



Adsorptive removal of acid blue 193 dye from wastewater using *Citrullus colocynthis* biomass

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Received: 4 January 2024 / Revised: 24 February 2024 / Accepted: 12 March 2024 / Published online: 2 April 2024
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Abstract

Due to their prevalence as contaminants in printing and textile industry wastewater, aqueous dyestuff decontamination approaches are receiving a lot of attention. Herein, the ability of powdered *Citrullus colocynthis* fruit peels (CCPs), a green agro-based adsorbent, to absorb an anionic acid blue 193 dye from an aqueous solution was further investigated. At pH 2.0 to 3.0, the monolayer adsorption capacity of CCP for the anionic dye species was 139.83 mg/g. Meanwhile, the successful dye uptake seen in the study is credited to the combined electrostatic interaction between the protonated adsorbent surface and the negatively charged sulfonic acid ($-\text{SO}_3\text{H}$) group of the anionic acid blue 193 dye. Another potential adsorption mechanism is the creation of hydrogen bonds between the highly polar $\text{C}=\text{O}$ and $-\text{OH}$ groups of the adsorbent and the nitrogen atoms on the dye backbone. These findings suggest that CCP adsorbent is a viable candidate for the elimination of anionic acid blue 193 dyes from aqueous solution.

Keywords *Citrullus colocynthis* shell · Acid blue 193 dye · Isotherm studies · Kinetic studies · Dye wastewater

1 Introduction

Dyes are chemical compounds, with inherent aromatic rings and a high degree of saturation [1]. They are mostly utilized for imparting colouration to a range of materials and products [2]. As a result of the production process in many process industries, enormous volumes of wastewater that is tainted with dyes are produced. These dyestuffs are potentially toxic and difficult to decompose when released into water, where they severely harm living things [3]. Additionally, the continual and unhealthy release of colored wastewater causes significant environmental deterioration and, thus, attracts serious attention from environmentalists and researchers.

To date, several physical, chemical, biological, and hybrid remediation approaches have been explored for dye wastewater treatment, while the pros and cons of the respective treatment techniques have been extensively reviewed [4, 5]. In brief, the chemical methods are flexible, require less operational space, and depict fast sorption kinetics [6]. However, their associated high operational cost and generation of secondary waste (in the form of sludges) are major drawbacks. Similarly, biological treatment techniques are highly sensitive to pH change and, hence, are not very efficient at removing complex varieties of dye pollutants [6]. Meanwhile, adsorption, a physical treatment technique, is considered an effective dye wastewater treatment approach because of the process flexibility in terms of overall adsorption [7] and adsorbent regeneration cost [8, 9]. Also, the ready availability of the adsorbent precursor materials and high wastewater treatment efficiency are some of the merits of the adsorption technique.

Unquestionably, activated carbon has proven to be efficient at adsorbing an array of both organic and inorganic pollutants from wastewater. However, its extensive application is often constrained by its high cost [10, 11]. As a result, efforts have been made to synthesize inexpensive alternative adsorbents using readily accessible lignocellulosic biomasses. Studies have shown that biowastes are

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made up of several functional groups that act as sorption sites for a variety of dye contaminants [12, 13]. For instance, crystal violet dye [14], rhodamine B dye [14], and methyl orange dye [15] were successfully adsorbed using *Raphanus caudatus* leaf biomass. Other common waste materials previously utilized as adsorbents include *Cortaderia selloana* flower spikes [16] and Moroccan cactus [17] for adsorbing methylene blue dye, coconut waste [18], and cabbage waste powder [19] for congo red adsorption and the use of apricot seed shell powder for acid blue 193 dye adsorption [20].

Citrullus colocynthis is a perennial herb that grows well in arid climates and several parts of the plant, ranging from its roots, fruit, and leaves have many medicinal applications. The *Citrullus colocynthis* fruit peels, on the other hand, have no recognized uses other than being disposed of as biowaste. Acid blue 193 dye, like all other acid dyes, is an anionic dye that has negative effects on the ecosystem because it contains organic sulphonic groups. Previously, the *Citrullus colocynthis* biowaste has been efficiently utilized for the adsorption of crystal violet [21], congo red [22], methylene blue [23], and brilliant green [24] dye from wastewater. Therefore, this work aims to elucidate the potential of *Citrullus colocynthis* fruit peel (CCP) for adsorbing acid blue 193 dye from wastewater. Employing a range of analytical techniques, the prepared CCP was thoroughly characterized. Subsequently, the CCP sorbent was utilized to adsorb acid blue 193 dye in batch mode. Moreover, the established sorption mechanisms governing the interaction with acid blue 193 dye were successfully investigated and discussed. However, to our best knowledge, there exists no work on the adsorption of acid blue 193 dye onto *Citrullus colocynthis* biowaste, hence making this work plausible.

2 Materials and methods

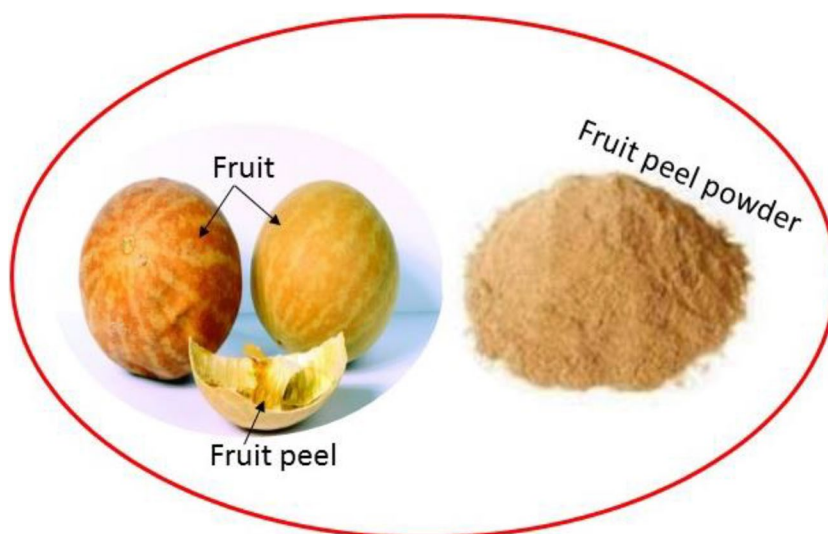
2.1 Adsorbent preparation

Citrullus colocynthis is a desert plant and its fruits were obtained from the Matrouh desert in Egypt. Its fruits were obtained and washed several times with distilled water to remove any attached dust particles. The clean fruit was sun-dried for 7 days until constant dry weight. Afterwards, the fruit peels were subsequently separated from the rest of the contents of the fruit and further ground to fine particle size (~ 50 – $125\ \mu\text{m}$) to obtain the desired *Citrullus colocynthis* powder (CCP). The *Citrullus colocynthis* fruit, the obtained fruit peel, and the *Citrullus colocynthis* fruit peel powder are shown in Fig. 1.

