

Article

Removal of Brilliant Green Cationic Dye Using Bioadsorbent Material from Oyster Shells

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Abstract: This study explored the potential of coral rock, specifically coquina derived from oyster shells, as a bioadsorbent for the removal of dyes from wastewater generated by the textile industry. The investigation included an examination of particle size fractions (300 μm and less than 300 μm) and thermal treatment; the investigation involved drying at 120 °C and calcination at temperatures ranging from 200 °C to 800 °C. The material was subjected to a comprehensive analysis through various characterization techniques. Laboratory-scale experiments were conducted to evaluate the removal capacity and adsorption kinetics of the bioadsorbent utilizing brilliant green dye. The experiments involved varying dye concentrations (25, 50, and 75 mg L^{-1}), pH levels (2 to 12), and different doses of biosorbent material (0.2 to 0.6 g L^{-1}), with constant agitation. Various kinetic models were applied to fit the experimental data, with the pseudo-second-order model demonstrating the best fit. The findings reveal that coquina rock, characterized by a temperature of 120 °C and a particle size of greater than 300 μm , exhibits remarkable effectiveness. It achieved a removal efficiency of 90% within 15 to 20 min at pH 7.8. This study concludes that coquina rock not only stands out as demonstrating remarkable efficacy in dye removal but also underscores a sustainable approach, leveraging readily available and environmentally friendly materials for wastewater treatment.

Keywords: bioadsorbent; dye; oyster shells; coquina rock; removal



Citation: Moreno-Ríos, A.L.; Coronado-Herrera, C.; Rhenals-Navarro, J.C.; Hernandez-Palma, H.G.; Dotto, G.L.; Gindri Ramos, C.; Gómez-Plata, L. Removal of Brilliant Green Cationic Dye Using Bioadsorbent Material from Oyster Shells. *Sustainability* **2023**, *15*, 16443. <https://doi.org/10.3390/su152316443>

Academic Editor: José Carlos Magalhães Pires

Received: 29 October 2023
Revised: 26 November 2023
Accepted: 27 November 2023
Published: 30 November 2023



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1. Introduction

The textile industry significantly contributes to the economies of developing countries, accounting for 5% of the total textile trade and 5% of total exports, creating 120 million jobs, and representing a market value of USD 2000 million. Nonetheless, it generates substantial quantities of highly polluting wastewater characterized by its dark appearance due to it containing dyes and toxic chemicals. Apart from environmental contamination, these effluents pose a health risk as they can easily infiltrate the food chain through animals, given that most dyes do not completely adhere to the fibers. Moreover, these wastewater residues persist in the environment for extended durations, emerging as a threat to living organisms, water quality, and soil integrity [1–3].

The textile industry stands as the second largest global water consumer, requiring 200 L of water to produce 1 kg of fabric [4]. Additionally, it holds a prominent position as a major contributor to global pollution, particularly in terms of liquid waste. Consequently, substantial volumes of effluents, often comprising millions of gallons, are discharged into water bodies.

These effluents predominantly contain dyes engineered for resistance, making their removal treatment contingent upon the specific characteristic of the utilized dye [5,6].

Numerous methods have been employed for the mitigation of dye contamination in wastewater originating from the textile industry, encompassing biological degradation, coagulation, flocculation, Fenton, photo-Fenton, ozonation, and electrochemical methodologies, among others [1,7]. However, a significant portion of these approaches necessitates the utilization of chemical agents, thereby incurring substantial costs. Consequently, there is a pressing need for sustainable and cost-effective alternatives.

The bioadsorption process has garnered significant attention as it facilitates the removal of various contaminants in solution by effecting mass transfer from the liquid phase to the solid phase. The substance to be eliminated from the liquid phase is referred to as the adsorbate, and the bioadsorbent serves as the repository for the accumulated adsorbate [8]. The significance of this process lies in the utilization of readily accessible materials, often considered waste [9,10].

Several factors influence biosorption, including the type of material and adsorbate, textural and structural properties, initial dye concentration, adsorbent quantity, contact time, pH, and temperature. Consequently, the evaluation of these variables is imperative for new bioadsorbent materials. This comprehensive assessment allows for the selection of optimal treatment and operation conditions, ensuring higher yields and guaranteeing both material and process sustainability [11,12].

Materials derived from agricultural waste, particularly biosorbents, have proven effective in the removal of dyes from wastewater. These materials, characterized by their low cost and abundant availability, present a viable option for such applications, exemplified by the utilization of rice husks. Rice husks have demonstrated success in adsorbing various dyes, including Congo red, methylene blue, crystal violet, and brilliant green. Notably, removal percentages of 93.4% for Congo red, 95.8% for methylene blue, 96.3% for crystal violet, and 96.6% for brilliant green have been achieved through its application [13].

In the same way, Singh et al. [14] conducted a study focusing on the adsorption of malachite green dye using powder seeds derived from *Mangifera indica* (mango). They achieved a maximum removal percentage of 96% with an adsorption capacity of 22.8 mg g^{-1} at pH 6 and with an initial concentration of 100 mg L^{-1} of malachite green [14]. Similarly, in their research, Sartape et al. [15] employed apple peel, as a solid residue of fruits and food, for the removal of malachite green. With this adsorbent, they obtained a removal efficiency of 98.87% at an initial concentration of 100 mg L^{-1} and pH in the range of 7–9, establishing it as a highly effective and economical alternative [15].

Another of the biosorbents implemented for dye removal is the biomass derived from the roots of water hyacinth (*Eichhornia crassipes*), a floating aquatic species indigenous to the Amazon region, where it proliferates abundantly, exerting a significant impact on aquatic ecosystems through oxygen depletion. Consequently, this biomass has been harnessed for the adsorption of the red reactive dye BF-4B, achieving an impressive 95% removal efficiency. This application presents itself as a viable alternative for mitigating the eutrophication induced by the prolific growth of water hyacinth [16].

Likewise, many bioadsorbents have been implemented, from which good results have been obtained in the removal of dyes and other contaminants [10,17]. An example of these materials is the oyster shell, which represents an environmental problem as it is a waste generated in large quantities by the fishing and food industries, leading to its accumulation and generation of bad odors [18–21]. However, oyster shells are rich in calcium carbonate (CaCO_3), and due to its textural properties, it has been considered a potential adsorbent of contaminants [22]. For example, this material has been used for the removal of heavy metals [23,24] and nutrients such as nitrates, nitrites, phosphates [25], sulfates [26], and dyes [18,26].

Coquina dust has been used in wastewater treatment processes [27–29]. This sedimentary rock, classified within the limestone group, is predominantly composed of unconsolidated aggregates of oyster shells, other mollusks, and fragments of coral skeletons. Owing to its inherent porosity, coquina typically presents a substantial surface area along

with numerous adsorption sites. Its mineral composition, primarily CaCO_3 , encompasses minerals with adsorbent properties, including clays or iron minerals, thereby facilitating the effective removal of dyes and other contaminants [29].

Coquina, derived from readily available sources, emerges as a sustainable alternative that avoids the depletion of scarce resources [26,27,29]. In comparison with synthetic adsorbents, coquina is natural and biodegradable, positioning it as an environmentally conscientious choice. The extraction and processing of coquina, being less energy-intensive than the synthesis of synthetic adsorbent materials, holds the potential to mitigate the carbon footprint associated with the production and utilization of such materials. Unfortunately, reports on this topic are less available [27,29].

According to the above, in this study, coquina rock obtained from oyster shells was assessed as a bioadsorbent material for dye removal in textile industry wastewater. The material underwent an initial process of crushing and thermal modification, succeeded by an assessment of its textural, elemental, and thermal properties. After these characterizations, the adsorption capacity of the coquina rock was evaluated using simulated textile wastewater containing bright green dye. Furthermore, to understand how various operational conditions affect the speed and efficiency of dye adsorption over time and the adsorption capacity of the bioadsorbent, the impact of the initial dye concentration, pH, and bioadsorbent dosage on the adsorption kinetics was assessed.

