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Phosphate Adsorption from Aqueous Solutions Using Eggshell and Sacha Inchi *(Plukenetia volubilis*) Mixture

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Abstract

The use of bioadsorbents for the removal of pollutants is being increasingly investigated worldwide due to their high efficiency and the potential use of various natural sources. The present study introduces a novel approach for phosphate adsorption using sacha inchi cuticle and eggshell mixture. These materials were pyrolyzed (400°C for 20 min) and mixed in a 1:10 (eggshell:cuticle) ratio. An adsorption study was carried out using synthetic phosphate solution concentrations of 0–300 mg/L and adsorbent masses of 0.1–1 g/100 mL. The temperature, pH and stirring were kept constant (25°C, pH:5 and 150 rpm) during the tests. The phosphate adsorption capacity increased as higher phosphate concentrations were used, reaching a maximum of 300 mg/L. However, differences in removal were observed when varying the amount of adsorbent used, reaching equilibrium in approximately 1 h, with a percentage of phosphate removal between 31 and 41%. The adsorption process followed a Freundlich isotherm with a correlation coefficient of 0.97, suggesting a multilayer adsorption process. According to the SEM-EDX results confirmed a high concentration of carbon and oxygen in the sacha inchi cuticle, in that sense, this by-product could be evaluated for the removal of other contaminants from water.

Keywords: Adsorption; Phosphates; Sacha Inchi; FTIR; SEM.

1. Introduction

In recent years, the study of pollutants presents in water and the technologies used to eliminate them have become more dynamic due to the scarcity and progressive degradation of water resources [1, 2]. Several studies have been carried out on phosphate pollution of water [3, 4]. These substances can be present in the effluents of industries, such as tanning, pharmaceuticals, agriculture and mining, and can also be found in domestic effluents. If these effluents are not adequately treated, they can affect aquatic systems and cause uncontrolled macrophyte proliferation, altering the ecological and ecosystemic dynamics of waterbodies [5-7].

The phosphate removal and recovery from wastewater becomes even more pressing considering that, according to the International Fertilizer Association (IFA), the amount of P_2O_5 -based fertilizers applied had increased by more than 343% by 2020, compared to the 11 million tonnes (Mt) consumed in 1961. At the same time, significant amounts of phosphorus are lost annually in urban and industrial wastewater—losses that could reach 2.4 Mt by 2050 [8]. In that sense, the recovery of phosphorus from wastewater can not only reduce the environmental impact of its anthropogenic discharge but also help to compensate for the global shortage of phosphorus resources [9].

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Different treatments have been proposed to avoid the environmental problems caused by the increase in phosphate concentration in aquatic systems, including biodegradation, precipitation, ion exchange, cementation, electrochemical techniques, chemical oxidation, solvent extraction, evaporation, membrane filtration, incineration, coagulation, and adsorption [10-13]. Adsorption is currently one of the most studied due to its simplicity, high removal efficiency, and the potential use of different natural sources as adsorbent media. Specifically, the use of biochar as an adsorbent is one of the most efficient, cost-effective, and environmentally friendly processes for removing and recovering phosphorous from water wastes [14].

By-products from the food industry, especially those with a high calcium oxide content, such as crab shells, oyster shells, and mussel shells, have been used for phosphate removal through adsorption processes. The efficiencies found under different variables, such as phosphorus concentration and pH, have shown removal ranging from 50 to 80% [15-17]. It has been suggested that dried eggshells should be pre-treated, including through crushing and calcination. Experiments have been performed on different time scales, showing phosphate removal rates ranging from 63.7 to 99.5% [18-21]. Eggshells have a very high global importance, as eggs are one of the most produced and consumed foods in the world. In 2023, world egg production was 86 million tons, with eggshells representing 11% of the total weight of eggs [22]; thus, the volume of this waste generated globally could be approximately 9.46 million tons [23].

Mixing adsorbent materials has also been proposed to improve phosphate removal from water. For example, research has been carried out using mixtures of eggshells and rice straw [24], eggshells and palm fiber [25], and eggshells and potato peel [26]. The results have shown high phosphate removal efficiencies, indicating that there is a need to identify new biomass sources to be used in adsorption processes. Table 1 shows some studies related to biomass and eggshell mixtures for phosphate removal.

Table 1. Use of biomass and eggshell for phosphate removal

Biomass	Method	Maximum adsorption capacity (mg/g)	Model	Reference
Eggshell and corn straw	Co-pyrolysis	288.83	Sips Isotherm and pseudo second order kinetics.	[27]
Eggshell and ashes	Geopolymers synthesis	49.92	Langmuir isotherm, pseudo second order kinetics.	[28]
Eggshell and peanut	Pyrolysis	-	Comparative analysis.	[29]
Eggshell and wheat straw	Granular formation	23 – 30	Yield at different pH conditions	[30]
Eggshell with and without thermal treatment	Thermal treatment	1.72	Sorption property analysis	[31]

As a result of the literature review, various studies have identified the high potential of using eggshells and various biomass residues as functional and sustainable adsorbents for removing phosphates from wastewater. They offer multiple environmental benefits, ranging from their applicability as a treatment system to their potential as a tool for resource recovery (circular economy models) [32].

On the other hand, Sacha inchi (*Plukenetia volubilis L.*), also known as star peanut or bush peanut, is an Amazonian plant found in countries including Peru, Bolivia, Brazil, and Colombia. Its seeds contain approximately 27.4% protein and 50% oil, including essential unsaturated fatty acids, such as omega-3 (alpha-linoleic acid 47.7–51.9%) and omega-9 (oleic acid 7.9–8.9%), making it a product of great interest to the food industry [33]. The extraction of oil from this seed produces several by-products, including the shell and cuticle, which represent approximately 30–35% of the weight of the seed. In countries such as Peru, where an annual production of 1200 tons of sacha inchi has been reported [34], an amount between 360 and 420 tons of residues is generated. This material is composed of fiber (77.8%), non-nitrogenous extract (17.3%), protein (2.75%), ash (1.75%), potassium (3736.2 mg/kg), calcium (2668.2 mg/kg), and magnesium (684.7 mg/kg). In this case, carbon and calcium are highlighted as key elements when considering this material for use as an adsorbent for phosphate removal [35]. Studies on the uptake of iodide (I^- and IO_3^-) in the aqueous phase by sacha inchi cuticle and shell have shown that the pyrolysis of the original biomass transforms its magnesium (Mg^{2+}), potassium (K^+), and calcium (Ca^{2+}) cations into active sites, which enhances the sorption process [36]. And these wastes were also studied as adsorbents for the removal of lead (Pb^{2+}), copper (Cu^{2+}), and arsenic (As^{+4}) from wastewater [37].

The present study introduces a novel approach for phosphate removal using pyrolysis of a sacha inchi cuticle and eggshell mixture as an alternative to promoting the valorization of agro-industrial by-products in sustainable water treatment applications.

