Article


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Highlights:
• The use of inexpensive, easily obtained, and ecological adsorbents.
• New bio-adsorbents were made for colorant adsorption from an aqueous solution.
• EBT dye adsorption capacities ranged from 1.8 to 2.8 mg·g⁻¹.
• Adsorptions of EBT dye by the activated carbon of cannabis.
• This study provides cost-effective and sustainable production of activated carbon.
• Application of mathematical modeling to develop new relevant mathematical models based on experimental results.

Abstract: In the present work, the adsorption behavior of Eriochrome Black T (EBT) on waste hemp activated carbon (WHAC) was examined. The surface of the WHAC was modified by H₃PO₄ acid treatment. The surface and structural characterization of the adsorbents was carried out using Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analysis. The effect of influential adsorption parameters (pH, contact time, dosage, and initial concentration) on the adsorption of EBT onto WHAC was examined in batch experiments; some adsorption parameters such as pH, concentration and dose were improved by new mathematical models. The adsorption behavior of EBT on the surfaces of WHAC was evaluated by applying different isotherm models (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich) to equilibrium data. The adsorption kinetics was studied by using pseudo-first-order, pseudo-second-order, Elovich and intraparticle models on the model. Adsorption followed the pseudo-second-order rate kinetics. The maximum removal of EBT was found to be 44–62.08% by WHAC at pH = 7, adsorbent dose of 10–70 mg, contact time of 3 h and initial dye concentration of 10 mg·L⁻¹. The maximum adsorption capacities were 14.025 mg·g⁻¹ obtained by calculating according to the Langmuir model, while the maximum removal efficiency was obtained at 70 mg equal to 62.08% for the WHAC. The adsorption process is physical in the monolayer and multilayer.
1. Introduction

Hemp or (*Cannabis sativa* L.), is an annual herbaceous plant, belonging to the family of Cannabaceae, and originating in Central Asia. Regardless of its origin, hemp is commonly grown and cultivated not only in Asian countries [1] but in Africa, Europe, Canada, and the United States, and is one of the oldest cultivated plants known to humans. Since 5000–4000 BC, [2], it has been used as a food and fiber source, as well as playing an important role in medical use. It contains several chemically bioactive compounds, such as cannabinoids, terpenoids, flavonoids, and alkaloids [3]. It contains more than 100 active chemical compounds well-known as ‘cannabinoids’ [4].

Waste is a major worldwide problem and produces severe ecological and socio-economic troubles. The exploitation of waste has become of vast scientific and industrial importance in order to reduce ecological harm, attain sustainability and progress, apropos a circular economy. Energy, fuels, and other value-added products can be recuperated from waste [5]. Moreover, owing to the fast growth in the quantity and nature of agricultural waste biomass, which comes from the growth of population and rigorous agricultural behaviors, these wastes are deemed as a consequential cause of pollution with an annual growth frequency of 5–10%. People produce about 150 billion metric tons of agricultural waste [6].

As a biological and ecological alternative, the application of agro-waste as precursors of materials with high adsorptive abilities is being explored [7]. Bio-adsorbents (bioproducts) are natural elements suitable for water treatment in view of the many benefits and remarkable characteristics of these assets. They are ample, inexhaustible, decomposable, and economic [8], moreover, they have macromolecular chains with various extremely reactive chemical functions [9]. In addition, adsorption is designed within the effective methods for the elimination of water contaminants because of its facility of function and the aptitude to eliminate various kinds of contaminants, providing larger application in water quality management [10].

Amid the diversity of adsorbents, activated carbon has been demonstrated to remain efficient in the elimination of contaminants from water and even in a gaseous atmosphere [11]. Activated carbon, a commonly used adsorbent in industrial procedures, is constituted of a pored, consistent organization with a great surface area and displays radiation stability [12]. On the other hand, its application is restricted because it is expensive and very difficult to be regenerated [13,14]. Therefore, an investigation of the fabrication of activated carbon from inexhaustible, inexpensive native farming waste has won interest due to its reduced cost and extremely plentiful qualities [15,16]; in this context, certain of the farming wastes that have been investigated as an alternative source of activated carbon are barley seeds [17], orange peel [18], cassava peel [19], eucalyptus bark [20], coconut shells [21], hazel nuts [22], and tobacco steam [23].