2. Experimental Procedure

2.1. Preparation of the Biosorbent Material

The coquina was collected from the foothills located on the beaches of Salgar in the municipality of Puerto Colombia, in the department of Atlántico, Colombia. The preparation of the material used in this study was carried out following the methodology presented in Figure 1. Initially, the bioadsorbent material was washed with a diluted solution of sodium hypochlorite (NaClO) to eliminate microorganisms, traces of organic residues, and other decomposing materials present in the samples. Subsequently, the material was air-dried, crushed in porcelain mortars, and subjected to a sieving process in a tower comprising sieves with hole sizes of $<300\ \mu\text{m}$ (a) and $>300\ \mu\text{m}$ (b) [26,27].

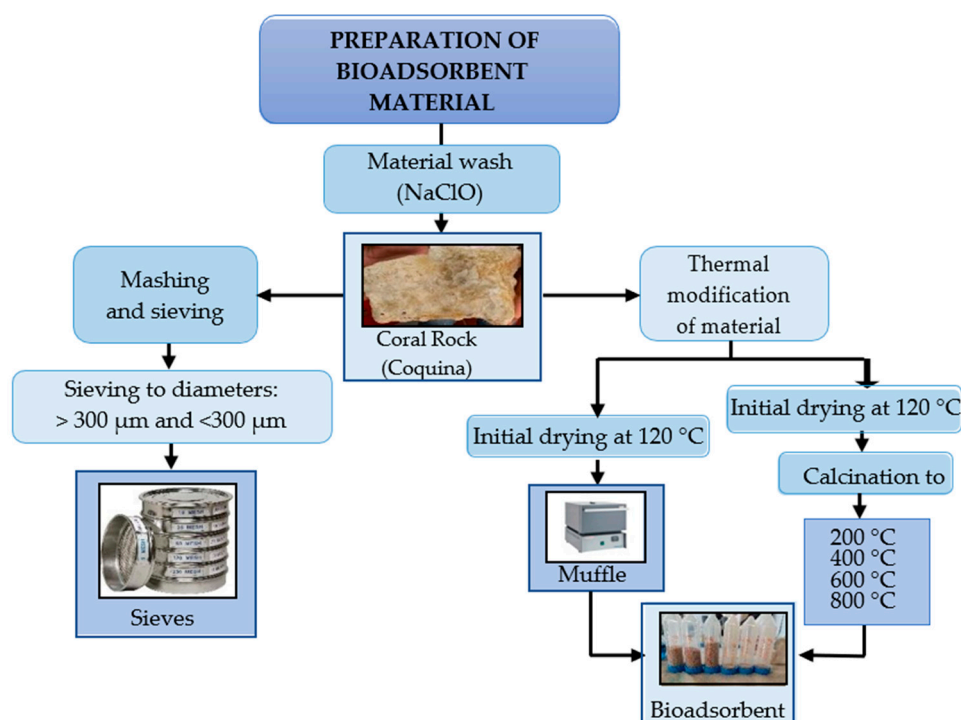


Figure 1. Preparation of the biosorbent material.

After the preceding procedure, a sample was taken without modification of the material, and another sample was subjected to thermal treatment at 120 °C for 2 h in a muffle furnace to eliminate humidity.

For the thermal modification of the biosorbent material, the samples underwent a gradual heating process at a rate of 5 °C min^{−1} until reaching a temperature of 120 °C, which was maintained for 2 h. Subsequently, the temperature was further increased at a rate of 5 °C min^{−1} to 200 °C, 400 °C, 600 °C, and 800 °C, each maintained for a specified duration of 2 h. Following this, the resulting samples were placed in a desiccator to avoid contamination.

2.2. Characterization of the Biosorbent Material

In assessing the material's adsorption behavior, the point of zero charges (PZC) was determined. Likewise, to characterize the textural and elemental features of the material, evaluations were conducted using the Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and thermal gravimetric analysis (TGA) [26,28].

It is important to highlight that initial tests were conducted using the bioadsorbent material, and among the tested conditions, coquina rock exhibited the most promising results for dye removal at a temperature of 120 °C. Specifically, this material underwent a drying process without thermal modification (Figure 1). Therefore, the characterization of this material will be presented, which was also used for the kinetic evaluation due to its efficiency.

2.2.1. Point of Zero Charges (PZC)

After obtaining the material and performing the heat treatment, the zero-charge point, also known as zeta potential (PCC or PCZ), was determined [30,31]. In a 100 mL Erlenmeyer flask, 50 mL of distilled water was utilized, and the pH of the solution was adjusted to 2, 4, 6, 8, 10, and 12 by adding appropriate amounts of 0.1 M HCl and 0.1 M NaOH. Then, 0.2 g of adsorbent material sample (of each diameter) was added to these solutions. After 48 h of stirring at 220 rpm and room temperature (25 °C), the final pH value was measured.

Considering the previous procedure, the adsorption capacity of the adsorbent material was validated in preliminary tests by employing two cationic dyes, brilliant green, and rhodamine B. Brilliant green dye was chosen due to its higher removal percentages observed with the studied bioadsorbent material. Consequently, this dye was selected for use in the subsequent simulations of textile wastewater.

2.2.2. BET Analysis

This study aimed to assess surface area measurements using nitrogen absorption at low temperatures. The experiment was conducted in the SENA laboratory using the ASAP 2020 Micromeritics equipment (Micromeritics Instrument Corporation, Norcross, GA, USA), indicating that the samples might primarily consist of calcium oxides and/or calcium carbonate due to their origin. A 0.1 g sample was analyzed under degassing conditions maintained at 50 °C for 1 h. The temperature was then incrementally raised at a rate of 5 °C min^{−1} until reaching 120 °C, sustained for 12 h. Nitrogen (N₂) served as the sorbate at 77 K for approximately 7 h. Pore size determination was executed using the adsorption isotherm, with 8 data points being collected for the adsorption isotherm.

2.2.3. X-ray Diffraction Analysis

This analysis yields insights into the composition and crystalline structure of the material [30–33]. The X-ray diffraction (XRD) analysis was carried out at the University of Antioquia laboratory using X-ray diffraction (XRD) XPert PANalytical Empyrean Series II-Alpha1, Model 2012 equipment (Malvern Panalytical, Malvern, UK). Standard conditions were applied for the reflection, with a step size of 0.05 and 50 s per step.

2.2.4. FTIR Analysis

A Fourier-transform infrared spectroscopy (FTIR) analysis was employed to examine the vibration modes of the inorganic structure of the adsorbent, facilitating the identification of modifications influenced by the organic molecules within the structure or on the surface [30,34]. The analysis was carried out at the SENA laboratory using IRAffinity-1 FTIR SHIMADZU equipment, Series: A213749, under standard conditions.

2.2.5. Thermogravimetry Analysis

This analysis provides information on the mass loss of the solid following thermal modifications and potential phase transformations [30]. The analysis was conducted at the laboratory of the University of Antioquia utilizing Thermal Analysis—TA Instruments, TGA 2950 equipment (TA Instruments, Inc., New Castle, DE, USA), under a nitrogen atmosphere with a heating rate of 5 °C min^{−1} until the temperature reached 900 °C.

2.3. Colorant Removal Evaluation

The efficiency of the bioadsorbent materials for eliminating recalcitrant dyes from the textile industry was assessed on a laboratory scale at the Center for Research in Environmental Technologies (CITA) of the Universidad de la Costa. For this purpose, brilliant green dye was used as a model pollutant representative of the textile industry. Preliminary tests were conducted on the bioadsorbent materials prepared (including different temperatures and particle sizes). Later, the material demonstrating the most effective dye removal was chosen and characterized using PCZ, BET, XRD, FTIR, and TGA. Removal tests were carried out with time-dependent monitoring to delineate adsorption curves, establish adsorption kinetics, and determine optimal operating conditions.

Adsorption tests were conducted using 100 mL of brilliant green dye solution and the bioadsorbent material under examination in borosilicate flasks. All experiments were duplicated and performed under constant agitation at 220 rpm using a six-speed Oxitop shaker. The progress was monitored over 2 h, with samples being collected at 0, 10, 20, 30, 40, 50, 60, 75, 90, 105, and 120 min.

