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Sustainable Banana-Waste-Derived Biosorbent for Congo Red Removal from Aqueous Solutions: Kinetics, Equilibrium, and Breakthrough Studies

Samah Daffalla ^{1,2,*}, Amel Taha ^{3,4}, Enshirah Da'na ⁵ and Mohamed R. El-Aassar ⁶

- ¹ Department of Environment and Agricultural Natural Resources, College of Agricultural and Food Sciences, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia
- ² Department of Chemical Engineering, College of Engineering, University of Khartoum, Khartoum P.O. Box 321, Sudan
- ³ Department of Chemistry, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia; ataha@kfu.edu.sa
- ⁴ Department of Chemistry, Faculty of Science and Technology, Al-Neelain University, Khartoum P.O. Box 11121, Sudan
- ⁵ Faculty of Engineering Technology, Al-Balqa Applied University, P.O. Box 15008, Amman 11134, Jordan; ensherah.azmi@bau.edu.jo
- ⁶ Department of Chemistry, College of Science, Jouf University, Sakaka 2014, Saudi Arabia; mrelaassar@ju.edu.sa
- * Correspondence: sbalal@kfu.edu.sa; Tel.: +966-135898731

Abstract: This study investigates the adsorption of Congo red (CR) dye from wastewater using banana peel biochar (BPBC) in both batch and fixed-bed column modes. BPBC was characterized using FTIR, SEM, XRD, TGA, and BET analysis, revealing a predominantly mesoporous structure with a surface area of 9.65 m²/g. Batch adsorption experiments evaluated the effectiveness of BPBC in removing CR, investigating the influence of the BPBC dosage, initial CR concentration, and solution pH. Results showed optimal CR removal at pH levels below 4, suggesting a favorable electrostatic interaction between the adsorbent and the dye. Furthermore, a pseudo-first-order kinetic model best described the adsorption process. The Freundlich isotherm provided a better fit compared to the Langmuir and Dubinin–Radushkevich (D-R) models, implying a heterogeneous adsorption surface. The calculated maximum adsorption capacity (Q_m) from the Langmuir model was 35.46 mg/g. To assess continuous operation, breakthrough curves were obtained in fixed-bed column experiments with varying bed heights (1–3.6 cm). The results demonstrated efficient CR removal by BPBC, highlighting its potential for wastewater treatment. Finally, this study explored the feasibility of BPBC regeneration and reuse through four adsorption–desorption cycles.

Keywords: banana peel biochar; Congo red; adsorption kinetics; adsorption isotherms; breakthrough; regeneration

1. Introduction

A biomass is a substance that comprises organic material (plant and animal byproducts) that is available naturally. Biomass can also be produced from sludge and industrial wastes. Many contaminants are currently removed from wastewater using biomass-based adsorbents. In addition to being eco-friendly and inexpensive, these materials are also abundant. The use of biomass can significantly reduce carbon emissions, contributing to the mitigation of global warming [1–4]. Wastewater can be treated effectively with biochar. Using thermochemical technology, biochar can be produced from biomass. Low pyrolysis, however, is one of the most effective thermochemical processes for producing biochar from biomass [1]. A variety of factors (temperature, reaction time, nitrogen flow, etc.) affect biochar production during pyrolysis. Biochar yield and quality are influenced



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). by the parameters listed above. The structure and content of cellulose, hemicelluloses, and lignin in biomass also affect biochar yield [1,5].

Dye pollution is a major problem in industrial effluents that causes significant damage to the environment [6]. Various types of dyes are available, including natural and synthetic ones. Natural dyes have almost been replaced by synthetic dyes due to the growing population and specific customer demands. In order to meet the demands of industries, over 1 million tons of dyes are manufactured each year worldwide [6,7]. A wide variety of industries utilize synthetic dyes, including textiles, paper, leather, and many others. Approximately 54% of the total dye effluent is generated by the textile industry [7]. As a result of dye effluents harming the ecosystem, their carcinogenicity, and their accumulation in organisms, dye effluents have drawn considerable attention in recent years [7]. When dyes are present in water, they prevent sunlight from reaching aquatic plants, cause degradable products to contaminate water and the increase water's COD [8]. It is difficult to treat dye-containing wastewater because of dyes' synthetic origins and complex structures, making them non-biodegradable and stable [3]. Even at very low concentrations, dyes decrease water clarity, making their treatment a primary concern [8].

To date, biological oxidation, coagulation, membrane separation, photocatalytic degradation, and adsorption have been evaluated as effective methods for removing dyes from wastewater [3,9–11]. Nevertheless, adsorption has demonstrated some success in the removal of dyes from aqueous solutions, and it is a technically feasible process as well [12,13]. Numerous studies have investigated the removal of dyes from aqueous solutions using a variety of biochars derived from agricultural by-products [13–18]. Biochar is an ideal adsorbent that can be developed from biomass through low-pyrolysis processes to adsorb dyes easily, sustainably, and in an environmentally friendly way [18].

