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Removal of Reactive Black 5 *Dye* by Banana Peel Biochar and Evaluation of Its Phytotoxicity on Tomato

Riti Thapar Kapoor [1], Mohd Rafatullah [2,*], Masoom Raza Siddiqui [3], Moonis Ali Khan [3] and Mika Sillanpää [4]

[1] Amity Institute of Biotechnology, Amity University Uttar Pradesh, Noida 201 313, India; rkapoor@amity.edu
[2] Division of Environmental Technology, School of Industrial Technology, Universiti Sains Malaysia, Penang 11800, Malaysia
[3] Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; mrsiddiqui@ksu.edu.sa (M.R.S.); mokhan@ksu.edu.sa (M.A.K.)
[4] Department of Biological and Chemical Engineering, Aarhus University, Nørrebrogade 44, 8000 Aarhus C, Denmark; mikasillanpaa@bce.au.dk
* Correspondence: mrafatullah@usm.my

Abstract: Removal of Reactive Black 5 (*RB*5) *dye* from an aqueous solution was studied by its adsorption on banana peel biochars (BPBs). The factors affecting *RB*5 *dye* adsorption such as pH, exposure time, *RB*5 *dye* concentration, adsorbent dose, particle size and temperature were investigated. Maximum 97% *RB*5 *dye* removal was obtained at pH 3 with 75 mg/L adsorbate concentration by banana peel biochars. Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were used to characterize the adsorbent material. The data of equilibrium were analyzed by Langmuir and Freundlich isotherm models. The experimental results were best reflected by Langmuir isotherm with maximum 7.58 mg/g adsorption capacity. Kinetic parameters were explored and pseudo-second order was found suitable which reflected that rate of adsorption was controlled by physisorption. Thermodynamic variables exhibited that the sorption process was feasible, spontaneous, and exothermic in nature. Banana peel biochar showed excellent regeneration efficiency up to five cycles of successive adsorption-desorption. Banana peel biochar maintained >38% sorption potential of *RB*5 *dye* even after five cycles of adsorption-desorption. The phytotoxic study exhibited the benign nature of BPB-treated *RB*5 *dye* on tomato seeds.

Keywords: banana peel biochar; reactive black 5; isotherm; kinetic; phytotoxicity; tomato

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1. Introduction

The exponential growth in global population, industrialization, urbanization, and unskilled utilization of natural water resources has enhanced the requirements of freshwater. Due to the limited availability of freshwater resources, currently 1 billion people have no safe drinking water but this number may rise as world population is predicted to increase up to 10 billion by the year 2050 [1]. *Dyes* are widely used for the coloration of materials in textile, plastic, cosmetics, pharmaceutical, and paper industries [2–5]. Increasing demand for *dyes* in different industries has exacerbated the release of *dye* wastewater into the environment [6,7]. The textile industry, one of the big industries globally, utilizes synthetic *dyes* and approximately 8×10^5 tons of *dye* are produced per year [8,9]. Most of the textile industries are located in developing nations where they enhance employment opportunities and boost the economy of a country by foreign exchange earnings [10]. The textile industry consumes approximately 56% of total *dye* generated every year at a global level and releases >280,000 tons of *dyes* as industrial effluent which poses serious threat to the ecosystem [11,12]. The presence of a small amount of *dye* in water (<1 ppm) is quite visible and unacceptable [13,14]. Most of the industries do not follow effluent discharge norms properly and they release large quantities of untreated or partially treated *dye* effluents in water resources, resulting pollution of the environment with a decrease in the availability of clean water [15,16]. The presence of *dyes* not only degrades the aesthetic value of water but also alters pH, BOD, and COD, enhances toxicity and turbidity, and reduces the sunlight penetration into water which leads to the deterioration of aquatic ecosystems [17,18]. *Dyes* show mutagenic and carcinogenic effects on animals and humans [11]. *Dye* adversely affects brain, kidney, liver, heart, respiratory, immune, and reproductive systems in humans [19]. Reactive *dyes* are utilized in fabric industries because of fast coloration, availability of reactive groups to form covalent bonds with different types of fibers, wide ranges of colors for printing and their permanent effect under a wide range of temperature [20]. According to Jozwiak et al. [21] around thirty percent of total coloring materials in the world are composed of reactive *dyes*. Reactive Black 5 (*RB*5), tetrasulphonated disazo *dye*, is used in fabric industries for coloring nylon and cotton stuff, etc. [22]. Reactive Black 5 and its intermediates are highly toxic in nature; however, no information is available in literature on the adverse effects of *RB*5 *dye* on animals, most of the reports revealed its deleterious impacts on human health. Some reports are available on Reactive red 120 which exerts genotoxic impact on *Catla catla* and damage DNA in the cells [23]. Reactive Black 5 exhibited adverse impacts on aquatic animals such as zebrafish embryo and digestive and central nervous system of humans [24,25]. The exposure to the *RB*5 *dye* causes allergy, skin irritation, nausea, bronchitis, confusion, high bold pressure, headache, cancer, etc., [26]. Removal of *dye* from industrial runoff is an arduous task due to stability of *dyes* against light, oxidation, temperature, and complex aromatic structure [27]. Different conventional methods such as coagulation, flocculation, electrochemical degradation, oxidation, membrane separation, ultra-filtration, microbial degradation, reverse osmosis, ion exchange, ozonation, and adsorption have been exploited to treat *dye* containing effluent [28–33]. Commercial adsorbents such as activated carbon, chitosan, graphene, and zeolite have been applied for removal of harmful contaminants from wastewater [34–36]. The Abovementioned wastewater treatment technologies are expensive, complex in operation, take a long operation time and are ineffective for *dye* removal on a large scale with sludge production at the end of the process.