2. Methods

2.1. Sacha Inchi

The cuticle of sacha inchi seeds was obtained from the Agroindustrial Plant of the Universidad de La Salle, located at the Utopía Campus in Yopal, Casanare, Colombia (coordinates 5°19'23.1"N 72°17'31.3"W, Figure 1). This cuticle was obtained after the dehulling process of the sacha inchi seed in a stage prior to the oil extraction process. Once obtained, this material was separated and characterized through analysis of its moisture, volatile, ash, and fixed carbon contents (ASTM D3302/D33202M-19, ASTM D782-15, ASTM D3172-13).

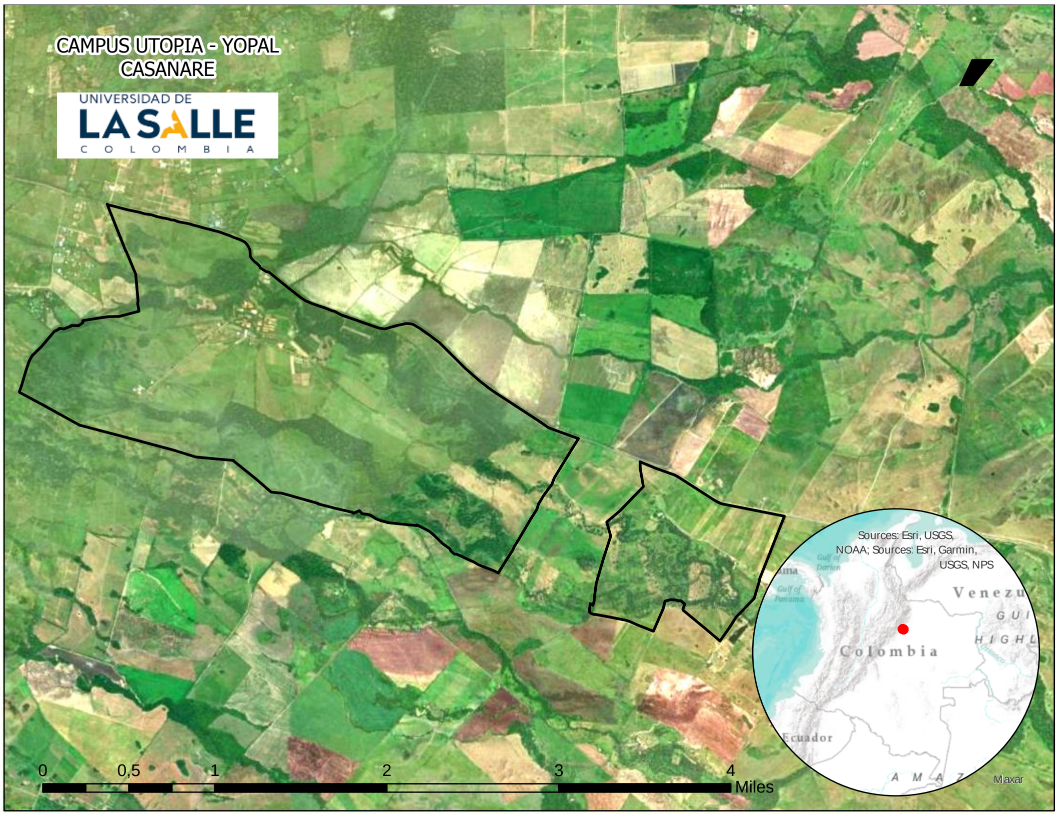

Figure 1. Utopía Campus in Yopal, Casanare, Colombia (adapted from [38])

2.2. Eggshell

The eggshell used in this research was collected from a commercial food processing facility located in Bogotá, Colombia. After its arrival at the laboratory, this material was washed with distilled water to remove the membrane and any type of contaminant adhered to its surface.

2.3. Bioadsorbent Preparation

For bioadsorbent preparation, previous research suggested the development of mixtures containing eggshell as a calcium source and biomass, in this case, sacha inchi cuticle, as a carbon source. A mixture of eggshell and sacha inchi cuticle at a ratio of 1:10 was therefore developed [24]. In addition, pre-treatment of these materials was considered to improve the efficiency of phosphate removal. In this sense, the sacha inchi cuticle and eggshell were subjected to a grinding and pyrolysis process. Pyrolysis was carried out at 400°C for 65 min (15 min preheating, 20 min at set temperature, and 30 min cooling) [39]. The material obtained was transferred to a desiccator and sieved, retaining the fraction with a particle size between 0.150 and 0.420 mm. This material was then characterized using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy with an attenuated total reflectance ATR module before being used for phosphate removal.

2.4. Evaluation of the Bioadsorbent for Phosphate Removal

Three batch tests were carried out to evaluate phosphate removal using the bioadsorbent obtained from the mixture of eggshell and sacha inchi cuticle in a ratio of 1:10. The first was designed to evaluate the effect of the phosphate concentration on the removal process. The second was carried out to evaluate the effect of the amount of bioadsorbent used in the adsorption process, and the third was related to the kinetic study of the process. Each of these experiments is described below.

2.4.1. Evaluation of the Effect of Phosphate Solution Concentration

To evaluate the effect of the phosphate solution concentration on the removal process, synthetic phosphate ion solutions were prepared using the reagent KH_3PO_4 (Merck). The evaluated concentrations were 25, 50, 75, 75, 100, 150, 200, 250, and 300 mg/L. In this case, the experiments were carried out at a constant temperature (25°C), pH (5), adsorbent solution ratio (1 g of adsorbents per 100 mL of solution), stirring speed (140 rpm) and contact time (1 h). After the set time, the solution was filtered, and the phosphate content was determined using the ascorbic acid method with a HACH DR 6000 spectrophotometer [40]. The experiments were performed in triplicate, and the data obtained were analyzed using an analysis of variance (ANOVA) in Minitab 16®. The results obtained at this stage were used to evaluate the behavior of the adsorption process using the Freundlich and Langmuir models.

2.4.2. Evaluation of the Effect of the Bioadsorbent Amount Used

To determine the effect of the adsorbent amount used on adsorption, 6 tests were carried out with different amounts of adsorbent material (0.1, 0.2, 0.4, 0.6, 0.8, and 1 g), while maintaining the volume of the solution used (100 mL) and the contact time (1 h). For the development of these tests, the pH (5), temperature (25°C), phosphate solution concentration (300 mg/L), and stirring speed (140 rpm) remained constant. After the set time, the solution was filtered, and the phosphate content was determined using the method described above. The experiments were carried out in triplicate, and the data obtained were analyzed by ANOVA (Minitab 16®).

2.4.3. Kinetics of the Bioadsorption Process

To carry out a kinetic study of the adsorption process, 100 mL of phosphate solution was prepared with an initial concentration of 300 mg/L. To this solution, 0.1 g of bioadsorbent was added, and the adsorption process was started, maintaining a stirring speed of 140 rpm and pH of 5. During the test, samples were collected after 5, 15, 30, 45, 60, 90, 120, 180, 300 and 1320 min, and the phosphate content in the solution was determined at each time. The tests were carried out in duplicate, and the data were analyzed using pseudo-first-order and pseudo-second-order models [41, 42]. After the adsorption process, the solid material obtained after filtration was separated and subjected to a drying process, after which it was characterized by FTIR tests using the ATR module and SEM.