After the contact period between the bioadsorbent and the dye, the mixture was centrifuged at 4000 rpm for 15 min, and the dye concentration was quantified using a GENESYS 10UV UV-visible spectrophotometer at a pre-calibrated wavelength of 640 nm. Dye solutions ranging from 5 to 100 mg L^{−1} were utilized. The impact of initial dye concentration (25, 50, and 75 mg L^{−1}), bioadsorbent material concentration (0.2, 0.4, and 0.6 g L^{−1}), and pH variations (2, 4, 6, 8, 10, and 12) were studied to elucidate the adsorption kinetics. The pH of the solutions was adjusted by the addition of HCl and NaOH to achieve the required experimental values.

The adsorption efficiency was assessed using the adsorption capacity at time t (q_t), adsorption capacity at equilibrium (q_e), and removal percentage (R , %) using Equations (1), (2), and (3), respectively:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

$$R(\%) = \frac{(C_0 - C_e)}{m} \quad (3)$$

The variables in the equations are defined as follows: C_0 denotes the initial concentration of brilliant green (mg L^{−1}), C_t signifies the concentration of brilliant green in the liquid phase at time t (mg L^{−1}), C_e represents the equilibrium concentration of brilliant green in the liquid phase (mg L^{−1}), m is the mass of the adsorbent (g), and V is the volume of the solution (L) [35].

The statistical differences among means for the various treatments were assessed using a two-way analysis of variance (ANOVA) followed by Tukey's honestly significant difference (HSD) post hoc test. In all cases, p -values < 0.05 were considered indicative of significantly different relationships from zero, with a confidence level of 95.0%. It is important to note that the statistical analyses were conducted using Microsoft Excel and GraphPad Prism software (version 10.1.0).

2.4. Estimation of Kinetic Parameters

To determine the reaction speed, 4 highly referenced kinetic models were used in previous research studies [36,37]. These include the pseudo-first-order, pseudo-second-order [38] intraparticle [39], and Elovich models [40,41], as shown in Table 1.

Table 1. Kinetic equations are used to determine the rate of degradation of dyes.

Kinetic Model	Equation	Parameters
Pseudo-first-order [38].	$q_t = q_e \left(1 - e^{-k_1 t}\right)$	k_1 (L min ⁻¹): first order rate constant; q_e (mg/g): amount of adsorbate adsorbed at equilibrium; q_t : amount of adsorbate adsorbed at time t . The values of q_e and k_1 can be obtained by fitting the nonlinear curve of the experimental data $\log(q_e - q_t)$ against t .
Pseudo-second-order [38].	$q_t = \frac{k_2 t}{1 + k_2 q_e t}$	k_2 (g mg ⁻¹ min ⁻¹) second order rate constant; q_e (mg/g): amount of adsorbate adsorbed at equilibrium; q_t : amount of adsorbate adsorbed at time t .
Elovich Model [40,41].	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	α : initial rate of adsorption (mg g ⁻¹ min ⁻¹); β (g mg ⁻¹) desorption constant related to surface reach and chemisorption activation energy; q_t : amount of adsorbate adsorbed at time t .
Intraparticle model [39].	$q_t = k_{ip} t^{1/2} + C$	Donde k_{ip} (mmol g ⁻¹ min ^{-1/2}) is the intraparticle diffusion rate constant.

3. Results and Discussion

3.1. Characterization of the Bioadsorbent Material

Once the biosorbent material was prepared, the selection of particle size and optimal heat treatment temperature was carried out to define the material with the best efficiency in the adsorption process for brilliant green dye and to proceed with its respective textural and elementary characterization. Figure 2 shows the removal percentages obtained for the different temperature values at which the material was prepared and for the two particle sizes evaluated (greater than 300 μ m and less than 300 μ m). Subfigure (a) depicts the significant variations exhibited by the coarse material compared with the fine material under the same thermal treatment, while (b) illustrates the notable distinctions among the thermal treatments applied to the fine material. The coarse material did not show statistically significant changes in response to variations in the thermal treatment temperature during its preparation. Notably, treatments at 120 and 200 $^{\circ}$ C did not yield significant variations in the material's thickness.

The results show that the percentage of dye removal obtained with the thick coquina did not show statistically significant changes in response to variations in the temperature of the thermal treatment. In contrast, the fine particle bioadsorbent displayed a reduction in the removal percentage as the thermal treatment temperature increased from 200 $^{\circ}$ C to temperatures within the range of 400 to 800 $^{\circ}$ C. Furthermore, it is evident that the thick material (particle sizes $> 300 \mu$ m) exhibited higher removal percentage values compared with the fine material (particle sizes $< 300 \mu$ m). Notably, the fine material encountered operational issues at temperatures exceeding 400 $^{\circ}$ C. Consequently, the particle size that was selected for further analysis was $>300 \mu$ m, as this size exhibited no significant changes

at temperatures below 200 °C. This selection implies a larger contact surface area and minimal thermal modification at lower temperatures [26].

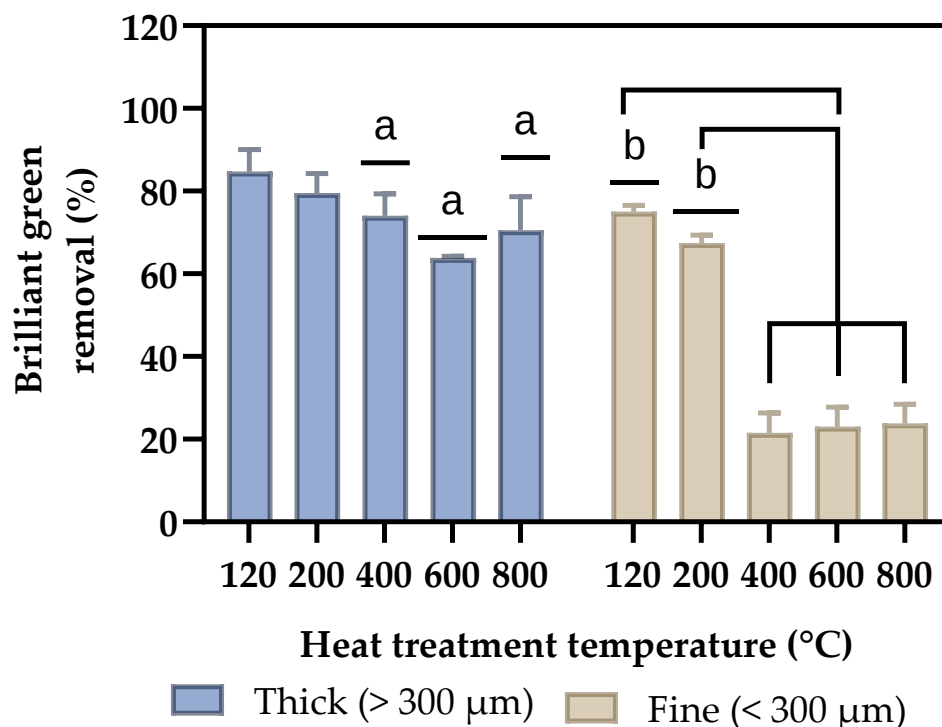


Figure 2. Removal percentage of fine and coarse material at different treatment temperatures. Conditions: bioadsorbent dosage = 0.2 g. L⁻¹; C₀ = 25 mg L⁻¹; natural solution pH; t = 120 min). Results are presented as the means ± SEM. Significant differences between treatments: $p < 0.05$. (a) Significant changes of the coarse material compared to the fine material under the same heat treatment. (b) changes between heat treatments applied to the fine material.

It is important to note that, although it is well known that the removal percentage of most adsorbents increases with smaller particle sizes, this consideration may vary depending on the type of material used [26]. In this case, the coquina with particle sizes of less than 300 μm experienced operational issues during the experiments, particularly in materials obtained at temperatures exceeding 400 °C. This is reflected in the decrease in the dye removal percentage shown in Figure 2.

