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A Study of the Feasibility of *Pinus patula* Biochar: The Regeneration of the Indigo Carmine-Loaded Biochar and Its Efficiency for Real Textile Wastewater Treatment

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Abstract: The feasibility of an adsorbent material like biochar (BC) depends on its regeneration capacity and its ability to achieve high removal efficiencies on real wastewater (WW) effluents. In this study, the regeneration capacity of the *Pinus patula* BC previously used in the removal of Indigo Carmine from water was evaluated. The regeneration technique that resulted in the highest desorption efficiency was a thermo-chemical method that consisted of heating the spent BC in a stove at 160 °C for 45 min followed by regeneration with ethanol (C_2H_6O) at a concentration of 75% for 6 h. Through this regeneration method, it was found that *Pinus patula* BC could be used in seven consecutive adsorption–desorption cycles. The feasibility of this BC was also assessed by evaluating the adsorbent's efficiency in real textile WW. Under optimal operational conditions (solution pH = 3, BC dose = 13.5 g/L, and BC particle size = 300–450 µm), the highest removal efficiencies in terms of colour and dissolved organic carbon (DOC) were 81.3 and 76.8%, respectively, for 120 min of treatment. The results obtained in the regeneration studies and the treatment of real textile WW suggested that the use of *Pinus patula* BC could be suitable to be scaled to an industrial level, contributing to sustainable development and the circular bioeconomy by using a waste to solve the dye pollution problem of another waste.

Keywords: adsorption; biochar; indigo carmine; regeneration; scalability

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1. Introduction

Water pollution stemming from the unregulated discharge of organic dyes into aquatic environments poses a grave risk to both human health and the biodiversity of ecosystems [1]. Mitigating the detrimental effects of these substances necessitates the development of effective removal methods and materials [2,3]. Various technologies have been proposed to tackle this issue, including coagulation and flocculation, ion exchange, membrane separation, electrochemical, and biological processes, among others [2,4]. However, these methods often suffer from drawbacks such as having a low efficiency, high operational costs, or dependences on specific parameters for optimal performance [3,5]. Thus, there is an urgent need for innovative or combined approaches to efficiently eliminate organic dyes from wastewater (WW), and adsorption stands out as a promising method due to its cost-effectiveness, high efficiency, and ease of operation [1,5].

Several adsorbent materials have been used in the treatment of real textile WW. Zarandona et al. [5] synthesized, characterized, and used the semiconductor bismuth sulfide iodide in treating a WW matrix with Rhodamine B due to its adsorption, and the sonocatalytic and photocatalytic properties of this material. This study found a maximum removal capacity of 28.7 mg/g in a short period of time when exposed simultaneously to ultrasonic

waves and ultraviolet irradiation [5]. In turn, Raj et al. [6] used graphene oxide as an adsorbent material to treat textile WW after a coagulation-flocculation process. The authors being referred to here found that graphene oxide was able to remove 99.54% of the initial chemical organic demand (COD) and 99.79% of the colour. After the adsorption process, the effluent was able to be recycled, increasing the potential of a zero discharge of colour [6]. On the other hand, Tokay et al. [7] used a corn-cob-based adsorbent material, achieving a total organic carbon (TOC) elimination of 49.37%. The researchers stated that adsorption processes are required to treat textile WW since the processes aid in the reduction of water quality parameters like TOC and conductivity, which are commonly present in high values in real textile WW effluents [7].

One of the adsorbent materials that has been demonstrated to be highly efficient for the treatment of WW is biochar (BC) [3]. Along with its proven efficiency, BC contributes to circular bioeconomy principles since it allows waste to be used for solving the problem of WW pollution [1,3]. Nevertheless, the viability of the application of an adsorbing material like BC relies on its regeneration capacity, allowing for a decrease in the cost of treatment, while maintaining its efficiency in the treatment of real WW [8,9]. BC's regeneration efficiency is closely related to the capacity to maintain its adsorption properties [10]. Considering the number of adsorption–desorption cycles that can be conducted with the same BC, its regeneration potential makes it a competitive and efficient material [11]. The regeneration ability of BC not only impacts its cost of production but also has environmental importance [12] due to the reduction in the amount of sludge produced during the adsorption process [13].

The most widely used methods for the regeneration of BC are those that are thermal and chemical. In thermal regeneration, BC is heated up at high temperatures to achieve the degradation of the pollutant molecules that are adsorbed on the BC's surface. Even though the thermal regeneration of BC can reach desorption efficiencies of 80%, this process is limited by the high energy consumption required, which increases the cost of the treatment [14]. Additionally, high temperatures can cause damage to the BC's organic porous structure, leading to a decrease in its adsorption capacity [10]. Chemical regeneration, in turn, is based on the use of acids, bases, or solvents to either desorb or degrade the adsorbate molecule from the BC's surface. For this purpose, inorganic reagents like hydrochloric acid (HCl) and sodium hydroxide (NaOH), and organic compounds such as methanol (CH_4O), ethanol (C_2H_6O), acetic acid (CH_3COOH), acetone (C_3H_6O), and a mixture of solvents with other organic substances have been used [15–18]. Microwave irradiation and supercritical fluid regeneration are techniques that have been under study. In microwave irradiation, the dipole polarization of polar substances is induced by the irradiation of microwaves. Moreover, heat is produced by the conversion of electromagnetic energy, which causes the volatilization of the adsorbate. In microwave regeneration, the distortion of BC mesopores can be produced by the heat generated by the waves [19]. In supercritical fluid regeneration, a supercritical fluid is used as a desorption agent to desorb the adsorbate from the adsorbent surface through the means of pressure adjusting. Even though supercritical fluid regeneration can be performed under low temperatures and there is a low loss of BC, this method is expensive, and its investigation is still at a laboratory scale [19,20].