On the other hand, banana peel can be used as a low-cost adsorbent. The peels of fruits generally contain lignin, cellulose, hemicelluloses, carboxyl, hydroxyl, and pectin substances, which enhance the interactions between the adsorbent and adsorbate [6]. Approximately 250 million tons of bananas are produced worldwide [6]. Once banana peel is used up, it is no longer useful and is free of charge. Banana peel is disposed of as market waste, causing environmental problems. As a result, carbon-rich agricultural residues disposed of in landfills can contribute to greenhouse gas emissions. Thus, making biochar from waste materials, particularly agricultural residues, would be economically beneficial, reduce waste, and add economic value.

In this paper, biochar produced from banana peel is investigated for its dye-binding properties. An examination of the characteristic of the developed biochar was conducted. Batch and continuous experiments were conducted to investigate Congo red (CR) dye adsorption. Pseudo-first-order and pseudo-second-order models were used to study the CR adsorption kinetics. A model of Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherms was used to predict the adsorption isotherms. Moreover, studies were conducted on adsorbent regeneration and re-use.

2. Materials and Methods

2.1. Materials

Congo red (CR), nitric acid (HNO₃), potassium hydroxide (KOH), sodium chloride (NaCl), sodium phosphate (Na₃PO₄), sodium nitrate (NaNO₃), and sodium hydroxide (NaOH) were supplied from Merck. Banana peel (BP) was collected from a nearby market. After thoroughly rinsing with distilled water, the banana peel was dried at 70 °C for 24 h, and ground into fine particles. A particle size of between 125 and 250 μ m was selected. Subsequently the ground banana peel was pyrolyzed for one hour at 600 °C without oxygen in a furnace to produce banana peel biochar (BPBC). The selected temperature was part of the input series applied to assess the best conditions for production of biochar from banana peel as per the literature [19,20]. The yield value of the produced biochar was 31%.

2.2. Instrument Analysis

The morphology of the BPs and developed biochar (BPBC) was directly observed with a scanning electron microscope (SEM model FEI, QUANTA FEG, 250). The SEM was operated at an accelerating voltage of 15 keV. The surface area and pore size distribution of the BPBC was obtained using the surface area and pore size analyzer model Micromeritics ASAP 2020 with nitrogen sorption at -196 °C. The sample was first degassed at 200 °C for 4 h. In order to calculate the surface area, the Brunauer-Emmett-Teller (BET) method was used, while Horwarth-Kavazoe and BJH methods were used to evaluate the micropores and mesopores, respectively. Thermogravimetric differential thermal analysis (TG-DTA, Perkin Elmer STA 6000), was performed at 30 °C to 800 °C with heating rates of 10 °C per minute using N^2 gas at 20 mL/min in order to determine the sample's weight loss and thermal stability. Crystalline and chemical compositions were determined using X-ray diffraction analysis (XRD analysis, model D8 Advance). The diffraction was operated at 40 kV and 40 mA for one hour over the range of 2 θ . Fourier-transform infrared spectroscopy (Cary 630 FT-IR Spectrophotometer model) was applied to analyze the structural properties of the biochar before and after adsorption. The spectra were taken in transmission mode in the region of $400-4000 \text{ cm}^{-1}$.

2.3. Determination of the pH of the Zero Charge Point (pH_{ZC})

To determine the pH_{ZC} of the BPBC, an equilibrium routine was established as described by [21]. Eight beakers were prepared with a 20 mL solution of 0.1 M NaCl; the pH value of these solutions was varied from 2.0 to 11.0 using 0.1 M NaOH and HNO₃ using a pH meter (Orion 2 star) to achieve the initial pH (pH_i). Next, 0.1 g of the BPBC was added to each beaker and stirred at room temperature for 24 h. Lastly, for each sample, the equilibrium pH (pH_e) was measured.

2.4. Adsorption Studies

The experiments were performed in a thermostatic shaker using an elementary flask (200 mL) containing 50 mL of the working solutions. Batch studies investigating the effects of several parameters on dye removal, including the pH (2–10), concentration (20– 100 mg/L), and BPAC dose (0.025–0.15 g), were conducted. In order to maintain the pH of the solution, 0.1 M NaOH or 0.1 M HNO₃ was added to the solution. A thermostatic shaker was used to shake the flasks for the required time period. Kinetic studies involved agitating flasks containing BPBC and a fixed concentration (20 mg/L) of CR dye at 120 rpm and 25 °C for varying durations (0–120 min). A Whatman syringe filter was used to filter the suspension at a predetermined time after the flask had been withdrawn from the shaker. The CR concentration in the filtered was measured at a wavelength of 557 nm with a UV-Vis spectrophotometer (Shimadzu, Tokyo, Japan). Equilibrium studies explored the effect of the initial CR concentration (20-100 mg/L) by shaking 0.1 g BPBC with different CR solutions for 24 h at 25 °C. A similar procedure was used to investigate the effect of salts on CR adsorption. In 50 mL of 20 mg/L CR dye solutions containing 0.1 M NaCl or 0.1 M Na₃PO₄, 0.1 g of BPBC was added. It was then shaken until equilibrium was reached. Upon reaching equilibrium, the dye concentration in the solution phase was determined.