Eriochrome Black T (EBT) is one of the colorants that are employed in water hardness resolution, in the production of paper and textiles, and also in the biomedical research field [24]. It was identified as a water pollutant which causes substantial damage to the environment. EBT is an organic azo colorant that is tolerant to natural treatment as most azo colorants are, due to their aromatic rings and sulfonate groups. Even at reduced amounts, it is not easily decayed by chemical or bacterial deterioration [25].

The overall objective of this study is to report the synthesis and characterization of hemp waste (*Cannabis sativa* L.) and its activated carbon. The as-synthesized materials were used as adsorbents for the removal of Eriochrome Black T dye in an aqueous solution. The effects of various experimental parameters on the adsorption of the dye were examined. The adsorption parameters (pH, concentration, and dose) were improved by new mathematical models obtained with a polynomial interpolation.
2. Materials and Methods

In the current study, activated carbon was geared up from residues of Cannabis sativa L. with the saturation of a chemical activating agent at reduced temperatures. We note there are only a few limited studies on the elimination of Eriochrome Black T dye using Cannabis sativa L. activated carbon as an adsorbent. All chemicals employed in this work were of analytical grade and were used without additional purification.

2.1. Preparation of Waste Hemp Activated Carbon (WHAC)

The method of preparation applied for the WHAC has two steps: carbonization and activation, as already described in our previous works [26,27]. After impregnation, to remove any excess of phosphoric acid, the solid was filtered under a vacuum. Then afterwards the waste hemp powder was pyrolyzed at 600 °C for 90 min in a muffle furnace (PR Series Hobersal). Furthermore, the carbon was completely washed with ultra-pure water to remove the remaining phosphoric acid until reaching a pH of (6.5). Lastly, the solids were dried in the oven at 105 °C for 24 h.

2.2. Characterization of the Activated Carbon

In order to approximate the temperature of distribution at which waste hemp responds under a latent climate, a thermogravimetric analysis (TGA) was applied. Thermal analyses were conducted with STD 2960 TA and SDT Q600 instruments under a nitrogen flow of 100 mL/min. A temperature ramp of 10 °C/min from room temperature to 800 °C was employed during the analyses.

FTIR spectroscopy was used to examine the surface functionalities. A Thermo IS5 Nicolet (USA) spectrophotometer was used to obtain FTIR spectra, acquired from 400 to 4000 cm\(^{-1}\) at room temperature (16 scans and spectral resolution of 4 cm\(^{-1}\)); the peak positions were revealed using Origin software (Version 2021). Origin Lab Corporation, Northampton, MA, USA.

2.3. Functional Group Analysis by FTIR

To characterize the different functional groups at the surface of the precursor and the prepared activated carbon, FTIR spectra of the various materials (EBTA, WHAC, WHNAC, WH, WHAFC) were recorded between 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). Figure 1 depicts the obtained spectrum. From this figure, the precursor presents vibration bands around 607.46, 691.12, 862.02, 953.62, 1028.83, 1086.69, 1230.20, 1306.5, 1394.28, 1616.05, 1741.4, 2851.52, 2920.66 and 3291.89 cm\(^{-1}\). The infrared spectrum of the mixture remaining after the adsorption of the EBTA colorant displays a total absence of the waves linked to the dye, obtaining two bungs which correspond to the water molecule, one bung at 3291.89 cm\(^{-1}\) and the other at 1616.05 cm\(^{-1}\). On one hand, the WHAC carbonization and the WHAFC activation of the carbon present cyclic carbon compounds, and functional groups have disappeared such as alcohols, ketones, and aldehydes. On the other hand, the biomass is rich in witness groups and also present in addition to the OH groups linked to 3300 cm\(^{-1}\). The table indicates the different leaves that contain cannabis. The other bonds are grouped in Table 1, where:

- EBT-A: Eriochrome Black T after adsorption and filtration.
- WHAC: waste hemp activated carbon.
- WHNAC: waste hemp non-activated carbon.
- WH: waste hemp (Cannabis sativa L.).
- WHAFC: waste hemp activated carbon after adsorption.
Figure 1. FTIR (Fourier transform infrared spectroscopy) spectra.