Chemical regeneration has been applied for regenerating the BC used in the removal of dyes in water and efficient results have been found. The BC regenerated by chemical methods has been proven to be able to obtain high removal efficiencies even after five adsorption–desorption cycles [21–25]. It is worth noting that even though chemical regeneration has presented promising results, a more adequate regeneration method to achieve a high desorption of an adsorbed organic pollutant has not been reported yet [15]. Therefore, studies must focus on finding the best regeneration method to prolong the life of BC as an adsorbent and reduce the cost associated with the implementation of the process [24]. When an adsorbent like BC decreases its efficiency in the removal of dyes and it is not possible to use it in another adsorption cycle, the final disposal of this material must be considered. There is a need to reduce the probability of the secondary pollution

that can come with the disposal of the exhausted BC with dyes. Therefore, the BC with dyes adsorbed on its surface must be converted into a non-toxic BC before giving it a final disposal, or an in-depth study about the toxicity of the exhausted BC before choosing a final disposal method must be carried out [2,26]. As a consequence, the comprehension of BC's regeneration and final disposal is fundamental to contributing to the circular bioeconomy and sustainable development [23].

On the other hand, the study of the efficiency of BC in the removal of dyes has been focused on the treatment of synthetic WW (i.e., distilled water doped with a known concentration of dye). When an adsorbent material is used to treat real WW, its efficiency tends to decrease due to the competition of the target contaminant with other constituents contained in the WW matrix for the active adsorption sites on the surface of the adsorbent [24]. In the case of textile WW, dissolved salts, heavy metals, acids, bases, binders, surfactants, and biocides can compete with the dye molecules and reduce the efficiency of the adsorption treatment [27]. Textile WW also exhibits high pH values, CODs, biochemical oxygen demands (BODs), and turbidity that make the effluent complex to be treated [6]. The effect of other textile WW constituents on the adsorption of dyes by BC must be assessed not only to evaluate the performance of this adsorbent material in a real scenario but also to assess the applicability of the process [28].

Under this scenario, the regeneration of the *Pinus patula* BC previously used in removing Indigo Carmine was studied using chemical regeneration with both organic and inorganic reagents to find the solvent that achieves the highest desorption capacity. Additionally, the efficiency of *Pinus patula* BC was evaluated in real textile WW from the processing of denim. Finally, information regarding the final disposal of the spent BC was covered.

2. Materials and Methods

2.1. Chemicals and Reactants

NaOH (>99%) was purchased from Sigma Aldrich (Darmstadt, Germany), and HCl (37.20%), from VWR chemicals (Radnor, PA, USA). CH_3COOH (99.85%) and C_2H_6O (96%) were bought from Dunamis, SAS (Medellín, Colombia). The textile WW was provided by a company located in La Estrella-Department of Antioquia, Colombia, that specialises in denim wash and fibre dyeing. The WW samples were collected in an opaque polyethylene container and stored at 4 °C. Indigo Carmine (99%) was obtained from Carlo Erba (Sabadell, Spain). All reactants were used as received.

2.2. Biochar Generation and Characterization

BC was generated from the gasification of *Pinus patula* wood pellets and was used in the regeneration studies and the treatment of a real textile WW effluent. *Pinus patula* wood pellets were provided by a sawmill in Medellín, Colombia. During gasification, *Pinus patula* wood pellets (10–15 mm in length and 8 mm in diameter) were placed in a TLUD (top-lit updraft) reactor under atmospheric pressure. Further information about the gasification process and the TLUD reactor can be found in Gutiérrez et al. [29]. To obtain the particle size of 300–450 μm, the BC was cooled down, crushed, and sieved to be stored in zipper bags.

In a previous study, *Pinus patula* BC was characterized through ultimate, elemental, and proximate analyses. To determine the specific surface area and the pore volume, BET and BJH were used, respectively. To assess a structural analysis, SEM was performed, and to estimate the functional groups present in *Pinus patula* before and after gasification, a FTIR was conducted as presented in Table 1 and as reported by Gutiérrez et al. [29]. Further details on BC characterization methods and the equipment used were reported in [29].

Table 1. *Pinus patula* biochar's physicochemical properties.