To test the BPBC's reusability, dye-laden BPBC was first desorbed with 0.1 M KOH. Then, to wash the adsorbent, distilled water was used first, followed by 0.1 M HNO₃ until a pH close to 7.0 was achieved. A study of fourth-cycle adsorption–desorption adsorbent regeneration and reuse was conducted. All of the experiments were performed in duplicates. Equations (1) and (2) were used to determine the CR dye removal efficiency and adsorption capacity:

% Removal efficiency of
$$CR = \frac{(C_i - C_t)}{C_o} \times 100$$
 (1)

Amount adsorbed
$$(q_t) = \frac{(C_i - C_t)V}{W}$$
, (mg of adsorbate/g of adsorbent) (2)

where C_i and C_t (mg/L) are the influent and effluent concentrations (mg/L); *V* is the volume (L); and *W* is the mass of BPBC (g).

For practical applications, the performance of the BPBC was also tested in a column with a diameter of 1.4 cm and a length of 11 cm, with the BPBC packed in the column between glass wool as a support layer to prevent sorbent loss and clogging during operation. The BPBC was packed onto the column in quantities of 0.6 g (bed height: 1 cm), 1.2 g (bed height: 2 cm), and 2.17 g (bed height: 3.6 cm) at a 0.65 mL/min flow rate, with an initial pH of 3.0 and an initial CR concentration of 20 mg/L. Samples were taken from the bottom of the packed bed and analyzed. Based on the area under the plot of the adsorbed CR concentration, the maximum uptake capacity (q_{total} , mg) was calculated for a given inlet concentration and flow rate as follows [22]:

$$q_{total} = \frac{FA_r}{1000} = \frac{F}{1000} \int_{t=0}^{t=t_{total}} (C_i - C_t) dt$$
(3)

where the flow rate (mL/min), area under the curve (area), and total flow time (min) are represented by *F*, *Ar*, and t_{total} , respectively.

According to the equation below, the equilibrium uptake $(q_{e, exp})$ was calculated as the weight of CR adsorbed per unit dry weight of the adsorbent (mg/g):

$$q_{e, exp} = \frac{q_{total}}{x} \tag{4}$$

where *x* is the mass of the adsorbent in the bed (g).

To calculate the porosity of the packed bed column, we needed to determine the volume occupied by the adsorbent (BPBC) and the total volume of the column. Here is how we calculated this [23]:

$$V_{Column} = \pi r^2 L \tag{5}$$

$$V_{BPBC} = \frac{m_{BPBC}}{\rho_{BPBC}} \tag{6}$$

$$Total \ Porosity \ (\varepsilon_{total}) = \frac{V_{void}}{V_{column}}$$
(7)

where V_{Column} , V_{BPBC} , V_{void} , m_{BPBC} , ρ_{BPBC} , r, and L are the total volume of the column (cm³); total volume of the BPBC (cm³); void volume of the column (cm³), which is equal to $(V_{Column} - V_{BPBC})$; total mass of the BPBC (g); bulk density of the BPBC (g/cm³); radius of the column (cm); and height of the column (cm), respectively.

3. Results and Discussions

3.1. Characterizations

3.1.1. FTIR Analysis

An FTIR analysis of an adsorbent is essential for identifying its functional groups. Figure 1 shows the FT-IR spectra of the banana peel and produced biochar. According to Figure 1a, banana peel exhibits sharp peaks at 3280 cm⁻¹, which account for the -OH group or C-O-(H) bonds that are raised from the surface hydroxyl species for the adsorbed water molecules or intermolecular-bonded hydroxyl group involving phenols and alcohols [24]. The peaks at 2911 and 2851 cm⁻¹ are the result of C-H stretching vibrations [6,25]. The peak at 1722 cm⁻¹ (C=O) represents the symmetrical stretching vibration of carboxylic acids and ketones [14,25]. The observed peak at 1591 cm⁻¹ belongs to the vibrations of (C=C) in the aromatic ring from lignin. The peaks at 1025 and 801 cm⁻¹ represent C-OH and C-H stretching vibrations, respectively [24,25]. The origins of these functional groups are summarized in Table 1. The FTIR spectra of the banana peel biochar (Figure 1b) show a reduction in relative intensity, mainly as a result of the breakdown of carboxyl groups, at levels ranging from 4000 cm⁻¹ to 2000 cm⁻¹. The peak at 1594 cm⁻¹ may be attributable to aromatic C=C, which suggests that there were some relatively stable aromatic compounds

and/or graphitic structures present [24]. In a comparison between the BPBC and BP, we notice a decrease in or disappearance of significant peaks at 1050 and 1150 cm⁻¹, which are related to symmetric and asymmetric C-O stretching, demonstrating that hemicellulose, lignin, and cellulose present in the raw material were depolymerized and degraded owing to the pyrolysis process [26].



Figure 1. FT–IR spectra of (a) BP and (b) BPBC.

Table 1.	FTIR	functional	group	com	positions	of BP.

