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Potential Use of Agricultural Waste—Carob Kibbles (*Ceratonia siliqua* L.) as a Biosorbent for Removing Boron from Wastewater

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Abstract: The release of boron (B) into the environment as a result of anthropogenic activity modifies sustainable natural conditions, thus affecting ecosystems. To meet water quality regulations, commercial and natural boron adsorbents are available to reduce its concentrations in industrial effluents, with the former being not only more expensive but also less sustainable. In the publication, the biosorption parameters of carob kibbles (*Ceratonia siliqua* L.) were optimized in order to remove boron from aqueous solutions using batch experiments. The biosorbent used in the present research was agro-waste biomass provided by the local locust-beam gum industry. Boron removal by carob kibbles was favored at high initial pH values, and this capacity was found to be a function of boron initial concentration, biosorbent content in the solution, and particle size. The change in temperature did not affect the potential of biomass to remove boron. The highest boron removal efficiency (55.1%) was achieved under the following optimal conditions: 50 g/L biosorbent dose (Cs), with particle size range 0.025–0.106 mm, for the initial concentration (C_0) of boron in the solution of 100 mg/L, at an initial pH of 11.5, for 5 h at 25 °C. This investigation suggests that carob kibble agro-waste can be valorized as a biosorbent to remove boron from wastewater, and the boron-loaded residue may eventually be explored as a new boron-fertilizer.

Keywords: carob kibbles; biosorption; boron; aqueous solutions; wastewater treatment

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1. Introduction

The element boron can be found in all the systems that sustain life: soil, atmosphere, and water. However, it is present with a relatively small (10 mg/kg) crustal abundance, limited availability, and may face a future supply risk [1–5]. Since boron reacts with oxygen and other elements to generate boric acid or inorganic salts like B_2O_3 (boric oxide), known as borates, it is not found in its elemental form in nature. The latter is of commercial interest. Turkey, the USA, Chile, Argentina, Russia, Tibet, and Italy are the countries with the most significant mines. Borate deposits are linked to volcanic activity and arid conditions [2,6]. The common ionic species of boron that exist in aqueous medium are boric acid and borate ions, but the relative concentration of these species depends on the pH of the media. $B(OH)_3$ exists in solution at low pH, whereas a higher percent of $B(OH)_4^-$ species is present at high pH [1,7]. Except for areas whose soils naturally contain borates and borosilicates, where boron concentrations in groundwater can be as high as 100 mg/L, natural boron levels in surface and seawater are generally a few milligrams per liter (in freshwater, boron concentrations range between 0.01 mg/L and 1.5 mg/L, while in seawater, boron concentrations range between 1.0 and 10 mg/L) [6,8].

The global biogeochemical boron cycle has resulted in the evolution and adaptation of living species to natural boron concentrations that support key biochemical reactions within these organisms. Boron traces are part of the vital functions of various life forms. For example, it is one of the essential elements for plants due to its key roles in plant growth and yield [9–14]. In the case of humans and other animals, boron is an essential element in the life cycle of zebrafish or frogs, and for higher animals, boron is required for the normal metabolism of specific biomolecules that include major minerals, glucose, lipids, hormones, and other nitrogen-containing compounds, as well as reactive oxygen species at physiological levels [15,16]. According to the World Health Organization (WHO), a daily consumption of 1.0 to 13 mg of boron for humans (adults) could be safe [16].

Amounts of boron (or boric acid) in the environment that exceed what living organisms (including humans) are adapted to tolerate are detrimental both on a short- and long-term basis, according to several ecotoxicological studies [17–19]. The literature suggests that the line between the required amount of boron and what is harmful is relatively narrow, and organism tolerances vary as well. In terms of crop plant sensitivity to boron in irrigation water, carrot (*Daucus carota* L.) is classified as tolerant (4.0 mg/L), while orange (*Citrus sinensis* L.) is regarded as sensitive (1.0 mg/L) [17–19].

Because of the discharge of wastewater of industrial or residential origin into natural watercourses, which may contain significant concentrations of boron residual products, the boron global cycle has been altered. This imbalanced mobilization of boron from anthropogenic sources increases its concentration in waterways [6]. Ceramic wastewater without treatment can contain boron concentrations as high as 36 mg/L. Indeed, boron concentrations in effluents from this source are typically about 14 to 15 mg/L, according to the literature [20,21]. Therefore, before being released, boron-containing wastewater produced from human activities needs to receive suitable treatment in order to maintain a safe environment for organisms. In this context, water quality standards are key components of regulatory bodies from local and regional governments to provide safe water for human consumption and irrigation activities, as well as to protect life in ecosystems. These guidelines establish the maximum acceptable concentration for boron in drinking and surface water [18,22–24]. For instance, even though the US EPA has not set a boron limit for drinking water, boron drinking water standards or guidelines vary from 0.6 to 1 mg/L in several states [25].

To meet these standards, the actors involved in wastewater treatment and potable water provision are developing effective technologies to remove boron from drinking water and wastewater. As an example, some of these methods use the chemical behavior of boron as a function of pH to reject or gather it. Boron removal is based on various techniques recognized as adsorption, membrane technologies, coagulation, and hybrid methods. On the surface of an adsorbent, boron is immobilized through the adsorption process. Activated carbon, chelating resins, and fly ash are some of the materials used as boron sorbents [26]. Boron adsorption capacity, adsorption selectivity, removal percentage, and retention time determine the utility of the sorbents [26–29]. For example, the low adsorption selectivity of activated carbon demands chemical modification in order to get beyond this limitation [27,28].

In membrane technology, feed water with a high boron concentration is passed across a membrane that preferentially retains boron to remove it. The retentate stream exits the membrane with a reduced boron concentration. This method groups reverse osmosis, electrodialysis, and ion exchange resins [29]. The most desirable lifetime and good selectivity and permeability properties require systems to be adjusted, for example, by modifying the physical structure or the functional groups of the membrane surface, which increases the cost of the membrane and the regeneration process [30–32].

Chemicals that render the present borates less soluble are added to the solution in coagulation by chemical precipitation or electrocoagulation, which results in the formation of a low-soluble borate [33]. Chemical precipitation may necessitate using large amounts of chemicals or energy. Electrocoagulation is not suited for the treatment of wastewater with a high boron concentration, and it requires the use of certain metals as the anode material and an appropriate electrolyte [33]. Newly developed hybrid methods combine two technologies in one process, but the process of synthesizing polymers necessitates the use of chemicals that, for example, according to the globally harmonized system, represent a health risk [34,35].

Some of the mentioned processes are described as effective (up to 99% of boron removal). However, in most applications, these technologies tend to be costly to manage, consume large amounts of energy, lose significant amounts of water, and/or generate large amounts of waste, making them unsustainable for the sector. On the other hand, a small number of review articles focused on biosorbents employed in boron removal methods that would ultimately not require excessive use of chemicals to be produced since the sorbent is already accessible or would open the potential of food waste valorization.

Given the opportunity to find good and low-cost boron removal solutions, the use of waste biomass as a biosorbent material in biosorption processes is promising. This nonconventional opportunity is presented as an alternative and environmentally safe approach to removing metal/metalloid ions from aqueous matrices [36], since it has the potential to be both effective and inexpensive, and additionally, the boron-loaded waste materials can be reused as new boron fertilizers. The utilization of biomass (e.g., olive bagasse [37], cotton [38], rice husk [39], algae [40]), and waste materials of organic origin (e.g., wheat, rice, green shell of walnut, cellulose) [41,42] for boron biosorption from solutions is documented by researchers under various experimental settings. The findings are generally positive, with one species of marine seaweed, *Caulerpa racemosa* [40], able to adsorb up to 63% of boron from solutions. However, there are only a few studies on boron removal by biosorbents. These studies are significant because they highlight the usefulness of biosorbents by demonstrating their strong boron adsorption capacities and high boron removal percentages. Given the wide range of biomass available in nature as a residue, as well as the fact that boron has a unique chemical behavior, studies on boron biosorption are extremely important to discover new low-cost boron removal processes.