Physicochemical Properties	*Pinus patula* Wood Pellets	*Pinus patula* Wood Pellets' BC
Volatile matter (wt%)	84.64	20.59
C (wt%)	47.01	97.94
H (wt%)	5.69	0.97
N (wt%)	0.02	0.19
O (wt%)	47.28	0.9
H/C	1.45	0.12
O/C	0.75	0.01
BET	1.16	367.33

2.3. Adsorption and Desorption Studies

Adsorption studies were carried out to determine the optimal operational conditions for a solution pH (3, 6, and 9), a BC dose (9, 13.5, and 18 g/L), and a BC particle size (150–300, 300–450, and 450–600 µm) that maximize the removal of Indigo Carmine using *Pinus patula* BC. The adsorption studies were conducted in a batch mode using 200 mL and 25 mg/L of Indigo Carmine, which was prepared from an Indigo Carmine stock solution of 10,000 mg/L. The change in the concentration of Indigo Carmine was analysed by visible spectrophotometry using a DR 2700 visible spectrophotometer (Hach, Loveland, CO, USA) that was set at a maximum wavelength of 612 nm. A calibration curve with a correlation coefficient (R^2) of 0.9991 was constructed to measure the initial and final levels of the target dye. During the optimization studies, a central composite design was used [3]. It was determined that the values of pH, BC dose, and particle size that maximize the removal efficiency of Indigo Carmine in water were 3, 13.5 g/L, and 300–450 µm, respectively. Therefore, for every adsorption–desorption cycle, the optimum values of these factors were used. Further details on the optimization process can be found in Gallego-Ramírez et al. [3].

To conduct the first adsorption–desorption cycle, 200 mL of a 25 mg/L solution of Indigo Carmine was maintained in contact with 13.5 g/L of BC with a particle size of 300–450 µm, the solution's pH was adjusted to 3 and stirred in a stirring plate at 200 rpm for 5 min, since the equilibrium was reached after this amount of time [3]. After 5 min of treatment, an aliquot of 10 mL was collected with a syringe and filtered with a 0.45 µm syringe filter. Once the aliquot was collected, the *Pinus patula* BC was separated from the solution using a paper filter with a pore diameter < 375 µm, and dried for 12 h at room temperature.

The BC exhausted with Indigo Carmine was immersed in 100 mL of a 0.1 M NaOH solution for 30 min and stirred [16,21,23]. C_2H_6O was also evaluated for the desorption process, according to the method used by Jiang et al. [30]. C_2H_6O was tested at a concentration of 75%, and the BC loaded with Indigo Carmine was submerged in 100 mL of C_2H_6O and stirred for 30 min. The method used by Park et al. [18] was also used, but it was modified. The authors being referred to here used a mixture of CH_4O and CH_3COOH; nevertheless, CH_4O has a toxicity potential associated with the formation of formaldehyde (CH_2O) when digested. Therefore, to avoid this possible disadvantage in the application of this process [15], C_2H_6O was used instead as it has a similar regeneration performance and exhibits less toxicity potentials than CH_4O [30]. Consequently, in the modified method, the BC loaded with Indigo Carmine was immersed in 100 mL of a mixture with a proportion of 95:5 (C_2H_6O:CH_3COOH) and stirred for 30 min. C_6H_6O and CH_3COOH were used at a concentration of 75% and 99.85%, respectively.

After the performance of each desorption process, an aliquot of 10 mL of the solution was taken and filtered with a 0.45 µm syringe filter. The aliquot was then analysed via visible spectrophotometry to calculate the level of Indigo Carmine desorbed from the *Pinus patula* BC's surface by the solvent. The experiments were carried out in triplicate.

The desorption efficiency was calculated as described in Equation (1), where D (%) is the desorption percentage, q_{des} (mg/g) is the desorption capacity of the BC, and q_{ads} (mg/g) is the BC's adsorption capacity [16]. q_{des} and q_{ads} were determined according to Equations (2) and (3), respectively. C_s (mg/L) is the concentration of Indigo Carmine in the solvent, vs. (L), which is the volume of the solvent used, m (g) is the mass of the BC, V (L) is the volume of the solution used, C_0 and C_t (mg/L) are the initial and final levels of Indigo Carmine, respectively.

$$D(\%) = \frac{q_{des}}{q_{ads}} * 100 \quad (1)$$

$$q_{des} = \left(\frac{C_s}{m}\right) V_s \quad (2)$$

$$q_{ads} = \frac{(C_0 - C_t)V}{m} \quad (3)$$

2.4. Regeneration Studies

The method with the highest desorption efficiency was selected and used to evaluate the number of adsorption–desorption cycles for the *Pinus patula* BC to be used in the WW polluted with Indigo Carmine. For this purpose, the same procedure followed in the adsorption experiments was carried out. After each adsorption treatment, an aliquot of 10 mL was filtered with a 0.45 µm syringe filter to calculate the removal efficiency in each adsorption–desorption cycle. The BC was separated from the solution using a paper filter that had a pore diameter < 375 µm, dried out at room temperature for 12 h, and regenerated. After regeneration, the BC was again filtered using the paper filter, and used in another adsorption cycle. All the treatments were conducted in triplicate.