2.2 Adsorption experiment and data modeling

The adsorption experiment was conducted following the experimental protocol reported in our previous work [25]. Briefly, 0.1 g of the adsorbent was contacted with 100 mL of the simulated wastewater (30 mg/L). The setup was mildly agitated using a magnetic stirrer (150 rpm) at a given duration (180 min). Meanwhile, test samples were intermittently collected from the setup at 5-min intervals until the equilibrium point was reached. The final dye concentration in each of the collected test samples was obtained using a laboratory spectrophotometer (Shimadzu UV/Visible Spectrophotometer, model: UV-1900 UV–VIS Spectrophotometer) at ~ 580 -nm wavelength. Subsequently, the amount of solute adsorbed was evaluated using Eq. (1). Furthermore, the effect of process variable variation on the adsorption capacity was evaluated via one-factor-at-a-time (OFAT) methodology in the

Fig. 1 Pictorial presentation of the *Citrullus colocynthis* fruit, fruit peel, and fruit peel powder



range of 0.01–0.2 g (adsorbent mass), pH 2.0–pH 10.0, and 313–343 K (solution temperature).

$$q_e = \frac{(C_o - C_e) \times V}{W} \quad (1)$$

where C_o , C_e , V , and W are the starting dye concentration (mg/L), dye concentration at equilibrium point (mg/L), volume of wastewater used (mL), and mass of adsorbent (g).

The isotherm studies were conducted at varying initial concentrations (10–100 mg/L) and the generated equilibrium data was modeled using the nonlinear forms of the Langmuir (Eq. 2) [26], Freundlich (Eq. 3) [27], and Temkin (Eq. 4) [28] isotherm models.

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2)$$

$$q_e = K_F (C_e)^{\frac{1}{n_F}} \quad (3)$$

$$q_e = \frac{RT}{b_T} \log(K_T C_e) \quad (4)$$

Similarly, the adsorption kinetics and mechanistic investigation were conducted within the contact time range of 0–180 min. The experimental kinetics data were modeled using the nonlinear forms of the pseudo-first-order (Eq. 5) [29] and the pseudo-second-order (Eq. 6) [30] kinetic models, while the mechanistic investigation was achieved using the linear form of intraparticle diffusion (Eq. 7) [31] and Bangham models (Eq. 8). Furthermore, the goodness of fit on the nonlinear adsorption models was determined based on the value of the sum of the normalized error value. The

details of the mode of evaluating the SNE values for the respective nonlinear adsorption models have been extensively elucidated in our previous publication [32].

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (5)$$

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{(1 + k_2 \cdot t)} \quad (6)$$

$$q_t = K_{id} \sqrt{t} + C \quad (7)$$

$$\log \left[\frac{C_o}{C_o - q_t M} \right] = \log \left[\frac{k_b}{2.33V} \right] + \alpha \log t \quad (8)$$

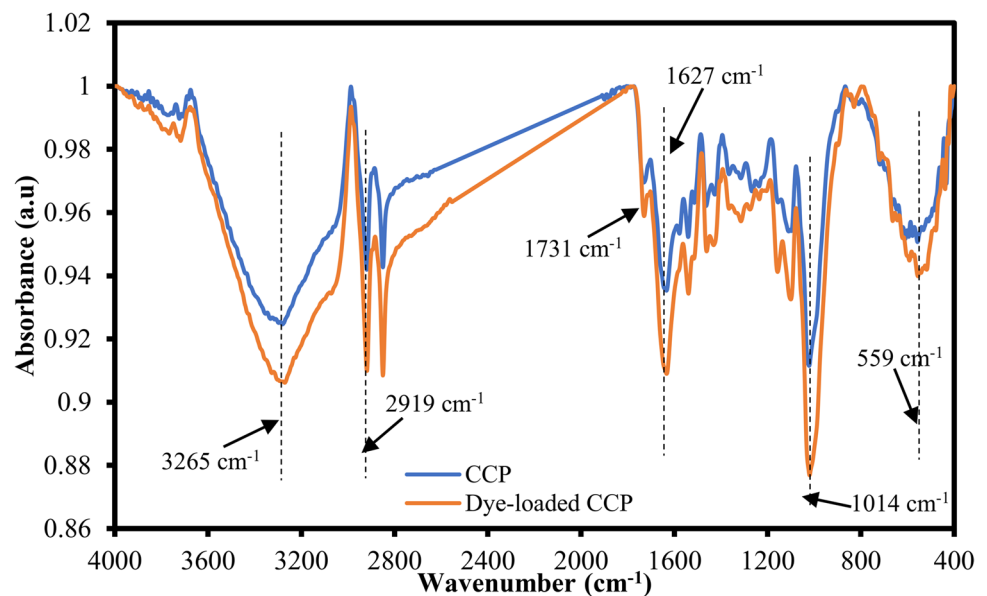
3 Results and discussions

3.1 Adsorbent's characterization result

3.1.1 Fourier transform infrared spectroscopic analysis

The Fourier transform infrared (FTIR) spectra of the raw and dye-loaded CCP were obtained on a PerkinElmer spectrophotometer (LAMBDA 365 UV–Vis Spectrophotometer, USA) and shown in Fig. 2. The raw CCP sample showed five predominant functional groups, in addition to other groups with weak absorption bands. The predominant groups are the carboxylic –OH (3265 cm^{-1}), aliphatic C–H stretching (2919 cm^{-1}), C=C stretching (1627 cm^{-1}), and C–OH bending vibration (1014 cm^{-1}) groups. Also, wavenumbers

Fig. 2 FTIR spectra of the raw and dye-loaded CCP



around 400–800 cm^{-1} are assigned to the aromatic and out-of-plane C–H bending bands whose degrees of substitution vary significantly [33]. Other sublime peaks observed in the raw CCP sample are H-bonded carboxyl (1535 cm^{-1}), carboxylic (1423 cm^{-1}), aliphatic C–H bending (1315 cm^{-1}), and P=O/P–OH stretching (1151–1093 cm^{-1}) [33].