The scientific name of the carob tree, *Ceratonia siliqua* L., is derived from the Greek word *keras*, which means horn, and the Latin word *siliqua*, which describes the hardness and shape of the pod [43]. It is mostly grown and produced in Spain, Italy, Portugal, Northern Africa, the larger Mediterranean islands, Iran, the Canary Islands, and Macao, where it is employed in the food and pharmaceutical industries because of its chemical composition [44]. Major polyphenols found in carob kibbles have been tentatively identified, including gallic acid, myricetin 3-O-rhamnoside, quercetin p-hydroxy benzoyl 3-O-rhamnoside, and quercetin 3-O-rhamnoside [45]. Every year, 50,000 tons of carob fruit are grown in Portugal's Algarve region, which makes it difficult to dispose of the waste generated by this sector [46]. This waste requires the use of environmentally friendly and effective disposal methods. In the present study, the biomass of carob kibbles (deseeded chopped pods) was used to remove boron from wastewater. The literature presents more information on the biosorption properties of carob kibbles and emphasizes its utilization for metal ion removal. The maximum biosorption capacity for this biosorbent, calculated from the Langmuir equation, for Cd(II), Ni(II), Cu(II), and Zn(II) ions at optimum conditions (pH 5.0–6.0, biosorbent dose 5.0 g/L, and initial concentration of boron in the solution of 100 mg/L) was 14.3 mg/g, 42.2 mg/g, 21.7 mg/g, and 31.4 mg/g, respectively [47]. Furthermore, it was reported that phosphoric acid-activated locust bean (carob kibbles) may remove considerable quantities of Cr(VI) and Cd(II) ions. For a sorbent dose of 0.8 g (reaching the best boron adsorption performance with 100 mg/L as an initial concentration), the adsorbent was able to bind a maximum of 4.13 mg/g (82.5%) when removing Cr(VI) ions and 3.17 mg/g (63.3%) when removing Cd(II) ions [48].

The present experimental investigation examines, by using batch sorption experiments, the effect of contact time (5.0 min–30 h), initial pH of solution (3.0–11.5), initial concentration of boron (20–200 mg/L), biosorbent dose (10–100 g/L), solution temperature (25–55 °C), and biomass particle size (0.025–2.00 mm) on boron removal from aqueous media employing carob kibbles as a biosorbent [49]. To our knowledge, this is the first time that the biosorption properties of this sorbent have been comprehensively characterized. As a result, this study provides a new and effective boron biosorption strategy from aqueous solutions as well as a way for valorizing carob kibbles using the residues from the local agro-food industry, which, when boron-loaded, may eventually be reutilized as a new boron fertilizer to provide the needed boron for plants.

2. Materials and Methods

2.1. Chemicals

Chemicals supplied by Merck Germany were used in this study. To obtain calibration curves and quality control samples, the Certified Reference Material (CRM) in the form of boric acid was diluted in water to prepare a stock solution of boron (100 mg/L). The sorbate solution for the batch studies was prepared by dissolving boric acid in distilled water to prepare a solution with a boron concentration of 1000 mg/L.

2.2. Biosorbent Preparation

Carob kibbles (*Ceratonia siliqua* L.) residues provided by the Industrial Farense Lda, a local agro-food company from Faro (Portugal), were dried for 2–3 h at 50 °C, deseeded, then powdered in a blender and sieved before being utilized as a biosorbent without prior treatment. A general scheme of the experiments is presented in Figure 1.

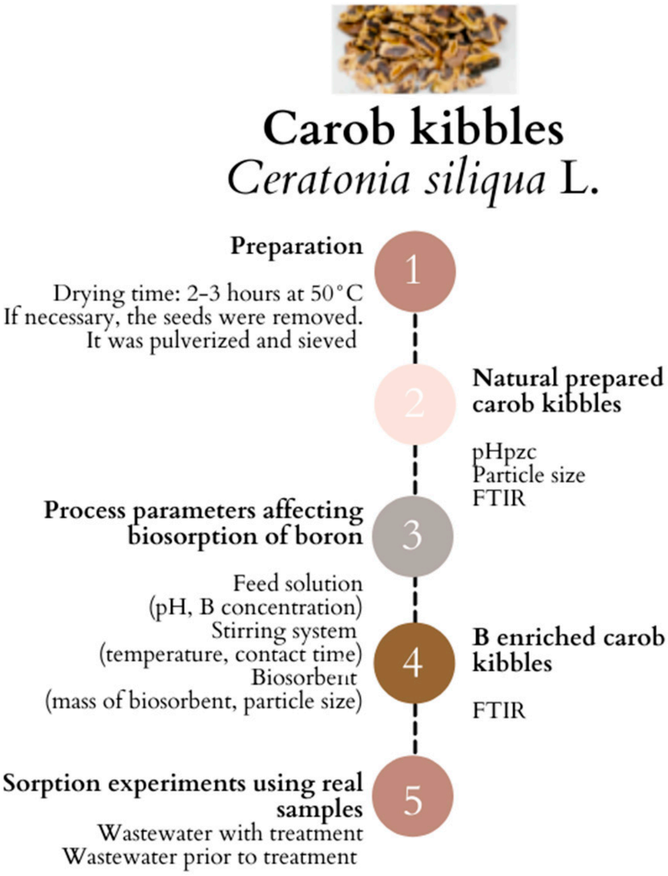

Figure 1. General scheme of the experimental investigation.

2.3. Biomass Characterization

2.3.1. Isoelectric Point (pHpzc)

The isoelectric point (pHpzc) provides numerical and graphical data on the pH value at which the surface of a particular material is neutral (carries no net electrical charge). It is related to the biosorption process since the biosorbent's surface would be positive and eventually attract anions at pH levels lower than pHpzc. The material surface would be negatively charged at pH levels over pHpzc, and this would cause positively charged ions to bind. The method described by Mahmood et al. [50] was employed to determine the isoelectric point of carob kibbles. Accordingly, 50 mL of KNO_3 solution (0.1 mol/L) held in a 100 mL Erlenmeyer flask were mixed with hydrochloric acid or sodium hydroxide (0.1 mol/L) to obtain an initial solution pH (pHi) ranging between 1.8 and 12.0. After adding the powdered biomass (0.1 g) without sieving, the biomass-liquid preparation was mixed with constant shaking (48 h) at a stirring speed of 120 rpm and at room temperature. The pH of the solution was also measured at the end (pHf). pHi was plotted against the difference between the final and initial pH readings (ΔpH = pHf − pHi). In the pHpzc, the ΔpH is numerically equal to zero.

2.3.2. Particle Size Distribution

The particle size distribution was obtained by employing granulometric analysis. Raw carob kibbles (150 g) were oven dried, powdered, and sieved with a Sieve Shaker (Retsch, AS 200, Haan, Germany) in vibratory mode (10 min). Seven sieves of increasing diameters (0.025, 0.106, 0.200, 0.250, 0.500, 1.0, and 2.0 mm) were used to characterize the biosorbent. Triplicates of the identical essay were performed, with the average value being used as the result.

2.4. Batch Biosorption Experiments

Batch sorption experiments were used to test the removal of boron by the biomass of carob kibbles from aqueous media. In an Erlenmeyer flask (250 mL), a prepared mass of powdered carob kibbles was mixed with a boric acid solution (100 mL) with a known initial boron concentration and pH. In a shaking water bath (Julabo, SW 22, Seelbach, Germany), the aqueous mixture was constantly agitated at a controlled temperature, reaction time, and speed of 150 rpm. Following the experimental investigation of the biosorption parameter, samples were collected to determine the remaining boron concentration in the solution. Except when otherwise mentioned, all of the tests were performed twice. In the experiments on the biosorption kinetics and in the experiments on the effect of the initial concentration of boron in the solution (C_0), pH, biosorbent dose (Cs), and temperature on the boron removal, a biosorbent with a size in the range of 0.025–1.0 mm was used.