Although the decrease presented with the temperature of the thermal treatment in the larger coarse material was not statistically significant, the results indicate a favorable removal of up to 80% for the thermal treatment at 120 °C. Therefore, this material was chosen for comprehensive characterization using techniques such as zero charge point determination, BET, XRD, FTIR, and TGA. Likewise, for the determination of adsorption kinetics, it should be noted that at a temperature of 120 °C, the material underwent no thermal modification; instead, it was solely subjected to drying to eliminate residual moisture from the previous preparation process.

3.1.1. Points of Zero Charge (PZCs)

The point of zero charge is a crucial parameter for understanding the aggregation and agglomeration behavior of particles. When dispersed in solutions at the PZC pH, the surface charge of the particles approaches zero, and their electrostatic force decreases, leading to the formation of agglomeration among them [42]. This parameter helps define the most suitable pH range for achieving efficient removal of a specific contaminant, whether it is of an anionic or cationic nature [8,43].

Figure 3 shows the pH measurements before and after the removal process using the bioadsorbent (coquina rock). The graph indicates the point at which surface charges neutralize each other, identified as 8.37. This finding suggests that there is no substantial impact of particle size on the surface charges of coquina rock.

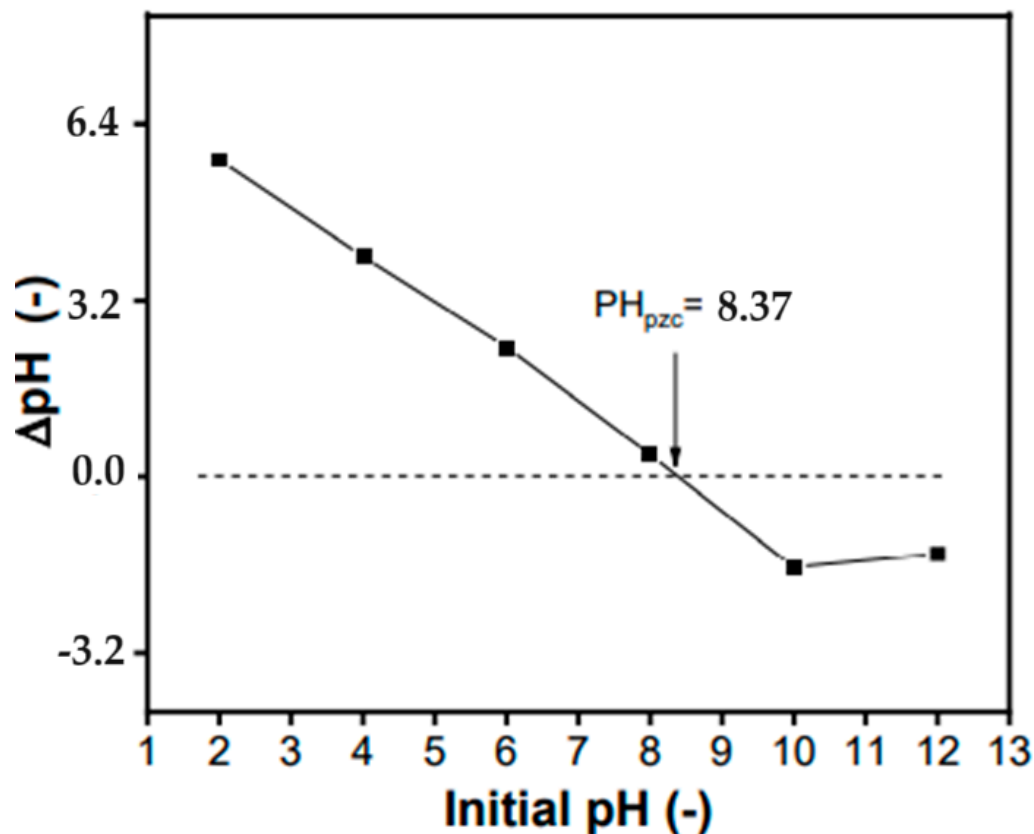


Figure 3. Point of zero charges. Experimental conditions: bioadsorbent dosage = 0.2 g L⁻¹; C₀ = 25 mg L⁻¹; t = 48h.

In comparison with other studies, such as Wu et al. [44], who employed recycled crab shell residues for the removal of brilliant green, our obtained zero charge point (PZC) is 8.37. Notably, their study revealed a PZC of 9.17, indicating the use of basic compounds to ensure efficient performance in aqueous solutions and the neutralization of surface charges.

3.1.2. BET Analysis

Figure 4 shows the N₂ adsorption isotherm for coquina rock at 120 °C. The exponential increase in the amount of adsorbed nitrogen can be observed as the relative pressure changes. According to the IUPAC classification, the observed behavior aligns with a type II adsorption isotherm associated with non-porous or macroporous adsorbent materials, indicating multilayer adsorption [45,46]. This is consistent with the non-porous characteristics of the studied material, characterized by pore diameters exceeding 50 nm.

Coquina rock exhibits a behavior like that found in earlier studies investigating the adsorption isotherms of dolomite and modified clinoptilolite zeolite, both of which contain calcium in their structure and display type II and III isotherms [44]. Regarding surface area, coquina rock demonstrated an area of 1.4163 ± 0.1134 m² g⁻¹, which is comparable with the value of 1.83 m² g⁻¹ observed for dolomite [46–48].

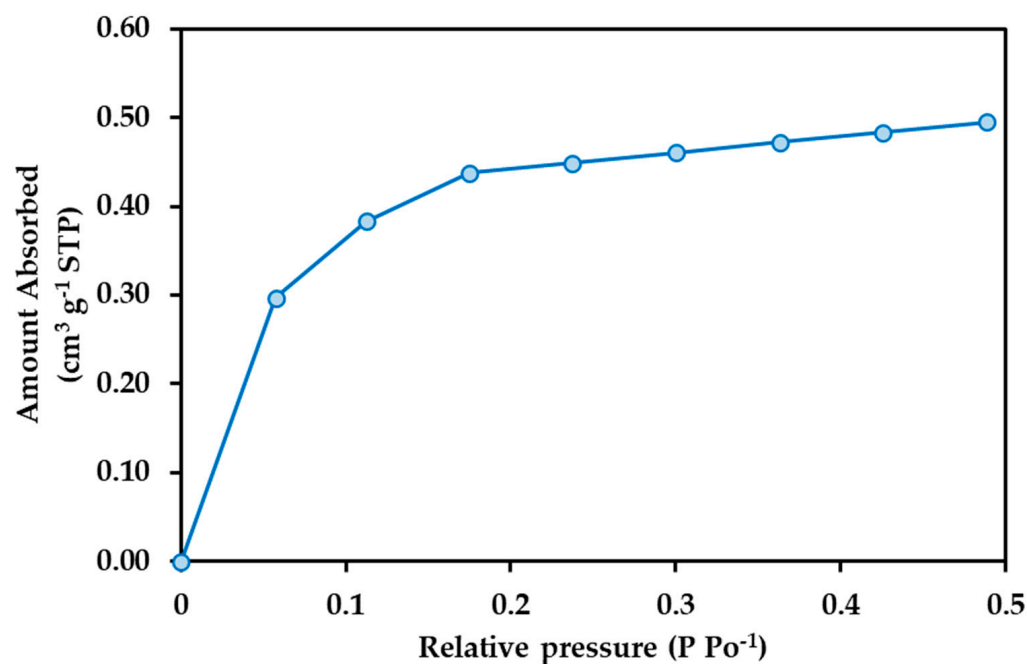


Figure 4. Bioadsorbent material adsorption isotherm.

3.1.3. XRD Analysis

Figure 5 shows the diffractogram resulting from the X-ray diffraction analysis of the chosen bioadsorbent (dried at 120 °C). Several distinct peaks are evident, with notable occurrences at $\theta = 26.2^\circ$, 27.3° , 38.7° , 46° , 48.3° , 50.3° , 52.8° , and 53.2° . These peaks are indicative of compounds associated with calcium carbonate, specifically the mineral calcite. This aligns with findings from prior investigations involving materials such as oyster waste clams and limestone, which demonstrate a parallel behavior to the outcomes of this study [47,49].