Table 1. FTIR analysis of WHAC.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Functional Group</th>
<th>Wave Numbers Range (cm⁻¹)</th>
<th>σ&lt;sub&gt;th&lt;/sub&gt;</th>
<th>σ&lt;sub&gt;exp&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>C-H</td>
<td>Alkane</td>
<td>2850–2925</td>
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<td>2851.52</td>
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<tr>
<td>C=O</td>
<td>Aliphatic Ketone</td>
<td>1710–1735</td>
<td>1741.40</td>
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<tr>
<td>C-H</td>
<td>Aldehyde</td>
<td>1370–1390</td>
<td>1394.28</td>
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<tr>
<td>C-OH</td>
<td>Third Alcohol</td>
<td>1110–1250</td>
<td>1230.20</td>
<td>1146.47</td>
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<tr>
<td>C-H</td>
<td>Cycloalkane</td>
<td>1012–1031</td>
<td>1028.83</td>
<td></td>
</tr>
<tr>
<td>=C-H (E)</td>
<td>Alkene</td>
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<tr>
<td>Ar-C</td>
<td>Aromatic</td>
<td>850–890</td>
<td>862.02</td>
<td></td>
</tr>
<tr>
<td>=C-H (Z)</td>
<td>Alkene</td>
<td>650–750</td>
<td>691.12</td>
<td></td>
</tr>
</tbody>
</table>

2.4. SEM/EDX

SEM micrographs and elemental analysis spectra of various prepared materials shown in Figure 2 show that all the materials have cracks and pores on their surfaces. This may be due to the escape of gases released during the carbonization process [28,29]. As the rate of impregnation increases, the development of cracks and pores becomes more pronounced. The prepared materials consist mainly of carbon (47.85 to 54.70%), oxygen (28.72 to 36.57%), phosphorus (0.35 to 12.14%), calcium (0.88 to 6.41%), and silicon (0.27 to 1.09%). Other elements such as magnesium, aluminum, sulfur, potassium, and sodium are present in the form of traces, in Figure 3. The high carbon content coupled with the porous structure of all the materials prepared are important criteria for an adsorbent suitable for the elimination of colorants and heavy metals in an aqueous media [30].
Figure 2. SEM (scanning electron microscopy) micrographs.

Figure 3. EDXA (energy dispersive X-ray analysis) diffractograms.
2.5. TGA/DTA Analysis

The waste hemp (*Cannabis sativa* L.) thermal performance was examined employing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 4 depicts the TGA/DSC curve of WH for the heating rate of 50 °C/min. As a result, the thermal decomposition of WH was detected at three phases. The first phase occurs from room temperature to about 125 °C with a corresponding weight loss of 9.9%. The endothermic process that takes place at 81 °C could be assigned to the vaporization of water. The low value of weight loss at this stage is a result of the low moisture content of WH. In the second phase, which extends up to about 320 °C, the weight loss has considerably increased to a value of 56.33%. At this stage, the broad and intense exothermic peak detected at 304 °C can be attributed to the decomposition of celluloses, hemicelluloses, and part of lignin. According to Haykiri et al. [31], hemicellulose and part of lignin decomposes in the range 265–310 °C. During the third phase, there is a narrow peak centered at 405 °C which relates to the degradation of residual lignin. This phase corresponds to the combustion of released gases during the decomposition of lignin. In this phase, the mass loss was lower than in the previous phase corresponding to 31.07%. The shoulder at 373 °C corresponds to the transition from the combustion of celluloses to lignin [32]. Above 505 °C the weight loss becomes constant. This shows that all the lignocellulosic content has been decomposed. Therefore, T = 505 °C appears as a minimum temperature to produce WH-based activated carbon.

![Figure 4. TGA/DTA Analysis.](image)

3. Experimental Procedure

The adsorption tests were conducted, in triplicate, by adding 10 mg of activated carbon to 25 mL of the mixture, containing EBT dye. The stock concentration of the three mixtures was diluted to draw the calibration curve in a concentration range of EBT dye (from 10 to 70 mg.L\(^{-1}\)), and the absorbance measured using a spectrophotometer. The tests were disposed on a shaker with a stirring speed of 150 rpm. For adsorption kinetics, samples were taken at time intervals varying from 20 to 160 min, centrifuged for 2 min at 3000 rpm, and then the absorbance was measured. Regarding the isothermal tests, the initial concentrations used were 10; 20; 30; 40; 50; 60; and 70 mg.L\(^{-1}\). Samples were taken after an equilibrium time of 90 min. The quantity of EBT adsorbed per gram of activated carbon \(q_e\) (mg.g\(^{-1}\)), was determined based on the following formula:

\[
q_e = \frac{(C_i - C_e) \times V}{M}
\]  

(1)
where $C_i$ and $C_e$ are the initial and final ion concentrations, respectively, expressed in (mg.L$^{-1}$). $V$ is the volume in liters of the solution and $M$ represents the mass of activated carbon in (g), and R%: removal.