Wavenumber Range (cm $^{-1}$)	Wavenumber (cm $^{-1}$)	Details
3200–3600	3280	O–H bond from lignocellulose [24]
2850-3000	2851, 2911	C–H stretching vibration from hemicellulose [24]
1400–1600	1591	C=C aromatic-ring vibrations from lignin [24]
1210–1320	1261	C–O stretching from carboxylic acids of hemicellulose [27]
300–1100	801, 1025	O-H bending [25], C–O stretching [27]

3.1.2. SEM Analysis

Scanning electron micrographs of the raw banana peel and biochar are shown in Figure 2. In Figure 2a, a rough, irregular, and uneven external surface of the morphology of the raw banana peel is revealed in the micrograph [28]. In contrast, the biochar SEM image reveals a very porous surface and a surface that is not too smooth due to the pyrolysis process, which enhanced the porosity of the material (Figure 2b). By pyrolyzing carbonaceous raw materials, a large number of pores are created, which are suitable for adsorption [29]. According to the pyrolysis decomposition reactions, pyrolysis volatiles were produced and released from the banana peel, while a biochar with pores of varying sizes and shapes was formed from the remaining nonvolatile components (Figure 2b) [29,30]. The porous structure of the biochar supports its potential use as an adsorbent, as the pores could provide a large number of adsorption sites to bind desired molecules.



Figure 2. SEM images of (a) BP and (b) BPBC.

3.1.3. XRD Analysis

X-ray diffraction patterns were collected for the sample powders to identify the phases. The XRD patterns of the BP and BPBC samples are revealed in Figure 3. The diffraction peaks show a sharp peak for banana peel near $2\theta = 22.0^{\circ}$ and 40.6° , which corresponds to the reflection's planes (002) and (100) of the graphite carbon structure, respectively (JCPDS 41–1487) [31]. These diffraction peaks broaden after the pyrolysis process, which indicates the destruction of the biomass's graphite crystal structure during the pyrolysis process, resulting in the biochar composite material being amorphous [32]. Additionally, there is a relatively weak diffraction peak at $2\theta = 43.8^{\circ}$ in BPBC, which is characteristic of carbon structures. This resulted from the cracking of the graphene structure during pyrolysis. Sima et al. reported the appearance of the same peaks in rice husk biochar at $2\theta = 26^{\circ}$ and 43° [33]. Some other sharp peaks centered at 28.2 and 28.0° in both the BP and BPBC, respectively, are attributed to carbonate minerals such as calcite [34]. This result is in agreement with our FTIR results. It was reported by Liu et al. [35] that the adsorption efficiency of dye removal generally increases due to the formation of π - π interactions between the dye molecule and graphited carbon surface; this broadening initiated from the small dimensions of crystallites perpendicular to the aromatic layers, as confirmed with the IR spectra [35].

3.1.4. Thermogravimetric Analysis

The thermogravimetric analysis and resulting TGA curves were used to determine the thermal stability of the BP and BPBC. The BP and BPBC TGA curves showed a pattern of weight loss with increasing temperature (Figure 4). There was a 6.51% loss in BP weight from 45.00 °C to 145.52 °C at the first stage, as a result of moisture adsorbed on the surface

of the biochar, as well as functional groups [24]. Thermal degradation of the BP's cellulose and hemicellulose content could explain the 49.73% weight loss at the second stage from 145.52 °C to 377.14 °C [30]. The third stage, with a weight loss of 31.179% from 377.14 °C to 530.32 °C, shows that the pyrolysis reaction continued to decompose the cellulose and hemicelluloses [24]. In contrast, there was a two-step degradation of BPBC, where the weight loss decreased by 13% at the first stage, as a result of moisture adsorbed on the surface of the biochar as well as functional groups [24]. Upon reaching 550 °C, the weight loss reached 78.90% at the second stage. Based on the results, hemicellulose, cellulose, lignin, and polycyclic aromatic structures dominate biomass-derived biochar. It is possible to decompose hemicellulose when the temperature is between 220 and 315 °C. Between 315 and 400 °C, the cellulose and lignin decompose [30]. Further increases in temperature will cause the polycyclic aromatic structures to be destroyed completely [30]. Our FTIR and XRD results are also consistent with this result. The disappearance of many functional groups and the destruction of the graphite crystal structure of the banana peel after pyrolysis, as shown in the FTIR and XRD results, respectively, confirm that the structure of the banana peel was changed after pyrolysis, with a 91% weight loss in the BPBC.



Figure 3. XRD profile of BP and BPBC.



Figure 4. TGA curves of BP and BPBC.

3.1.5. BET Analysis

To determine the surface texture of the BPBC sample, a N₂ adsorption/desorption analysis was conducted using the BET method (Figure 5). Type-II and IV behavior with H3-type hysteresis can be deduced from Figure 5a, indicating complex material containing both mesopores and macroporous [36]. According to the BET results, the BPBC sample had a BET surface area of 9.649 m²/g and a total pore volume of 0.0086 cm³/g. A plot of the pore size distribution (PSD) for the BPBC sample is shown in Figure 5b. A Barrett–Joyner–Halenda (BJH) analysis was used to determine the PSD within a range of 13–130 nm. Macropores were detected in the BPBC sample, and the shape of the curve below 50 nm indicates mesopores as well. A large distribution of mesoporous sites makes the treatment procedure suitable for adsorption [36].