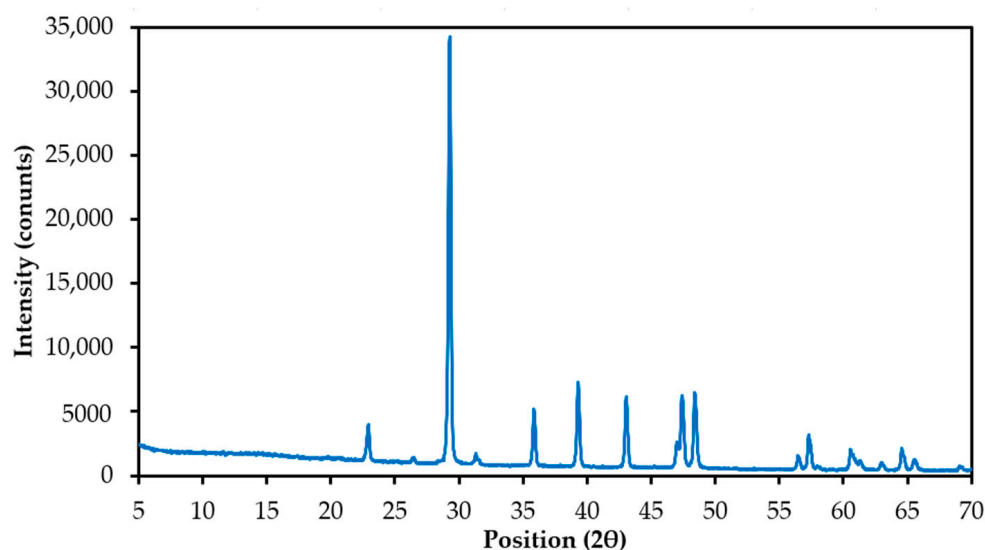


Figure 5. X-ray diffraction—XRD.

Moreover, Figure 5 reveals that the analyzed sample exhibits increased intensity in the 30 range when compared with reference patterns and similar studies involving comparable samples. This heightened intensity peak can be attributed to the presence of calcium carbonate (CaCO_3) in its structure. A relevant example is found in the study conducted by

Wu et al. [44], which utilized recycled crab shells for malachite green removal; the identical compound was identified in the same position, thus substantiating the findings presented in this study.

3.1.4. FTIR Analysis

The spectrum that is observed in Figure 6 represents the absorption peaks at 1450 cm^{-1} that are consistent with the C-O stretching and bending vibrations of carbonate anion (CO_3^{2-}). This evidences the presence of calcite in the selected sample, as mentioned previously, making comparison possible with investigations carried out with similar characteristics of bioadsorbents, such as other shells and clams [47,50]; the characteristics correspond to the composition of materials containing calcium carbonate.

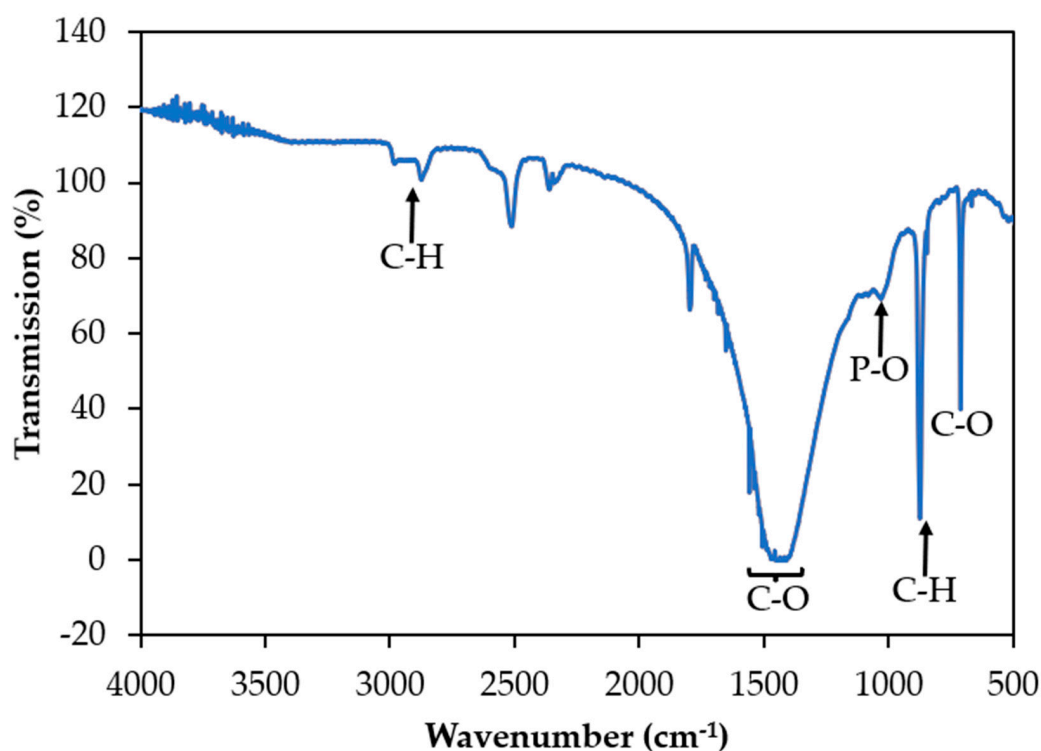


Figure 6. FTIR spectrum of the bioadsorbent studied.

Additionally, peaks are evident in the curve between 2800 and 3000 cm^{-1} , at 1030 cm^{-1} , and between 850 to 700 cm^{-1} , which are consistent with H-O, P-O, C-H, and C-O related to hydroxyapatite, bearing similarity to the hard tissues of human bones and teeth as reported by Wang et al. [51]. This material has also demonstrated adsorption properties for dye removal.

Finally, it is important to mention that, despite the well-known composition of coquina primarily consisting of calcium oxides, in this investigation, XRD and FTIR techniques were employed to analyze the composition and functional groups present in the structure of the bioadsorbents. This approach was adopted due to the variability in the composition of coquina rock based on its origin and source materials, such as oyster shells [45]. Upon analyzing the results obtained from these techniques, it was confirmed that the utilized material indeed corresponds to a type of coquina that, in its structure, also exhibits characteristics related to phosphorus-based compounds and even similarities with hydroxyapatite, indicating an affinity for dye removal.

3.1.5. TGA Analysis

In the thermogram presented in Figure 7, a noticeable mass loss is observed at a temperature ranging from 600 °C to 800 °C, resulting in a loss of up to 42.57% of the mass, equivalent to 9.059 mg. These findings, when compared with those of other authors, reveal a similar trend of losses determined at 35% in materials such as eggshells, oyster shells, and clams, among others [52,53]. This aligns with the presence of calcium carbonate as the primary compound in the study. It is important to note that at temperatures exceeding 600 °C, the material begins to undergo changes in its characteristics. However, the material chosen at 120 °C exhibits promising results and remains in a phase where it does not undergo a significant modification in its characteristics.

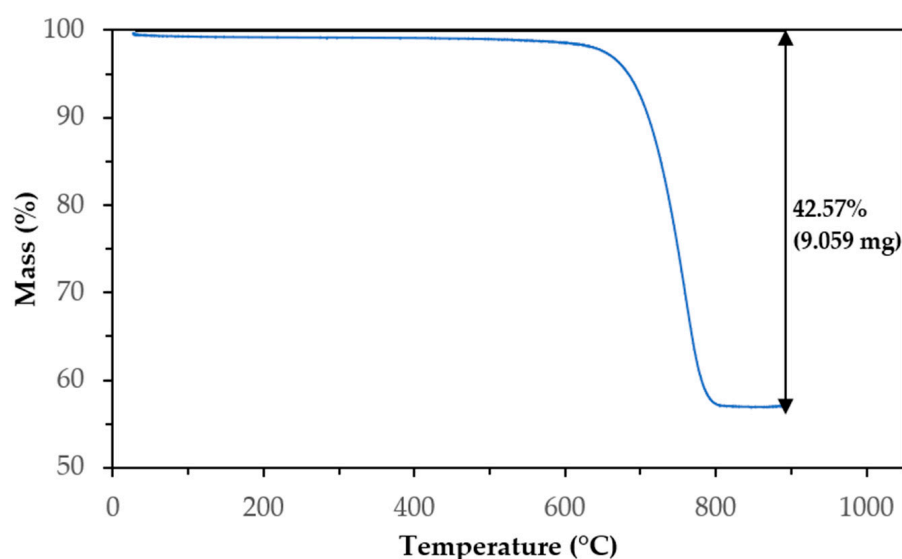


Figure 7. TGA thermogram for the bioadsorbent studied.