In the initial tests, the effect of contact time (0.083–30 h) and solution pH (3.0, 5.5, 7.5, 9.5, and 11.5) on boron biosorption by carob kibbles was evaluated. This was done using an initial boron concentration (C_0) adjusted to 100 mg/L, a biosorbent dose (Cs) of 50 g/L, and 25 °C. HNO_3 and NaOH solutions (0.1 mol/L) were used to adjust the initial pH, monitored with a GLP 21 pH Meter (Crison, Barcelona, Spain). This experiment also served to investigate biosorption kinetics—the determination of the time necessary to reach equilibrium. The optimum contact time was 5 h, while the optimal pH was 11.5, and this was employed throughout the investigation.

To test the effect of initial boron concentration (C_0) on its removal by carob kibbles, C_0 was prepared in the range of 20–200 mg/L and agitated with a biomass dose of 50 g/L at 25 °C.

To verify the influence of the biosorbent dose (Cs) on boron biosorption, the following solutions of biosorbents were prepared: 10, 50, and 100 g/L. Such sorbent concentrations were selected based on literature data, which mention that this content presented good performance for boron removal with organic-origin sorbents. The resulting sample was then agitated at 25 °C with an initial boron concentration of 100 mg/L.

The influence of temperature on boron biosorption by carob kibbles was investigated by agitating a 50 g/L biosorbent dose (Cs) with 100 mg/L of boron (C_0). One bath test was conducted at 25 °C, followed by a batch test at 45 °C, and a third test was conducted at 55 °C as the initial temperature.

The effect of the particle size of carob kibbles on boron removal was investigated by combining 50 g/L of biosorbent dose (Cs) with 100 mg/L of boron (C_0) at 25 °C. The particle sizes of the powdered carob kibbles used for this experiment were >1.0–2.0, >0.5–1.0, >0.2–0.5, >0.106–0.2, and >0.025–0.106 mm.

2.5. Fourier Transform Infrared (FTIR) Spectroscopy

To detect and measure the frequencies at which the functional groups and bonds that may be present in biosorbent vibrate, FTIR was performed with a Tensor 27 FTIR spectrophotometer (Bruker, Ettlingen, Germany). For this purpose, the powdered biomass (natural before biosorption and loaded with boron after biosorption) was prepared in the form of tablets by mixing it with powdered potassium bromide [40]. Then, the mixture was pressed with the help of a hydraulic press to produce a transparent disk. In the instrument, the operative parameters wavenumber (400 to 4000 cm^{-1}) and resolution (4 cm^{-1}) were established. A total of 98 scans were performed on each sample (on average).

2.6. Sorption Experiments Using Real Wastewater Samples

Once the optimal removal conditions for boron were established, the batch approach was carried out to estimate the removal of boron from real wastewater samples from the ceramics industry. For this, carob kibbles were contacted with effluents with two different characteristics: wastewater that did not receive treatment and wastewater with treatment. Wastewater from ceramics production processes has dissolved and suspended heavy metals (including lead and zinc), sulfates, boron, and traces of organic matter. Suspended solids (such as clays and insoluble silicates) are also present [51].

The treatment unit consisted of cooling towers and a plain sedimentation tank, and the annual concentration of boron in its effluent varied between 1 and 44 mg/L. The Laboratory of Environmental Technologies of the Center of Marine Sciences at the University of Algarve provided a characterization of both effluents. Results with the differences between both streams are presented in Section 3.5. As part of quality assurance, to confirm the signal of the analyte (boron) and avoid matrix effect, both real solutions (250 mL) were independently transferred into a 500 mL volumetric flask and filled up to the mark (spiked) with boric acid (100 mg/L). During these experiments, a blank spiked with a known amount of CRM was analyzed. Triplicates of the identical essay were performed, with the average value being used as the final result. A single measurement's standard deviation was less than 5%.

2.7. Instrumental Analysis

Before instrumental analysis, samples after biosorption were centrifuged (5 min, 4000 rpm) in a bench centrifuge Rotofix 32A (Hettich, Kirchlengern, Germany). As a result, a clear solution was obtained that was acidified ($pH < 2.0$) with concentrated HNO_3 (65% *w*/*w*). An MP-AES instrument (Model: Agilent 4200, Agilent Technologies, Santa Clara, CA, USA) was used in all boron determinations. Boron concentration was determined using the method described by Hettipathirana [52]. The instrument operating conditions included the following: (1) wavelength 249.77 nm; (2) read time 3 s; (3) nebulizer flow 0.75 L/min; and (4) calibration fit linear through blank. The instrument used nitrogen extracted from the air. The arithmetic average of two measurements is provided (otherwise it is specified). Only results with a standard deviation of individual results less than 5% can be used. An analysis of aliquots of certified reference material with a certified value was also performed.

2.8. Calculations

The pseudo-second-order model is frequently used to describe the kinetics of boron biosorption because it is based on the assumption that chemical sorption, or chemisorption, is the rate-limiting step and because a number of investigated adsorbents have multiple hydroxyl or alcoholic hydroxyl groups that may react with borate to form chelate complexes [53,54]. The pseudo-second-order model (Equation (1)) was employed to characterize overall boron biosorption kinetics [40,55,56].

$$t/q_t = t/q_e + 1/k_2q_e^2 \tag{1}$$

The most common approach to evaluating how much boron in solution is removed by the biosorbent is to find the percentage (%) removal (Equation (2)) [40,55,56]. This percentage of boron removal (%R) can be calculated by first using the starting, or C_0, or initial concentration of boron in the solution (mg/L) before the biosorption experiment and then using the concentration of boron that continues in the solution (C_t, mg/L) after a specified biosorption time t:

$$\%R = (C_0 - C_t) \times 100/C_0 \tag{2}$$

In practice, the most common way to estimate the biosorption capacity at a given time of biosorption (q_t, mg/g) of the biosorbent is to calculate its value from Equation (3) [57].

$$q_t = (C_0 - C_t) \times V/m \tag{3}$$

Both C_0 and C_t are concentrations of metal ions before biosorption and at a given time t, respectively (mg/L), V corresponds to the volume (L) of a sorbate-bearing solution, and m is a mass of dry raw biomaterial (biosorbent) (g).

2.9. Statistical Analysis

Comparisons between the boron removal (%) results of real wastewater samples were performed with a two-sample *t*-test with equal variances (95% confidence level).

3. Results

3.1. Isoelectric Point (pHpzc)

The determination of the isoelectric point helped to better understand boron biosorption onto carob kibbles. The pHpzc of raw carob kibbles is 5.15 (Figure 2). The pHpzc observed in this investigation is consistent with the 5.4 pHpzc reported in the literature for raw carob shells [58]. Below pHpzc, the biomass surface is positively charged, and above pHpzc, it is negatively charged.

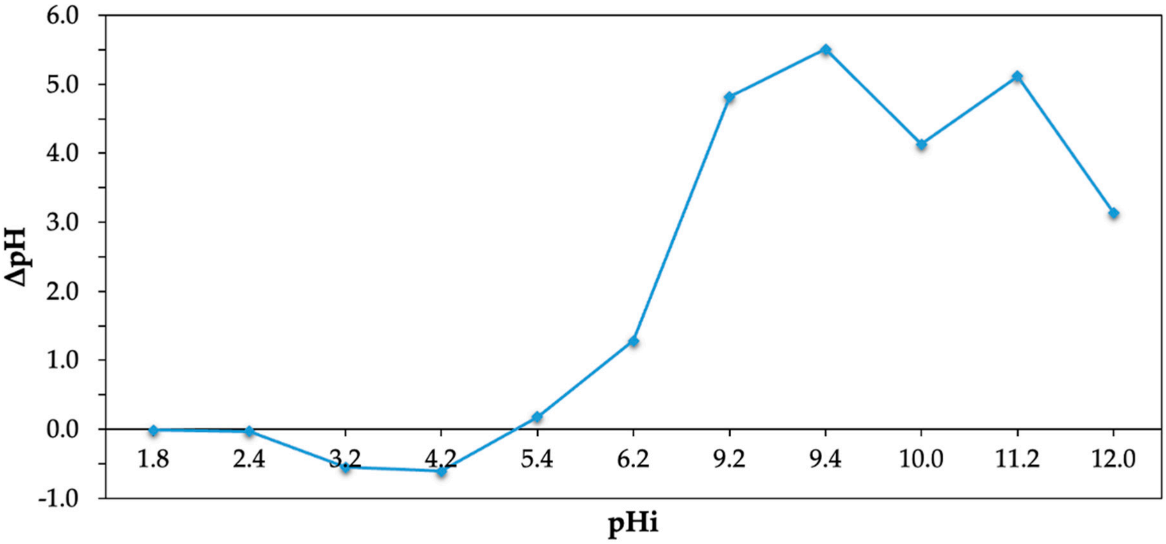

Figure 2. Point of zero charge of carob kibbles before biosorption.