4. Results and Discussion

4.1. pH Effect

Figure 5 shows the effect of pH on the elimination of the dye, it is observed that with the increase in pH the quantity adsorbed reduces this decrease due to the presence of ions (H$^+$) which causes the birth of protonation of the OH groups to dye in the acid medium by elimination of the water molecule and formation of a cycle of seven with two nitrogen atoms. In the basic medium, the existence of ions (HO$^-$) in the solution inhibits the adsorption of the dye on the surface of the cannabis and the adsorption becomes very hard with a minimum quantity of 1.7 mg g$^{-1}$ at pH = 12.

\[
R\% = \frac{(C_i - C_e)}{C_i} \times 100
\]  

(2)

Figure 5. pH effect on the adsorption of EBT dye by activated carbon of cannabis ($t = 90$ min, $T = 20 \pm 1 \, ^\circ C$, adsorbent dose 10 mg, ($C_0 = 10$ mg.L$^{-1}$), stirring speed = 150 rpm.

We present in (Equation (3)) the formula for predicting adsorption as a function of pH. This formula is obtained using polynomial interpolation. The interpolation error is given by the formula (Equation (4)).

\[
Ad = 9.25926e - 5 \times pH^3 - 5.92593e - 3 \times pH^2 + 2.69444 \times pH + 2.07
\]  

(3)

where, $Ad$ is the value of the adsorption

\[
\forall x \in [pH_{min}, pH_{max}] \text{we have, } Er = \frac{Ad^{(n+1)}(x)}{(n+1)!} \prod_{i=0}^{n}(x - pH_i)
\]  

(4)

where $Er$ is the interpolation error, $n$ is the polynomial degree. $pH_{min}$ and $pH_{max}$ are, respectively, the minimum and maximum pH values in the experiment. $pH_i$ is the nth value of pH in the experiment. $Ad^{(n)}$ is the nth derivative of $Ad$, and $n! = n \times (n - 1) \times \cdots \times 2 \times 1$. Figure 6 shows the comparison of the results of our model (Equation (3)) and the observed results.
The coefficients in (Equation (3)) are calculated using the Lagrange interpolation formula given by:

$$\text{Ad}(pH) = \sum_{j=0}^{n} pH_{j}(\prod_{i=0, i\neq j}^{n} \frac{pH_{i} - pH_{j}}{pH_{i} - pH_{j}})$$

4.2. Dose Effect

The histogram presented in Figure 7 gives the effect of the dose of cannabis on the elimination of the dye; it is observed that the yield increases with the increase in mass, this yield goes through 44.12% for m = 10 mg then continuously increases up to a yield of 60% when m = 40 mg, but for masses m $\geq$ 50 mg the yield remains almost constant, fixed at 62% at this moment in equilibrium.

Figure 7. Influence of the mass of activated carbon of cannabis on adsorption of EBT dye (stirring speed = 150 rpm, $t$ = 90 min, pH = 7 ± 0.2; $C_{0}$ = 10 mg.L$^{-1}$ and temperature = 20 ± 1 °C).
The mathematical model describing the effect of the mass of the activated carbon on the adsorption of EBT is given by the formula (Equation (5)).

\[
Re = 2.92222 \times 10^9 \times d^6 - 6.53083 \times 10^8 \times d^5 + 5.60264 \times 10^7 \times d^4 - 2.31604 \times 10^6 \times d^3 + 47473.1 \times d^2 - 183.715 \times d + 0.673
\]  

(5)

where Re is the removal and d is the dose in g. This formula is obtained by using the same technique used in (Equation (3)). We give in Figure 8 the comparison between our new mathematical model and the detected findings.

4.3. Effect of the Initial Concentration

With the aim to identify the impact of the preliminary concentration of EBT dye suggested for these studies on retention phenomena, solutions of 100 mL were prepared at different concentrations of metal ions between 10 to 70 mg.L\(^{-1}\). The achieved results are presented in Figure 9 below. The illustrious results show that the adsorbed amount of EBT dye increases with increasing initial concentration. In fact, after an equilibrium time of 90 min, the adsorption capacity registers an increase from 2.21 to 10.17 mg.g\(^{-1}\), for concentrations from 10 to 70 mg.L\(^{-1}\). This action is explained by the fact that the more the concentration of EBT dye increases, the more the number of molecules in the solution increases, involving a higher absorption capacity [33–35].