A summary of the methodology developed is presented in Figure 2.

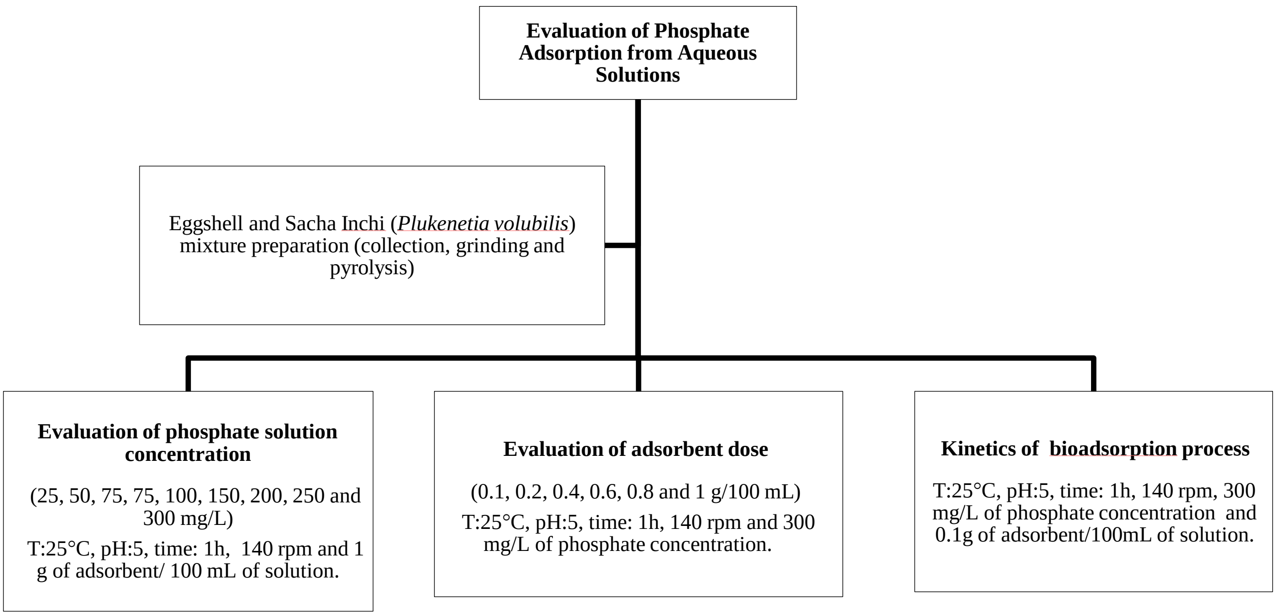

Figure 2. Methodology summary

3. Results and Discussion

3.1. Characterization of the Bioadsorbent

Figure 3 shows the husk, cuticle and kernel of sacha inchi, distinguishing the materials that make up the fruit, with a view to obtain and characterize the raw material. The cuticle was specifically used for this work.

Figure 3. Parts of the sacha inchi fruit: A) husk, B) cuticle and C) seed

With regard to the characterization of the cuticle, which was the material evaluated as a bioadsorbent, Table 2 shows its total moisture, volatile matter, ash and fixed carbon content.

Table 2. Characterization of the sacha inchi cuticle

Analysis	Dry basis	Wet basis
Total humidity (ASTM D3302/D3302M-19)	11.04	-
Volatile matter (% by weight) (ASTM D 7582-15)	57.92	65.11
Ashes (% by weight) (ASTM D 7582-15)	1.13	1.27
Fixed carbon (% by weight) (ASTM D 7582-15)	29.92	33.63

The carbon content, which was 29.92%, shows the potential of this material for use as a bioadsorbent material [24, 25]. However, the ash content, which was 1.13%, is related to the presence of components, such as Ca, which also contribute to the adsorption processes, especially phosphates.

During the pyrolysis process, the eggshell acquired a dark brown color, indicating the partial decomposition of the organic matter present in its structure. The sacha inchi cuticle became black and gray, indicating the formation of pyrolysis products, such as amorphous carbon. These color changes are characteristic of thermal decomposition processes, in which organic materials disintegrate and break down into simpler products under the influence of high temperatures. Additionally, other authors have also shown pyrolysis may transform calcium (Ca^{2+}) cations into active sites, which subsequently enhances the sorption process [36].

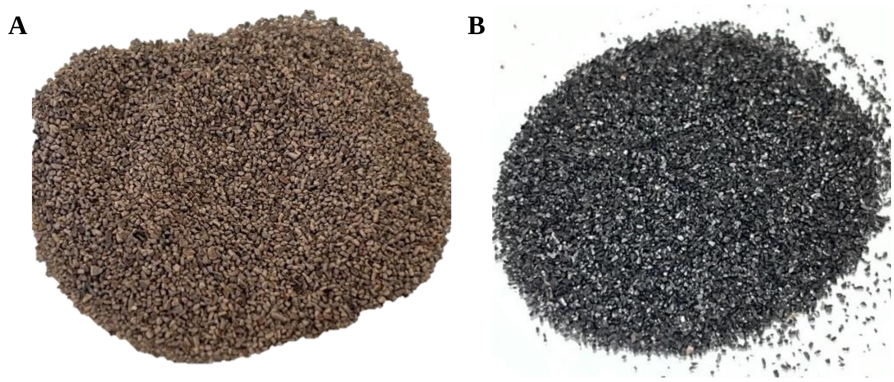

Figure 4. Pyrolyzed sample: A) eggshell, B) sancha inchi cuticle

Analysis of the FTIR spectrum of the eggshell, shown in Figure 5-a, revealed prominent peaks in the 713, 871 and 1406 cm^{-1} regions, indicating the presence of characteristic CO_3^{-2} vibrations. These peaks were consistent with the main composition of the eggshell, in which calcium carbonate ($CaCO_3$) predominated. Furthermore, peaks detected in the high-frequency range, such as the one observed at 1232 cm^{-1}, were indicative of vibrations associated with specific functional groups, which could correspond to phosphate (PO_4^{3-}) or C-O groups [43]. Figure 5-b shows the FTIR spectrum of the sacha inchi cuticle, in which a peak was observed at 3354.21 cm^{-1}, possibly related to the presence of phenols (O-H) and N-H bonds characteristic of hydroxyl groups (-OH) derived from fatty acids and alcohols. The peak observed at 1595.13 cm^{-1} could be related to vibrations caused by aromatic groups, C=C bonds of aromatic rings, which could be tocopherols and aromatic phytosterols. This peak could also be attributed to the C=O groups present in the amides, indicating the presence of proteins or peptides in the sample. The peak present at 1128.36 cm^{-1}, associated with the C-O bonds of esters, may be related to the presence of fatty acid esters.