3.2. Particle Size Distribution of Biomass

Most of the mass of biosorbent (powdered carob kibbles) (32.6%) had a particle size ranging from 0.025 to 0.106 mm, preceded by particles ranging in size from 0.25 to 0.5 mm (22.8%) (Figure 3). Since particles in the range of 0.025–1 mm constituted the largest fraction after sieving, they were used in experiments on biosorption kinetics and equilibrium. Results on the effect of a given size range of carob kibbles (>1.0–2.0, >0.5–1.0, >0.2–0.5, >0.106–0.20, >0.025–0.106 mm) on boron biosorption are discussed in the following Section 3.3.6. These studies provide a better understanding of the ideal biomass size to be used for biosorption in future studies.

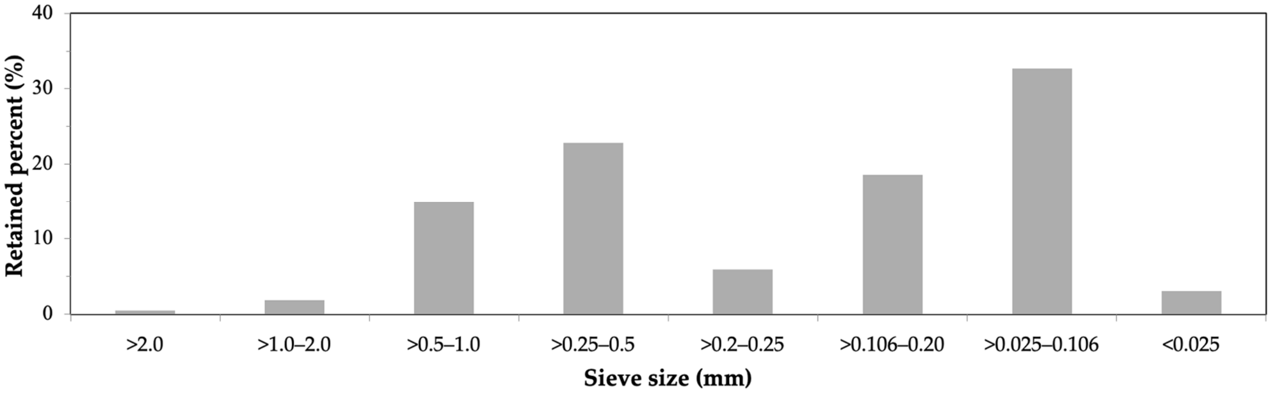

Figure 3. Particle size distribution of carob kibbles expressed as a mass fraction (%).

3.3. Batch Biosorption Experiments

3.3.1. Kinetic Experiments

In Equation (1), the gradient and intercept of the plot were analyzed to calculate the biosorption capacity at equilibrium (q_e, mg/g) and the constant rate, k_2, expressed in g/mg·min (Table 1). Because the coefficients of determination for the linear plots were close to or greater than 0.990, the experimental findings, as shown in Figure 4, supported the suggested model.

Table 1. Pseudo-second-order model parameters on boron biosorption onto carob kibbles with Cs 50 g/L, particle size range 0.025–1.0 mm at varied pH: 3.0, 5.5, 7.5, 9.5, 11.5 (mean and standard deviation, n = 2), at 25 °C, and initial boron concentration, C_0 100 mg/L.

pH	q_e (mg/g)	k_2 (g/mg·min)	R^2
3.0	0.402 ± 0.005	0.0601 ± 0.0275	0.995 ± 0.002
5.5	0.545 ± 0.091	0.169 ± 0.183	0.998 ± 0.002
7.5	0.516 ± 0.008	0.0715 ± 0.0084	0.997 ± 0.002
9.5	0.595 ± 0.024	0.119 ± 0.022	0.999 ± 0.000
11.5	0.672 ± 0.030	0.220 ± 0.137	0.996 ± 0.003

Two remarkable features can be derived from Table 1. In one aspect, it may suggest that pH is a key parameter for removing boron [38,40], and from this, the parameters of the model describe that the highest constant rate for biosorption of boron by carob kibble powder (k_2 = 0.220 g/mg·min) is attained when the solution has a pH of 11.5.

The estimation of the optimal conditions of time and pH of solution for attaining equilibrium is shown in Figure 5. The results include a series of contact time points with pH ranging from 3.0 to 11.5.

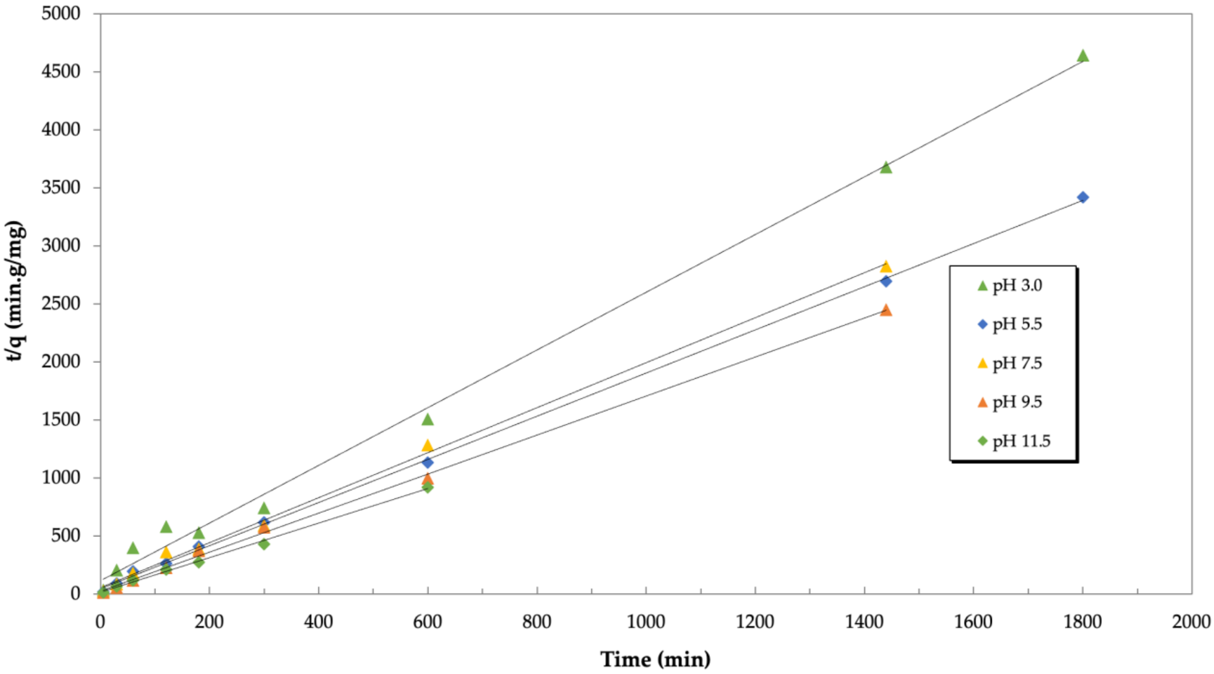

Figure 4. Plots of the pseudo-second-order kinetic model for boron biosorption onto powdered carob kibbles with Cs 50 g/L, particle size range 0.025–1.0 mm for various pHs, at 25 °C, and initial boron concentration, C_0, 100 mg/L.