Furthermore, the functional groups reported by other authors who worked on different shell-based adsorbents are in line with those reported in this study. For instance, during the FTIR analysis of walnut shell powder, Miyah et al. [34] reported the presence of –OH stretching (from the carboxylic groups), C–H stretching, C=O stretching, and C–H in-plane bending vibrations at 3339, 2920, 1731, and 1368–1437 cm^{-1} , respectively. Similarly, the FTIR analysis of wood apple shell powder revealed the presence of –OH (at 3406 cm^{-1}), C–H (at 2925 cm^{-1}), C=O stretch (1738 cm^{-1}), and C=C bending groups (at 1634 cm^{-1}) [35]. Acid-treated palm shell powder also depicted –OH stretching, C–O stretching and carboxylic acid groups at ~ 3419.42 , ~ 1200 , and ~ 1739 cm^{-1} , respectively.

The FTIR spectra pattern of the raw and dye-loaded CCP samples did not, however, show any appreciable

differences, although the dye-loaded sample's absorbance reading was lower than that of the raw CCP sample. This observation indicates successful adsorption and suggests the depletion of the functional groups that would have otherwise absorbed the light rays transmitted through the CCP sample.

3.1.2 Scanning electron microscopic analysis

Using a scanning electron microscope (JEOL JSM 6060, Jeol Ltd., Tokyo, Japan), the raw and dye-loaded CCP samples' surface morphology and elemental distribution mapping were obtained (Fig. 3). A rough, porous surface with apparent fissures and irregularly shaped pores was observed on the surface morphology of the raw CCP sample (Fig. 3a). These pores, which are present in the CCP structure, play a crucial role in the process of adsorbing the molecules of the acid blue 193 dye. The dye-loaded CCP sample (Fig. 3c) showed less porosity, with the fissures visibly disappearing and a whitish film of the adsorbed dye being deposited, thus suggesting a successful dye adsorption.

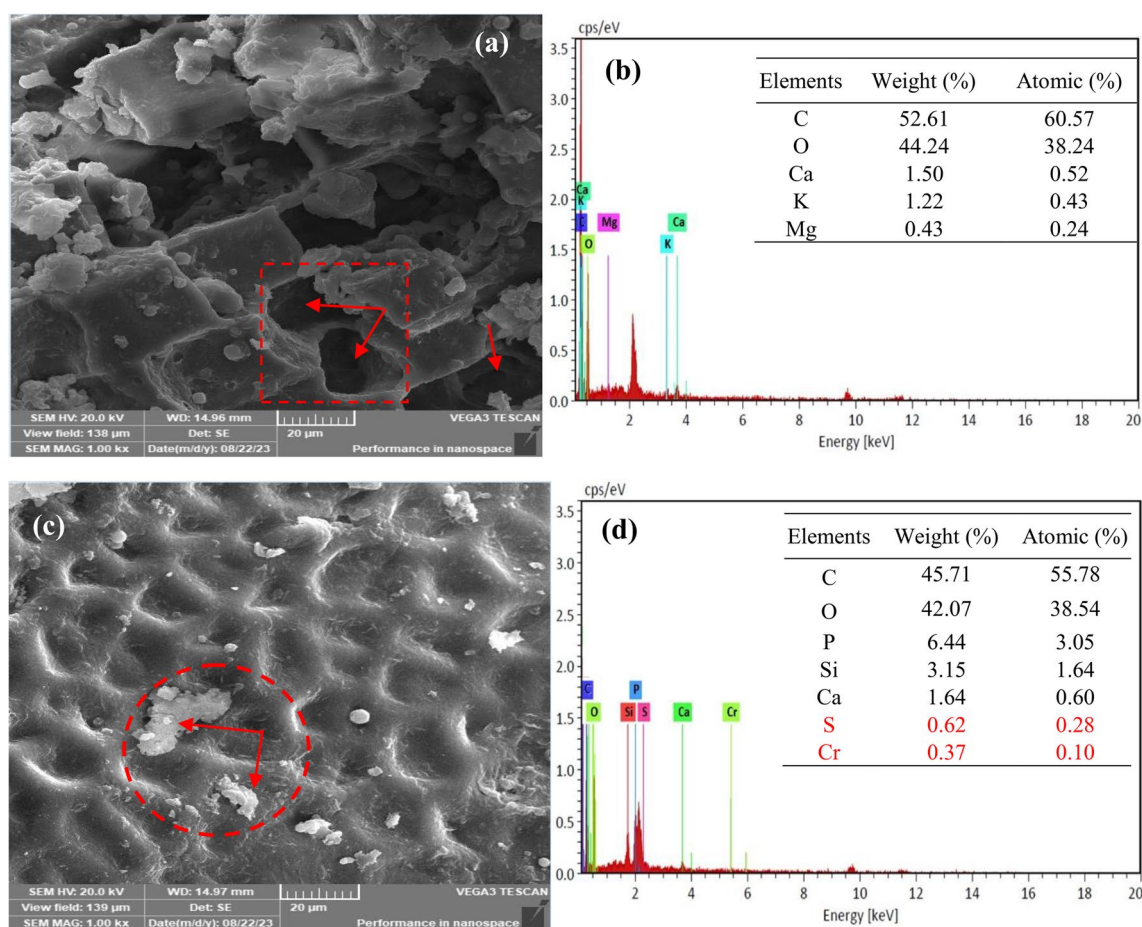


Fig. 3 a SEM image of the raw CCP, b EDX mapping spectra of the raw CCP, c SEM image of the dye-loaded CCP, d EDX mapping distribution of the dye-loaded CCP

Further proof for the dye biosorption can be found in the identification of about 0.37 and 0.62% of chromium and sulfur ions, respectively, in the scanning electron microscopic (SEM)-EDX elemental distribution of the dye-loaded CCP sample (Fig. 3d), which was absent in the raw sample (Fig. 3b), given that the acid blue 193 dye is chromium-based.