Figure 5. (a) N₂ absorption/desorption isotherms for the BPBC sample; (b) pore size distribution plot for the BPBC sample.

3.1.6. pH of the Zero Charge Point (pH_{ZC})

The pH of the zero charge point (pHzc) of BPBC depends on the chemical and electronic properties of the functional groups on its surface. Figure 6 shows the initial pH (pHi) measurement for NaCl solution after mixing with 0.1 g of BPBC with the pH varying from 2 to 11. In Figure 6, the BPBC has a pH_{ZC} of approximately 4.8. This value shows that this BPBC would be an efficient adsorption candidate for CR removal if the pH of the solution was adjusted to be less than 4.8. The BPBC surface can be protonated to have a positive charge if the solution has a pH value less than 4.8, and since CR is an anionic dye, there will be an attraction between them. Therefore, BPBC is expected to be an efficient anion adsorbent in a solution with a pH less than 4.8.

Many factors can affect CR dye removal using a biochar: (i) the dye's molecular weight and charge; (ii) the charge of the biochar functional groups; (iii) the capacity for cation exchange; (iv) the π - π interaction. The possible suggested adsorption mechanism for CR removal by BPBC is electrostatic attraction/repulsion between the dye charge and biochar surface. The pyrolysis process at a high temperature leads to the presence of electron-rich or electron-poor functional groups, which theoretically have the ability to interact with both electron donors and electron accepters [37,38]. The repulsion (electrostatically) between the functional groups in the biochar and the negatively charged CR could accelerate the adsorption process due to H-bonding. The same results were confirmed by Teixidó et al. [39]. This clearly indicates that the ionic strength effect on the surface of the adsorption material is completely pH-dependent. Accordingly, the adsorption efficiency of CR removal using BPBC depends on the pH of its zero charge point.



Figure 6. Effect of pHi on pHe for a 20 mL solution of 0.1 M NaCl containing 0.1 g of BPBC.

3.1.7. Post-Adsorption Characterization

According to Figure 7, the BPBC was tested before and after adsorption using FTIR. Based on a comparison of the FTIR spectra of BPBC and BPBC containing CR, a reduction in band intensities in the region between 1600 cm⁻¹ and 1731 cm⁻¹ caused by CR adsorption can be observed (Figure 7). It has been observed by other researchers as well that band intensities decrease after adsorption [40,41]. In addition, the BPBC spectrum after the adsorption of Congo red showed an absorption band corresponding to an azo group (N=N) at 1558 cm⁻¹. The stretching vibration at 1021.28 cm⁻¹ is due to the C-N bands [42]. It is therefore evident that banana peel biochar (BPBC) has an affinity for CR removal due to the presence of certain functional groups which result in its attraction during the adsorption process.



Figure 7. FT–IR of BPBC before and after CR adsorption.

3.2. Adsorption Studies

3.2.1. Effect of Adsorbent Type on CR Uptake

The adsorption capacities of banana peel and BPBC for the removal of 20 mg/L initial CR solution were evaluated for 24 h at pH 2.0 and 23 $^{\circ}$ C. Both adsorbents were

3.2.2. Influence of pH

further analysis due to its higher performance.

In this experiment, dye uptake and removal were tested at pH levels ranging from 2 to 10, while the remaining operating conditions were kept constant. The results shown in Figure 8a indicate that an acidic medium facilitates the removal of the dye. The removal rate is reported to decrease from 85.42% at pH 2 to 2% at pH 10. At a pH value of 2, a higher dye uptake of 6.83 mg/g was achieved, while at pH 10, it decreased to 0.16 mg/g. In alkaline media with an operating pH above 5, the OH ion concentration is high, creating an anionic charge on the BPBC and reducing the removal of anionic dyes. On the other hand, acidic media with a lower operating pH (less than 4) have high hydrogen-ion concentrations. The corresponding increase in hydrogen ions creates a positive charge on the BPBC, which improves the removal of anionic dyes by electrostatic attraction [43].



Figure 8. Influence of (a) $pH(C_i = 40 \text{ mg/L}, W = 0.1 \text{ g})$, (b) adsorbent dose ($C_i = 40 \text{ mg/L}, pH = 3$), and (c) initial dye concentration (pH = 3, W = 0.1 g) on CR removal and adsorption capacity using BPBC.