Adsorption is considered as a significant treatment method because of its simple, affordable, and cost-effective nature and capacity to use locally available waste biomass [33]. Agricultural wastes such as wheat straw, cabbage and coconut waste, peanut husk, pumpkin seed hulls, mango seed husks, cashew nutshell, bamboo, spent tea leaves, walnut shells and orange peel have been used in preparation of carbon materials that can absorb *dye* from wastewater [37–40]. Biochar produced from agro-wastes are a rich source of bioavailable nitrogen, phosphorus, potassium, and magnesium [41]. Due to the high specific surface area and availability of functional groups on their surface, biochar can be used for the adsorption of contaminants. Banana (Family: Musaceae) plant grows around the year in the places with tropical climate. Banana peels are rich in carbon amount due to cellulose, hemicellulose, chlorophyll, and pectin presence and can be considered an excellent source of activated carbon [24]. The presence of functional groups such as hydroxyl, carboxyl, carbonyl, and amide groups on banana peel surface act as a binder in the adsorption process [24]. Banana peel has the potential to remove heavy metals, and pharmaceutical and phenolic compounds as reported by earlier workers [42,43]. Application of banana peel as an adsorbent removes contaminants from wastewater as well as solves the disposal problem of biowaste. In the earlier published work of Munagapati et al. [24], they used chemically modified banana peel powder for removal of *RB*5 *dye*. Their process was not eco-friendly as they utilized chemicals such as HCHO and HCOOH for modification/activation of banana peel biochar. They did not report the effect of chemically modified banana peel powder-treated *RB*5 *dye* solution on the growth of plants. In our study, we did not utilize any chemicals, so our process is environmentally benign. We also checked the impact of banana peel biochar-treated *RB*5 *dye* solution on germination and growth of tomato seeds. The irrigation of agricultural fields with *dye* contaminated water or industrial effluent inhibits crop growth and reduces land productivity [44,45]. In the present study, we wanted to evaluate the applicability of BPB-treated *RB*5 *dye* contaminated water for irrigation purposes. Wastewater after biochar treatment can be reused for various purposes and it can reduce the demand of fresh water. To the best of our knowledge, the phytotoxic effect of Reactive Black 5 *dye* and banana peel Biochar (BPB)-treated RB 5 *dye* solution on the development of tomato plants was not reported previously. Hence, the objective of the present investigation was to develop efficient and cost-effective adsorbent from banana peel for Reactive Black 5 *dye* removal from contaminated water and to analyze its impact on various growth parameters of tomato plants.

2. Materials and Methods

2.1. Preparation of Banana Peel Biochar and Proximate Analysis

Bananas were purchased from the local market of Noida, Uttar Pradesh, India. Banana peel was washed in tap water for 4–5 min, washed thrice with double deionized water to remove dust from its surface [46,47] as the presence of dust may provide different results of proximate analysis. Banana peel was cut into small pieces and dried at room temperature for 5 days to reduce moisture. The pyrolysis reactor was used for generation of biochars with nitrogen gas inside a pyrolyzer and the temperature was regulated by an electric heater. Dried banana peel was crushed and pyrolyzed at 500 °C for 3 h. Banana peel biochar was washed with lukewarm double deionized water and kept at 75 °C for 2 h in an electric oven to check micro-organisms growth [48]. The proximate analysis of BPB was conducted to confirm its stability for thermochemical transformation procedure. The proximate analysis was performed to verify ash, moisture, volatile material, and carbon contents.

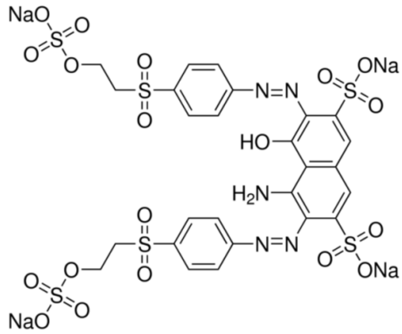
2.2. Preparation of Dye Stock Solution

Reactive Black 5 *dye* was obtained from Sigma Aldrich (Mumbai, India). *RB*5 *dye* (1000 mg/L) stock solution was prepared with sterilized double deionized water which was used to prepare different concentrations as per requirements. The absorbance of *dye* was measured by UV-vis spectrophotometer (Shimadzu 1800, Kyoto, Japan) and the maximum absorbance (λmax) for *RB*5 *dye* was recorded at 597 nm (Table 1).

Table 1. Properties of *RB*5 *dye*.

Dye	***RB5***
Chemical name	Remazol Black B
Solubility	High solubility in water, easily forms covalent bonds with cellulosic fibers, resistant to sunlight and aerobic decomposition
Melting point	>300 °C
CAS number	17095-24-8
Dye type	Anionic *dye*
Appearance	Black colored powder
IUPAC Name	4-amino-5-hydroxy-3,6-bis[[4-(2-sulfonatooxyethylsulfonyl)phenyl]diazenyl]naphthalene-2,7-disulfonate
Empirical Formula	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Molecular Weight	991.82 g/mol

Table 1. *Cont.*

Dye	***RB5***
Molecular Structure	
λmax	597 nm

2.3. Characterization of Banana Peel Biochar

Functional groups available on banana peel biochar (BPB) prior and afterwards *RB*5 *dye* sorption were analyzed by FTIR (Fourier-transform infrared spectroscopy) (Perkin Elmer 2000, Waltham, MA, USA) in wavenumber (400–4000 cm^{-1}) by utilizing KBr pellet method. Outer surfaces of BPB prior and afterwards *RB*5 *dye* sorption were observed by scanning electron microscopy (SEM) (Quanta FEG 650, Thermofisher, Beverly, CA, USA).

2.4. Batch Adsorption Experiments

The batch study was carried out to detect applicability of BPB as an adsorbent for removal of *RB*5 *dye*. The impact of various variables such as pH (3–11), adsorbent dose (0.2–1.0 g), size of particles (0–500 µm), concentration of *dye* (25–150 mg/L), temperature (25–65 °C), and contact time (30–180 min) were assessed at stirring speed 120 rpm for *RB*5 *dye* removal from aqueous solution by BPB. The experiment was conducted in six sets and in each set eighteen Erlenmeyer flasks were taken as triplicate, each flask with 100 mL of *RB*5 *dye* concentrations (25, 50, 75, 100, 125, and 150 mg/L) and 0.2, 0.4, 0.6, 0.8, 1, and 1.2 g BPB, respectively. The experiments were performed in triplicate. In the control set, no banana peel biochar was used in the *RB*5 *dye* containing flasks but in treatment, different concentrations of BPB were added in *RB*5 *dye* solution to study its *dye* sorption capacity. The UV-vis spectrophotometer (λmax = 597 nm) was utilized to detect concentration of *RB*5 before and after BPB treatment and the absorption efficiency was measured by the following formula:

$$Removal\ of\ RB5\ dye = {C_0 - C_t}\Big/{C_0} \times 100 \tag{1}$$

C_0 and C_t are initial and final *RB*5 *dye* concentrations in mg/L.

The isotherm models were applied for determination of sorption equilibrium. A total of 100 mL of *RB*5 *dye* (25–150 mg/L) solution were taken with different dosages of BPB to confirm the feasibility of the isotherm by comparing the adsorption potential. The Langmuir isotherm indicates that adsorption energy is constant over the adsorbate layer on the adsorbent surface at a constant temperature [49]. Langmuir equation is expressed as:

$$C_e\Big/q_e = \frac{1}{q_e}K_L + \frac{C_e}{q_m} \tag{2}$$

where q_e (mg/g) = *RB*5 *dye* adsorbed at equilibrium, q_m (mg/g) = maximum *RB*5 adsorbed, C_e = *dye* concentration at equilibrium (mg/L), K_L = Langmuir constant for binding ability of *RB*5 on BPB.