2.5. Textile WW Treatment

The textile WW was characterized before the adsorption studies; the measured parameters were the COD, the BOD after 5 days of incubation (BOD_5), the pH, conductivity, temperature, dissolved organic carbon (DOC), TOC, and the true and apparent colour. To obtain the wavelength at which the absorbance of the textile WW was at a maximum, a sample of the textile WW was scanned from 500 to 700 nm with visible spectrophotometry using a DR 2700 visible spectrophotometer. The wavelength tested was chosen considering the maximum wavelength of Indigo Carmine (612 nm) since the textile WW came from the denim washing industry and Indigo Carmine is the main dye used in the dyeing of denim [31]. Before evaluating the maximum wavelength, the WW was filtered with a syringe filter of 0.45 µm to remove the suspended solids and reduce the interference that these solids can represent when measuring the absorbance. Afterwards, a calibration curve with the Indigo Carmine previously filtered with a syringe filter of 0.45 µm was constructed at the obtained wavelength. The equation of the calibration curve was used to calculate the efficiency of the BC (%) for the removal of colour from the WW effluent used according to Equation (4).

$$Removal\ (\%) = \frac{C_0 - C_t}{C_0} * 100 \quad (4)$$

The adsorption studies were carried out in triplicate in a batch mode and according to the optimal conditions obtained for the removal of Indigo Carmine using *Pinus patula* BC as presented in [3]. Therefore, the solution pH was adjusted to 3, the concentration of *Pinus patula* BC was 13.5 g/L in 200 mL of WW, and the BC particle size was 300–450 µm. A number of 10 mL volume aliquots were taken at 5, 15, 30, 60 and 120 min, and filtered with a nylon syringe filter (0.45 µm of pore diameter) to analyse the performance of the elimination process throughout the treatment time. The aliquots were analysed through visible spectrophotometry at the wavelength obtained in the absorbance assays to determine the removal in terms of colour according to Equation (4).

Additionally, for the analysis of the DOC, a TOC analyser (Shimadzu Corporation, Columbia, MD, USA) was used. Samples were previously filtered using a 0.45 µm nylon filter.

2.6. Final Disposal of Biochar

For the final disposal of the dye-loaded BC, scientific databases were used to find the disposal methods and techniques that have been proposed or evaluated.

3. Results and Discussion

3.1. Adsorption and Desorption Studies

If the adsorption of a dye is favoured by an acid medium, a basic medium is expected to break the adsorption equilibrium that exists between the adsorption active sites of the adsorbent and the adsorbate. An increase in hydroxide ions (OH^-) is going to deprotonate the surface of the adsorbent and create a driving force to cause the desorption of the dye molecules [24]. In the optimization studies previously conducted, it was found that a pH solution had a major influence in the removal of Indigo Carmine, and an electrostatic interaction was an adsorption mechanism involved in the removal process [3]. Therefore, a medium with an unfavourable pH value is expected to cause the desorption of the dye molecule [32]. Since the adsorption of Indigo Carmine by *Pinus patula* BC was enhanced in an acid medium (pH = 3), a solution of NaOH at 0.1 M was used to cause the desorption of Indigo Carmine molecules. Nonetheless, it was observed that the effect of a 0.1 M NaOH solution was negligible. This can be ascribed to the fact that multiple adsorption mechanisms like hydrogen bonding (H-bonding), π–π interactions, electrostatic attraction, and pore filling were involved in the adsorption of Indigo Carmine by the BC of interest [3]. Hence, the stable adsorption of Indigo Carmine on the BC surface does not depend only on the desorption of the Indigo Carmine molecules adsorbed via electrostatic attraction, resulting in a low desorption efficiency and an insignificant regeneration [32].

The efficiency of C_2H_6O at 75% (v/v) to desorb Indigo Carmine from *Pinus patula* BC was also estimated and a value of 2% was reached. The low desorption efficiency obtained by C_2H_6O (75%) could be related to a high affinity between Indigo Carmine and *Pinus patula* BC. Since the principle of adsorption relies on the affinity that the adsorbate and adsorbent have between each other, C_2H_6O (75%) was not able to break the adsorption equilibrium created between the Indigo Carmine molecules and the *Pinus patula* BC adsorption sites [20]. In addition, as the adsorption mechanism involved in the process is mainly a chemical, the solvent alone does not have the required energy to break the bonds between the Indigo Carmine molecules and the studied BC [13]. The performance of a mixture with a proportion of 95:5 C_2H_6O (75%) and a concentrated CH_3COOH solution was also evaluated. Under these conditions, the Indigo Carmine desorption was negligible.

Because of the low desorption efficiency obtained for the BC spent with Indigo Carmine, a method that combined thermal with chemical generation was used according to the information reported by Momina et al. [13]. Accordingly, the Indigo Carmine-loaded BC was first heated in a furnace at 160 °C for 45 min. Afterwards, the BC was cooled down at room temperature and submerged in a solution of C_2H_6O (75%), since this was the solvent that performed better in the desorption of Indigo Carmine. The contact time between the solvent and the spent BC was also increased to test its effect and evaluate whether a higher contact time could result in a better desorption efficiency. The contact times evaluated were 3, 4, and 6 h. Table 2 presents the desorption efficiency of the tested methods.