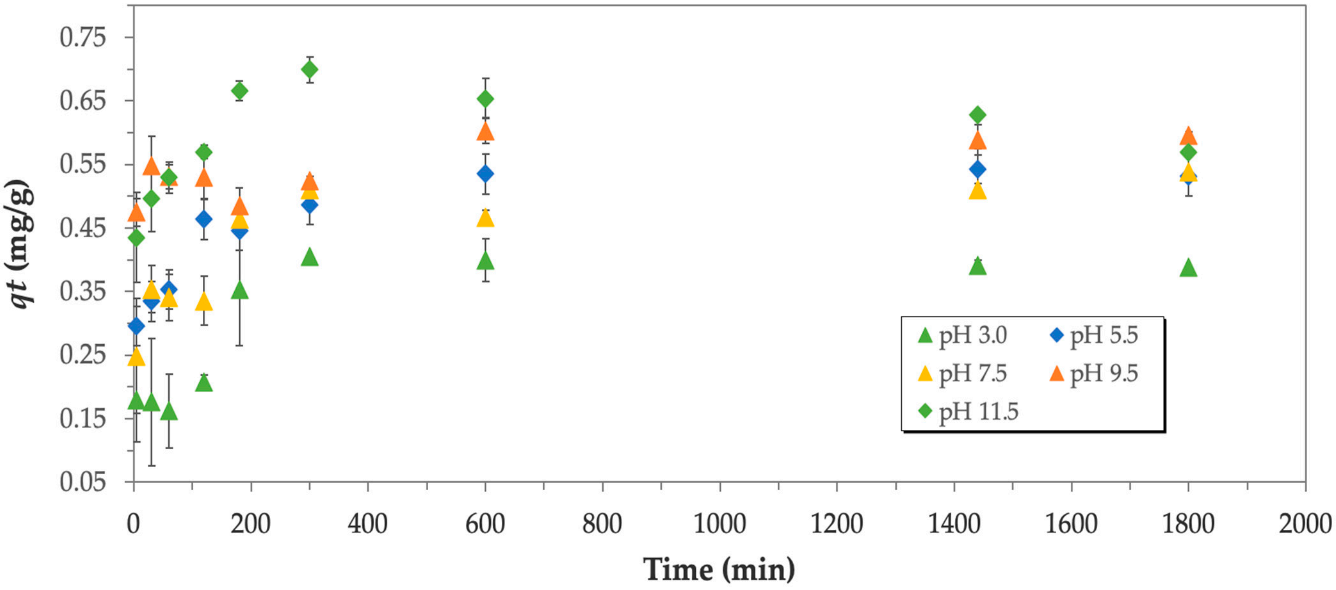

Figure 5. Influence of time on biosorption of boron onto powdered carob kibbles with Cs 50 g/L, particle size range 0.025–1.0 mm, for various pH, at 25 °C, and initial boron concentration, C_0 100 mg/L (n = 2).

From Figure 5, it can be seen that, in general, the sorption of boron only required a minimal reaction time. The highest biosorption capacity (0.700 mg/g) was achieved within 5 h (300 min) when the pH of the prepared solution was 11.5, followed by 600 min at the initial solution pH of 9.5 (q_t equal to 0.604 mg/g). The dynamics of rapid boron binding observed for the 50 g/L biomass dose can be explained by the fact that there is still sufficient space available to bind sorbate (boron) dissolved in solution (100 mg/L). Allowing the adsorption to take place for more than 300 min at pH 11.5, an improvement in the biosorption performance was not observed. This is likely because the hydroxyl ions $B(OH)_4^-$ may compete for the same accessible adsorption sites in the biomass [40].

Some studies suggest that the equilibrium for boron attracting to the surface of biosorbents can take between 2.5 h for marine seaweed, *Caulerpa racemosa* [40], and 48 h for biomass from olive bagasse modified into activated carbon [37]. With this perspective, the optimal contact time obtained for the bioremoval of boron by carob kibbles falls within the time interval found in the literature. In a similar way, this implies that the chemical composition of biomass's surface influences boron biosorption, as evidenced by FTIR analysis of biosorbent before and after biosorption of boron (Section 3.4).

3.3.2. Influence of pH on Boron Biosorption

According to Equation (4), the concentration of hydrogen or hydroxide ions in acidic or alkaline media controls the dominant species of boron in a solution, either as boric acid (molecular form, pH < 9.0) or as borate anions (pH > 9.0). Similarly, the overall pH of a biosorbent-liquid solution can modify the chemical composition of the biosorbent's surface [7,59,60].

$$H_3BO_3 + 2H_2O \rightleftarrows B(OH)_4^- + H_3O^+ \tag{4}$$

By changing the pH of the solution, there is an opportunity to enhance the efficiency of boron ions biosorption onto carob kibbles. This efficiency is highly influenced by the pH of the media. According to batch test results, the biosorption of boron is modest (0.405 mg/g) for pH < 7.0, with boric acid as the dominant species in solution, which may prove that the acidic environment suppresses boron binding independent of the source of biosorbent [37–41]. Results obtained in the present study indicate that carob kibble biosorbent has the highest boron biosorption capacity at an initial pH of 11.5. Therefore, the pH was set to 11.5 and the contact time was set to 300 min in subsequent experiments.

Considering the chemical behavior of boron in an aqueous environment (Equation (4)), the borate ions can be better retained by the carob kibbles than the boric acid. This may be linked to carob kibbles' surface charge in an alkaline environment (pHpzc 5.15). The borate ions bond to the biomass surface because they are negatively charged. Higher pH values and the resulting hydroxyl groups, which may activate negative charges on the sorbent surface, also increased the ratio of H_3BO_3 to $B(OH)_4^-$(aq) in the media, which might have a better tendency to eventually replace OH^- groups in the surface of carob kibbles via a ligand exchange mechanism [41]. Chelation between $B(OH)_4^-$ species and OH^- groups that are present on carob kibbles surface is still attainable [54].

Findings obtained in another study with olive bagasse as a biosorbent [37] showed that the highest boron removal from solution (approximately 30%) was observed at pH 5.5 (Cs 20 g/L, 25 °C, particle diameters in the range of 0.425–0.600 mm, and an initial boron concentration of 100 mg/L). This seems similar to the removal obtained during the present investigation (28%) with a boron-bearing solution at the same initial acidic conditions.

As it was previously shown, boron biosorption is influenced by the solution pH, regardless of the source of biomass. For instance, using cotton as an adsorbent, it was demonstrated that the adsorption capacity of boron was affected by pH, and the highest value was 11.3 mg/g at pH 7.0 (C_0 500 mg/L, Cs 2 g/L, room temperature) [38]. In the case of the rice husk used as a biosorbent, boron adsorption capacity was 43.2 mg/g at an optimal pH of 5.0 (at room temperature, C_0 300 mg/L, Cs 2 g/L) [39]. Another biomaterial, seaweed—*Caulerpa racemosa* var. *cylindracea*—that was used for the biosorption of boron at solution pH ranging between 7.5 and 8.5 (C_0 10 mg/L, Cs 4 g/L, 25 °C), showed 70% as maximum and constant removal [40]. In this investigation, 28% was the best removal percentage at 7.5 as the initial solution pH. In addition, the adjustment of the pH of the solution to around 11 is a common practice in the improvement of some reverse osmosis membranes, ion exchange membranes, and nanofiltration for water desalination, including boron rejection, according to other reports [32,61,62].

3.3.3. Influence of the Initial Concentration of Boron Ions in the Solution on Its Biosorption

In Figure 6, it can be observed that the removal of borate ions is a function of the boron initial concentration. The removal potential gradually decreased from 59% at an initial boron concentration of 20 mg/L to a minimum of 19% up to an initial boron concentration of 200 mg/L with a biosorbent dose of 50 g/L. This could be attributed to the availability of binding sites on the surface of the biomass that were initially unoccupied, which would result in a higher removal of boron. Following that, as the boron content increased, the biosorbent active sites would be less accessible, and the biosorption of boron would be reduced [63]. In the case of active sites, biosorbents have a finite number that will eventually reach a saturation point at a specific concentration [55,64,65].