The Freundlich isotherm illustrates distribution of *dye* molecule between BPB and solution at equilibrium. The isotherm defines an expanding inconsistency of active sites surface energy during adsorption and reduction in adsorption heat [50]. The Freundlich equation can be mentioned as:

$$lnq_e = lnK_F + \left(\frac{1}{n}\right)lnC_e \tag{3}$$

where Freundlich constants n = intensity of sorption and K_F = uptake capacity (n shows nature of process, $n < 1$ indicates chemisorption, $n > 1$ implies physisorption and $n = 1$ shows linear sorption).

The kinetic study determines the equilibrium time and rate of adsorption through adsorption modelling. Two kinetic models such as pseudo-first and second order were applied for rate constant calculation in sorption procedure. The pseudo-first order [51] and pseudo-second order [52] reaction mechanism were calculated by given equations:

$$\ln(q_e - q_t) = lnq_e - K_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e and q_t are *RB*5 *dye* adsorbed at equilibrium and time, k_1 = pseudo-first order adsorption rate constant (min^{-1}), and k_2 = pseudo-second order adsorption rate constant (g/mg.min).

2.5. Regeneration Analysis

The regeneration analysis was performed by the procedure of Kapoor and Sivamani [53]. In *RB*5 *dye* solution (100 mL) of 75 mg/L concentration, 0.8 g BPB was added and kept in shaking incubator under constant shaking condition at 32 °C for 45 min. Banana peel biochar containing *dye* was segregated by centrifugation. After filtration with Whatman no. 1 filter paper, the filtrate was analyzed by measuring absorbance for determination of *dye* content adsorbed by BPB. The blank sample (without BPB) was taken to compare the impact of BPB on *RB*5 *dye* removal compared with those samples in which BPB was added. After that, 0.1 g of *RB*5 *dye* containing biochar was placed at 50 °C for 6–7 h as drying may influence the sorption ability and microstructure of BPB [54] which was mixed with the desorbing solution. For the desorbing solution, 1N HCl and 1N NaOH reagents each were prepared in two different flasks separately and BPB was first washed with 1N HCl. Then the same biochar was washed with 1N NaOH and agitated at 180 rpm for 45 min. *RB*5 present in desorbing solution was recorded by UV-vis spectrophotometer. BPB isolated from desorbing solution was washed with sterilized distilled water three to four times to remove the desorbing solution and particles of BPB were kept at 50 °C for 9 h. The regeneration analysis was conducted up to five cycles for identification of re-applicability of used biochar. *Dye* desorption (%) was calculated by following formula [55]:

$$Desorption\ (\%) = Amount\ of \frac{RB5desorbed}{Amount} of\ RB5\ adsorbed \times 100 \tag{6}$$

2.6. Evaluation of Phytotoxicity

Reactive Black 5 *dye* toxicity before and after treatment with BPB was tested on tomato seeds. A total of 9 test tubes, 9 petri plates, and 90 tomato seeds were taken for the phytotoxicity test. Seeds of tomato (*Solanum lycopersicum* L. variety Heera) were washed with tap water and the surface of seeds was sterilized with sodium hypochlorite solution (10% w/v) for 5 min for inhibition of microbial activities and cleaned again with sterilized distilled water. As the experiment was conducted in triplicate, nine test tubes were arranged and in each test tube, ten tomato seeds were kept in 10 mL of distilled water, *RB*5 *dye* solution (75 mg/L), and BPB-treated *RB*5 *dye* solution, respectively for 4 h according to the treatment. Soaking of the tomato seeds was performed for the activation of enzymes. Then, tomato seeds were transferred into sterilized petri plates (ten tomato seeds were placed in each petri plate) and the petri plates were kept in the seed germinator for 8 days under 87% relative humidity with 12 h photoperiod at 26 ± 2 °C. Three petri plates were taken for the control, three petri plates for *RB*5 *dye*, and three petri plates were taken for the BPB-treated *RB*5 *dye* solution. In the control set, distilled water was used for watering/irrigation of tomato seeds whereas two other sets were arranged in which tomato seeds of the second set were irrigated with *RB*5 *dye* solution (75 mg/L) and in the third set BPB-treated *RB*5 *dye* solution was used for watering of tomato seeds. *RB*5 *dye* concentration (75 mg/L) was selected for the evaluation of phytotoxic effects of *RB*5 *dye* on tomato seeds as maximum *dye* removal was obtained with this concentration in the batch study. Seed germination, length, and *vigor index* of 90 seedlings were measured in the control and treatment set of all the nine petri plates after 8 days of treatment [56]. The *germination percentage* and *vigor index* were analyzed by a given equation [57]:

$$\begin{aligned} Germination\ (\%) \quad &= Total\ number\ of\ tomato\ seedsgerminated \\ &/Total\ number\ of\ tomato\ seeds\ taken\ for\ germination \\ &\times 100 \end{aligned} \tag{7}$$

$$Vigor\ index = Total\ length\ of\ seedling\ in\ mm \times germination\ percentage \tag{8}$$

2.7. Estimation of Biochemical Components

The chlorophyll content was assessed in tomato seedlings through the Lichtenthaler [58] procedure. The total sugar and protein contents present in tomato seedlings were analyzed by the method of Hedge and Hofreiter [59] and Lowry et al. [60], respectively.

2.8. Statistical Analysis

Treatments with three replicates were arranged in a randomized block design. A randomized block design is an experimental design in which the experimental units are kept in groups called blocks. Data were analyzed by ANOVA and SPSS software and the treatment mean was calculated by DMRT at $p < 0.05$.

3. Results and Discussion

3.1. Proximate Analysis of Banana Peel Biochars

The proximate analysis was performed to confirm the amount of ash, fixed carbon, volatile material, and water content in banana peel biochar. Results reflected that BPB have 4.72% fixed carbon, 72.45% volatile material, 12.5% moisture, and 10.23% ash contents.

3.2. Characterization of Banana Peel Biochars

The spectrum 3407 cm^{-1} is assigned to OH stretching vibrations which may be due to the presence of moisture on BPB. The spectrum at 2920 and 2913 cm^{-1} was due to the CH-stretching vibration while the band at 2259 cm^{-1} showed the presence of C=C stretching vibration. The 1705 and 1726 cm^{-1} bands indicated C=O which showed the presence of carboxylic groups on BPB. The band at 1400 cm^{-1} reflected the CH bending vibration which showed stable binding and significant in adsorption process. There was a change in the CH stretching vibration at spectra 2130 cm^{-1} which reflected the presence of the methoxyl group as a result of the removal of lipids and lignin (Figure 1). The increase in the intensity of spectra after adsorption was due to the presence of C=C stretching vibration. Hydroxyl and carboxylic groups affected *RB*5 adsorption [61]. The decrease in C-O-H stretching vibration peak in secondary cyclic alcohol was recorded after adsorption.