When analyzing studies involving the use of sugarcane bagasse and barium carbonate for the removal of malachite green or brilliant green, it is evident that these materials undergo modifications at temperatures near 120 °C. Consequently, they begin to lose their physical characteristics and become unstable in the presence of elevated temperatures [54]. In comparison with the aforementioned research, the selected sample demonstrates better viability as it remains stable at high temperatures and does not exhibit mass loss as described above.

A particle size evaluation revealed variations in the dye adsorption capacity, with superior performance observed in particles larger than 300 µm. Characterization techniques (BET, XRD, FTIR, and TGA) confirmed the presence of calcite minerals, demonstrating a high affinity with the dye. The TGA analysis indicated a thermal modification of the material at temperatures exceeding 600 °C, resulting in material disintegration influenced by increased pH and turbidity during removal tests.

3.2. Brilliant Green Dye Removal Tests

3.2.1. Analysis to Determine Operating pH

Figure 8 illustrates the results of removal percentage and adsorption capacity at different pH values. Removal dye experiments were conducted at a fixed concentration of 25 mg L⁻¹ and duration time of 120 min. During this period, samples were collected every 10 min to monitor the dye removal process. Considering that adsorption equilibrium was achieved after 30 min, for comparison purposes, the removal percentages obtained at 90 min are depicted in Figure 8. The pH range that showed the highest removals of the bright green dye was between 6 and 8, as depicted in Figure 8A, where percentages of 82.8 and 81.7% are evident, along with adsorption capacities of 103.5 and 102.1 mg·g⁻¹ (Figure 8B),

respectively. Additionally, it can be observed that statistically significant changes were mainly noted at pH values of 2 and 10, resulting in a reduction in the removal percentage and adsorption capacity.

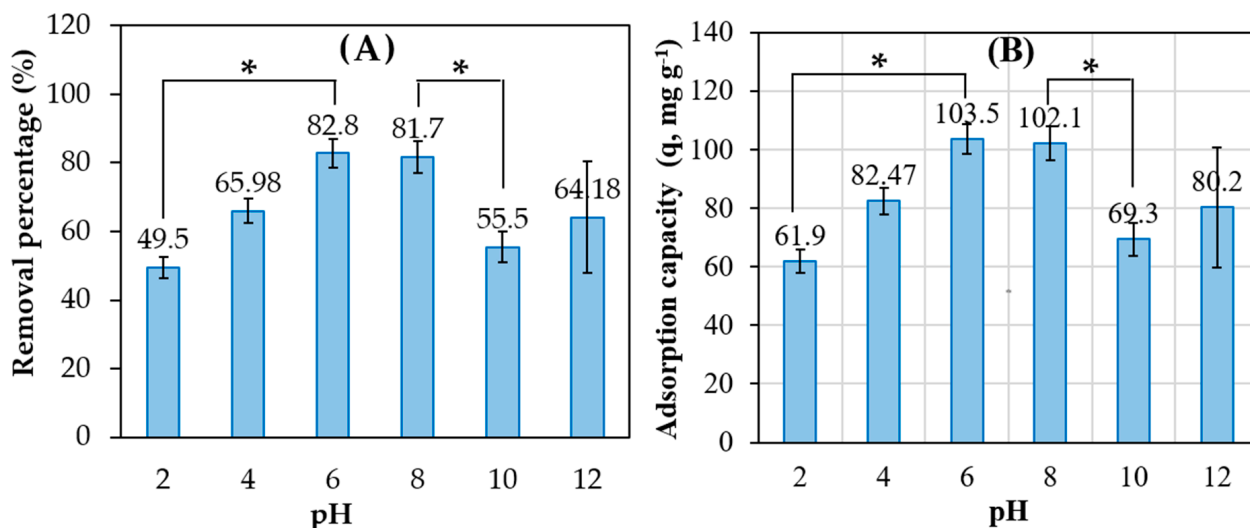


Figure 8. Effect of pH on dye removal (A) removal percentage and (B) adsorption capacity. Experimental conditions: bioadsorbent dosage = 0.2 g. L⁻¹; C₀ = 25 mg L⁻¹; t = 120 min. Results are presented as the means ± SEM. * Significant differences between treatments: $p < 0.05$.

The observations presented in Figure 8 are consistent with the earlier findings in Figure 3, particularly regarding the point of zero charge (PZC) at pH 8.37. Below this threshold, the material surface carries a positive charge, which transitions to a negative charge above the threshold. This dynamic suggests that, in acidic environments, the cationic brilliant green dye experiences repulsion, whereas in alkaline conditions, attraction occurs, significantly augmenting the overall removal efficiency.

However, it is crucial to note that, throughout the experiment, degradation was noted in both the adsorbate and the material under extreme pH conditions, specifically below a pH of 4 or above a pH of 10. Such instances could pose operational challenges on an industrial scale, potentially resulting in diminished removal percentages and adsorption capacities. As a strategic measure, a pH range of 6 to 8 was strategically chosen for subsequent tests, demonstrating superior removal efficiencies within this specified range.

Given that the natural pH of the brilliant green dye solution was around 7.8, closely aligning with the determined point of zero charge (PZC) pH, this value was selected for the subsequent adsorption experiments. Consequently, the need for introducing acidic or basic solutions to adjust the pH was eliminated, ensuring that the process was carried out under conditions closely resembling real-world scenarios.

If we conduct a comparison with other similar studies, it can be found, for example, that Singh et al. [14] even used a pH of 6 for the adsorption of the same dye, employing the powder of *Mangifera indica* (mango) seed. They achieved a maximum removal percentage of 96% with an initial concentration of 100 mg/L of malachite green [14]. Similarly, Sartape et al. [15] used pH values ranging between 7 and 9, achieving removals of up to 98.87%, also starting from the same initial concentration used by [14]. In this study, as can be seen below, removal percentages of around 94% were even found for an initial dye concentration of 75 mg/L when using the natural pH of 7.8. This demonstrates that the material obtained from coquina rock has significant potential for dye removal.

3.2.2. Variation of Initial Dye Concentration

The evaluation of a novel adsorbent necessitates careful consideration of its adsorption capacity with respect to the initial concentration. The adsorption process, which is inher-

ently linked to dye concentration and the active binding sites on the adsorbent's surface area, exhibits variable effects as the initial concentration is heightened [55].

The effect of the initial concentration was evaluated, maintaining constant pH, agitation, and material dosage during adsorption tests, as depicted in Figure 9. Notably, heightened removal percentages (Figure 9A) and enhanced adsorption capacity (Figure 9B) were observed within the initial 15 and 20 min, showcasing accelerated adsorption kinetics at a concentration of 25 mg L^{-1} . In line with previous investigations, it was established that an increase in dye concentration leads to prolonged adsorption times, attributed to a greater availability of dye molecules [56]. The adsorption process is intricately linked to the dye concentration and bonding sites on the adsorbent's surface area, exhibiting variable effects when the initial concentration is increased [55]. Consequently, it can be inferred that lower concentrations facilitate faster adsorption kinetics, maintaining a relatively linear behavior as a constant concentration is sustained before 25 min, indicating a consistent progression.