As observed in Table 2, the thermo-chemical method led to the highest desorption efficiency (21.4%) for 6 h of contact time. The relatively high desorption could be attributed to the weakening of the adsorption forces between the Indigo Carmine molecules and the active sites of the BC during the heating process. When the adsorption forces were debilitated, the solvent was able to break the bonds between the Indigo Carmine molecules and the BC [13]. Therefore, the above-mentioned method was selected to regenerate the Indigo Carmine-loaded BC.

Table 2. Desorption efficiencies of the tested desorption methods.

Desorption Method	Time (min)	Desorption Efficiency (%)
NaOH (0.1 M)	30	0
C_2H_6O (75%)	30	2
C_2H_6O (75%):CH_3COOH	30	0
Heat at 160 °C and C_2H_6O (75%)	180	18
Heat at 160 °C and C_2H_6O (75%)	240	18
Heat at 160 °C and C_2H_6O (75%)	360	21.4

According to the relatively low desorption efficiencies obtained in the present study, it can be concluded that the adsorption forces that contributed to the removal of Indigo Carmine from water by *Pinus patula* BC are strong and difficult to brake. The adsorption of Indigo Carmine was mainly influenced by mechanisms like the π–π interactions that occur between the π electron cloud in the benzene rings of the Indigo Carmine molecular structure and the π electrons on the surface of the BC [3]. Internal pore diffusion also influenced the adsorption of Indigo Carmine; therefore, the pathway that Indigo Carmine molecules must follow to be desorbed from the adsorbent is difficult to reach. Hence, π–π interactions and internal pore diffusion made the desorption of the target dye difficult [18]. Low desorption efficiencies were also obtained by Li et al. [9] for malachite green and sunset yellow. The authors being referred to here found that 0.1 M of NaOH was only able to reach a desorption efficiency of ~9% for bone BC loaded with Sunset Yellow. In turn, HCl at 0.1 M presented a desorption efficiency close to 5% for malachite green-loaded BC.

3.2. Regeneration Studies

BC loaded with Indigo Carmine was regenerated using a thermal-solvent method. The loaded BC was heated in a furnace at 160 °C for 45 min and subsequently submerged in C_2H_6O 75% for 6 h. The adsorption cycles were conducted with an initial Indigo Carmine concentration of 25 mg/L and a pH of three until equilibrium was reached (5 min). As presented in Figure 1, the removal efficiency of Indigo Carmine by the *Pinus patula* BC decreased from 99.1% to 55.3% after seven adsorption–desorption cycles.

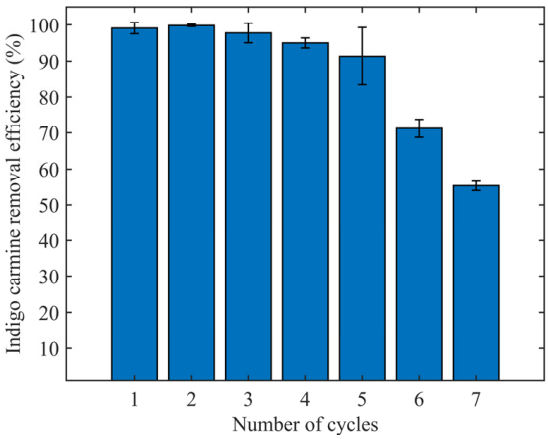

Figure 1. Adsorption–desorption cycles of *Pinus patula* biochar (BC). Operational conditions: BC dose = 13.5 g/L, Indigo Carmine concentration = 25 mg/L, BC particle size = 350–400 µm, solution pH = 3, time = 5 min.

The decrease in the removal efficiency of Indigo Carmine by *Pinus patula* BC with the increase in the number of adsorption–desorption cycles can be related to the remaining dye molecules that stay in the BC adsorption active sites, causing the saturation of the adsorbent and decreasing the availability of the adsorption active sites [33,34]. During the regeneration studies, it was observed that the amount of BC decreased as the number of cycles increased. Hence, during the cycle, there was a loss in the BC's weight that resulted in a decrease in the number of adsorption active sites available. The loss in the adsorbent weight was also observed by Mensah et al. [35]. As described in the desorption studies, the desorption efficiency was low; therefore, dye molecules were still adsorbed in the adsorption active sites of the BC, resulting in the blocking of the adsorption sites and the reduction in the removal efficiency [17]. Even though the desorption efficiency was low, high Indigo Carmine removal efficiencies were obtained by *Pinus patula* BC even after seven adsorption–desorption cycles. This can be explained by the unsaturation of the adsorbent, meaning that after the adsorption process, there were still adsorption active sites. *Pinus patula* BC presented a good performance in regeneration studies, meaning that the studied adsorbent is stable, and can be used in several adsorption–desorption cycles in the treatment of WW effluents [36]. Additionally, since *Pinus patula* BC exhibits good regeneration, the cost associated with the production and application of this adsorbent in the treatment of dyes is reduced [37]. Tomin et al. [38] evaluated the regeneration potential of red-straw BC and found that, with a thermal regeneration method, only two adsorption–desorption cycles could be conducted because the removal efficiency decreased from 72% to 17%. The inability of BC to be regenerated in that case was attributed to the thermal deterioration of the BC, which induced the change in its physicochemical properties. Ravindiran et al. [39] regenerated palm shell BC using a 0.01 M NaOH solution, and three adsorption–desorption cycles were conducted with the removal efficiency decreasing from 71.57% to 68.78%. The reduction in the removal efficiency was attributed to the loss of functional groups on the surface of the adsorbent.