3.2.3. Influence of Adsorbent Dose

The effect of BPBC dosage on the removal efficiency and dye uptake was tested by varying the dosage from 0.025 to 0.15 g. The obtained trends are shown in Figure 8b. Increasing the dose from 0.025 to 0.05 g significantly increased the removal rate from 79% to 85%. The maximum removal trend obtained can be attributed to the increased amount of BCBC available at higher loads and the significant increase in adsorption sites. When the addition amount was further increased from 0.05 g to 0.15 g, it was observed that the removal rate decreased from 85% to 77%. This is because excessive amounts of adsorbent suspended in the solution can lead to the formation of aggregates, resulting in improper site utilization and reduced removal rates of adsorbed dye [44]. qt values were reported to decrease from 25.4 g for the 0.025 g dose to 4.11 g for the 0.15 g dose. A similar trend of low dye uptake and maximum removal was reported for anionic dye removal using waste tea residue [43]. According to these results, the optimal BPPC dosage was determined to maximize adsorption efficiency while ensuring practical removal rates.

3.2.4. Influence of Initial Concentration

Figure 8c shows the influence of the initial dye concentration on the adsorption capacity of BPBC within the concentration range of 20-100 mg/L, pH = 3, and with 0.1 g of the adsorbent. It is obvious from this figure that the adsorption of CR molecules is drastically influenced by the starting concentration. As the dye concentrations increased from 20 mg/L to 100 mg/L, the adsorption capacity increased also by a factor of almost 5 (from 2.92 mg/g to 13.09 mg/g), indicating a direct linear relation between q (mg/g)and C (mg/L). This enhancement in uptake capacity could be related to the amplification of the concentration gradient through increasing the initial concentration (C_i) , which in turn facilitates the transfer of CR molecules from the bulk solution to the surface of the BPBC. Accordingly, reducing the mass-transfer resistance at a higher initial concentration led to faster kinetics and a higher adsorption capacity [45]. On the other hand, a decrease in the removal efficiency from 89% to 66% when increasing the initial concentration from 20 mg/L to 100 mg/L was observed. This phenomenon is related to the saturation of available adsorption sites on the surface of the BPBC at higher initial concentrations. Thus, CR becomes the excess component, while adsorption sites are the limiting factor. Despite the constant amount of active sites on the BPBC surface, the capacity to accommodate dye molecules becomes limited at higher C_i values, resulting in less remediation efficiency [45]. These findings highlight the importance of optimizing the initial dye concentration to maximize the adsorption efficiency while ensuring practical removal rates for commercial applications. One possible way to overcome this limitation is to increase the mass of adsorbent used to increase the number of available adsorption sites, as shown in Figure 8b.

3.2.5. Adsorption Kinetics

An analysis of experimental data was conducted using first-order and second-order kinetic models to understand the adsorption mechanisms. With 50 mL of the 20 mg/L CR solution mixed with 0.1 g of BPBC, the concentration of CR as a function of time was monitored by measuring the UV absorbance at 557 nm every 5 min for 120 min. The UV spectra of the CR solution during the adsorption by BPBC are shown in Supplementary Material Figure S1. Equation (8) can be used to express a first-order kinetic model in linear form [46].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

Using the second-order model, the kinetic data were further analyzed. The linear form of this model can be seen in Equation (9) [46].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(9)

Kinetic modeling of the CR dye adsorption process was performed using both pseudofirst-order and pseudo-second-order models. The corresponding linear regression plots are presented in Figure 9, and the extracted kinetic parameters are summarized in Table 2. Based on an analysis of Figure 9 and Table 2, the pseudo-first-order kinetic model exhibits the best fit to the experimental data for the adsorption rate of CR dye. This is evidenced by the higher coefficient of determination ($R^2 = 0.9456$) compared to the pseudo-secondorder model ($R^2 = 0.8585$). Additionally, the calculated adsorption capacity (q_e) obtained from the pseudo-first-order model (3.69 mg/g) demonstrates good agreement with the experimentally determined value (3.16 mg/g). Notably, prior research in [47] also reported the successful application of the pseudo-first-order model for the adsorption of Congo red dye onto industrial waste, suggesting the potential universality of this model for CR dye adsorption.



Figure 9. Linear plot of the (a) first-order and (b) second-order kinetic models.

Kinetic Models	Pseud	lo-First-Order		Pseudo-Second-Order		
Parameters	q _{e,cal} (mg/g)	k_1 (min ⁻¹)	R ²	q _{e,cal} (mg/g)	k₂ (g/mg·min)	R ²
$q_{e,exp}$ (3.16)	3.69	0.0265	0.9456	4.04	0.006	0.8585

Table 2. Constant parameters and correlation coefficients of the kinetic models.

3.2.6. Adsorption Isotherms

Three commonly used models, namely the Freundlich isotherm, Langmuir isotherm and Dubinin–Radushkevich (D-R) isotherm, were selected to simulate the adsorption isotherms between the dye and BPBC. The Langmuir equation is presented as follows [48]:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}.b} + \frac{C_e}{Q_{max}} \tag{10}$$

where the maximum adsorption capacity is Q_{max} , and the Langmuir constant is b (L/mg). The Freundlich isotherm is presented below [48]:

$$Log(q_e) = Log(K_F) + \left(\frac{1}{n}\right) Log(C_e)$$
(11)

where K_F (mg/g (L/mg)^{1/n}) and *n* are Freundlich constants.