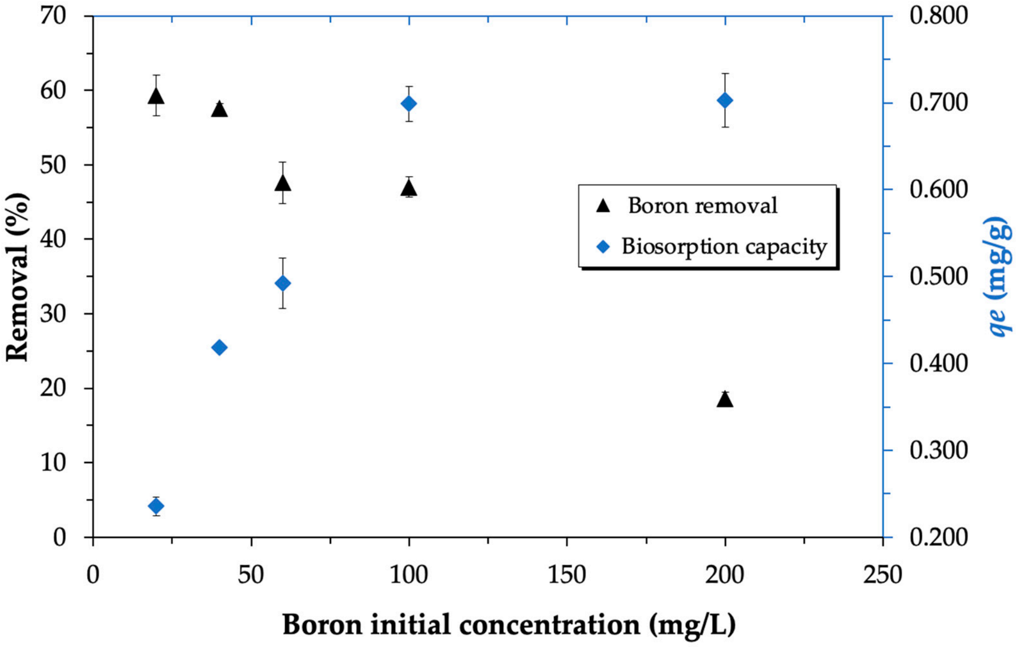

Figure 6. Influence of boron initial concentration on biosorption of boron onto powdered carob kibbles with Cs 50 g/L, particle size range 0.025–1.0 mm, and an initial pH of 11.5 at 25 °C for 300 min. The standard deviation for $n = 2$ is represented by bars.

Studies on other types of biomasses revealed that boron adsorption capacity increased with an increase in the boron concentration. Cotton cellulose biosorbent tested at varied pHs (5.0–9.0) and incremental concentrations of boron (5.0–500 mg/L) showed that with a higher boron concentration, there is a higher boron biosorption capacity equal to 11.3 mg/g (Cs 2 g/L, room temperature, pH 7.0) [38]. For rice husks used as a biosorbent, at the highest initial concentration of boron (300 mg/L, Cs 2 g/L, room temperature, and pH 5.0), the maximum sorption capacity at equilibrium (q_e 119 mg/g) was reached [39]. Using prepared activated carbon from olive bagasse to remove boron, a similar trend was observed: at a high initial boron concentration (100 mg/L, Cs 20 g/L, 25 °C, pH 5.5, particle diameters in the range of 0.425–0.600 mm), greater biosorption of boron (1.5 mg/g) occurred [37]. In theory, raising the starting concentration of adsorbate will result in a high concentration gradient, and hence the resulting driving force of adsorption will increase the adsorption capacity. This applies to most of the biomass used for boron removal.

3.3.4. Influence of Biosorbent Dose on Boron Biosorption

Figure 7 shows that the biosorbent dose and its removal potential are strongly related. The adsorption of boron increased gradually as the adsorbent dose rose from 10 to 100 g in 1.0 L of the solution, which was expected because as the content of biomass in the solution increases, more surface area of the biosorbent will come into contact with the boron to be removed. With a 100 g/L adsorbent dose, the highest boron removal potential (55.3%) was achieved (Figure 7). However, 50 g/L was selected as the best dose since there is not much difference in boron removal. Also, from an economic point of view, it is good to use as small amount of biosorbent as possible to remove boron.

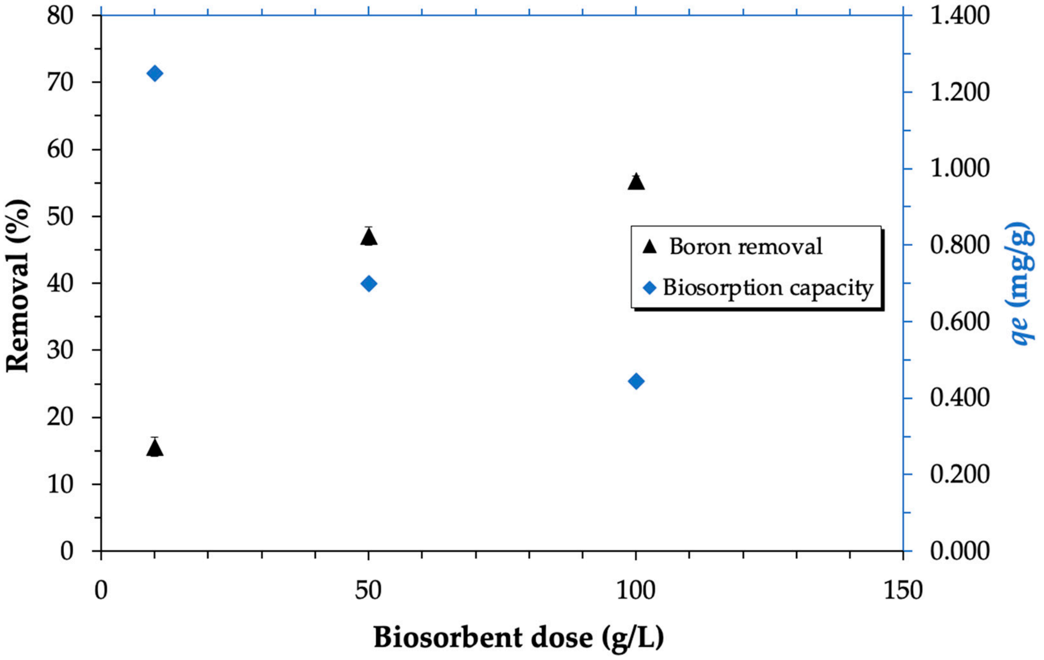

Figure 7. Influence of biosorbent dose on biosorption of boron onto powdered carob kibbles with a particle size range of 0.025–1.0 mm, an initial pH of 11.5 at 25 °C, for 300 min, and an initial boron concentration, C_0, 100 mg/L. The standard deviation for $n = 2$ is represented by bars.

Bursali et al. [40] observed a higher removal of boron by invasive marine seaweed—*Caulerpa racemosa* when its dose increased to 0.2 g of biomaterial in 25 mL of solution (8 g/L). Furthermore, boron removal remained constant at 50% beyond the 0.2 g/25 mL biomass-liquid ratio (0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 g). A similar trend was reported by Öztürk and Köse—the removal of boron also increased from 11% for 5 g/L to 50% for 20 g/L [66]. The adsorption capacity of rice husk biomass decreased as the adsorbent dose increased from 1.0 to 6.0 g in a 500 mL solution containing boron (C_0 100 mg/L, pH 5.0) [39]. The decrease in the boron adsorption capacity with increasing biosorbent dose suggests that the low biosorbent dose promotes boron removal via adsorption on powdered carob kibbles, as demonstrated by this study.

3.3.5. Influence of Temperature on Boron Biosorption

Compared to previously studied parameters, boron removal by carob kibbles is less dependent on the temperature at which the biosorption evolves. Nearly 47% boron removal was achieved at 25 °C, but gradually decreased at 45 °C (39%), but increased moderately as temperature increased to 55 °C (43%) (Figure 8). Using carob kibbles for the boron removal, the optimum temperature for adsorption was set at 25 °C, which corresponds to room temperature. This is economically significant as no additional thermal energy is required to achieve greater boron removal.