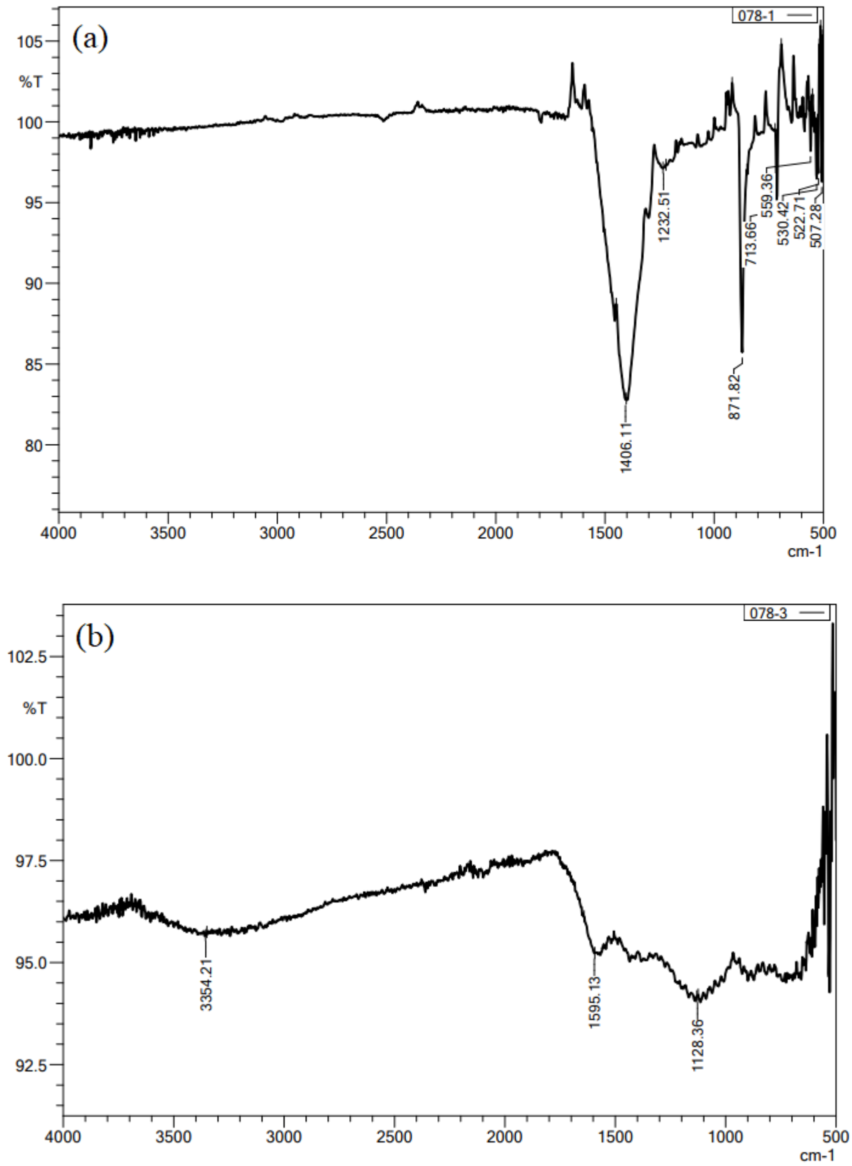

Figure 5. FTIR spectrum (modulus ATR) of pyrolyzed materials: (a) eggshell; (b) sancha inchi cuticle

With regard to the SEM analysis, Figure 6-a shows the pyrolyzed eggshell particles, demonstrating the characteristic morphology of this material [43]. These particles had a wide range of sizes, from 150 to 420 nm, and their surfaces were covered with small protrusions and ridges. Figure 6-b shows an SEM image of the cuticle of pyrolyzed sacha inchi, showing two distinct surfaces and a fibrous arrangement with long, thin fibers oriented in random directions, similar to the fibers of palm fruit

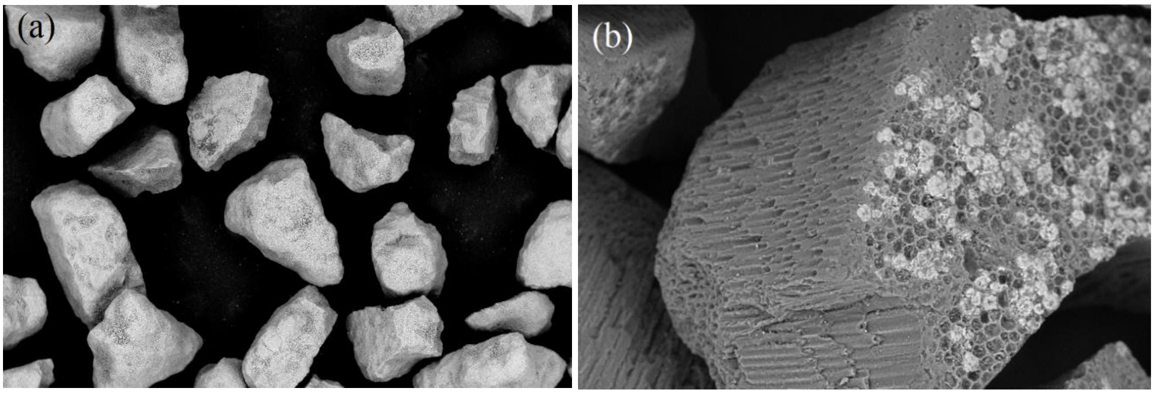

Figure 6. SEM images: (a) pyrolyzed eggshell 100 X, and (b) pyrolyzed sacha inchi cuticle 500 X

The scanning electron microscopy – energy dispersive X-ray spectroscopy SEM-EDX spectral map of the eggshell showed that calcium was the most abundant element in the sample (23.31 wt%), confirming the presence of calcium carbonate ($CaCO_3$) as its main component. Carbon was also present in a significant amount (26.46 wt%), which could be due to residual organic material from the eggshell membrane or incomplete pyrolysis. Oxygen accounted for 49.58 wt%, probably from calcium carbonate and other present oxides. Minor amounts of magnesium (0.40 wt%) and phosphorus (0.24 wt%) were also detected. These elements may be present as trace impurities in the eggshells or may be incorporated into the calcium carbonate structure. These results are very similar to those previously published by other researchers [43].

SEM-EDX analysis of the pyrolyzed sacha inchi cuticle sample revealed a predominant elemental composition of carbon and oxygen, accounting for 85.72 and 12.09% by weight, respectively. This high carbon concentration indicates the presence of a large amount of organic material in the sample, while the detection of oxygen indicates the presence of oxides and other organic components [37, 41, 44]. Trace amounts of magnesium, potassium and calcium were detected, indicating the possible presence of minerals. No significant phosphorus concentrations were detected in the sample. Thus, the potential of the mixture of these two materials for the development of a useful bioadsorbent for phosphate removal was established.