The Dubinin–Radushkevich (D-R) isotherm is presented as follows [49]:

$$Ln\left(q_{e}\right) = Ln\left(q_{m}\right) - \beta\varepsilon^{2} \tag{12}$$

where q_m is the Dubinin–Radushkevich monolayer capacity (mg/g), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol² /kJ²), ε is the Polanyi potential, which is equal to RTLn(1 + (1 + Ce)), R is the gas constant (8.314 kJ/mol K), and T is the absolute temperature (K). The sorption energy can also be worked out using the following Equation (13):

$$E = 1/\sqrt{2\beta} \tag{13}$$

where *E* is the mean adsorption energy (kJ/mol).

The Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) plots of CR adsorption on BPBC are shown in Figure 10. Table 3 shows the parameters and R^2 values for these isotherm models. This work specifies favorable adsorption with 1/n values smaller than unity [48], and according to Langmuir's constants, Q_{max} is 35.46 mg/g, and b is 0.016 L/mg (Table 3). In comparison with the Langmuir and D-R equations, the Freundlich equation R^2 value is very close to unity (mean of 0.9844), which describes a heterogeneous system that is not limited to monolayer formation [47,48]. According to the Freindlich model, BPBC surfaces are heterogeneous and can be divided into two regions based on their multilayer adsorption processes: as a result of geometric constraints, one region can support only a limited number of layers, while another region can support an unlimited number [47]. Similar results were reported for the uptake of CR on nanocrystalline hydroxyapatite and industrial waste, respectively [47]. The Dubinin–Radushkevich constant was calculated and is given in Table 3. Also, the correlation coefficient was determined and is shown in Table 3, and the value of this correlation coefficient is less than those of the Langmuir and Freundlich models. By calculating the mean adsorption energy (E), a D-R isotherm can be used to estimate the type of adsorption process. Adsorption is classified as an ion exchange or chemisorption process if (E) is between 8 and 16 KJ/mol, and as physical adsorption if it is less than 8 KJ/mol [50]. A physiosorption process is indicated by the E values of 0.316 kJ/mol calculated in this study.

Table 3. Isotherm model parameters.

Т (°С)	Langmuir Isotherm				Freundlich Isotherm]	Radushkevich (D-R) Isotherm		
25	b (L/mg)	Q _{max} (mg/g)	R ²	1/n	$K_{\rm F} ({ m mg/g} \ ({ m L/mg})^{1/n})$	R ²	q _m (mg/g)	β (mol ² /kJ ²)	E (kJ/mol)	R ²
	0.016	35.46	0.807	0.821	1.312	0.984	9.83	$5 imes 10^{-6}$	0.316	0.805

3.2.7. Comparative Study of BPBC with Other Adsorbents

As shown in Table 4, the BPAC's maximum adsorption capacity (Q_{max}) was compared to that of other adsorbents used by other researchers. Comparatively to other adsorbents, BPBC has a good adsorption capacity.

Table 4. A comparison of CR maximum adsorption capacity by different adsorbents.

Adsorbents	Q _{max} (mg/g)	References	
Acid-activated red mud	7.08	[51]	
Coir-pith-activated carbon	6.70	[52]	
Cashew nut shell	5.184	[53]	
Calotropis procera leaf	25.8	[54]	
Commercial silica gel (CSG)	66.5	[55]	
Tea waste	43	[56]	
Kenaf	14.2	[57]	
	35.84		
NaBentoniteKaolinZeolite	5.44	[58]	
	3.77		
Cabbage waste powder	2.313	[59]	
Banana-peel powder	164.60	[60]	
Banana peel	1.72	[61]	
BPBC	35.46	This study	



Figure 10. (a) Langmuir, (b) Freundlich, and (c) Dubinin–Radushkevich (D-R) isotherm plots for the removal of CR by BPBC.

3.2.8. Effect of Salt on Dye Adsorption

The impact of various salts (NaCl and Na₃PO₄) on CR removal efficacy was investigated, and these results are presented in Table 5. The data reveal a significant influence of both cation and anion types on the adsorption process. For the negatively charged CR dye adsorbing onto the positively charged BPBC adsorbent, the primary interactions are attributed to hydrophobic and electrostatic attractions, as previously reported [62]. The observed enhancement in CR removal with NaCl addition can be explained by the promotion of CR dye dimerization in the solution. Alberghina et al. [63] have extensively studied the effect of salt and temperature on this phenomenon. The aggregation is attributed to various intermolecular forces, including van der Waals forces, ion–dipole forces, and dipole–dipole forces. These forces are reported to strengthen with an increasing salt concentration in the solution [64].

Table 5. The effect of salt on CR adsorption.

	Normal	NaCl	Na ₃ PO ₄	
Adsorption capacity (mg/g)	3.572	1.868	1.076	

In contrast to NaCl, the higher valence phosphate anion (Na_3PO_4) resulted in a lower CR adsorption capacity. This suggests a potentially positive influence of cation valence and a negative influence of anion valence on CR removal [64]. This observation aligns with the decrease in electrostatic attraction observed at higher ionic strengths in other studies [62]. However, further investigations are warranted to elucidate the specific mechanisms governing these interactions.