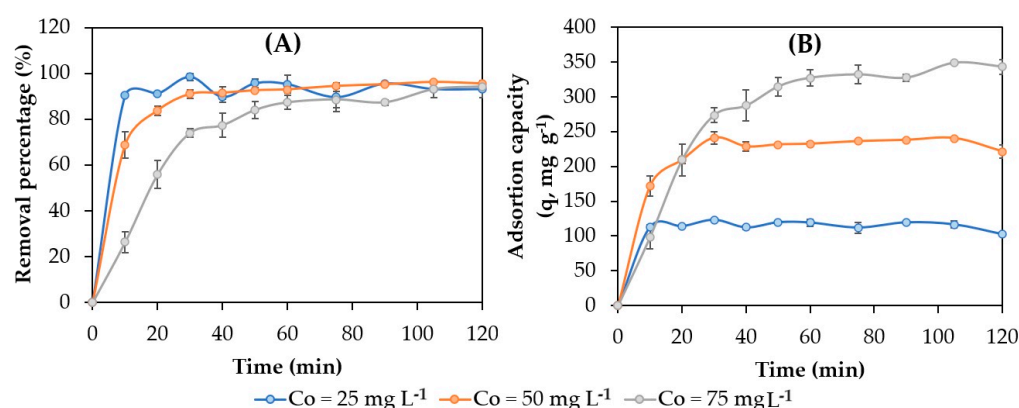


Figure 9. Removal of brilliant green dye at various initial concentrations. (A) Removal percentage; (B) adsorption capacity. Conditions: bioadsorbent dosage = 0.2 g L^{-1} ; natural solution pH 7.8; $t = 120 \text{ min}$. Results are presented as the means $\pm$ SEM.

To assess the efficiency of the study material, a comparative analysis was conducted with other materials implemented in prior studies. For instance, Haladu et al. [37] utilized a pH-sensitive cycloterpolymer resin, achieving a 90% removal of brilliant green dye within 65 min at a concentration of 50 mg/L . Our findings with coquina rock surpassed these results, achieving a comparable removal in a shorter timeframe (40 min) at the same concentration (see Figure 9).

In another study focused on the same dye (brilliant green), alkali-laccase immobilized with biocarbon was employed as an adsorbent [57]. The results indicated an adsorption capacity of up to 700 mg g^{-1} within 330 min, highlighting a more prolonged adsorption process compared with our study (Figure 9B). In our investigation, adsorption capacities of up to 375 mg g^{-1} were reached within a significantly shorter period of 120 min.

3.2.3. Bioadsorbent Dose Variation

The optimal bioadsorbent dose was determined through adsorption tests, varying only this parameter while maintaining constant pH, initial dye concentration (brilliant green), temperature, and agitation. In Figure 10A, a high removal percentage of approximately 96% was obtained after 20 min for all three doses, suggesting that within the evaluated adsorbent concentration range, there is no significant variation in the removal percentage. However, a closer examination of the adsorption capacity in Figure 10B reveals that at concentrations of 0.2 mg L^{-1} , both the removal and adsorption capacity are favorable. Based on these results, we identify 0.2 mg L^{-1} as the optimal adsorbent dose.

Figure 10B illustrates a decrease in adsorption capacity with the increase in bioadsorbent dose, contrary to the expected behavior where an increase in the dose typically leads to more active sites on the material's surface [8,18,22]. However, this observed behavior may

be attributed to the following factors: (1) rapid saturation of the bioadsorbent, resulting in a decrease in adsorption capacity; (2) at higher bioadsorbent doses, there may be enhanced interaction between adsorbent particles, leading to excessive agglomeration and blocking of adsorption sites, thereby limiting the diffusion of the adsorbate from the solution to the adsorption sites and negatively affecting adsorption capacity; and (3) with an increase in the adsorbent quantity, the dye concentration in the solution may become relatively low compared with the present bioadsorbent, diminishing the adsorption capacity [58].

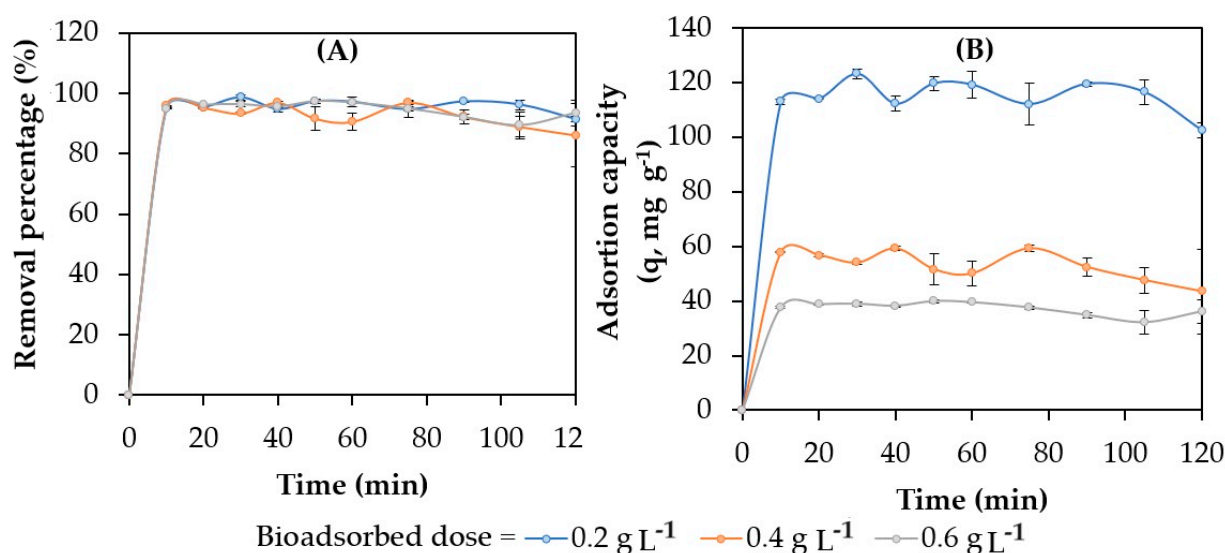


Figure 10. Dye removal according to the adsorbent dose variation. (A) Removal percentage; (B) adsorption capacity. Conditions: $C_0 = 25 \text{ mg L}^{-1}$; natural solution pH 7.8; $t = 120 \text{ min}$. Results are presented as the means $\pm$ SEM.

Finally, it is important to mention that although the possibility of reusing the coquina rock-derived material was not assessed in this study, a similar investigation conducted with calcined oyster shells and an anionic dye demonstrated the feasibility of material reuse after several washes and thermal treatments for regeneration. However, the study notes that the removal efficiency decreases after three recycling cycles with the material. Nonetheless, within these three cycles, a removal efficiency of up to 90% of the dye was achieved within 60 min [59]. This suggests that the material obtained in the present study may also have potential for reuse, given that coquina exhibits similar characteristics to oyster shell material in terms of composition, textural properties, and adsorption capacity.

3.3. Adsorption Kinetics

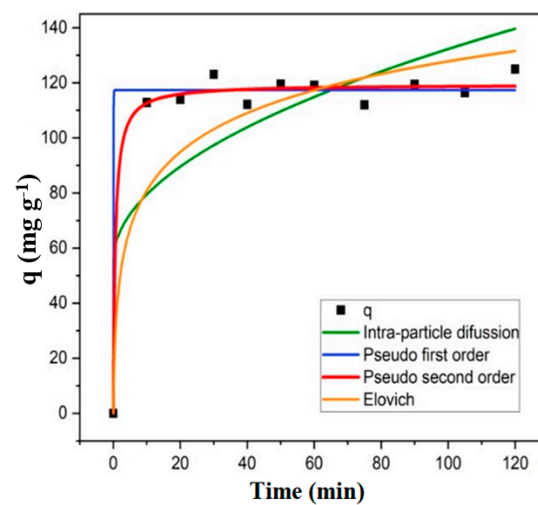
This kinetic study facilitates the observation of the rate at which the dye is adsorbed. Four well-referenced kinetic models, acknowledged in prior research, were considered: the pseudo-first-order, pseudo-second-order, Intraparticle, and Elovich models [36,37].

Table 2 presents the kinetic constant obtained using Origin 2022 software for different adsorbate concentrations when evaluating the various models. The analysis highlights that the pseudo-second-order model exhibits the best alignment with the experimental data for the assessed bioadsorbent material, displaying a regression coefficient that remarkably close to 1.

Figures 11–13 show the sequence of models utilized for non-linear adjustment at concentration levels of 25 mg L^{-1} with $R^2 = 0.9874$, 50 mg L^{-1} with $R^2 = 0.9904$, and 75 mg L^{-1} with $R^2 = 0.9972$, all under the pseudo-second-order model. Therefore, the pseudo-second-order model exhibited the most accurate fit and was selected for further analysis.