3.2. Evaluation of the Effect of the Phosphate Solution Concentration

After characterizing the materials comprising the adsorbent, the eggshell was mixed with the sacha inchi cuticle in a 1:10 ratio. This material was used to evaluate the effect of the initial phosphate solution concentration on the adsorption process. The results are shown in Figure 7.

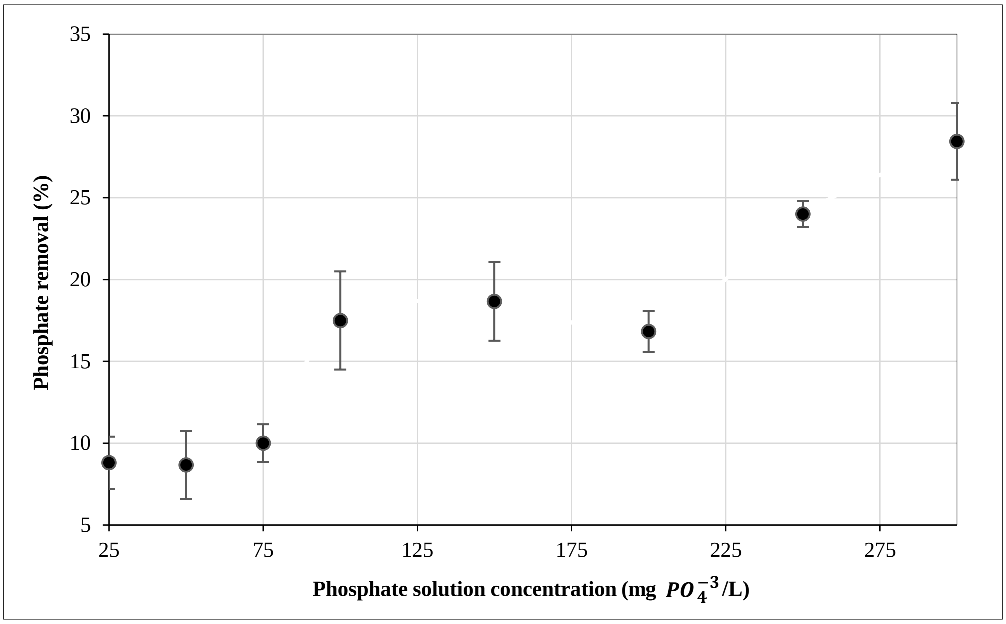

Figure 7. Phosphate removal vs. PO_4^{-3} solution concentration

The highest phosphate removal was achieved when the initial phosphate concentration was highest (300 mg/L), with an adsorption yield of 7.75–9.19 mg/g adsorbent, resulting in a removal rate of 28.44%. As the initial phosphate concentration decreased, the amount of phosphate adsorbed decreased. At concentrations of 100 mg/L or less, the ‘q’ values were much lower, between 1.44 and 2.02 mg/g, for a removal rate of 17.50%. These results suggest that at higher initial phosphate concentrations, the driving force for mass transfer increases, thereby facilitating more phosphate ions reaching and interacting with the available active sites on the adsorbent surface. Additionally, the low adsorption observed at concentrations below 100 mg/L could indicate a limitation in the number of high-affinity adsorption sites, which may be rapidly saturated. This implies that the efficiency of this bioadsorbent is more pronounced in moderately to highly contaminated waters, making it potentially suitable for industrial or agricultural effluents rather than lightly polluted domestic waters.

These data were analyzed using an ANOVA with the phosphate solution concentration as the only variation factor, evaluated at 8 levels (25, 50, 75, 100, 150, 200, 250 and 300 mg/L) and the amount of phosphate removed per gram of adsorbent as the response variable, with a significance level of 95%. Statistical analysis showed that the initial phosphate concentration significantly influenced the removal efficiency ($p < 0.05$), indicating significant differences between the concentration levels evaluated. A Tukey test was then used to determine the differences between the mean values of the concentrations evaluated. This confirmed that the highest phosphate adsorption yields were obtained when the initial phosphate solution concentration was highest (300 mg/g), reaching an average of 8.5 mg PO_4^3 adsorbed/gram adsorbent. There were no significant differences between the treatments carried out using phosphate solution concentrations of 75, 50 or 25 mg/L, with mean adsorption yields of 0.75, 0.43 and 0.22 mg PO_4^{3-} adsorbed/g adsorbent, respectively.

Comparing these results with those of other work on phosphate removal, it was observed that the percentage of removal was lower than that obtained using only eggshells calcined at 800°C as the adsorbent material, in which case a percentage of removal higher than 90% was achieved [41]. This difference in phosphate removal is related to the use of a mixed adsorbent in which eggshell was a minority component, limiting the availability of CaO in the adsorbent. The difference can also be attributed to the pyrolysis conditions, as in this work, the treatment was less intensive (400°C) than in other investigations. For example, in a study in which this process was carried out at 600°C using mixtures of eggshell and palm fiber as adsorbents, removal rates of up to 83% were achieved [18]. However, this evaluation was carried out at a lower temperature, with the belief that this could reduce the environmental impact of pyrolysis. Furthermore, it was selected not only because it represents a condition evaluated for producing pyrolysis biofuel from sacha inchi waste as an energy alternative [39], but also because it provides an opportunity to establish the basis for a biorefinery to obtain various products like biofuel and an adsorbent material.

The data obtained from this test were used to determine whether the process fits better to a Langmuir or Freundlich isotherm. The model was fitted to the data using the following formula [45]:

$$\frac{C_e}{qe} = \frac{1}{Q_o} \times C_e + \frac{1}{Q_o b^*} \tag{1}$$

Where; C_e is the equilibrium phosphate concentration (mg/L); qe is the amount of phosphate adsorbed at equilibrium (mg/g); and Q_o and $b*$ are the Langmuir constants related to the adsorption capacity in a monolayer and the sorption energy, respectively [41].

The results corresponding to this fit are shown in Figure 8. In this case, the numerical data corresponding to Q_o and $b*$ were −2.396 and −0.0038, respectively, which, being negative, indicates that the Langmuir model did not adequately fit the experimental data. However, the coefficient of determination (R^2) obtained for this fit was 0.81. These results suggest heterogeneous adsorption with variations in the structure and functionality of the adsorbent surface, which prevents monolayer adsorption. This can be linked to the microscopic analysis, as evidenced by the results of the SEM analysis, suggesting an irregular and rough morphology in the eggshell and a fibrous structure in the sacha inchi cuticle, elements that would contribute to the low uniformity of the active sites available for adsorption.

