [43], pumpkin skins [44], orange peels [42], leaf dust of jackfruit [45], *Moringa oleifera* seed powder [46], brown macroalgae [47], and shell [48], as low-cost bio-sorbents.

The effectiveness of biomass suggests that it is useful as a substrate in continuous batch water treatment in fixed-bed reactors. Some studies have demonstrated the possibility of staggering water treatment using natural biomass through continuous batch fixed-bed reactors [49–51].

Evaluations of the water quality based on the *T. molitor* larvae can reveal the toxicity of the lagoon water (resulting from nitrogen compound contents), as well as the treatment efficiency. Based on the toxicity tests, the increase in the larvae survival percentage may have been directly related to a higher nitrogen compound content, considering that the plant-derived adsorbent was more efficient in reducing the content of these compounds than that of the animal adsorbent. Toxicity is a highly important parameter in water quality evaluations because, based on evaluations of living organisms, we can observe whether the accumulation of xenobiotic compounds in water influences the biology of the organism [52].

## 5. Conclusions

Based on our results, both adsorptives were efficient in the adsorptive treatment; however, the vegetal biomass, pineapple crown, was more efficient in the removal of organic contaminants in waterbodies compared with that of the animal biomass and chitosan. An alternative is its use in treatment plants for the removal of toxic compounds in water and effluents. The use of these biomass types represents a technique for reducing the accumulation of waste in dumps and sanitary landfills. It is an economical and viable alternative because no biomass treatments are required; they are a by-product of the consumption of the original material and have no commercial or domestic value, which reflects the final value of this process.

**Author Contributions:** T.F.N.—methodology; P.L.S.G.—methodology; C.D.d.S.P.—methodology; C.S.D.S.—methodology; F.N.S.C.—methodology; I.N.S.—methodology; R.R.d.J.T.—statistical analysis; A.S.d.S.A.—conceptualization and methodology; M.C.G.—review paper; W.C.G.—conceptualization and methodology; D.F.d.S.—software; M.R.C.S.—conceptualization and methodology; F.B.S.—methodology; Á.S.L.—conceptualization and methodology; E.d.B.G.—conceptualization and methodology; R.d.C.M.d.M.—conceptualization, writing, and original draft preparation. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Fundação de Amparo a Pesquisa do Maranhão (FAPEMA). Process number UNIVERSAL-00810/19.

**Data Availability Statement:** All research data are presented in the article.

**Acknowledgments:** The authors thank Ceuma University for providing infrastructure and logistical support.

**Conflicts of Interest:** The authors declare no conflict of interest.

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