Table 2. Fitting parameters for the evaluated kinetic models.

Model	Initial Concentration (mg L ⁻¹)		
	25	50	75
Pseudo-First-Order			
q_1 (mg g ⁻¹)	117.37 ± 1.46	227.80 ± 7.07	390.87 ± 2.08
k_1 (min ⁻¹)	5.39	43.11	0.03
R^2	0.99	0.91	0.93
R^2_{adj}	0.98	0.90	0.93
χ^2	21.28	499.64	518.16
MSE (mg g ⁻¹)	4.6139	22.3525	22.76
Pseudo-Second-Order			
q_2 (mg g ⁻¹)	119.37 ± 2.02	253.37 ± 4.32	515.55 ± 0.99
k_2 (min ⁻¹)	0.01	9.31	4.83
R^2	0.99	0.99	0.99
R^2_{adj}	0.99	0.99	0.99
χ^2	17.70	55.03	27.12
MSE (mg g ⁻¹)	4.21	7.42	5.21
Intraparticle Model			
q (mg g ⁻¹)	7.72 ± 2.55	17.99 ± 4.17	34.25 ± 4.02
k (min ⁻¹)	7.73	17.99	34.25
C	55.01	86.65	31.71
R^2	0.50	0.67	0.89
R^2_{adj}	0.44	0.64	0.87
χ^2	699.64	1870.53	1737.37
MSE (mg g ⁻¹)	26.45	43.25	41.68
Elovich Model			
a	102.62 ± 5.19	4934.43 ± 7433.91	16.91 ± 0.09
b	0.05	0.04	0.01
R^2	0.91	0.98	0.99
R^2_{adj}	0.91	0.98	0.99
χ^2	37.18	115.80	24.48
MSE (mg g ⁻¹)	6.09	10.76	4.95

**Figure 11.** Non-linear fit at a C_0 25 mg L⁻¹ concentration. Conditions: bioadsorbent dosage = 0.2 g L⁻¹; natural solution pH 7.8; t = 120 min.

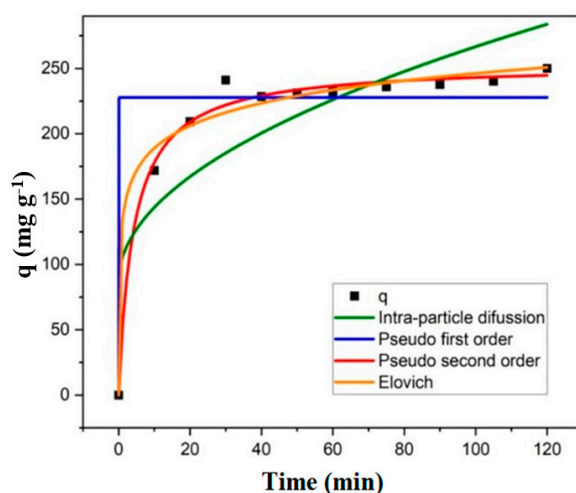


Figure 12. Non-linear fit at a C_0 50 mg L⁻¹ concentration. Conditions: bioadsorbent dosage = 0.2 g L⁻¹; natural solution pH 7.8; $t = 120$ min.

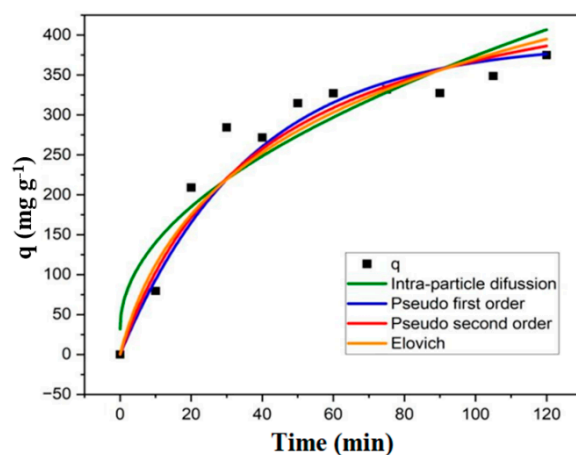


Figure 13. Non-linear fit at a C_0 75 mg L⁻¹ concentration. Conditions: bioadsorbent dosage = 0.2 g L⁻¹; natural solution pH 7.8; $t = 120$ min.

In the scientific literature, both the pseudo-first-order and pseudo-second-order models are commonly utilized. The former explains a particle diffusion process, while the latter suggests a process governed by the adsorption reaction in the liquid/solid phase within the adsorbent. It is noteworthy that, in this investigation and in others that are cited [36], the pseudo-second-order reaction kinetics consistently provide the most optimal fit with the experimental data.

This model implies that the adsorption rate is proportionally related to the available active sites on the adsorbent, suggesting that the adsorption process is controlled by the formation of chemical bonds between the adsorbate and the active sites on the adsorbent surface. It has been demonstrated to offer a superior fit to experimental data compared with other kinetic models, especially in scenarios characterized by rapid initial adsorption followed by an equilibrium phase [60,61], as observed in the present study.

However, the choice of kinetic model may depend on the specific nature of the adsorbate and adsorbent as well as the experimental conditions. Importantly, the system's adherence to the pseudo-second-order model does not inherently imply advantages over other systems or models. Model selection is based on alignment with the experimental data and the physical interpretation of the adsorption process in the specific system presented [60,61].

In another study focusing on the adsorption of brilliant green using hybrid-based magnetite stones, the Pseudo-second-order model was identified as the most suitable kinetic model, providing a comprehensive analysis of the adsorption process [19].

4. Conclusions

In this research, pulverized coquina rock proved to be a highly effective bioadsorbent for removing brilliant green dye from textile wastewater. The results from the characterization and kinetic modeling demonstrated excellent adsorption performance under standard conditions (material drying at 120 °C, pH 7, stirring at 220 rpm, and room temperature), with no need for thermal modification. Notably, particles larger than 300 µm exhibited superior dye adsorption capacity, and characterization techniques confirmed the material's affinity with the dye despite experiencing thermal modification at temperatures exceeding 600 °C.

Efficiency assessments under specific conditions revealed removal rates exceeding 80%, particularly at pH 8, which proved to be optimal for minimizing the impact of pH changes during the removal process. Coquina rock demonstrated rapid interactions, achieving a remarkable 96% removal within the first 30 min and surpassing the efficiency of other bioadsorbents. Applying the pseudo-second-order kinetic model to coarse particle sizes at various dye concentrations further validated the effectiveness of coquina rock. This study highlights coquina rock as a practical and environmentally friendly alternative for brilliant green dye removal, emphasizing its accessibility in coastal areas without generating adverse environmental effects or chemical byproducts.

Considering the aforementioned factors, coquina emerges as a promising alternative as a bioadsorbent material for the removal of dyes from effluents in the textile industry. Its environmental advantages and contribution to economic and operational sustainability underscore its advantageous role. The utilization of coquina as a local resource not only promotes environmental well-being but also has the potential to stimulate economic growth within local communities by advocating for the use of regionally available materials. However, further studies are needed to evaluate the conditions for its regeneration potential and its application on a larger scale.

Author Contributions: All authors made substantial contributions to this study. A.L.M.-R.: conceptualization, methodology, data curation, writing—original draft, and project administration; C.C.-H. and J.C.R.-N.: preparation of the bioadsorbent material, data collection, and analysis; C.G.R.: supervision and support in analyses and manuscript reviewing; H.G.H.-P. and G.L.D.: manuscript reviewing; L.G.-P.: experiments and calculations for determining the zero-charge potential as well as the determination of kinetic parameters. All authors have read and agreed to the published version of the manuscript.

Funding: The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors are grateful to the Vice-Rector of Science, Technology, and Innovation of Universidad de la Costa (CUC) for providing the necessary equipment and materials for the completion of this work.

Conflicts of Interest: The authors declare that they have no conflict of interest or personal relationships that could have influenced the work reported in this paper.

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