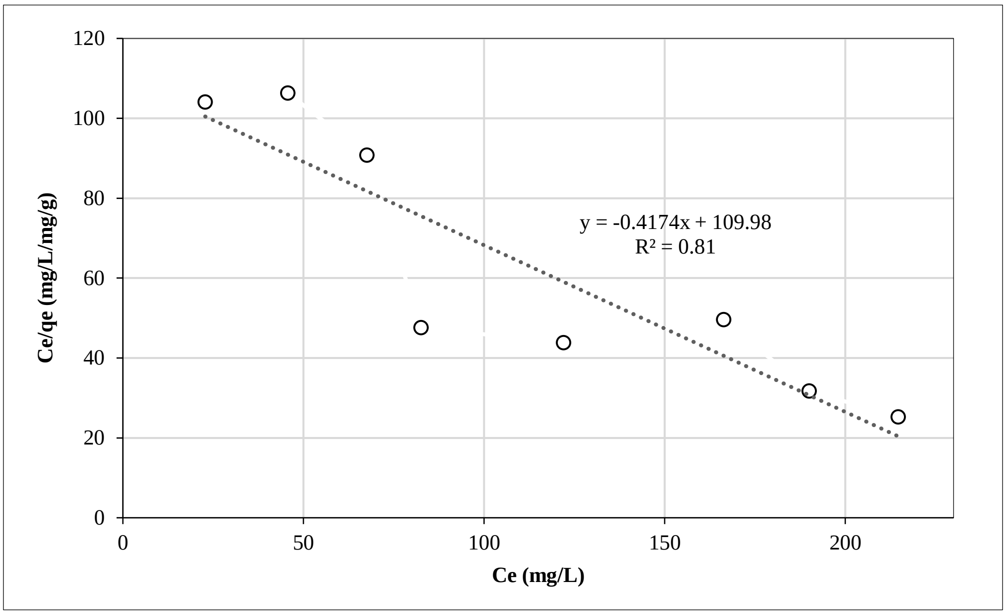

Figure 8. Langmuir isotherm for phosphate removal using a mixture of sacha inchi and eggshell as adsorbents

The following model was used for the Freundlich adsorption isotherms [46]:

$$log\, q_e = \frac{1}{n} \times log\, C_e + log\, K \tag{2}$$

here K (mg/g) is the Freundlich capacity constant; and n is the Freundlich intensity constant [41]. In this case, an n value of 0.612 and K value of 0.00104 were found. These values were determined using the fit information shown in Figure 9. R^2 was 0.97, indicating a better fit of the data to the proposed model.

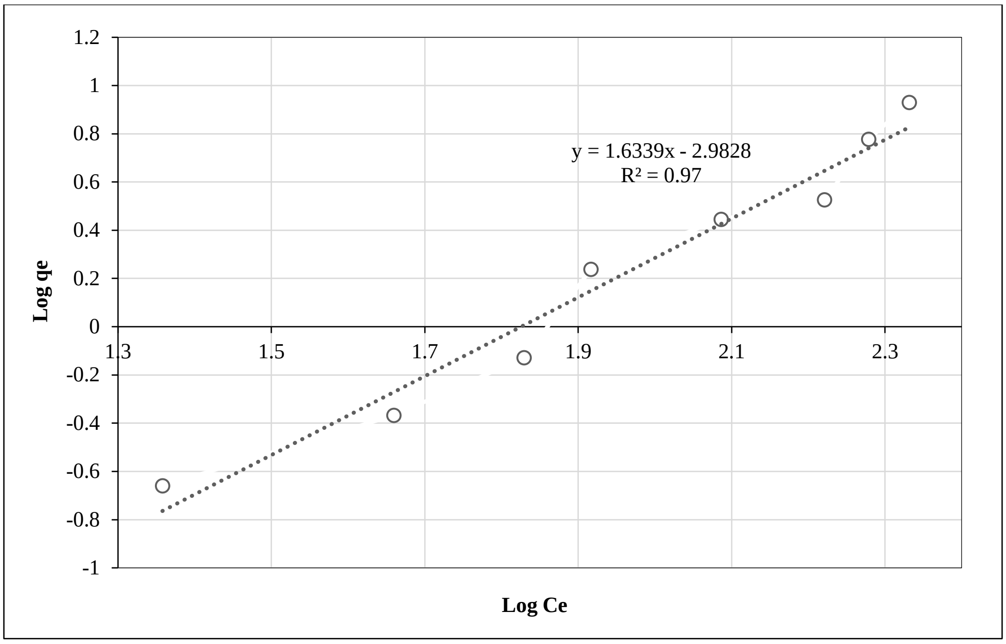

Figure 9. Freundlich isotherm for phosphate removal using a sacha inchi and eggshell mixture as the adsorbent

In general, the analysis of the isotherms is consistent with that presented in a study of phosphate adsorption with eggshells, in which the Freundlich model was found to be a better fit to the observed phenomenon than the Langmuir model. This was considered in this case, but the values of Q_0 and b^* were −44.25 and −0.35, respectively, for the Langmuir model. A k value of 23.02 and n of 0.79 was found for the Freundlich model [41].

A study using a mixture of eggshell and palm fiber found a better fit to the Langmuir model. However, they also observed a good fit with the Freundlich model, suggesting the formation of multiple phosphate layers on the adsorbent surface, which is consistent with the experimental results of the present study, in which multilayer adsorption and surface heterogeneity were determining factors in the adsorption efficiency [25].

3.3. Evaluation of the Effect of the Bioadsorbent Amount Used

The effect of the adsorbent amount used on the phosphate adsorption process was further evaluated. The results of these experiments are presented in Table 3.

Table 3. Effect of adsorbent amount on adsorption performance

Adsorbent amount (g/100 mL solution)	Average (mg of PO_4^{3-} adsorbed/ g adsorbent)	Deviation (mg PO_4^{3-} adsorbed/ g adsorbent)
0.1	89.05	26.07
0.2	52.90	15.14
0.4	24.89	6.34
0.6	19.74	2.13
0.8	14.17	2.75
1	12.09	0.87

Increasing the amount of adsorbent did not necessarily improve phosphate adsorption. Thus, when analyzing the results in terms of adsorption performance, an amount of 0.1 g adsorbent/100 mL solution maximized adsorption in relation to the adsorbent amount used in the process. This inverse relationship between adsorbent dose and adsorption efficiency could be due to particle aggregation at higher concentrations, leading to a decrease in total surface area and a reduction in the number of active sites effectively exposed to phosphate ions. Moreover, overlapping of adsorption sites may occur, resulting in internal diffusion resistance [47]. The percentage adsorbed for each adsorbent dose is shown in Figure 10.