The mathematical model describing the effect of the initial concentration of EBT dye adsorption by activated carbon of cannabis is given by the formula (Equation (6)).

\[
q_e = \frac{11 \times c^6}{7.2e8} + \frac{91 \times c^5}{2.4e7} - \frac{107 \times c^4}{2.88e4} + \frac{291 \times c^3}{1.6e4} - \frac{1.6657 \times c^2}{3.6e4} + \frac{1753 \times c}{300} - 25
\]  

(6)

where \(q_e\) is the amount adsorbed at equilibrium and \(c\) is the initial concentration of EBT in mg/L. This formula is obtained by using the same technique used in (Equation (3)).

The comparison between our new mathematical model and the observed results is given in Figure 10.
Figure 9. Effect of initial concentration of EBT dye adsorption by activated carbon of cannabis ($t = 90$ min, $T = 20 \pm 1 ^\circ C$, adsorbent dose $10$ mg, stirring= $150$ rpm and pH $= 7 \pm 0.2$).

The mathematical model describing the effect of the initial concentration of EBT dye adsorption by activated carbon of cannabis is given by the formula (Equation (6)).

$$q_e = -11 \times c_0^{7.2 \times e^{8}} + 91 \times c_0^{2.4 \times e^{7}} - 107 \times c_0^{2.88 \times e^{4}} + 291 \times c_0^{1.6 \times e^{4}} - 1.6657 \times c_0^{3.6 \times e^{4}} + 1753 \times c_0^{300^{-2.5}}$$

where $q_e$ is the amount adsorbed at equilibrium and $c$ is the initial concentration of EBT in mg/L. This formula is obtained by using the same technique used in (Equation (3)).

The comparison between our new mathematical model and the observed results is given in Figure 10.

Figure 10. Comparison between the mathematical model and the observed results.

4.4. Effect of Contact Time

The adsorptions of Erichrome Black T (EBT) by activated carbons obtained from hemp waste (Cannabis sativa L.) were studied at different time intervals (20 to 160 min) and a fixed amount of $10$ mg.L$^{-1}$. Figure 11 shows that the absorption speed is fast during the first 20 to 60 min, and afterwards proceeds at a slower rate with a constant phenomenon of adsorption–desorption until the 100 min. After this period, the amount adsorbed did not change significantly. The initial rapid reaction is due to many vacant sites available at the initial stage; as a result, there is an increased concentration gradient between the adsorbate in the solution and the adsorbate in the adsorbent. Generally, the rapid initial adsorption results in a surface reaction. Slower adsorption ensues as available adsorption sites decrease with increasing occupancy and repulsive forces between favorable negatively
charged dye (EBT) adsorption due to electrostatic attraction molecules on the phase’s solid and bulk [36]. The maximum absorption of EBT after reaching pseudo-equilibrium was 1.9 mg/g.

![Figure 11. Effect of contact time of EBT dye adsorption by activated carbon of cannabis (T = 20 ± 1 °C, adsorbent dose 10 mg, C₀ = 10 mg.L⁻¹, stirring speed = 150 rpm and pH = 7 ± 0.2).](image1)

4.5. Effect of Temperature

The following figure represents the effect of temperature on the amount adsorbed by EBT on cannabis. From Figure 12, we observe that the temperature is a kinetic factor favoring the adsorption of the dye and also that the quantity adsorbed increases from 1.89 to 2 mg.g⁻¹ when the temperature increases from 293°K to 313°K, then the continuous adsorbed amount increases up to 2.2 mg.g⁻¹ when the temperature equals 333°K. This increase is owing to the effect of vibration of the dye molecules with the increase in shock numbers on the surface of the cannabis. Therefore, the adsorption of the examined ions seems to be an endothermic phenomenon. This could be also due to a relative increase in the mobility of ions in solution, which improves their exposure to active adsorption sites on the one hand and sends them to difficult-to-access sites on the other.

![Figure 12. Effect of temperature of EBT dye adsorption by activated carbon of cannabis (adsorbent dose 10 mg, C₀ = 10 mg.L⁻¹, stirring speed = 150 rpm and pH = 7 ± 0.2).](image2)
4.6. Modeling of Adsorption Isotherms

To obtain the adsorption isotherm, a series of Erlenmeyer flasks were employed. In each Erlenmeyer were poured 25 mL of EBT solution dye of varying concentrations: 10; 20; 30; 40; 50; 60 and 70 mg.L$^{-1}$. The adsorption equilibrium study was carried out under the same optimum conditions mentioned above. After equilibration, the particles of the adsorbent were separated by centrifugation and the clarified mixture was analyzed by determination of the equilibrium concentration ($C_e$) of EBT using the same calibration curve used previously. The quantity of the adsorbed reagent at equilibrium ($q_e$, in mg.g$^{-1}$) was calculated by an equation (Equation (1)).