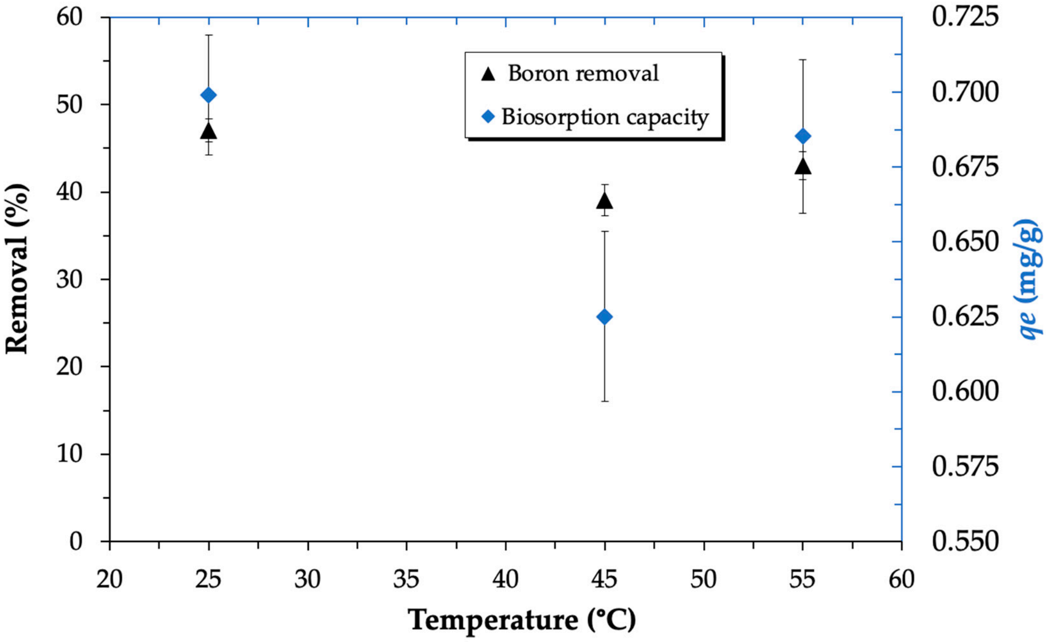

Figure 8. Influence of temperature on biosorption of boron onto powdered carob kibbles with Cs 50 g/L, particle size range 0.025–1.0 mm, initial pH of 11.5 for 300 min, and initial boron concentration, C_0, 100 mg/L. The standard deviation for $n = 2$ is represented by bars.

The results of this research differ to some extent from previous studies where various biosorbents were applied and indicated that boron adsorption can be favored at lower or higher temperatures. For instance, the adsorption efficiency of boron onto olive bagasse decreased as temperature increased (25, 45, and 55 °C), showing that the sorption process is promoted at low temperatures [37]. The opposite results were obtained by Bursali et al. (2009) for the boron sorption using marine seaweed—*Caulerpa racemosa* var. *cylindracea*—the biosorption capacity towards boron increased with increasing temperature (25, 35, and 45 °C) due to increased boron-biomass interaction [40]. The use of Dowex 2 × 8 ion exchange resin for boron removal showed that the sorption decreased as feed water was heated (25, 35, and 45 °C). The authors indicated that the sorption process is exothermic [66].

3.3.6. Influence of Particle Size

In addition to the initial pH, initial boron concentration in the solution (mg/L), and biosorbent dose (g/L) in the solution, the particle size of carob kibble powder can also affect the boron biosorption. The removal percentage was reduced from 55% (1.02 mg/g as biosorption capacity) at a particle size of 0.025—0.106 mm to 48% (0.904 mg/g as biosorption capacity) at a particle diameter of 1.0–2.0 mm, as Figure 9 shows. The higher surface area for mass adsorption per unit weight of carob kibbles may explain the increased boron removal capacity of the finer particles [67].

Man et al. (2012) reported that for agitating rice husks with particle sizes between 0.150 and 0.212 mm, 0.212 and 0.425 mm, and 0.425 and 1 mm, boron removal was the highest (84%) for particles with a larger size (0.425–1.0 mm) [39]. Kehal et al. (2010) showed that using micron-grade vermiculite with the smallest particle sizes (average particle size 6.6 μm), the highest adsorption was achieved (0.15 mmol/g). The authors concluded that the adsorption of boron is largely reliant on particle size [68].

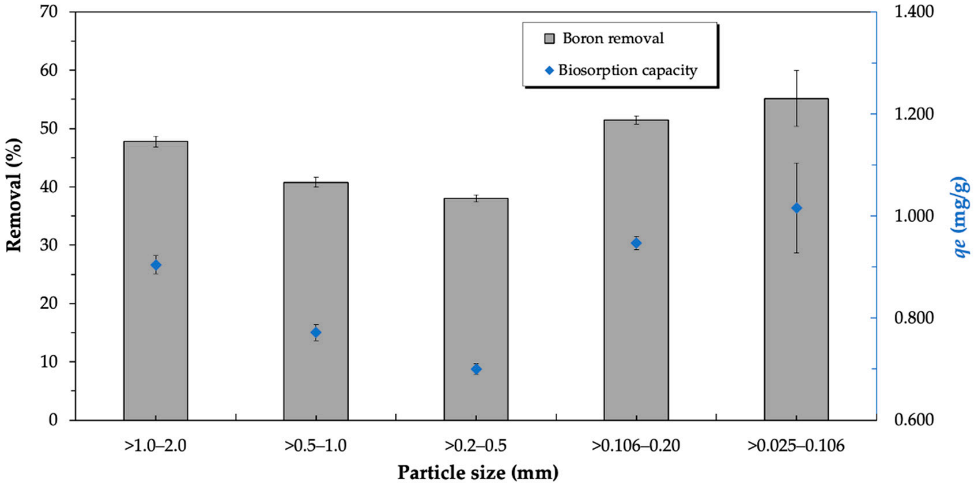

Figure 9. Influence of particle size on biosorption of boron onto powdered carob kibbles with Cs 50 g/L, an initial pH of 11.5 at 25 °C for 300 min, and an initial boron concentration, C_0 100 mg/L. The standard deviation for n = 2 is represented by bars.

To better understand the potential of carob kibbles for boron biosorption, the optimal experimental conditions obtained in the present study were compared to results from other studies using biomass of different origins. The table also includes the results of a commercially available adsorbent (ion exchange resin), which is also used to remove boron (Table 2).

Table 2. Comparison of results from other studies with the optimum experimental conditions for boron biosorption obtained with carob kibbles.

Biosorbent	Optimal Experimental Conditions						Removal Percent (%) or Biosorption Capacity (mg/g)	Reference
	Initial pH	Contact Time (h)	Temperature (°C)	Initial Boron Concentration (mg/L)	Biosorbent Dose (g/L)	Particle Size (mm)		
Carob kibble	11.5	5	25	100	50	0.025–0.106	55% (1.15 mg/g)	This work
Olive bagasse modified by pyrolysis: activation temperature of 850 °C	5.5	48	25	100	20	N.A.	30%	[37]
Cotton cellulose modified with 0.1 M NaOH	7	4	room	500	2	N.A.	11.3 mg/g	[38]
Rice husk	5	–	ambient	300	2	0.425–1.00	119 mg/g	[39]
Marine seaweed: *Caulerpa racemosa* var. *cylindracea* (0.1 M NaCl optimal ionic strength)	7.5–8.5	2.5	45	8	8	N.A.	63%	[40]
Natural minerals Organic waste material modified with 0.1 M $FeCl_3$ With 0.001 M $CaCl_2$ as background electrolyte for isotherm	9 (Waste calcite)/ 7 (Rice residues)	24 (Mineral sorbents)/ 48 (Organic sorbents)	N.A.	120	50 (Mineral sorbents)/ 2 (Organic sorbents)	N.A.	0.24 mg/g (Waste calcite) 2.88 mg/g (Wheat residues)	[41]
Dowex 2 × 8 ion exchange resin modified with 2 M NaOH/48 h	9	8	25	600	20	N.A.	55%	[66]

N.A.—not available.

3.4. FTIR Analysis of the Biosorbent before and after Biosorption of Boron

For the characterization of the biosorbent, FTIR spectra of both carob kibbles before biosorption and boron-loaded carob kibbles were recorded. The results are displayed in Figure 10.