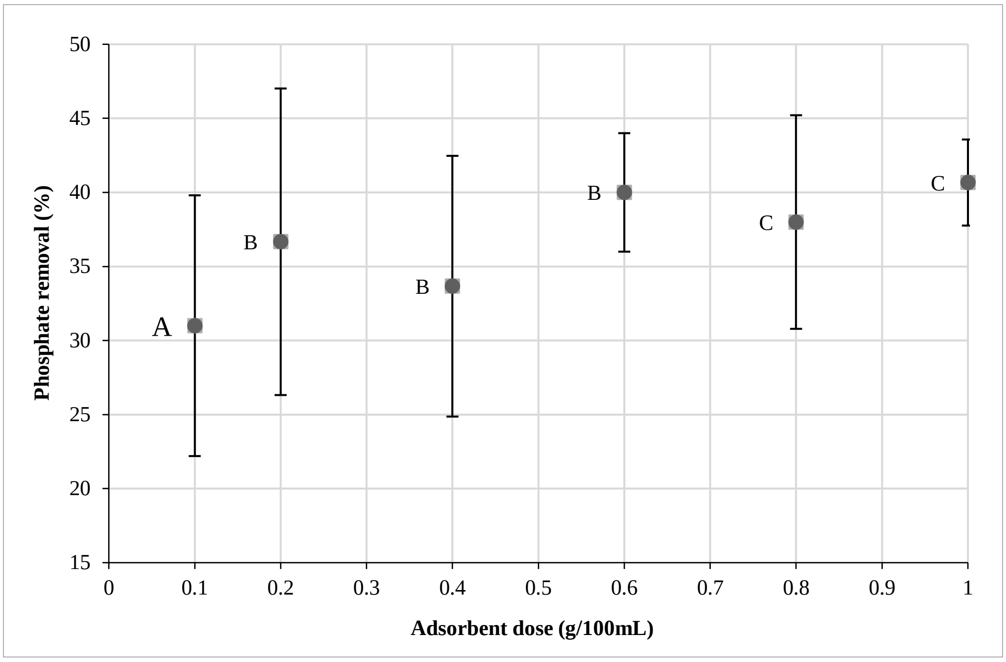

Figure 10. Phosphate removal percentage vs. adsorbent quantity (g/100 mL)

The non-linear relationship observed between final phosphate concentration and amount of adsorbent (Figure 10) indicates a decrease in adsorption efficiency with an increasing adsorbent amount, suggesting saturation of the bioadsorbent. To confirm this, ANOVA was performed using Minitab® software. At a 95% confidence level, there were significant differences in the means of the adsorbed mass concentrations for different adsorbent amounts ($p < 0.05$). A Tukey test was then used to determine the differences between the means, and three categories were identified: A (0.1 g/100 mL), B (0.2, 0.4 and 0.6 g/100 mL) and C (0.8 and 1.0 g/100 mL), as shown in Figure 10.

3.4. Kinetics of the Bioadsorption Process

The kinetic study involved monitoring the adsorption process using an initial solution concentration of 300 mg/L phosphate and 0.1 g adsorbent/100 mL solution. Samples were collected after 5, 15, 30, 45, 60, 90, 120, 180, 300 and 1320 minutes. The data obtained were used to evaluate the pseudo-first-order and pseudo-second-order models.

The pseudo-first-order model was represented by the Lagergreen equation [41]:

$$\log(q_e - q_t) = \log(q_e) - \frac{(k_1 \times t)}{2.303} \tag{3}$$

where q_e and q_t represent the amount of phosphate adsorbed (mg/g) at equilibrium and at time t, respectively; and k_1 is the adsorption constant (min^{-1}). The pseudo-second-order model evaluated was expressed by the following equation:

$$\left(\frac{t}{q_t}\right) = \frac{1}{(k_2 \times q_e^2) + (\frac{t}{q_e})} \tag{4}$$

where k_2 is the pseudo-second-order constant (g/mg×min); qe is the adsorption capacity at equilibrium; and q_t is the phosphate adsorption capacity at time t [41].

The regression coefficient of the pseudo-first-order kinetic model was lower than that of the pseudo-second-order kinetic model, which reached a regression coefficient of 1.0. These results support the selection of this model to explain the phosphate adsorption mechanism using the studied bioadsorbent. The fit of this model is shown in Figure 11 [41].

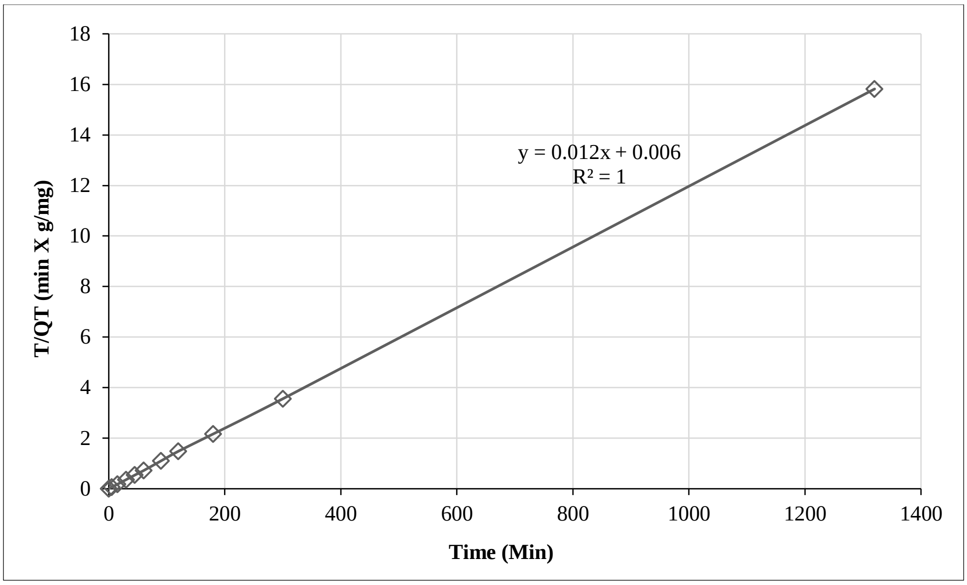

Figure 11. Pseudo-second-order kinetic model obtained from phosphate adsorption

The analysis corresponding to the FTIR and SEM (EDX) tests carried out on the adsorbent material after the adsorption process is presented in Figures 12 and 13. In this case, the sample studied corresponded to the adsorbent material prepared using eggshell and sacha inchi cuticle pyrolyzed in a ratio of 1:10.

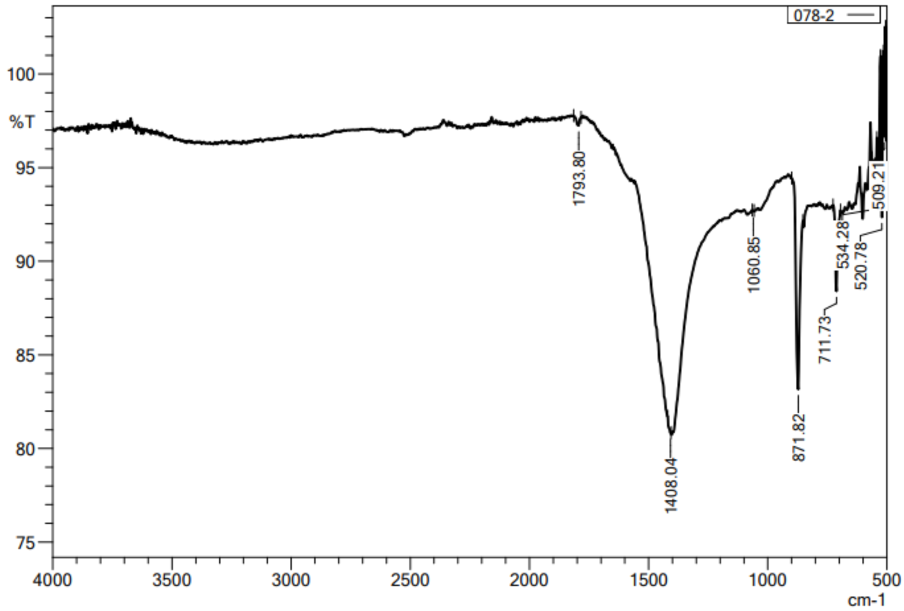

Figure 12. FTIR spectrum of a 1:10 mixture of eggshell and pyrolyzed sacha inchi cuticle after the adsorption process