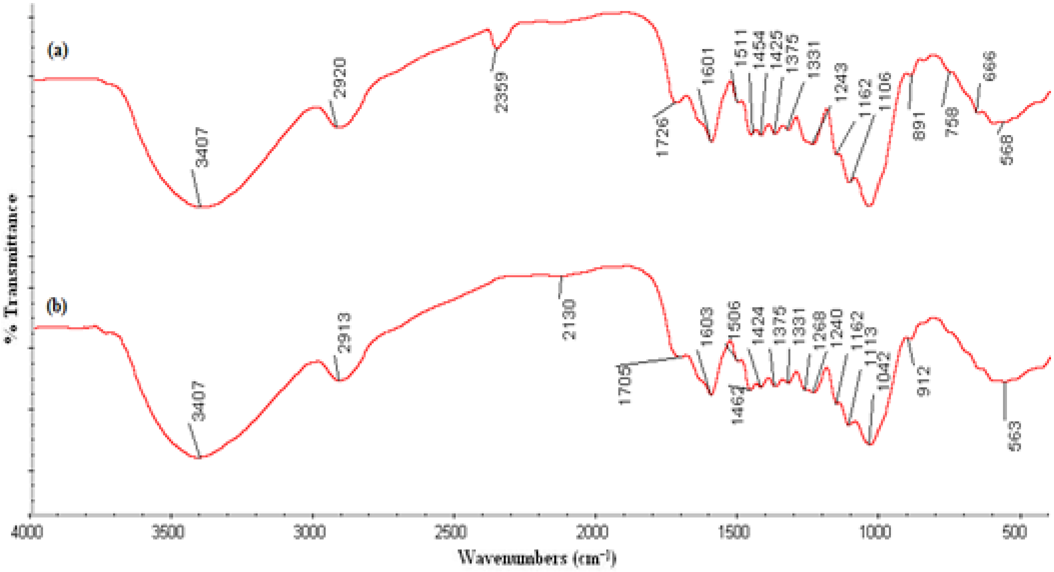


Figure 1. FTIR of banana peel biochars (**a**) before *RB*5 *dye* adsorption and (**b**) after *RB*5 *dye* adsorption.

The SEM micrograph of banana peel biochar before and after the adsorption process was recorded at the resolution of ×5000 magnification using 30 µm particle sizes. It was found that the morphology of the BPB before adsorption (Figure 2a) was different from banana peel biochars after adsorption of *RB*5 (Figure 2b). In Figure 2a, the micrograph revealed the rough and porous surface of the banana peel biochar and it is due to the presence of lignin, pectin, and vicious compounds [61]. Banana peel biochar after adsorption with *RB*5 can be observed with a rough and irregular surface because of the chemical alteration of the surface. Due to the *dye* uptake, lignin was oxidized and produced hydroxyl, carbonyl, and carboxyl groups which enhanced lignin solubility [62]. Functional groups present on the surface are responsible for improving the adsorption process through electrostatic interactions and chemisorption-based processes.

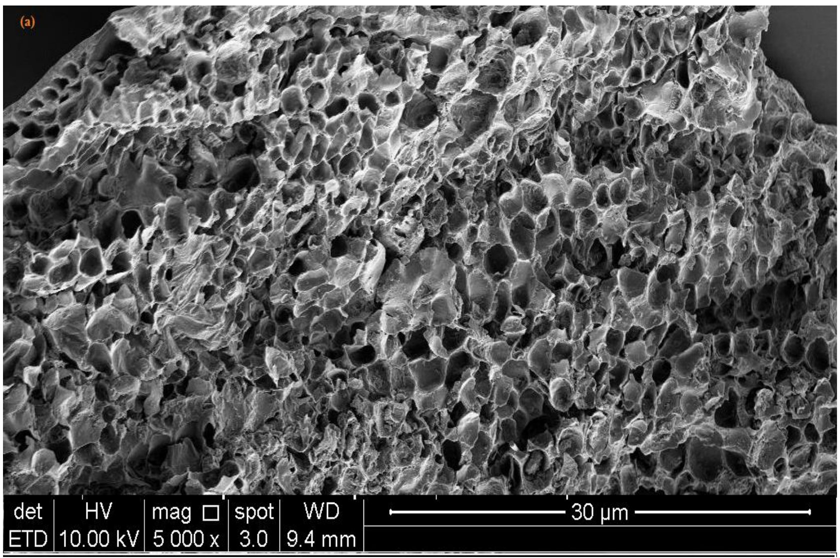


Figure 2. *Cont.*

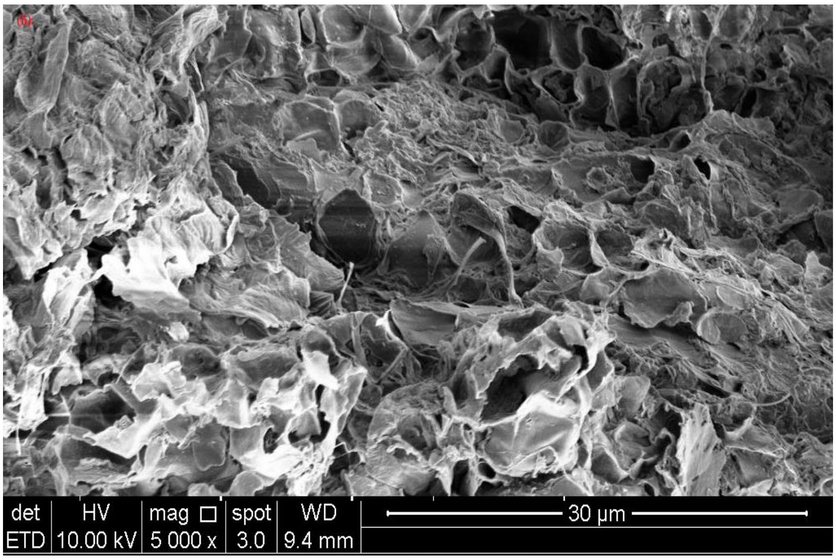


Figure 2. Scanning electron micrographs of banana peel biochar (**a**) before *RB*5 *dye* adsorption and (**b**) after *RB*5 *dye* adsorption.

3.3. Effect of Different Parameters on Reactive Black 5 Dye Adsorption by Banana Peel Biochar

3.3.1. pH

The solution pH plays a significant role in adsorption of *dye* on BPB. The degree of ionization, surface charge of adsorbent, and nature of *dye* solution were affected by the pH. The pH regulates electrostatic interactions between the functional groups available on the BPB surface and *dye* solution. The effect of pH on *RB*5 *dye* removal from an aqueous solution (25–150 mg/L *RB*5 amount) was analyzed through the change in pH from 3 to 11 at 27 ± 2 °C. Maximum 96% removal of 75 mg/L *RB*5 *dye* was reported by BPB at pH 3 while 77, 56, and 34% *RB*5 removal was observed at pH 7, 9, and 11, respectively (Figure 3a). The *RB*5 removal was reported more at less pH due to the involvement of H^+. The surface of adsorbent was positively charged at low pH and attracted *RB*5 which is anionic *dye*. At low pH, more *RB*5 adsorption by BPB was due to electrostatic attraction [24].