3.1.3 X-ray diffraction analysis

A Rigaku Miniflex II diffractometer (Japan) was used to obtain the X-ray diffraction (XRD) patterns of the raw and dye-loaded CCP, and the findings are displayed in Fig. 4. The amorphous structural property of the raw CCP sample was implied by the large peaks at $2\theta = 22.28^\circ$ and 34.91° . A pair of large diffraction peaks at $2\theta = 24^\circ$ (002) and $2\theta = 42^\circ$ (100) were similarly found by Jawad et al. [36]. for coconut shell powder. This discovery, in the author's opinion, is evidence of amorphous structural properties and further shows that the adsorbent is made up of crystallographic planes of

carbonaceous materials. *Penicillium* sp. [37] and *Aspergillus ustus* [25] both showed a large peak at $2\theta = 20^\circ$ and 19.80° , respectively, leading the authors to likewise conclude that both materials had amorphous structural properties. Notably, no structural changes were observed in the post-adsorption samples of the CCP.

3.1.4 BET surface area measurement

The surface area, pore volume, and pore radius of CCP were measured and found to be, respectively, $58.04 \text{ m}^2/\text{g}$, $0.041 \text{ cm}^3/\text{g}$, and 1.92 nm . According to the results in Table 1, the BET surface area value obtained in this study is significantly higher than those reported for other shell-based adsorbents. Further evidence for the CCP's adsorptive potentials in comparison to these other adsorbents was provided by the fact that the higher the surface area, the greater the adsorptive capacity. Additionally, the fact that the pore radius is smaller than 2 nm shows that the majority of CCP is made up of micropores.

Fig. 4 The XRD spectra of the raw and dye-loaded CCP

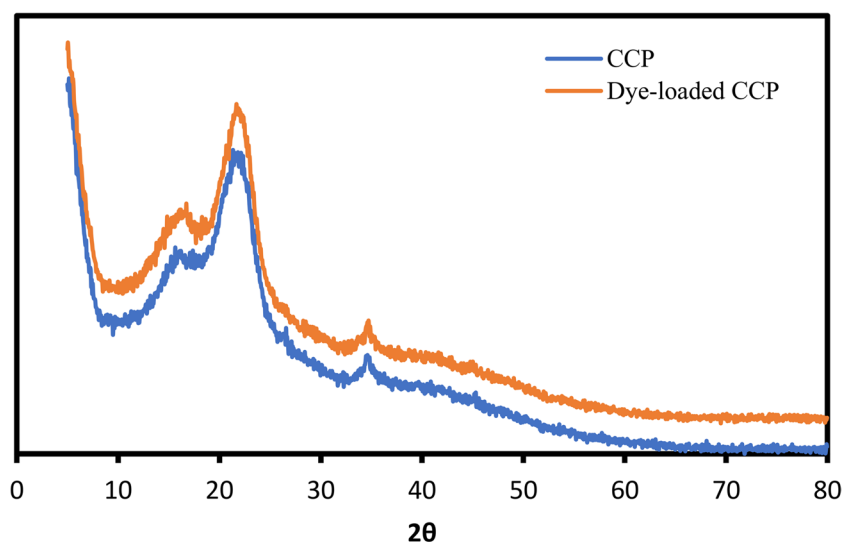


Table 1 BET surface area and pore properties of other shell-based adsorbent powders

Adsorbent	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)	Reference
Cashewnut shell powder	395.0	0.473	5.89	[33]
<i>Citrullus colocynthis</i> fruit peels powder	58.04	0.041	1.92	Present study
<i>Citrullus colocynthis</i> seed powder	24.679	0.023	1.49	[23]
<i>Citrullus colocynthis</i> peels powder	11.988	0.013	1.56	[23]
Hazelnut shell powder	2.850	–	–	[38]
Coconut shell powder	1.137	0.002	–	[36]
Palm shell powder	0.674	–	–	[39]
Acidified palm shell powder	0.298	–	–	[39]
Almond shell powder	0.20	–	–	[40]

3.2 Adsorption process variable investigation

3.2.1 Effect of pH

The point of zero charge is a parameter that describes the evolution of the surface charge in a particular adsorbent. As a result, an adsorbent can efficiently function as either an anion exchanger, a cation exchanger, or a neutral species when effluent pH is less than the adsorbent's pH_{pzc} , greater than the adsorbent's pH_{pzc} , or equal to the adsorbent's pH_{pzc} , respectively. According to Fig. 5 a, the pH_{pzc} of the CCP was measured at pH 5.8; thus, the successful adsorption of the acid blue 193 anionic species should typically take place within a strongly acidic pH range if electrostatic interaction dominates the entire adsorption process. This assertion was further corroborated by the result of the effect of pH on the adsorption capacity (Fig. 5b). Accordingly, a rise in the adsorption capacity, q_e (mg/g), was recorded between pH 2.0–3.0, with the optimum q_e value occurring at pH 3.0.

Other studies have also reported a similar trend of results. For instance, Alghamdi and El Mannoubi [23] utilized *Citrullus colocynthis* peel powder for the adsorption of cationic methylene blue dye. According to the authors, the adsorbent exhibited a zero-surface charge at pH 6.4 and an optimum dye uptake at pH 8.0. Also, Basharat et al. [24] investigated the adsorption of cationic brilliant green dye onto *Citrullus colocynthis* peel powder. The study reported an adsorbent pH_{pzc} at pH 5.0 and an optimum dye uptake occurred at pH 7.0. Furthermore, the optimum adsorption of acid blue 193 dye onto pumpkin seed shell (pH_{pzc} =pH 7.9) [41] and apricot seed shell (pH_{pzc} =pH 7.3) [20] occurred at pH 2.0 in both cases.

3.2.2 Effect of adsorbent concentration

Using different adsorbent doses (0.01 to 0.20 g) and a fixed volume of adsorbate solution (100 mL), the study on the impact of adsorbent concentration was carried out at an initial dye concentration of 30 mg/L. According to the experimental results depicted in Fig. 6, the amount of dye adsorbed per gram of the adsorbent (q_e , mg/g) continuously declined from 53.33 to 8.04 mg/g as the adsorbent concentration rose, correspondingly from 0.01 to 0.2 g. This discovery may be the result of the progressive unsaturation of the adsorption sites with increasing adsorbent concentrations, at constant contaminant concentrations. The likely aggregation of adsorbent particles, which tends to decrease the surface area accessible and lengthen the diffusion path, is another explanation [42].