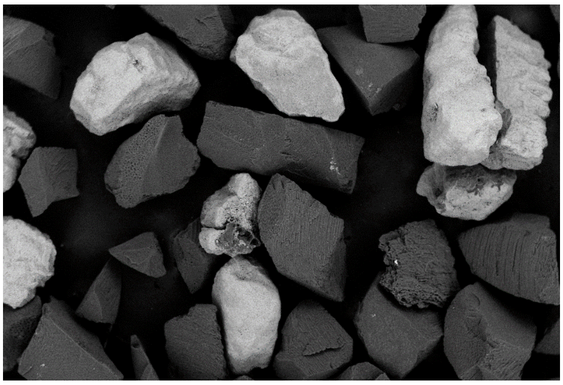

Figure 13. SEM image of the eggshell and sacha inchi cuticle mixture (100X)

The spectrum of the mixture after phosphate adsorption showed several significant peaks that provided information about the components present in the sample. The peak at 1793.80 cm^{-1}, associated with the C=O bonds of carbonyl groups, indicates the presence of calcium carbonates in the eggshell and aromatic compounds in the sacha inchi cuticle. The peak at 1408.04 cm^{-1}, associated with the C-O bonds of carboxylic groups, was attributed to carboxylic groups in the sacha inchi cuticle. The presence of the peak at 1060.85 cm^{-1}, corresponding to phosphate groups (PO_4^{3-}) and P=O bonds of inorganic phosphates, could indicate the presence of residual phosphates in the mixture coming from the adsorption process. However, the peaks at 871.82 and 711.73 cm^{-1}, which are characteristic of CO_3^{2-}, could be related to eggshells. The peaks at 534.28, 520.78 and 509.21 cm^{-1} are associated with bending vibrations of C-C and C-O bonds, which can be attributed to the presence of organic compounds on the adsorbent [43].

The SEM micrographs in Figure 12 show that the eggshell and calcined sacha inchi cuticle mixture consists of particles with an average size of 150–420 nm. They also showed the presence of particles with irregular morphologies and different sizes. The lighter particles belonged to the eggshell and the darker ones to the sacha inchi cuticle. Some particles had a higher porosity compared to others as well as a more compact structure. This morphological variability within the sample could influence its ability to adsorb phosphates, as porosity increases the contact surface and therefore improves adsorption efficiency.

EDX analysis revealed the presence of calcium (24.80% w/w), carbon (31.04% w/w), oxygen (43.61% w/w), phosphorus (0.3% w/w) and other elements in minor proportions, indicating a significant amount of organic and inorganic materials in the sample. Significant differences were observed in the elemental composition, with the presence of calcium and phosphates standing out. Particles with higher calcium concentrations also had more phosphates, suggesting that calcium in the eggshell facilitated phosphate adsorption more than the sacha inchi cuticle. When the concentrations of both adsorbents were compared, the eggshell and sacha inchi cuticle mixture had a significantly higher calcium content (24.80 wt%) than the sacha inchi cuticle alone (1.02 wt%).

4. Conclusions

Physicochemical characterization by FTIR analysis showed that the eggshell was mainly composed of calcium carbonate, while the sacha inchi cuticle had a complex composition that included fatty acids, alcohols, tocopherols, phytosterols and proteins. SEM-EDX studies confirmed the presence of calcium and carbon as the main components in the eggshell as well as a high concentration of carbon and oxygen in the sacha inchi cuticle. The irregular and rough morphology of the eggshell contrasts with the porous and fibrous structure of the sacha inchi cuticle. Therefore, these characteristics affected phosphate adsorption, resulting in low removal efficiencies compared to other adsorbent materials previously reported in the literature. Similarly, a clear relationship was found between the initial phosphate concentration and the phosphate amount adsorbed by the adsorbent material. Thus, the higher the initial phosphate concentration, the better the removal efficiency, peaking at an initial concentration of 300 mg/L with a phosphate removal rate of 28.44%.

Phosphate adsorption was more effective with 0.1 g of adsorbent, achieving a phosphate adsorption yield of 89 mg PO_4^{3-} adsorbed/g adsorbent. However, the Freundlich adsorption isotherm had a better fit to the experimental data with an R^2 of 0.97 compared to the Langmuir isotherm with an R^2 of 0.81 with respect to the observed phenomenon. This indicates multilayer adsorption and an energetically heterogeneous adsorbent surface. The kinetic study showed a rapid initial decrease in phosphate concentration during the first minutes of contact, followed by a slower decrease until equilibrium was reached in approximately 1 h. This behavior indicates that the adsorption process is fast in the initial stages due to the high availability of adsorption sites on the adsorbent surface, but as time progresses, the adsorption rate gradually decreases, suggesting a decrease in the availability of adsorption sites or saturation of adsorption sites.

The highest percentage of phosphate removal using the mixture of sacha inchi cuticle and eggshell was 41%, which was lower than that obtained with other adsorbents, such as calcined eggshell (99.4% removal percentage) and the eggshell and palm fiber mixture (87.74%), indicating the need to perform the previous pyrolysis of the material at a higher temperature condition. In addition, this by-product could also be evaluated for the removal of other contaminants from water, in which its composition and structure may allow it to perform better. Furthermore, post-adsorption analyses, such as FTIR and SEM-EDX, reveal that the material largely maintains its structure and functional elements. This suggests a promising potential for reuse across multiple treatment cycles. Future research could focus on evaluating its stability and efficiency after repeated regeneration processes, paving the way for this biosorbent to be considered a long-term, sustainable, and cost-effective solution

5. Declarations

5.1. Author Contributions

Conceptualization, C.A.P. and Á.M.O.A.; methodology, N.L.L.B., A.C.R.T., Á.M.O.A., and C.A.P.; formal analysis, N.L.L.B., A.C.R.T., Á.M.O.A., and C.A.P.; investigation, N.L.L.B. and A.C.R.T.; writing—original draft preparation, N.L.L.B., A.C.R.T., Á.M.O.A., and C.A.P.; writing—review and editing, N.L.L.B., A.C.R.T., Á.M.O.A., and C.A.P.; funding acquisition, Á.M.O.A. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available in the article.

5.3. Funding

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5.4. Conflicts of Interest

The authors declare no conflict of interest.

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