3.3.2. Particle Size

Reactive Black 5 adsorption was assessed by three types of BPB particle sizes such as 0–170, 230–300, and 320–500 µm. As the BPB size reduces, adsorption of *RB*5 molecules increases, because of the enlarged surface area of small particles, hence the surface area of BPB was directly proportional to *RB*5 absorption (Figure 3a). For large-sized particles, diffusion resistance to mass transport is high and internal surface cannot be used for adsorption and due to this, less *dye* amount was adsorbed.

3.3.3. Contact Time

Exposure duration of interaction between BPB and *dye* is an important factor which plays a pivotal function in the kinetics of the adsorption process. The *dye* removal percentage was enhanced by increasing contact time (Figure 3b). The removal of *RB*5 *dye* was significant at the earlier stages in comparison with the last stage of the procedure which may be due to the availability of free sites on banana peel biochar. However, after 120 min there was no significant change in the adsorption efficiency, and it was considered as the equilibrium point for the adsorption process. The impact of exposure time for adsorption of *RB*5 *dye* was calculated to analyze equilibrium time. Reactive Black 5 *dye* removal of 77, 81, and 87% was recorded after 30, 60, and 90 min, respectively, for 75 mg/L *RB*5 *dye*. Two hours (120 min) was taken as equilibrium time in adsorption process as after 2 h, increase in *dye* adsorption was not reported.

3.3.4. Adsorbent Dose

The adsorbent amount can affect the adsorption adequacy. Reactive Black 5 *dye* removal was increased from 65 to 69% as BPB enhanced from 0.2 to 0.6 g. Highest 97% of *RB*5 *dye* removal was recorded with 0.8 g of BPB. More *dye* uptake rate was observed with high biochar amount due to the rise in active sites because of increased surface area and functional groups accessible for adsorption, these facilitate frequent binding of *RB*5 on adsorption sites (Figure 3c).

3.3.5. *Dye* Concentration

The initial concentration of *dye* exhibits the significant effect on the adsorption capacity of the process. *Dye* concentration imparts energy for the regulation of mass transfer resistance of molecules between solid (adsorbent) and liquid (*dye* solution) stages [63]. Removal of *RB*5 *dye* by 0.8 g BPB was observed with different *dye* concentrations (25–150 mg/L). A significant amount of color was removed at a low concentration of *dye* whereas with high *RB*5 concentration, the rate of *dye* removal was decreased as the adsorbent surface was completely infused (Figure 3d). High *RB*5 *dye* removal efficiency at a low concentration may be because of more interaction of *dye* molecules with the active sites available on the BPB. Reduction in adsorption efficiency by increasing *dye* concentration might be due to the saturation of active spaces of BPB or less vacancy of adsorbent sites or enhanced repulsive electrostatic force between surface of BPB and *dye* solution.

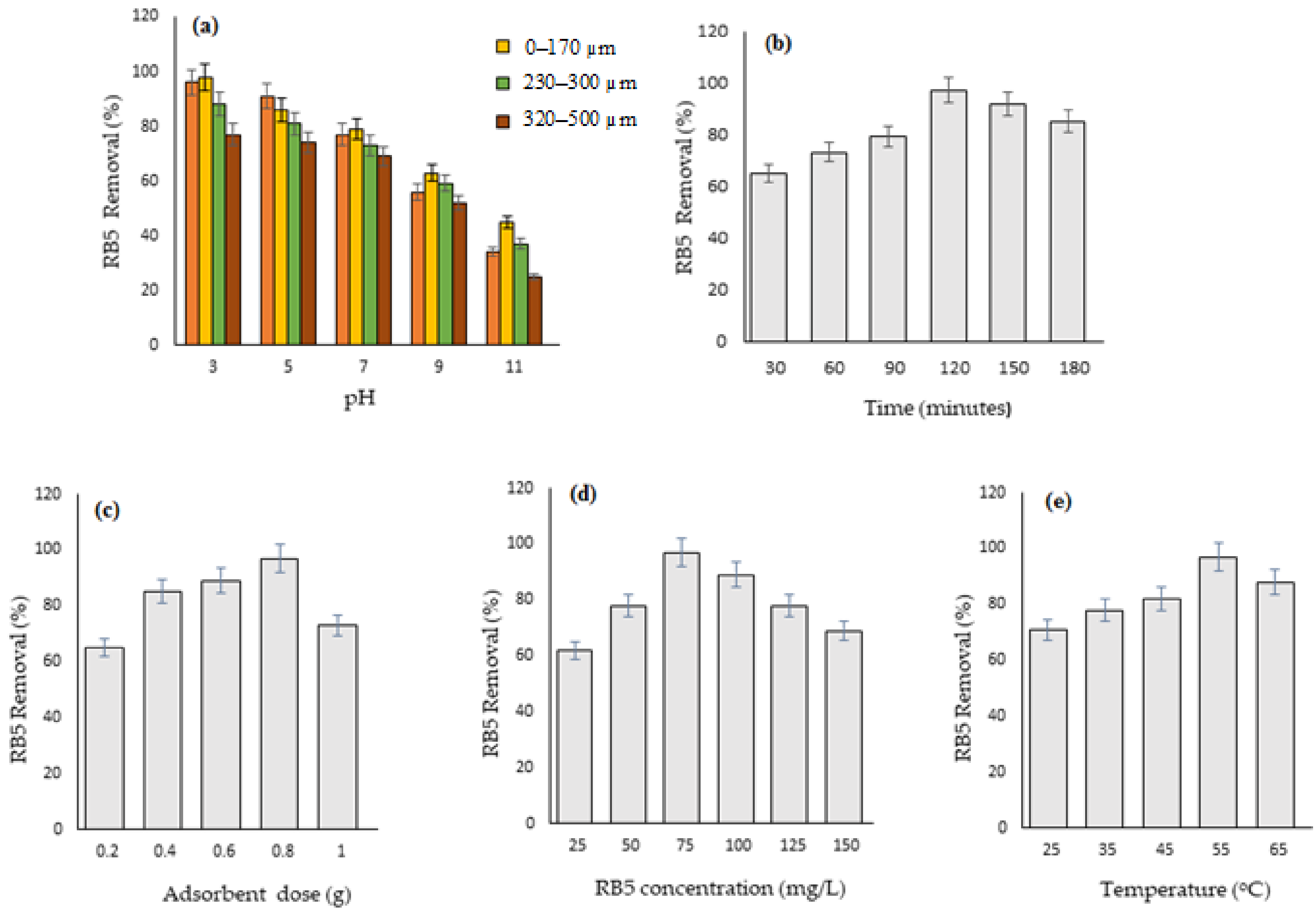


Figure 3. Impact of (**a**) pH and particle size for *RB*5 *dye* (75 mg/L), (**b**) contact period for *RB*5 *dye* (75 mg/L), (**c**) BPB dosage for *RB*5 *dye* (75 mg/L), (**d**) concentration of *dye*, (**e**) temperature on *RB*5 removal (75 mg/L) by BPB.