Other authors like Naseem et al. [43] and Naseem et al. [44] who worked on pollutant adsorption onto various adsorbents reported a similar trend of results. Also, Omorogie et al. [45] reported a consistent and significant decrease in the adsorption capacity of modified *Terminalia ivorensis* biomass due to increasing adsorbent concentration. According to the study, an increase in the adsorbent mass from 10 to 1000 mg reduced the amount of methyl orange and congo red dye adsorbed from 229.61 to 2.37 mg/g and 249.8 to 2.42 mg/g respectively. Also, according to Chukwuemeka-Okorie et al. [46], the increase in adsorbent mass from 0.1 to 0.5 g reduced the uptake capacity of biomass-derived activated carbon from 22.2 to 4.49 mg/g (for sunset yellow dye) and 29.4 to 5.78 mg/g (for tartrazine dye). Notably, all the referenced literature concluded that the decrease in the uptake capacity of the respective anionic dyes with

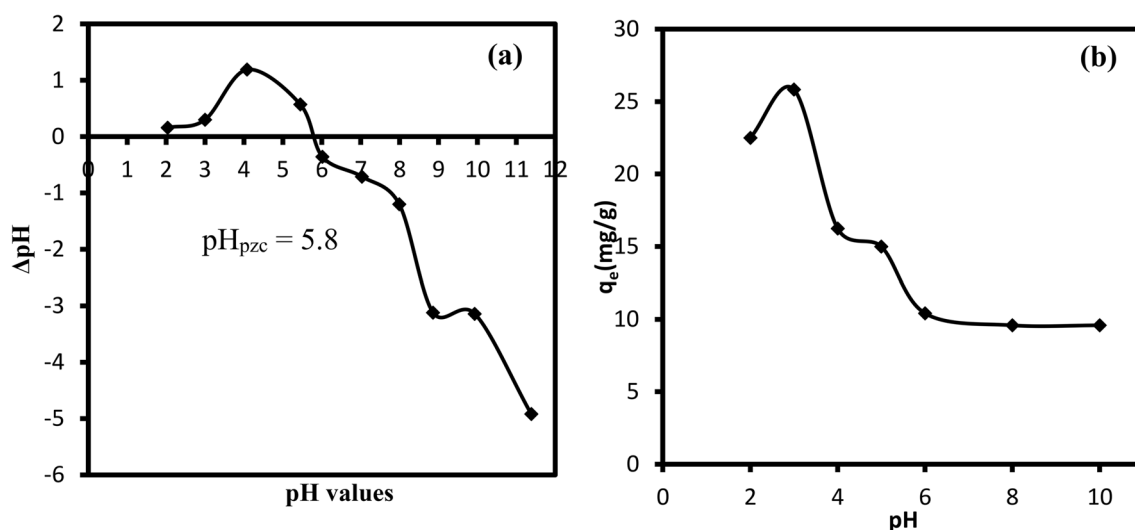


Fig. 5 **a** Titrimetric plot for the point of zero charge determination; **b** plot of the effect of solution pH on the adsorption capacity

Fig. 6 Plot of the effect of adsorbent concentration on adsorption capacity

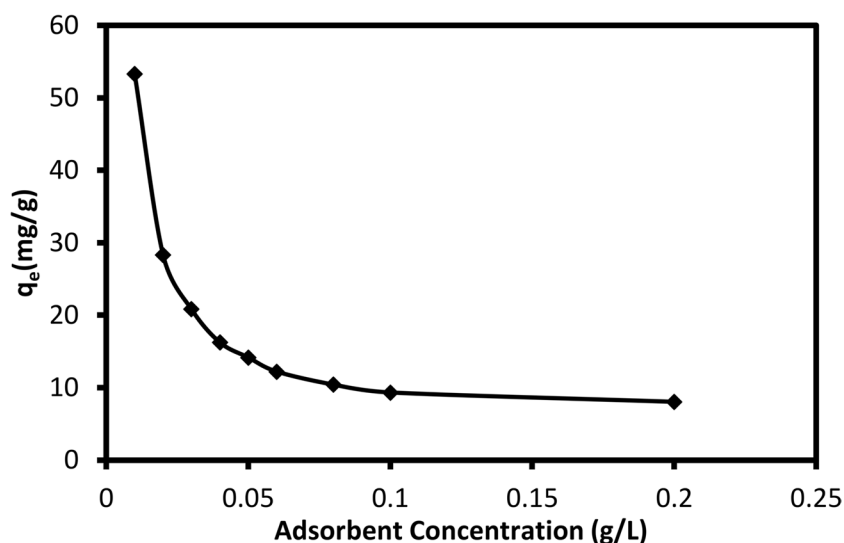


Table 2 Nonlinear isotherm model parameters

Langmuir	Freundlich	Temkin
$q_{\max} = 139.83$	$n_F = 1.49$	$A_T = 63.90$
$k_L = 3.13$	$1/n_F = 0.67$	$b_T = 122.90$
$R_L = 0.02$	$K_F = 6.35$	$R^2 = 0.906$
$R^2 = 0.939$	$R^2 = 0.990$	$SNE = 1.09$
$SNE = 1.08$	$SNE = 1.17$	

increasing adsorbent mass is due to possible aggregation/overlapping of the sites at higher doses, thus elongating the diffusion paths of solute towards the adsorption sites.

3.3 Adsorption modeling

3.3.1 Isotherm modeling

The equilibrium relationship between the amount of solute adsorbed onto the adsorbent (q_e) and the equilibrium concentration in the bulk fluid (C_e) under constant process conditions is described by the adsorption isotherms [47]. Three nonlinear models [Eqs. (2)–(4)] were used in this study to model the experimental equilibrium data. Table 2 displays the respective isotherm model parameters and the related goodness of fit (R^2 and SNE) values, while the data generated from the respective isotherm models are plotted in Fig. 7. In general, all of the models displayed reasonably high R^2 values ($R^2 > 0.9$); however, based on literature studies, R^2 values alone do not suffice to forecast the nonlinear model of best fit. Herein, some well-known error models that were earlier mentioned in Section 2.2 were adopted. The error values produced by the various error models were successfully normalized to yield the sum of normalized

error (SNE) values, and the lower the SNE value is for a given isotherm model, the better the model's fit.

