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The Optimization and Mechanism of Textile Dye Adsorption on the Surface of Pine Sawdust Biomass: Thermodynamic, Isotherm and Kinetic Studies

Abstract

Due to increasing problems of freshwater availability and wastewater treatment and management, there is a dire need to control water pollution. A major portion of wastewater is produced through dye contamination from textile industries. In this study, efforts were made to evaluate the renewable, environment-friendly, and biomass-based adsorbent for the effective removal of dyes from aqueous solution. Pine sawdust biomass samples were subjected to adsorption under different parametric studies to optimize the adsorption process efficiency. The maximum adsorption efficiency was observed around 50-60 % under different working conditions. This study demonstrates that the non-linear versions of the PSO and IPD kinetic models were better than the linear forms from the perspective of the dye adsorption mechanism. Comparably, the nonlinear fitting of the Freundlich model yielded lower χ^2 values and higher R^2 values than the linear fitting. Positive Gibbs free energy values imply that the adsorption is non-spontaneous and thermodynamically unfavorable at the investigated temperatures. The thermodynamic study shows that the adsorption of BBY onto the PSD adsorbent is an exothermic process.

Keywords: sawdust adsorbent, textile dye, adsorption, linear, nonlinear fitting

Introduction

Dye-contaminated water is becoming a huge threat to aquatic life survival and freshwater scarcity. Due to the rapid growth of art and fashion trends, there are numerous dyes used at the industrial level in the printing of cloth, from where a huge amount of dye-contaminated wastewater is produced every day (Tkaczyk et al., 2020).

Currently, there is insufficient installed technology for the treatment of such contaminated water which is discharged and mixed with freshwater resources such as lakes, rivers, and sea (Gadir et al., 2020). Treating this kind of wastewater is not an easy task because of the very fine particle size of dyes which cannot be filtered using ordinary membranes and the filtration process (Radjenovic & Sedlak, 2015). Biological process could be a suitable alternative (Grady et al., 2011). but the huge amount of wastewater produced cannot be cleaned every day because of the slow process efficiency of the biological process (Babuponnusami et al., 2023). Chemical processes are efficient processes that can meet the requirement of treating such a significant amount of wastewater (Shannon et al., 2008).

Chemical processes are of many subdivided methods, but the main two categories can be divided into two processes: adsorption and photocatalytic degradation which may be the economical way of treatment at the industrial level (Jo, Prajitno, Zeb, Kim, 2017; Solayman et al., 2023). The photocatalytic process is efficient in terms of cleaning the water from dyes, but it produces a lot of unknown organic free radicals which could perform several reactions with the other species present in the environment. Free radical accumulation and the production of secondary pollutants are more dangerous for human health and the ecosystem (Zeb et al., 2017; Khan et al., 2023).

So, the adsorption of such dye molecules over the surface of the suitable adsorbent and then their desorption under controlled conditions for their proper disposal off may be the future technology. Another aspect of the absorption of dyes over suitable adsorbent from dye-contaminated industrial effluent could provide the baseline to reuse the wasted dyes (Solayman et al., 2023)

There are various types of adsorbents (Shahbaz et al., 2019; Aljohani et al., 2023) in use such as metal oxide, metal nanoparticles, single atoms, bimetallic catalysts, organic-inorganic hybrid (Zeb et al., 2022; Mohan et al., 2023) and several biomass-based renewable and environmentally friendly materials (Hafiza et al., 2023; Siddigi et al., 2022) which may be used as adsorbent material for the effective adsorption of dyes. In biomaterials graphene, graphitic materials, metal-doped graphene, non-metal atom doped graphene, raw biomass, physical and chemical processed biomass, coal char (Asif et al., 2023; Agarwala, Mulky, 2023). and biochar could be used as an effective material for adsorption (Ravindiran et al., 2023; Hassan et al., 2023; Asif et al., 2024; Khan et al., 2024).

In this study, pine sawdust (PSD) was subjected to the adsorption of Bismarck brown dye from an aqueous solution. Before that many studies have been reported to evaluate the biochar produced after the pyrolysis of organic materials (Zeb et al., 2017; Asif et al., 2023), although this is a good approach there are huge changes during the pyrolysis which depends on the pyrolysis condition and reproducibility is very difficult. Here in this study raw biomass showed an adsorption efficiency of 50-60 % under various industrial relevant conditions, showing potential for commercialization for industrial wastewater treatment.

Material and Methodology

Pretreatment of Pine Sawdust

Pine sawdust (PSD) was used which was obtained from the nearby carpenter shop. The acquired sawdust was washed and then grounded using a disk mill, to get a 40-mesh size (420 μm) using an automatic sieve shaker. This type of particle size is well applied for adsorption purposes. The ground sawdust was left overnight in the oven at 80 $^{\circ}\text{C}$ using a muffle furnace and the moisture contents were removed completely (Nair et al., 2023).