3.3.6. Temperature

Reactive Black 5 *dye* adsorption on BPB was investigated under various temperature ranges from 25, 35, 45, 55, and 65 °C. *RB*5 *dye* exhibited 71 and 88% sorption at 25 and 65 °C respectively. Maximum 97% sorption of *RB*5 was observed at 55 °C (Figure 3e). Temperature is an important parameter and it affects the transfer process and adsorption kinetics of *dyes*. A higher *RB*5 sorption rate at high temperature was because of the increase in availability of sites on surface and more porosity and pore volume of adsorbent. Results reflected that the adsorption process was exothermic in nature.

3.4. Adsorption Isotherm

The adsorption isotherm indicated *RB*5 molecules dissemination between liquid and solid stages under equilibrium at constant temperature. The isotherm model provides significant information on the mechanism of sorption, surface characteristics, and BPB ability. The isotherm results of *RB*5 *dye* sorption on BPB was analyzed by Langmuir and Freundlich models (Table 2; Figure 4). The Langmuir isotherm model is based on the assumption that monolayer adsorption occurs at homogeneous active sites on adsorbent structure, whereas the Freundlich model describes that adsorption occurs at non-uniform surfaces.

Table 2. Isotherm constants for *RB*5 *dye* adsorption by banana peel biochar.

Isotherm	Equation	Parameters	Value
Langmuir	$C_e/q_e = 1/q_e\,K_L + C_e/q_m$	q_m (mg/g) K_L (l/mg) R^2	7.58 0.0053 0.9489
Freundlich	$\text{In}\ q_e = \text{In}\ K_F + (1/n)\ \text{In}\ C_e$	$1/n$ K_F (mg/g) R^2	7.813 1.90294 0.4471

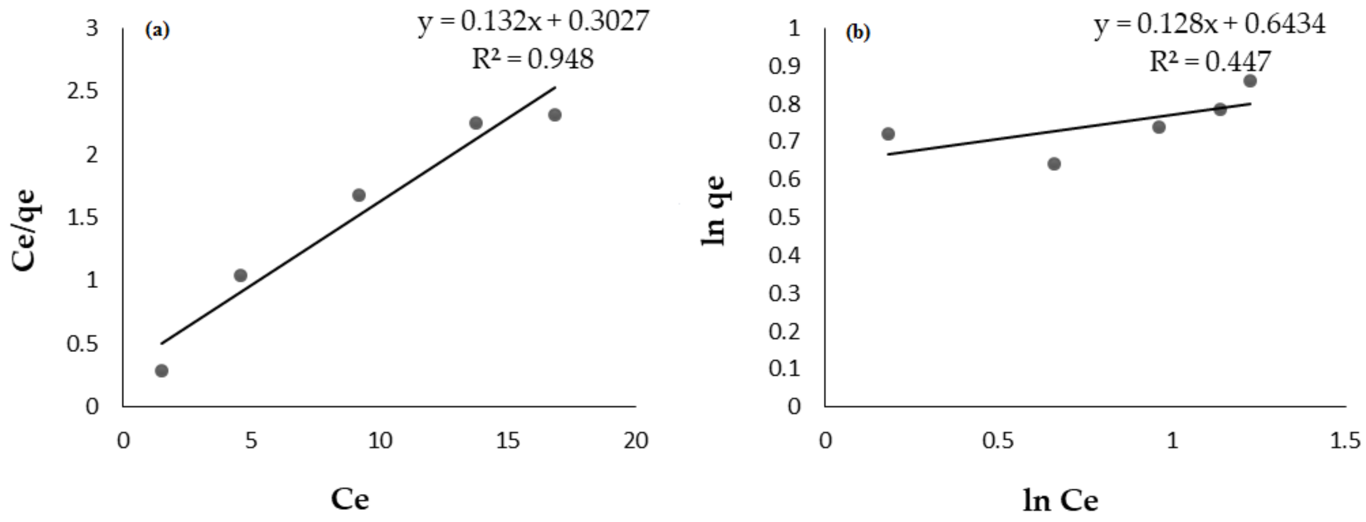


Figure 4. (**a**). Langmuir isotherm for *RB*5 *dye* adsorption by BPB (**b**). Freundlich isotherm for *RB*5 *dye* adsorption by BPB.

In this investigation, the Langmuir isotherm exhibited best fit model as it showed more correlation coefficient (R^2 = 0.9489) compared with Freundlich. It exhibited monolayer coverage of *RB*5 *dye* on banana peel biochar. After calculation, the values for Langmuir constants were q_m = 7.58 mg/g and k = 0.0053 mg^{-1} and Freundlich constants were K_F = 1.90294 and n = 7.813 and R^2 = 0.4471.

3.5. Adsorption Kinetic Models

A kinetic study provides information about adsorption efficiency and direction of reaction. Kinetic models were used to verify *RB5 dye* adsorption by BPB. The coefficient of determination (R^2) was 0.4111 and 0.9946 for pseudo-first and second-order models, respectively. Due to the high correlation coefficient value, the pseudo-second order kinetic model was followed (Table 3; Figure 5). Pseudo-second order kinetics exhibit chemisorption as the rate limiting step which was due to the physico-chemical interactions between the two phases. Data exhibited that the sorption procedure was controlled by uptake between the *RB*5 molecules and BPB surface. The pseudo-second order model was found suitable in earlier findings such as *RB*5 *dye* adsorption by pumpkin seed husks [64], coffee waste [65], and macadamia seed husks [66].

Table 3. Kinetic variables for *RB*5 *dye* adsorption on banana peel biochars.