The lowest SNE value was obtained for the Langmuir isotherm model, thus indicating that the binding of acid blue 193 dye onto CCP occurred via the formation of a homogeneous monolayer of adsorbed solute, with no molecular interactions between adjacent sites. The monolayer adsorption capacity ($q_{\max}$) was found to be 139.83 mg/g and the Langmuir isotherm constant (R_L) value of 0.02 indicates a favorable process. Besides the Langmuir model, the Freundlich and Temkin models also showed a reasonable description of the experimental equilibrium data judging from the low SNE values (SNE-value < 2.0). The Freundlich n_F value is useful for elucidating the isotherm curvature and according to Table 2, the n_F value = 1.49 indicates a favorable physorption interaction [48]. Also, the reciprocal of the n_F value ($1/n_F$) provides insight into the existence of either a cooperative ($1/n_F > 1$) or none cooperative sorption ($1/n_F < 1$) [49]. Notably, the $1/n_F$ -value is less than unity (0.67) and indicates the occurrence of non-cooperative sorption. The Temkin model parameters are related to the heat of adsorption and the minimal positive b_T -value recorded in Table 2 means that the adsorption is both a physical and endothermic process [50].

3.3.2 Kinetics modeling

For assessing the adsorption kinetics data, the kinetic models shown in Eqs. (5)–(7) were applied. Table 3 and Fig. 8 a–b respectively display the results of the kinetics model and the corresponding graphs generated at various initial solute concentrations. In general, two zones can be distinguished from the data points in Fig. 8 a–b, a region of rapid

Fig. 7 The nonlinear isotherm model plot for the adsorption of acid blue 193 dye onto CCP

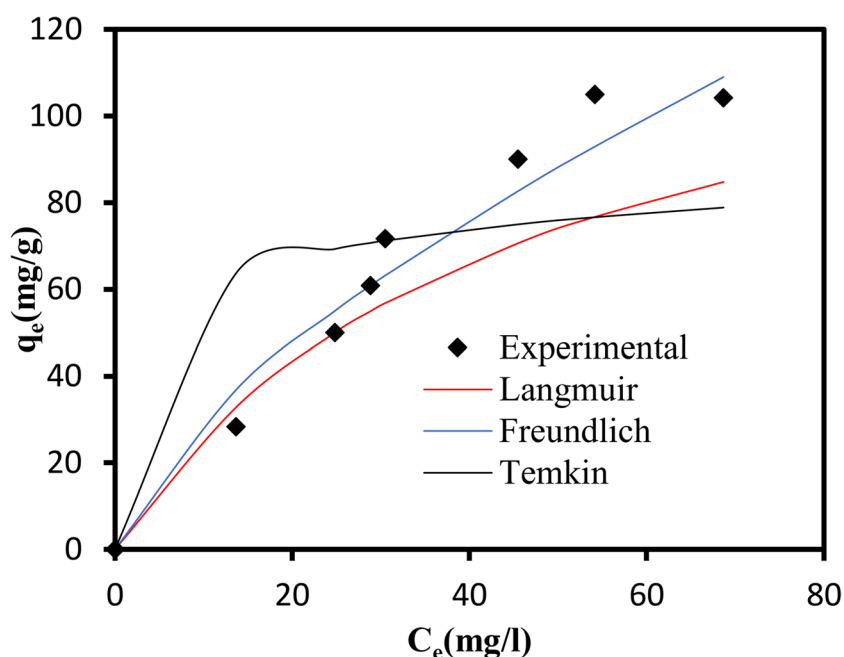


Table 3 Parameters determined from the kinetic and mechanistic studies

Initial conc	Kinetic models		Mechanistic models	
	PFO	PSO	Intraparticle	Bangham
30 mg/L	$q_e = 50.84$ $k_1 = 0.17$ $R^2 = 0.992$ SNE = 1.27	$q_e = 53.14$ $k_2 = 0.007$ $R^2 = 0.998$ SNE = 1.47	$k_{id} = 1.41$ $C = 37.85$ $R^2 = 0.999$	$k_b = 0.24$ $\alpha = 0.033$ $R^2 = 0.909$
40 mg/L	$q_e = 59.99$ $k_1 = 0.13$ $R^2 = 0.994$ SNE = 1.20	$q_e = 62.39$ $k_2 = 0.004$ $R^2 = 0.998$ SNE = 1.37	$k_{id} = 2.03$ $C = 37.72$ $R^2 = 0.989$	$k_b = 0.24$ $\alpha = 0.024$ $R^2 = 0.908$

uptake with spiked q_t value (which occurred within the first 30 min) and a zone of abated uptake with seemingly gradual improvement in the q_t -value over time. The fluctuation in q_t -value over time is explained by the variation in the number of accessible sorption sites [51]. Furthermore, all of the kinetic models depicted efficient correlation with the experimental data plot lines (Fig. 8a, b), and just like with isotherm modeling, the SNE value is utilized to identify which model provides the best match. The PFO model, having the lowest SNE value, is considered the model of best fit at both 30 and 40 mg/L concentration systems, for both adsorbents and suggests the predominance

of physisorption via interfacial diffusion. Additionally, because of the enhanced concentration gradient, which promotes qualitative affinity between the adsorbate and the adsorbents, the values of k_1 (L/min) and k_2 (g/mg/min) were higher at higher initial concentrations [52].

Using the linear versions of intraparticle diffusion (Eq. 8) and Bangham (Eq. 9), the stages of the adsorption process were also investigated. The plots of q_t vs. $t^{0.5}$ at both initial adsorbate concentrations are linear and exhibit acceptable R^2 values, despite the plot line's departure from the origin (Fig. 8c) (Table 3). This demonstrates that surface sorption and intraparticle diffusion both regulate the adsorption rate [53]. Additionally, based on the size of the intercept (C-value), it is possible to deduce the role intraparticle diffusion plays in regulating the adsorption rate. When the C-value is significantly more than unity, intraparticle diffusion contributes more, and vice versa [53, 54]. Thus, with C-values of 37.85 (for 30 mg/L initial dye concentration system) and 37.72 (for 40 mg/L initial dye concentration system), it is obvious that the acid blue 193 dye uptake was greatly aided by the intraparticle diffusion mechanism. Similarly, when the Bangham model produces a straight-line plot with a superior R^2 value, the possible involvement of pore diffusion is postulated. The results in Fig. 7 d and Table 3 indicate that the R^2 value for both adsorption systems is relatively high. As a result, the pore diffusion mechanism was equally crucial to the