3.3. Textile WW Treatment

The textile WW effluent used had an intense blue colour and had a pH near neutrality, as observed in Table 3, where the physicochemical characterization of the textile effluent is presented. Other studies on the characterization of textile WW reported similar results [28,40,41]. From the obtained findings, the high conductivity value was notable, which can be due to the high amount of salts used in the textile industry to enhance the fixation of the dye to the fibres [42]. Furthermore, according to the biodegradability index (BOD_5/COD), the textile WW had a low biodegradability; as a consequence, a physicochemical process like adsorption is more suitable than a biological process for the treatment of textile WW since the toxic substances contained can inhibit the organism growth used in biological processes [43,44]. The absorbance spectra of the real textile WW are illustrated in Figure 2; since it was known that Indigo Carmine was contained in the textile WW, the wavelength measured was within the range from 550 to 700 nm. The first absorbance spectrum depicted in Figure 2a shows that the absorbance peak could be between 650 and 660 nm; thus, another spectrum was obtained to have a more precise value. As observed in Figure 2b, the second spectrum with a smaller wavelength was measured to have wavelength values ranging from 650 to 660 nm. This absorbance spectrum showed that the absorbance peak for the textile WW effluent tested was located at 655 nm. In this regard, this wavelength was selected for the colour removal studies. The obtained wavelength for the textile WW was used to perform a calibration curve with an Indigo Carmine solution that was filtered with a syringe filter of 0.45 μm; the obtained equation was used to calculate the initial and final concentration of colour for each treatment. The R^2 obtained from the calibration curve was 0.9994.

Table 3. The textile wastewater's physicochemical characteristics.

Parameter (Units)	Value
Apparent colour (Pt-Co)	>90
True colour (Pt-Co)	201
Dissolved organic carbon (DOC) (mgC/L)	124.5
Total organic carbon (TOC) (mgC/L)	217.9
Chemical oxygen demand (COD) (mgO_2/L)	630.3
5 day biochemical oxygen demand (BOD_5) (mgO_2/L)	222.2
pH	6.4
Conductivity (mS/cm)	2.4
Temperature (°C)	24.9
BOD_5/COD	0.35

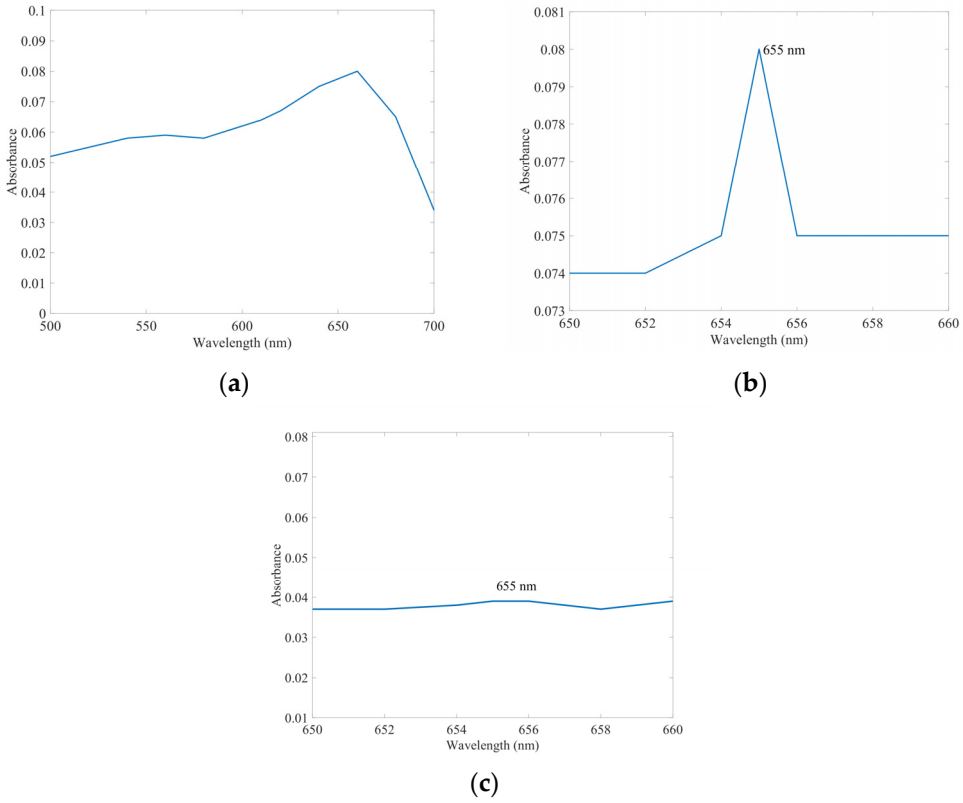

Figure 2. The real textile wastewater's (WW's) absorbance spectra. (**a**) The absorbance spectrum in a wide range of wavelengths, (**b**) the absorbance spectrum in a smaller wavelength range, and (**c**) the absorbance spectrum after adsorption with *Pinus patula* BC.