Model	Equation	Parameters	Value
Pseudo-first order	In $(q_e - q_t)$ = In $q_e - k_1 t$	k_1 (min^{-1})	0.0096
		q_e (mg/g)	3.1852
		R^2	0.4111
Pseudo-second order	$t/q_t = 1/k_2\, q_e + t/q_e$	K_2 (g/mg min)	0.0243
		q_e (mg/g)	8.9606
		R^2	0.9946

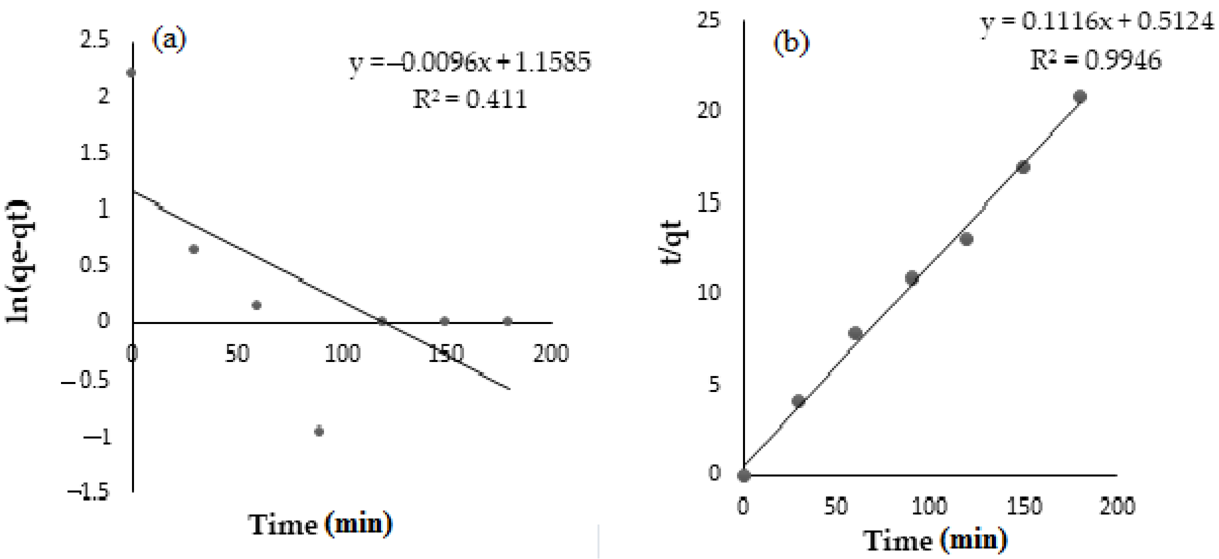


Figure 5. (**a**) Pseudo-first order model and (**b**) Pseudo-second order model for *RB*5 *dye* adsorption by BPB.

3.6. Thermodynamic Analysis

The change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were analyzed for RB 5 adsorption on banana peel biochar.

$$G^\circ = -2.303RT \log Kd \text{ and } Kd = q_e/C_e \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{10}$$

By repositioning the equation, we obtain $\log Kd = \Delta H^0/RT - (\Delta S^0)/R$, by applying the curve fitting method and ΔH° and ΔS° were calculated. Sorption experiments were conducted at 25, 35, 45, 55, and 65 °C (Table 4). The negative value of ΔG° at different temperature showed spontaneous nature of *RB*5 *dye* sorption on BPB [67].

Table 4. Thermodynamic variables for *RB*5 *dye* adsorption by banana peel biochar.

S.No.	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ mol^{-1})	ΔS° (J/K)
1.	25	−2363.79	−11.223	30.457
2.	35	−1506.13		
3.	45	−30.21		
4.	55	−3754.22		
5.	65	−596.03		

The negative value of ΔH° (−11.223 kJ mol^{-1}) established the exothermic nature of the process. The positive value of ΔS° (30.457 J/K) reflected an increase in the adsorbate content in solid state. Increased impermanence at solid-liquid confluence was recorded in sorption. The positive value of ΔS° reflects the randomness and stability of the adsorption procedure. Results revealed that *RB*5 *dye* adsorption on BPB was spontaneous and the exothermic procedure was consistent with our findings recorded in isotherm experiments.

3.7. Regeneration Analysis

Recyclability of BPB is an important parameter for the evaluation of total expenditure of the adsorption process which inhibits secondary pollution. Regeneration a is key indicator for the evaluation of the performance of an adsorbent. The regeneration process requires proper selection of eluent and it depends on the type of adsorbent and adsorption mechanism. Reactive Black 5 *dye* solution contains both positive and negative functional groups so both basic and acidic media are required to desorb *dyes* from the biochar surface. In an acidic medium, the solution consists of H^+ that attaches with the *dye* molecules with negative functional groups and desorbs from the adsorbent surface. Similarly, in basic medium, the *dye* molecules containing positive functional groups were removed [68]. Therefore, in the present analysis for obtaining maximum recovery, BPB was washed first with 1N HCl after that, the same biochar was washed with 1N NaOH. However, with the progression in the number of cycles, the efficacy of the *dye* removal reduced, which might be due to the blockage of the adsorption sites present in the micropores. For the regeneration analysis, 75 mg/L *RB*5 *dye* solution was used with 0.8 g banana peel biochar; as in batch experiments maximum 97% *RB*5 *dye* removal was observed with 75 mg/Ladsorbate concentration and 0.8 g BPB. Reproduced biochar exhibited 78, 62, 52, 43, and 38% *RB*5 *dye* adsorption efficiency from the first to fifth cycle (Figure 6). Hence, regenerated banana peel biochars can be reutilized for the uptake of *RB*5 *dye*.

3.8. Evaluation of Phytotoxicity

The phytotoxic effect of *RB*5 *dye* solution was analyzed prior and after the treatment with BPB by germination and morphological variables of tomato (*Solanum lycopersicum* L. variety Heera) seeds. Experiments were conducted in three sets: in the control set, distilled water was used for watering/irrigation of tomato seeds, whereas two other sets were arranged in which tomato seeds of second set were irrigated with *RB*5 *dye* solution (75 mg/L) and in the third set BPB-treated *RB*5 *dye* solution was used for treatment of tomato seeds. *RB*5 *dye* concentration (75 mg/L) was selected among the other *dye* concentrations for the evaluation of phytotoxic effects of *RB*5 *dye* on tomato seeds as maximum 97% *dye* removal was obtained with this concentration by 0.8 g of banana peel biochar. The seed *germination percentage* was calculated by counting the total number of tomato seeds germinated and after 8 days of seedling growth. Seedlings were used for the estimation of radicle and plumule length, *vigor index*, and analysis of biochemical components such as chlorophyll, sugar, and protein. Marked alterations were recorded among treatment for seed germination, seedling length, and *vigor index* of tomato seeds. In the control, 96% germination was noticed while tomato seeds treated with *RB*5 *dye* (75 mg/L) reflected

10% germination. Tomato seed germination was increased to 81% in *RB*5 solution with BPB treatment. The length of radicle and plumule were 2.97 and 13.67 cm in the control but reduced to 0.19 and 1.93 cm with *RB*5 *dye*. Banana peel biochars-treated *dye* solution exhibited escalation in length of seedling and *vigor index* of tomato in comparison with *RB*5 *dye*. The tomato seeds *vigor index* showed the order: Control > *RB*5 *dye* solution treated with BPB > *RB*5 *dye* (Table 5). The biochemical components such as chlorophyll, sugar and protein were analyzed both in the control and treated tomato seedlings. The maximum amount of chlorophyll, sugar, and protein were reported in the control. Banana peel biochar-treated *RB*5 *dye* solution exhibited a significant reduction, 70, 71, and 76%, respectively, in total chlorophyll, sugar, and protein contents of tomato seedlings over the control. The reduction in biochemical parameters might be due to the adverse impact of *RB*5 *dye* on the physiological activities of tomato seeds. Similar results were reported by Kapoor and Sivamani [53].