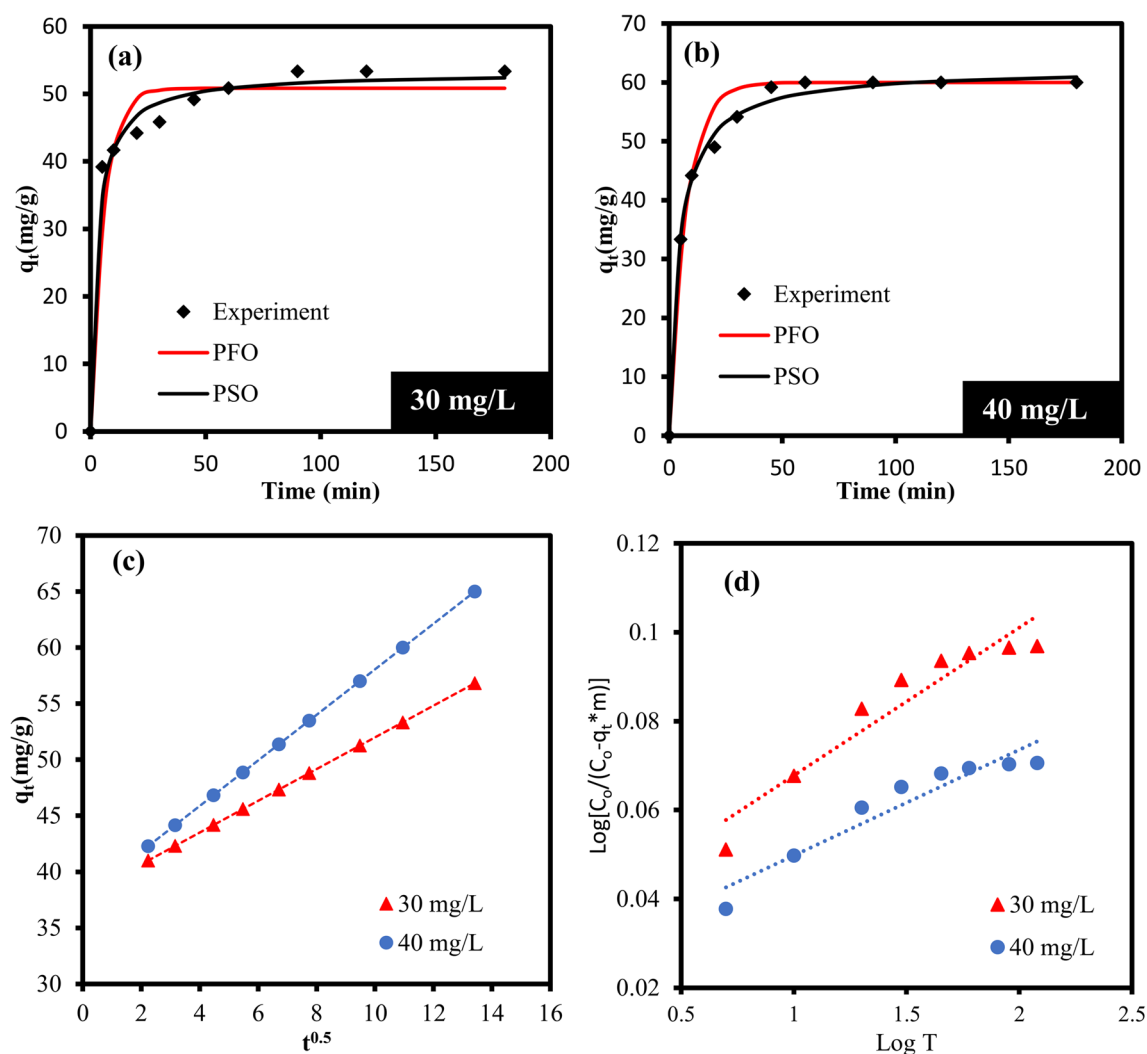


Fig. 8 **a** Nonlinear kinetic model plot at 30 mg/L adsorbate concentration. **b** Nonlinear kinetic model plot at 40 mg/L adsorbate concentration. **c** Intraparticle diffusion model plot. **d** Bangham model plot

Table 4 Thermodynamic parameters

Temp. (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)
313	3.988	31.086	513.570
323	3.738		
333	3.394		
343	3.063		

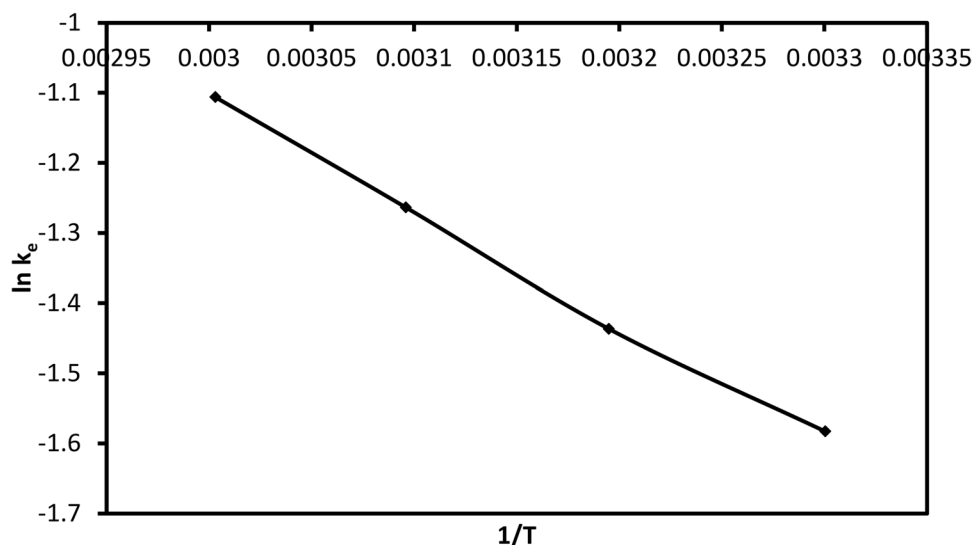
adsorption process. Therefore, it is noted that both the intraparticle and the pore diffusion mechanism control the present adsorption system at both 30 and 40 mg/L adsorbate concentrations.