The following four conventional models, in their linear forms, are used to describe the adsorption isotherms:

The four models tested in this adsorption are presented by their nonlinear equation and also their linear form.

The Langmuir model (Equation (7)) is linearized according to the form given in (Equations (8) and (9)) [37,38] the linear form of the Freundlich model (Equation (9)) [39,40], the Temkin model (Equation (10)) [41], and finally the Dubinin–Radushkevich model (Equation (11)) [42], the potential of Polanyi (Equation (12)) energy (Equation (13)) [43]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

$$\left(\frac{1}{q_e}\right) = \frac{1}{q_m K_L} \left(\frac{1}{C_e}\right) + \frac{1}{q_m}$$

$$R_L = \frac{1}{1 + K_L C_0}$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

$$q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln K_T$$

$$\ln q_e = -K_D \varepsilon^2 + \ln q_m$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$

$$E = \frac{1}{\sqrt{2K_D}}$$

Figure 13 represents the representation of the four linear forms of these isotherms and the choice of the model is subject to the correlation factor of the experimental points.

The linearization and the graphic representation of the four models tested in this study, and the obtained results synthesized in Table 2 above, indicate that the value of the linear correlation coefficient for the Freundlich model is closer to 1 for the EBT dye studied; these results also show the high value of the maximum adsorption capacity for the Langmuir model was 14.03 mg.g$^{-1}$. Similarly, some studies were written on the absorption phenomena of other such ions and dyes [44–52] (Table 3).

4.7. Modeling of Adsorption Kinetics

To evaluate the reaction parameters, a modeling of the adsorption kinetics is essential for the identification of the chemical or physical mechanisms that control the rate of adsorption. Four models are employed to link the experimental data of the adsorption kinetics of the studied systems, namely pseudo-first order, pseudo-second order, and intraparticle diffusion models. Figure 14 and Table 4 show the adsorption Kinetics obtained in this study.
Table 2. Constant adsorption of four isotherms models of EBT dye on activated carbon of cannabis (T = 20 ± 1 °C, mass of adsorbent = 10 mg, stirring speed = 150 rpm and pH = 7 ± 0.2).

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Constants</th>
<th>Activated Carbon of Cannabis</th>
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<tr>
<td></td>
<td>R²</td>
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<td></td>
<td>R_L</td>
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<td></td>
<td>K_L (L.mg⁻¹)</td>
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<td></td>
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<td>K_F</td>
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<td>n</td>
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<td>K_ad (mol².Kj⁻²) × 10⁻⁵</td>
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<td>q_m (mg.g⁻¹)</td>
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<td>Dubinin–Radushkevich</td>
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Table 3. The adsorption capacity of dyes and heavy metals in aqueous solutions by activated carbons of different biomass.

<table>
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<th>Adsorbate</th>
<th>Adsorbent</th>
<th>Dose (mg)</th>
<th>C₀ (mg L⁻¹)</th>
<th>pH</th>
<th>Kinetic</th>
<th>Isotherm</th>
<th>q_m (mg g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide-loaded activated char (ZnO-AC)</td>
<td>OG</td>
<td>8–30</td>
<td>50</td>
<td>7</td>
<td>Pseudo-second-order</td>
<td>Langmuir</td>
<td>153.8</td>
<td>128.2</td>
</tr>
<tr>
<td></td>
<td>Rh-b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Rice straw (RS) biochar Wood chip (WC) biochar</td>
<td>CV-CR</td>
<td>01</td>
<td>500</td>
<td>7</td>
<td>Pseudo-second-order</td>
<td>Langmuir</td>
<td>620.3</td>
<td>195.6</td>
</tr>
<tr>
<td>Charcoal (tree branches) (BCA-TiO₂)</td>
<td>MB</td>
<td>**</td>
<td>0.4</td>
<td>7</td>
<td>Pseudo-second-order</td>
<td></td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Cd²⁺</td>
<td>**</td>
<td>600</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>Sulfonated peanut shell (PNS-SO3H)</td>
<td>MB</td>
<td>20</td>
<td>900 ppm</td>
<td>10</td>
<td>Pseudo-second-order</td>
<td>Langmuir</td>
<td>1250</td>
<td>303</td>
</tr>
<tr>
<td></td>
<td>TC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[49,50]</td>
</tr>
<tr>
<td>Shrimp shell (SS) Coal acid mine drainage (AMD)</td>
<td>Mn</td>
<td>**</td>
<td>≤1</td>
<td>6–9</td>
<td>Pseudo-second-order</td>
<td>Freundlich</td>
<td>17.43</td>
<td>3.87</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>**</td>
<td>≤15</td>
<td>5–9</td>
<td></td>
<td></td>
<td></td>
<td>[51]</td>
</tr>
<tr>
<td>Waste hemp activated carbon (WHAC)</td>
<td>EBT</td>
<td>10</td>
<td>10</td>
<td>7</td>
<td>Pseudo-second-order</td>
<td>Langmuir</td>
<td>14.025</td>
<td>This work</td>
</tr>
</tbody>
</table>