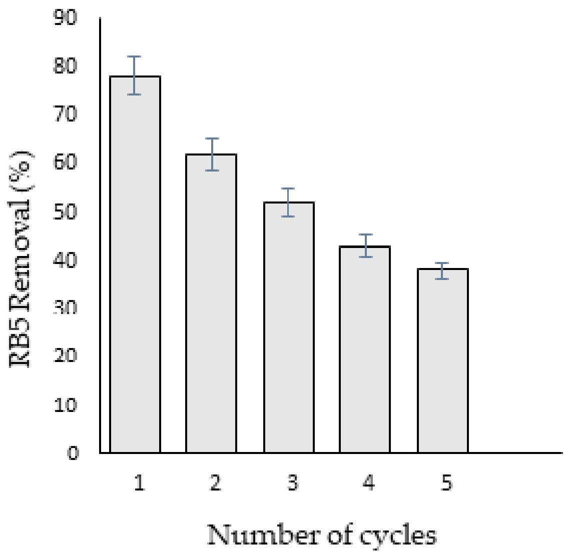


Figure 6. Reactive Black 5 adsorption by banana peel biochars up to five cycles.

Table 5. Phytotoxic effects of *RB*5 *dye* solution before and after treatment with banana peel biochar on germination, morphological and biochemical variables of *Solanum lycopersicum* L.

Treatment	Germination (%)	Length of Plumule (cms)	Length of Radicle (cms)	*Vigor index*	Total Chlorophyll (mg/g FW)	Sugar Content (mg/g DW)	Protein Content (mg/g FW)
Control	96 ± 1.41 ^{a}	13.67 ± 0.57 ^{a}	2.97 ± 0.29 ^{a}	15974.4 ^{a}	3.28 ± 0.36 ^{a}	3.74 ± 0.32 ^{a}	19.03 ± 0.57 ^{a}
*RB*5 *dye* solution (75 mg/L)	10 ± 0.71 ^{c}	1.93 ± 0.18 ^{d}	0.19 ± 0.01 ^{c}	212 ^{d}	0.99 ± 0.09 ^{c}	1.07 ± 0.06 ^{c}	4.53 ± 0.16 ^{d}
BPB-treated *RB*5 *dye* solution	81 ± 1.1 ^{b}	11.4 ± 0.74 ^{a}	2.4 ± 0.49 ^{a}	11178 ^{b}	2.33 ± 0.35 ^{b}	2.31 ± 0.32 ^{b}	15.57 ± 0.47 ^{b}

Values are mean ± standard error mean of 3 replicates from three independent experiments. Values showing different letters indicate significant difference among treatment at $p < 0.05$ significant level as per ANOVA.

3.9. Performance of Banana Peel Biochars

The prepared BPB capacity for *RB*5 *dye* adsorption was compared with similar studies as reported in Table 6. The development of adsorbent from biomass waste provides substitution of commercially available activated carbon and enhances cost effectiveness of the process [67]. Sorption ability (qmax) was utilized for comparison and it is in the line with previous findings, showing that *RB*5 *dye* can be easily adsorbed on BPB. The biochar prepared from different waste biomass resources showed a wide range of adsorption capacity for *RB*5 *dye*. It might be due to the difference in the surface area, pore size and availability of functional groups on the surface of biochar.

Table 6. Adsorption capacity (q_{max}) of *RB*5 *dye* with various adsorbents.

Biochars	Optimum Experimental Conditions	q_{max} (mg/g)	References
Coconut shell	pH = 2; exposure time = 60 min	0.82	Jozwiak et al. [69]
Pumpkin seed husk	pH = 3; exposure time = 60 min	1	Kowalkowska and Jozwiak [64]
Macadamia seed husk	pH = 3; exposure time = 510 min	1.21	Felista et al. [66]
Cotton fibers	pH = 3; exposure time = 240 min	2.74	Jozwiak et al. [70]
Potato peel	pH = 3; exposure time = 120 min	3.61	Samarghandy et al. [71]
Fly ash	pH = 5.64; exposure time = 60 min	7.94	Eren and Acar [72]
Pumpkin seed hulls	pH = 2; exposure time = 30 min	9.18	Celebi [46]
Eggshells	pH = 6; exposure time = 15 min	18.46	Celebi [46]
Coffee waste	pH = 7; exposure time = 50 min	77.52	Wong et al. [65]
Wood waste	Temperature = 25 °C; exposure time = 90 min	35.67	Figueiredo Do Nascimento [73]
Tobacco stalk biomass	pH = 2; exposure time = 120 min	92.84	Shah et al. [74]
Banana peel biochars	pH = 3; exposure time = 120 min	7.58	This study

Adsorption is considered as the most promising technology owing to its low cost, high selectivity and ease of operation. Banana peel biochar can be applied as an efficient adsorbent for removal of anionic *dyes* as observed in the findings of the present study. Further investigations are required for the utilization of the potential waste materials easily available at zero cost for its effective translation from laboratory scale treatment to real industrial effluent treatment at a large scale.

4. Conclusions

Azo *dye* treatment is an arduous task as these *dyes* are electron deficient xenobiotic compounds and recalcitrant to degradation. An FTIR analysis confirmed interactions between *RB*5 *dye* and functional groups available on the BPB surface. The Langmuir adsorption isotherm model best represented the experimental points and reflected highest 7.58 mg/g adsorption capacity. The negative value of ΔH^0 reflected that sorption was spontaneous and an exothermic process. Reproduced BPB showed positive results up to five successive cycles for removal of *RB*5. Hence, biochar prepared from renewable bio-waste i.e., banana peel, is a simple, inexpensive, sustainable, and efficient adsorbent for *RB*5 *dye* removal from contaminated water. Our findings represent promising alternatives for *RB*5 removal from aqueous phases, but needs further research on a larger scale.

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Abbreviations

The following abbreviations are used in this manuscript:

ANOVA	Analysis of Variance
BPB	Banana Peel Biochar
DMRT	Duncan's Multiple Range Test
FTIR	Fourier Transform Infrared Spectroscopy
*RB*5	Reactive Black 5
SEM	Scanning Electron Micrograph

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