3.3.3 Thermodynamics modeling

The temperature effect was elucidated in terms of process thermodynamics using the values of the change in Gibbs free energy, (ΔG°), change in enthalpy (ΔH°), and change in entropy (ΔS°). These thermodynamics parameters were evaluated using the appropriate version of Eqs. (10)–(10). Consequently, the generated thermodynamic data as presented in Table 4 is generated from the thermodynamics plot shown in Fig. 9.

$$\Delta G^\circ = -RT \ln k_c \quad (10)$$

Fig. 9 The thermodynamic plot for the adsorption of acid blue 193 dye onto CCP



$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$k_c = \frac{C_o - C_e}{C_o} \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

According to the results, positive values of ΔG° , ΔH° , and ΔS° were recorded. Despite the positive ΔG° values, the present system is thermodynamically favorable and spontaneous. This is because Doke and Khan [55] and Saha and Chowdhury [56] earlier reported that the spontaneity of a given adsorption process is guaranteed, even with positive ΔG° values, provided both ΔH° and ΔS° also retain positive values. Also, the system is predominantly physisorption, with an endothermic characteristic, judging from the fact that its ΔH° -value is respectively larger than zero and is also positive. Similarly, the positive value of ΔS° suggests an increase in the degree of entropy of this adsorption system. The aforementioned results are well related and logical, noting that external energy (positive ΔH° value), accompanied by increased system disorderliness (positive ΔS° value) is required to sustain the spontaneity of the adsorption system. Positive ΔH° and ΔS° values have been previously reported in several adsorption studies [57, 58]. Furthermore, during the adsorption of methylene blue dye onto coconut coir dust, Etim et al. [59] recorded positive ΔH° and ΔS° values at varying initial adsorbate concentrations. Similarly, Lyu et al. [60] reported positive ΔH° and ΔS° values during the adsorption of anionic azo dye Acid Red G onto magnetic polyaniline nanofibers.

3.4 Adsorption mechanism

The results of the different parameters, physical characterization, kinetic, and isotherm modeling were adopted to understand the adsorption mechanism. Based on the obtained results, acid blue 193 dye adsorption onto CCP involves different interaction mechanisms.

During the adsorption kinetics studies, an initial rapid solute uptake (occurring within the first 30 min of adsorption), which abated later upon equilibration at 180 min, was recorded. Also, the solute binding at the different initial concentration studies was well described by the pseudo-first-order model, thus highlighting the extensive role of physisorption interaction.

The effect of pH on the adsorption capacity can provide useful insight into prevalent adsorbent-adsorbate binding interaction. The pH_{pzc} of the CCP was recorded at pH 5.8 and optimum adsorption of acid blue 193 dye occurred within a strongly acidic pH range (between pH 2.0–3.0). Notably, at a strongly acidic pH range (where solution $\text{pH} < \text{pH}_{\text{pzc}}$), there is the protonation of the adsorbent surface groups and as a consequence, they electrostatically attract the negatively charged sulfonic acid ($-\text{SO}_3\text{H}$) group of the anionic acid blue 193 dye. This is an indicator of the importance of electrostatic interaction between the dye and biosorbents.

Furthermore, dipole-dipole hydrogen bonds might be formed between the highly polar $\text{C}=\text{O}$ and $-\text{OH}$ groups acting as proton donors on the surface of the CCP adsorbents and nitrogen atoms on the dye backbone (proton acceptors). This development is further buttressed by the decrease in the % absorbance of the aforementioned functional groups in the post-adsorption FTIR spectra. It is therefore proposed that the adsorption of acid blue 193

Table 5 Comparison of the adsorption capacities of different dyes onto agro-waste

Agro waste	Operating conditions				Surface area (m ² /g)	Adsorbate	q_e (mg/g)	Ref
	pH	Adsorbent dose (g/L)	Contact time (min)	Initial conc. (mg/L)				
Rice husk	2.0	0.2	60.0	5.0	342.5	Tartrazine	1.24	[61]
Coconut dreg	11.0	0.25	240.0	50.0	–	Methylene Blue	5.72	[62]
	2.0	0.25	180.0	50.0	–	Brilliant Red Remazol	3.76	
<i>Lupinus albus</i> seed peel	4.0–6.0	0.2	60.0	30.0	1170.0	Malachite Green	6.60	[63]
Lemon peel	2.0	0.5	60.0	25.0	–	Eosin	8.24	[64]
Macadamia shells	11.0	0.25	150.0	30.0	2.76	Methylene Blue	25.77	[65]
<i>G-seed</i>	2.0	0.2	180.0	25.0	38.25	Acid Violet 90	30.05	[66]
<i>Citrullus colocynthis</i> fruit peel	3.0	0.01	120	30	58.04	Acid Blue 193	139.83	Present study
Rice straw	7.0	0.1	60.0	140.0	4.42	Methylene Blue	158.0	[67]

dye onto CCP occurred via physisorption, electrostatic, and hydrogen bonding interactions.

Table 5 displays the dye adsorptive performance of different biomass-based adsorbents as compared to those of the adsorbent utilized in this study. From the presented data, it is observed that the adsorption performance recorded in this study is well-situated among the previously published works.

4 Conclusion

Waste *Citrullus colocynthis* fruit peel was utilized to prepare an adsorbent, termed CCP which is utilized for the removal of acid blue 193 dye from simulated wastewater. The CCP underwent characterization via FTIR, SEM, EDX, XRD, and BET analysis. Due to its inherent functional groups, CCP exhibited strong adsorption capabilities for acid blue 193 dye, with a monolayer adsorption capacity of 139.83 mg/g. The surface area, pore volume, and pore radius of CCP were measured at 58.04 m²/g, 0.041 cm³/g, and 1.92 nm, respectively. Furthermore, the adsorption capacity varied with solution pH. Optimal dye uptake was attributed to electrostatic interactions between the protonated surface groups of the adsorbent and the negatively charged sulfonic acid (–SO₃H) group of the anionic acid blue 193 dye, along with hydrogen bond formation between the highly polar C=O and –OH groups of the CCP adsorbents and nitrogen atoms on the dye backbone. This successful adsorption study holds significant implications for addressing dyeing wastewater by offering a promising avenue for utilizing agricultural waste.

Author contribution A. Hashem: project administration, experimentation, visualization of the original draft and provided critical feedback on the manuscript draft.

Chukwunonso O. Aniagor: conceptualization; data curation; writing—original draft; writing—review and editing and provided critical feedback on the manuscript draft.

Osama Morsy: investigation, methodology, data analysis, and provided critical feedback on the manuscript draft.

S. Farag: investigation, methodology, data analysis, and provided critical feedback on the manuscript draft.

A.A. Aly: investigation, methodology, data analysis, and provided critical feedback on the manuscript draft.

All authors have read and approved the final manuscript.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB).

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

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