** Undetermined.
Figure 13 represents the representation of the four linear forms of these isotherms and the choice of the model is subject to the correlation factor of the experimental points.

Figure 13. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models curves of activated carbon of cannabis adsorption towards BET dye.

Table 2. Constant adsorption of four isotherms models of EBT dye on activated carbon of cannabis (T = 20 ± 1 °C, mass of adsorbent = 10 mg, stirring speed = 150 rpm and pH = 7 ± 0.2).

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Constants</th>
<th>Activated Carbon of Cannabis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>R²</td>
<td>0.9904</td>
</tr>
<tr>
<td></td>
<td>RL</td>
<td>0.2636–0.7143</td>
</tr>
<tr>
<td></td>
<td>KL</td>
<td>(L.mg⁻¹) 0.0399</td>
</tr>
<tr>
<td></td>
<td>qm</td>
<td>(mg.g⁻¹) 14.025</td>
</tr>
<tr>
<td>Freundlich</td>
<td>R²</td>
<td>0.9996</td>
</tr>
<tr>
<td></td>
<td>KF</td>
<td>0.8052</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>1.4892</td>
</tr>
<tr>
<td>Temkin</td>
<td>R²</td>
<td>0.9545</td>
</tr>
<tr>
<td></td>
<td>KT</td>
<td>(L.g⁻¹) 0.00012</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>(J.mol⁻¹) 3.4945</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>697.096</td>
</tr>
<tr>
<td>Dubinin–Radushkevich</td>
<td>R²</td>
<td>0.7805</td>
</tr>
<tr>
<td></td>
<td>Kad</td>
<td>(mol².Kj⁻²) x 10⁻⁵ 0.5</td>
</tr>
</tbody>
</table>

Figure 14. Adsorption kinetics models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich and (d) interparticle diffusion of BET dye on activated carbon of cannabis, (T = 20 ± 1 °C, adsorbent dose 10 mg, Cₒ = 10 mg.L⁻¹, stirring = 150 rpm and pH = 7 ± 0.2).
Table 4. Adsorption kinetics constants of BET dye on activated carbon cannabis (temperature = 20 ± 1 °C, mass of adsorbent = 10 mg, initial concentration of dye = 10 mg.L⁻¹; stirring speed = 150 rpm and pH = 7 ± 0.2).

<table>
<thead>
<tr>
<th>Models</th>
<th>The Constants</th>
<th>Cannabis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>0.8576</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>K₁ (mL.min⁻¹)</td>
<td>0.0588</td>
</tr>
<tr>
<td></td>
<td>qₑ,cal (mg.g⁻¹)</td>
<td>1.353</td>
</tr>
<tr>
<td></td>
<td>qₑ,exp (mg.g⁻¹)</td>
<td>1.903</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9998</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>k₂ (g.mg⁻¹.min⁻¹)</td>
<td>0.0968</td>
</tr>
<tr>
<td></td>
<td>qₑ,cal (mg.g⁻¹)</td>
<td>1.9774</td>
</tr>
<tr>
<td></td>
<td>qₑ,exp (mg.g⁻¹)</td>
<td>1.903</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9079</td>
</tr>
<tr>
<td>Elovich</td>
<td>α (mg.g⁻¹.min⁻¹)</td>
<td>45.4475</td>
</tr>
<tr>
<td></td>
<td>β (g.mg⁻¹)</td>
<td>5.5803</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.8031</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>Kᵢ (mg.g⁻¹.min⁰.⁵)</td>
<td>0.0422</td>
</tr>
<tr>
<td></td>
<td>C (mg.g⁻¹)</td>
<td>1.4355</td>
</tr>
</tbody>
</table>