3.2.9. Recycling Test

Figure 11 illustrates the four-cycle reusability trend. From 73% in the first cycle to 16% in the fourth cycle, the percent removal efficiency decreased. Several possible reasons may have contributed to this drastic drop in efficiency. First, adsorbent degradation upon the repeated exposure of the adsorbent to the target adsorbate is expected to cause some physical or chemical changes, affecting its performance over multiple adsorptiondesorption cycles. Second, the desorption and regeneration protocol followed in this work may not have been sufficient for the complete leaching of all dye species from the surface, resulting in a lower number of free active sites after each successive cycle. The third possible reason is agglomeration of the adsorbent particles during the adsorption process, which may have added extra mass-transfer limitations, thereby decreasing the overall adsorption capacity over successive cycles. To solve these issues and enhance the reusability of the adsorbent, an optimization study of the regeneration conditions should be performed to find the optimum regeneration protocol that ensures complete desorption of the dye molecules and minimizes the possibility of any degradation of the adsorbent. This can be achieved via comprehensive characterization to clarify the mechanisms of this observed drastic loss in adsorption capacity [43].



Figure 11. Recycling BPBC for the repeated adsorption-desorption of CR.

3.2.10. Column Study

The effects of different packing heights of the BPBC (1, 2, and 3.6 cm) on breakthrough profiles in our column adsorption studies is illustrated in Figure 12. Supplementary Material Figure S2 presents the corresponding changes in UV spectra of the Congo red (CR) solution during the column adsorption by BPBC at a bed depth of 3.6 cm. According to Figure 11, both the breakthrough and exhaustion times increased with the bed depth. For instance, the breakthrough time increased from 70 min for a 1 cm bed depth to 240 min and

560 min for bed depths of 2 cm and 3.6 cm, respectively, which highlights the implication of bed depth in controlling the efficiency of the adsorption process. Increasing the bed height expanded the contact time between the dye solution and the adsorbent, leading to a higher adsorption capacity and allowing a larger amount of solution to be treated. The increase in the breakthrough time with higher bed depths is mainly related to having more adsorbent in the column and thus more active sites available for capturing the dye molecules, leading to a higher adsorption capacity and longer time of treatment before the break. Furthermore, it may be attributed to the reduction in axial dispersion of mass transfer within the column. With a greater mass of adsorbent available for interaction, there is a more efficient diffusion of dye molecules towards the adsorbent surface [43]. Consequently, the extended contact time facilitates greater adsorption capacity and delays breakthrough as a result of improving the efficiency of the adsorption process. The results obtained from the column studies show that BPBC is a very promising adsorbent with high efficiency in capturing CR from aqueous solutions. With a bed height of 3.6 cm, BPBC achieved a maximum equilibrium capacity $(q_{e,exp})$ of 7.02 mg/g, and the porosity of the column was 0.827, emphasizing its potential as an effective and promising adsorbent for the adsorption of CR from water systems. Furthermore, the breakthrough curve obtained for the three bed depths is very steep (sharp), indicating a small mass-transfer zone and high mass-transfer coefficient. These results highlight the significance of bed depth in continuous adsorption processes to minimize the mass-transfer resistance and thus to enhance the efficiency and effectiveness of BPBC.



Figure 12. Breakthrough for CR at bed depths of 1, 2, and 3.6 cm.

4. Conclusions

Batch and column adsorption experiments were conducted to measure the effectiveness of using a BPBC adsorbent to adsorb Congo red dye. It was found that BPBC can efficiently remove CR from aqueous solutions. The SEM results show that BPBC is a viable alternative for CR removal based on its potential use as an adsorbent. According to our BET calculations, this BPBC adsorbent removes CR effectively from aqueous solutions based on its specific surface area, pore volume, and average pore diameter. Electrostatic attraction enhances dye removal under acidic pH conditions. The adsorption capacity was found to decrease with increasing ionic strength. Freundlich, Dubinin–Radushkevich, and Langmuir isotherm equations were employed to elucidate the CR's adsorption onto the BPBC. The Freundlich model revealed the highest R^2 value (0.984) among the four models. The kinetics were well described by employing a pseudo-first-order model. BPBC's suitability for applications on a commercial scale was confirmed by performing a continuous study conducted in a packed bed with an adsorption capacity of 7.02 mg/g. Furthermore, the breakthrough curve obtained for the three tested bed depths was very steep (sharp), indicating a small mass-transfer zone and high mass-transfer coefficient. For an industrial-scale remediation application, BPBC appears to be an effective, cost-effective, and environmentally friendly adsorbent.

Supplementary Materials: The following supporting information can be downloaded at https://www. mdpi.com/article/10.3390/w16101449/s1: Figure S1: The change in UV spectra of the CR solution during the kinetic adsorption by BPBC for wavelengths of 200–900 nm. Figure S2: The change in UV spectra of the CR solution during the column adsorption by BPBC (3.6 cm bed depth) for wavelengths of 200–900 nm.

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