The treatments for the real textile WW were conducted under the optimal operation conditions found in [3]. Aliquots at 5, 15, 30, 60, and 120 min were taken to evaluate the efficiency of the process in terms of colour removal. As observed in Figure 3, the removal efficiency in terms of colour was 64% at 5 min of treatment and rose to 75.7% when the contact time was increased up to 30 min. The maximum elimination efficiency in terms of colour was observed at 120 min of treatment and had a value of 81.3%. The removal efficiency in terms of colour was lower than that obtained in the optimization experiments in simulated WW for Indigo Carmine (99%). The reduction in the efficiency in the real textile WW is attributed to the presence of substances like mordants, perfluorinated compounds that function as surfactants, salts, ions like chlorides (Cl^-) and sulphates (SO_4^{2-}), solvents,

and ammoniacal nitrogen (NH_3-N) that can compete with the dye molecule to take up the adsorption active sites on the surface of the BC [45–48]. Nevertheless, the decrease in colour was evident and can be represented by the removal efficiency in terms of the colour obtained in the adsorption process. The colour removal was also observed in the absorbance spectrum of the treated WW (Figure 2c) for 2 h of contact time. The decrease in the absorbance peak at 655 nm indicated that the chromophore of the dye, which is responsible for colour, was removed [28]. In this regard, according to the results, *Pinus patula* BC can be suitable for the removal of dyes contained in textile WW effluents.

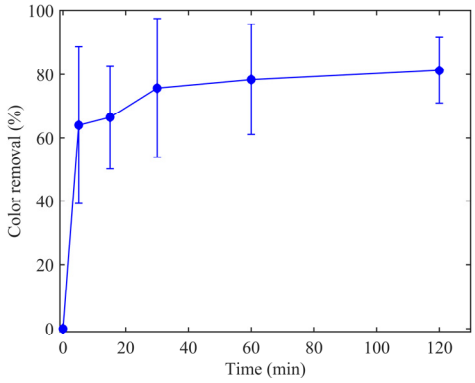

Figure 3. The treatment of real textile WW by the BC derived from *Pinus patula* wood pellets in terms of colour removal vs. time. Operational conditions: BC dose = 13.5 g/L, pH = 3, BC particle size = 300–450 µm.

Other authors have reported a decrease in colour or TOC due to the application of an adsorption process. Pandey et al. [28] used pine needle BC with laccase enzymes immobilized on the BC's surface to treat a textile WW effluent. The tested WW presented two types of dyes, one in the yellow region and another in the blue region. After the adsorption with laccase-BC, the dye in the yellow region was removed completely, and for the dye in the blue region, a removal of 35.7% was obtained. Furthermore, in the WW absorbance spectrum after the adsorption treatment, the peaks that represented the presence of dyes were flattened, indicating that the removal of colour was caused by the breakdown of the chromophore group in the dye molecules. Pessoa et al. [48] modified açai BC with NaOH to treat WW from the textile industry. Before the adsorption process, coagulation-flocculation was conducted to remove metallic ions, surfactants, and soaps. The authors being referred to here obtained a removal of colour of 32.5%; however, the treatment caused a significant decrease in the COD, indicating that the combined treatments could reduce the organic load of the WW. In turn, Tokai et al. [7] used a corn-cob BC that was activated with zinc chloride ($ZnCl_2$) to treat textile WW. They found that the corn-cob-$ZnCl_2$ BC was able to remove 49.37% of the initial TOC present in the textile effluent. Before conducting the adsorption process, the textile WW was treated with a photo-Fenton process and a removal of TOC of 86.63% was achieved. The authors being referred to here stated that adsorption improves the quality of the textile WW; hence, it is a process that should be considered when designing a WW treatment facility for textile industry effluents. Additionally, the improvement of water quality due to the application of an adsorption process makes WW suitable for the irrigation of plants [7]. Kumari et al. [49] evaluated the efficiency of a zero-valent iron nanocomposite to treat a WW derived from the textile industry. The authors found that the nanocomposites were able to achieve a removal of colour of 89.73%. Additionally, the textile WW presented a dark green-to-black colour before the adsorption process and after conducting the process, the intensity in colour decreased due to the adsorption of substances that imparted colour into the water [49].

The reduction in the DOC was also measured. Within 120 min of residence time, the DOC decreased from 124.5 ± 21.2 mg/L to 28.86 ± 3.61 mg/L, which represented a DOC removal of 76.8%, as observed in Figure 4. These results suggest that *Pinus patula* BC can

eliminate dyes and other organic compounds contained in a real WW matrix from the textile industry.