For a pseudo-first-order kinetics, Lagergen suggested in 1898 [53] the following equation:

\[
\frac{dq}{dt} = K₁(qₑ - q)
\]

From the integration of (Equation (13)) and the application of the boundary conditions we find the following equation:

\[
Ln(qₑ - qₜ) = Ln(qₑ) - K₁t
\]

The pseudo-second-order model, or the Ho and McKay model [54,55], turns out to be more appropriate for writing experimental data; this model is given by its following linear equation:

\[
\frac{t}{qₜ} = \frac{1}{K₂qₑ²} + \left(\frac{1}{qₑ}\right)t
\]

The models established, respectively, by Morris and Weber and Urano Tachikawa [56] for internal diffusion were used with the aim of selecting the model or models best suited to the physical processes implicated in the adsorption of adsorbate on the activated carbon of cannabis used. This model is expressed in the following form:

\[
qₜ = Kᵢt^{1/2} + C
\]

With: t the time in (min); qₑ: the amount adsorbed at equilibrium (mg.g⁻¹); qₜ: the quantity adsorbed at the instant t (mg.g⁻¹); K₁: the first-order rate constant (min⁻¹); K₂: the second-order rate constant (g.mg⁻¹.min⁻¹); C: the boundary layer thickness value (mg.g⁻¹); Kᵢ: diffusion speed coefficient (min⁻¹/2).

4.8. Thermodynamic Study

The thermodynamic parameters were determined to qualify the phenomenon of absorption of EBT dye on activated carbon of cannabis. Thus, Gibbs free energy or free enthalpy of absorption; ΔG° (kJ.mol⁻¹), the enthalpy of adsorption; ΔH° (kJ.mol⁻¹)
and adsorption entropy; $\Delta S^0$ (KJ.mol$^{-1}$.K$^{-1}$) were calculated according to equations (Equations (18) and (19)) [52].

$$\Delta G^0 = -RT \ln(K_d) \quad (19)$$

$$\ln(K_d) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (20)$$

$$K_d = \frac{q_e}{C_e} \quad (21)$$

where, $K_d$ is the adsorption equilibrium constant, $R$ is the gas constant perfect, and $T$ is the temperature in (°K). From the results illustrated in Table 5 and Figure 15, the positive value of ($\Delta S^0$) shows the good nature of the present adsorption phenomenon. Furthermore, positive values of ($\Delta G^0$) show that the examined adsorption process is spontaneous up to a temperature of 60 °C. In addition, the positive value of ($\Delta H^0$) demonstrates the endothermic nature of this phenomenon.

Table 5. Thermodynamics parameters data of EBT dye adsorption on activated carbon of cannabis.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cannabis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0$ (KJ.mol$^{-1}$)</td>
<td>16.8467</td>
</tr>
<tr>
<td>$\Delta S^0$ (J.mol$^{-1}$.K$^{-1}$)</td>
<td>11.0808</td>
</tr>
<tr>
<td>$\Delta G^0$ (kJ.mol$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>T = 293°K</td>
<td>13.5999</td>
</tr>
<tr>
<td>T = 303°K</td>
<td>13.48917</td>
</tr>
<tr>
<td>T = 313°K</td>
<td>13.37838</td>
</tr>
<tr>
<td>T = 323°K</td>
<td>13.26756</td>
</tr>
<tr>
<td>T = 333°K</td>
<td>13.15675</td>
</tr>
</tbody>
</table>

Figure 15. The 95% confidence intervals for the main analysis of influential adsorption parameters.

5. Conclusions

In this study, the performance of phosphoric acid-activated carbonaceous materials derived from waste hemp (Cannabis sativa L.) to remove Eriochrome Black T (EBT) from an aqueous mixture was investigated. The effects of the activator (liquid) to adsorbent (solid) on the textural, structural, and adsorption characteristics were investigated. The porosity of the adsorbents increased with increasing the activator:adsorbent ratios resulting in increased adsorption capacities. Equilibrium data were well explained by the Langmuir model with upper limit adsorption abilities of 14.03 mg.g$^{-1}$ for WHAC corresponding to
the activator: adsorbent ratios of 1:1. The second-order kinetic model was suitable with the experimental results. It was found that the prepared activated carbons worked as a potent adsorbent for the elimination of EBT from an aqueous medium. Since the *Cannabis sativa* L. plant is available in abundance in Morocco, it may be considered as an economically viable raw material.


All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Not applicable.

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

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