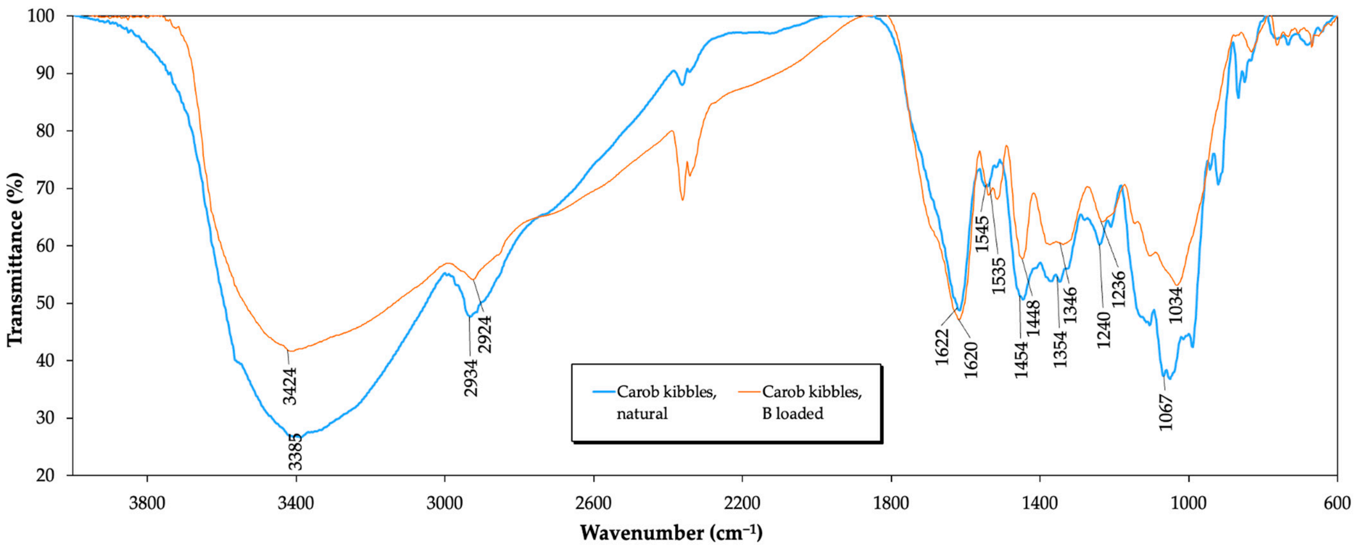

Figure 10. FTIR spectra of carob kibbles (before and after biosorption of boron).

A shift from 3385 cm^{-1} (carob kibbles, natural) to 3424 cm^{-1} (carob kibbles, boron-loaded) can be seen, as well as a change in the peak's intensity, which may indicate an O-H bending vibration's participation on the *Ceratonia siliqua* surface after contact with boron solution. Comparable shifts in the frequencies of the FTIR spectrum of *Caulerpa racemosa* var. *cylindracea* (natural and loaded with boron) because of boron biosorption revealed some reducing bands from 3409 cm^{-1} to 3403 cm^{-1} for OH stretching vibration [40]. The formation of OH groups in the adsorbent outer layers improved boron adsorption when working with modified vermiculite [68]. Hydroxyl groups are fundamental for boron adsorption from aqueous solutions, according to the authors. Figure 10 also shows that the band at about 1622 cm^{-1} (natural carob kibbles), corresponding to carbonyl C=O stretching vibration, does not present changes. In the bands at 1535 cm^{-1} (natural carob kibbles), 1545 cm^{-1} (carob kibbles, boron-loaded), 1067 cm^{-1} (natural carob kibbles), and 1034 cm^{-1} (carob kibbles, boron-loaded), some structural changes are noticed (wavenumber and percentage of transmittance), which may indicate that N–H and C–O bending vibrations are involved in the biosorption of boron.

The FTIR spectra of both carob kibbles before biosorption and boron-loaded carob kibbles provided valuable qualitative information in the identification of the adsorbing species participating in boron biosorption. Table 3 presents the wavenumber and changes of the functional groups that are probably involved in boron adsorption onto carob kibbles.

Table 3. FTIR description for carob kibbles before and after boron biosorption.

Functional Group	**Wavenumber (cm^{-1})**		**Changes**	**Involved in Boron Removal**
	Natural Biosorbent	**Boron-Loaded Biosorbent**		
Alcohol; O-H	3385	3424	Intensity	Yes
Group; C-H	2934	2924	Intensity	No
Carbonyl; C=O	1622	1620	No	No
Amine; N-H	1535	1545	Intensity	Yes
Alkene; C=C	1454	1448	Intensity	Yes
Hydroxyl; O-H	1354	1346	Intensity	Yes
Phenols; C-O	1240	1236	Intensity	Yes
C-O phenols and C-OH	1067	1034	Intensity	Yes

3.5. Boron Biosorption from Real Wastewater from the Ceramic Industry: Batch Tests

Two categories of wastewater samples from the ceramic industry, namely, effluent prior to wastewater treatment and effluent with wastewater treatment, were tested by batch adsorption onto carob kibbles to validate the boron removal from real samples. The characterization of the examined wastewater samples is presented in Table 4.

Table 4. Characteristics of wastewater from the ceramic industry *.

Parameter (mg/L)	Effluent Prior to Wastewater Treatment (I)	Effluent with Wastewater Treatment (II)
B	36	19
Fe	<1.141	<1.141
Al	1.6	2.9
Cu	<0.531	<0.531
Zn	<0.143	<0.143
SO_4^{2-}	24	10.5
pH (units)	9.5	7.8

* no spiked solutions.

The removal of boron from the wastewater samples with powdered carob kibbles was investigated under the following conditions: Cs 50 g/L, particle size range 0.025–0.106 mm, initial pH of 11.5 at 25 °C, for 300 min, since these were the optimum conditions obtained in this study. Both types of samples were spiked with boric acid (concentration of boron equal to 100 mg/L) prior to testing using the biomass, and the concentration of boron after biosorption was 72.9 mg/L for effluent with no wastewater treatment (I) and 56.2 mg/L for effluent with wastewater treatment (II). The boron removal observed for samples I and II was 64.6% (q_e 0.942 mg/g, n = 3) and 70.2% (q_e 0.789 mg/g, n = 3), respectively. The results suggest that significant quantities of boron can be removed from real solutions (effluents) using carob kibble biosorbent under the right conditions. As a result, the complex nature of this wastewater does not appear to have a negative impact on boron biosorption. In fact, results from a statistical hypothesis *t*-test suggest that there is no evidence that the type of sample affects the values of the percentage of boron removal.

4. Conclusions

In the present study, it was shown that non-modified carob kibbles have the potential to remove boron from wastewater. Boron was chosen because of the widespread interest in removing this element from industrial wastewater to meet water quality requirements. The proposed approach is also a way to valorize this waste biomass. Experiments have shown that the boron biosorption onto carob kibbles was strongly dependent on the initial pH of the solution. Increased boron biosorption was observed at a high pH (11.5). Additionally, the boron removal potential of the biosorbent was also a function of the initial boron concentration, biosorbent dose and particle size. A greater removal percentage was obtained at low concentrations, high doses of biosorbent, and using a smaller particle size. Changing the temperature of boron biosorption had no effect on the adsorption properties of carob kibbles, which ensures the favorable profitability of using this biosorbent, since it may not require additional energy input. Work in the following optimal conditions: agitating a biosorbent dose of 50 g/L with a particle size in the range of 0.025–0.106 mm, in a boron solution with an initial concentration of 100 mg/L and an initial pH of 11.5, for 5 h at 25 °C, ensured the highest efficiency of boron removal (55.1%) from the artificial aqueous solution. When real effluents from the ceramic industry were used, the obtained values of the percentage of boron removed were similar (from 64 to 70%). As shown by the FTIR analysis, the hydroxyl and carboxyl groups mainly participated in the biosorption of boron by carob kibbles. Due to the easy access to the raw material and its low price, we propose to test this biosorbent enriched with boron as a possible component of fertilizers rich in this important microelement.

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Data Availability Statement: Apart from the data reported in this study, no supplemental data were obtained.

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