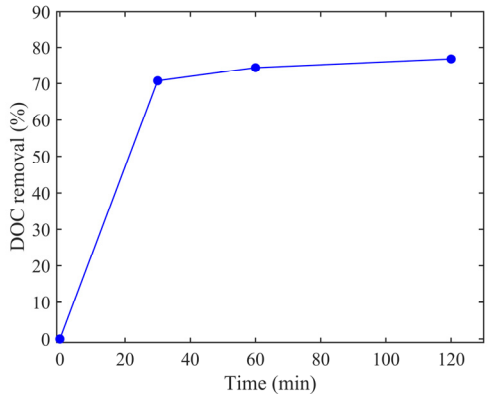

Figure 4. Dissolved organic carbon (DOC) removal vs. time. Operational conditions: BC dose = 13.5 g/L, pH = 3, BC particle size = 300–450 µm.

3.4. Disposal of the Spent Biochar

The application of BC in a WW treatment facility can be limited by the final disposal of the dye-loaded BC since the selection of the adequate disposal method should avoid secondary pollution due to the toxicity associated with dyes [23]. The disposal of dye-loaded BC represents a hazard and is a new challenge for researchers due to the mobility that can put dyes into the environment at the disposal of the spent adsorbent [50]. Choudhary et al. [22] evaluated the calorific value of malachite green-loaded BC and obtained a value of 20.37 MJ/kg, which accomplished the required minimum calorific value for incineration. They concluded that the spent BC could be utilized in energy recovery and could be used as a source of energy in some industries.

Another method of disposal that has been proposed is landfilling [51]. Even though this disposal method is cost-effective, it is important to guarantee that the dye would be adsorbed on the BC for a long time or that the leaching of the dye molecule from the BC surface could not occur. Consequently, the possibility of the release of the dye molecule into another environment is low and secondary pollution could be avoided [52].

BC can be used in soil to enhance the cation exchange capacity and improve the growth of plants by reducing the leaching of nutrients from the soil [53]. Hence, a proposed disposal of spent BC is its use as a soil amendment [52]. Nonetheless, regarding the previous utilization of BC in the removal of dyes in water, the toxicity potential of the dye-loaded BC should be evaluated before its soil incorporation [54]. To assess the toxicity of the dye-loaded BC in soil, a study similar to that performed by Han et al. [55] should be conducted. In the referred-to study, the toxicity of different concentrations of a mixture of raw BC and soil was evaluated using *Eisenia fetida* as a sentinel organism. They concluded that the BC assessed was suitable for soil amendment. Nevertheless, it is notable that the disposal of the loaded BC has not been investigated in depth yet; therefore, further investigations are required to determine whether the application of the spent BC in the agroindustry is viable [56]. For example, Kar et al. [57] evaluated the use of phosphorus-doped BC previously used in the treatment of textile WW as a compost and its effect on the growth of *Solanum lycopersicum* L. The tomato plant achieved its maximum height when the soil was mixed with the compost generated from the spent adsorbent since the BC had a high carbon content. As a consequence, the BC could be used as a soil conditioner to favour the growth of plants [57]. When the existing gap in knowledge about the final disposal of spent BC is filled, BC's feasibility would increase as well as its contribution to sustainable development and the circular bioeconomy.

4. Conclusions

The desorption efficiency of Indigo Carmine was relatively low with all the solvents evaluated. The highest Indigo Carmine desorption efficiency was obtained with a dual thermo-chemical process that consisted of heating the spent BC loaded with Indigo Carmine at 160 °C for 45 min before putting it in contact with a solution of 75% $C_6H_{10}O$ for 6 h. Regardless of the desorption efficiency of the *Pinus patula* BC loaded with Indigo Carmine, the same adsorbent could be used during seven adsorption–desorption cycles, indicating that the *Pinus patula* BC had a high regeneration ability and that its production cost could be decreased, as well as that of the WW treatment.

The BC derived from *Pinus patula* showed high efficiencies in the removal of the target dye from real textile WW (86%). In addition, the absorbance spectra of the pre-and post-treated textile WW showed a flatted area on the absorbance peak, indicating the removal of the chromophore group of the dye of interest. In the DOC studies, it was observed that the treatment of the textile WW with *Pinus patula* BC reached a removal of 76.8%. Therefore, the BC used could be considered as a potential adsorbent for the treatment of dyes in textile WW in a cost-efficient way.

Concerning the disposal of the dye-loaded BC, further research is required to fill the existing gaps, particularly due to the toxic effects that could be ascribed to the spent adsorbing material and the benefits of incorporating it as a soil amendment, since this is the application that can have a positive impact on the circular bioeconomy and sustainable development when comparing it with other disposal methods that have been proposed.

The regeneration studies and the study using real textile WW showed that *Pinus patula* BC could be scaled to an industrial level and used in the treatment of textile effluents. Nonetheless, to be certain about this statement, the disposal of the dye-loaded adsorbent needs to be studied at a deeper level to conclude whether the dye-loaded BC is adequate as a soil restoration material or if it could pose an added risk to the living organisms that are in contact with the exhausted BC.

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