Preparation of BBY Stock Solution

The 1000 mg/L BBY dye concentration stock solution was produced by dissolving 1 gm analytical grade (Merck) for both dyes in 1000 mL of deionized water. Solutions with lower dye concentrations were made through appropriate dilutions using deionized water (Eq. 1).

$$C_1V_1 = C_2V_2 \quad (\text{Eq. 1})$$

Whereas C_1 and C_2 are the concentrations of stock and the required solutions respectively. V_1 and V_2 are the volumes of stock solution and the required volume for dilution respectively.

Preparation of 0.1M HCl and 0.1M NaOH solution

In this experiment, the adsorbent is tested on different pH to check the adsorbent's performance for adsorption. The experiments are conducted on different acid and base pH adjusted through acid and base solutions that are HCl and NaOH respectively. For this 0.1 molar HCl and 0.1 molar NaOH were prepared by adding 0.8 mL HCl into 100 mL of deionized water providing 0.1 molar of HCl. Likewise, 0.1 molar of NaOH solutions were obtained by adding 400 mg of analytical grade NaOH in 100 mL of deionized water (Tabish).

Batch adsorption experiments

The Kinetics batch experiment was conducted with 0.05 g of PSD (raw, physically modified, and chemically modified) by attachment with 50 mL of BBY and MG dye (concentration ranging from 25-150 mg/L) in Erlenmeyer flasks. The pH was not adjusted initially, and it was 6.5 for MG and for BBY adjusted at 4 pH which was determined by the PHS-38W microprocessor pH/temperature meter. After preparation, the solution was kept in a shaking incubator (wise cube WIS-20) and was used to shake the flask for 120 mins at 150 rpm at room temperature which is 30 $^{\circ}\text{C} \pm 1$. The adsorbed dye was then measured through a T80+UV/VIS Spectrometer at 616 nm for MG and 416 for BBY. The values were then used to estimate the concentrations. All the experiments were carried out in triplicates. The amount of dye adsorbed on the adsorbent was calculated using the following equation (Kalengyo et al., 2023):

Percentage removal was calculated by the following equation:

$$S(\%) = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (\text{Eq. 2})$$

Where S % is the removal percentage, C_i and C_f were the initial and final concentrations (mg L^{-1}).

$$qe = (C_i - C_f) \frac{V}{M} \quad (\text{Eq. 3})$$

Here q_e is the equilibrium concentration of dye (mg g^{-1}), C_i and C_f are the initial and final dye concentrations (mg L^{-1}), V is the solution volume (L) used and M is the adsorbent mass (g).

Equilibrium time

The experiment was conducted at several contact times, 5 to 300 mins, and the sample was taken twenty minutes apart each (i.e. 2, 5, 10, 20, 40, 60, 80, 100, and 120), while other parameters were kept constant. Equilibrium time is important to find out the time in which the equilibrium for adsorption occurs.

Initial dye concentration

The experiment was carried out by varying the dye concentration, i.e., from 25 mg L^{-1} to 200 mg L^{-1} 25, 50, 70, 100, 150, and 200 mg/L .

Particle size

Experiments were carried out to study the impact of different particle sizes, ranging from mesh size 40 to 140 (400 to $105 \mu\text{m}$) i.e. 40, 60, 80, 100, 120, and 140.

Adsorbent dose

The adsorbent dose experiment was examined from 25 mg to 300 mg, i.e. 25, 50, 75, 100, 150, 200, 250, and 300 mg L^{-1} .

Temperature

Adsorption capacities of adsorbents were studied at different temperatures ranging from 30 to 50°C , at the intervals of 5°C i.e. 30, 40, and 50°C .

pH

pH is the most influential parameter in adsorption studies as it affects the adsorption capacity of the adsorbent. The experiment was carried out at different pH values pH 4-10 for BBY.

Kinetic Analysis

Adsorption capacity was determined as follows:

$$q_t = \frac{(C_o - C_t) * V}{m} \quad (1)$$

Where V (mL) denotes the volume of the dye solution and m (g) represents the mass of the adsorbent. C_o represents the initial concentration (mg/L) of the dye and C_t is the concentration of dye at time t (mg/L).

The percentage removal is calculated using Equation 2.

$$\% \text{ Removal} = \frac{(C_o - C_t)}{C_o} * 100 \quad (2)$$

PSO and Intraparticle diffusion models

Linear and non-linear kinetic models curve fitting and error function analysis

The adsorption kinetics modeling explains the rate of adsorption of adsorbate from liquid to solid phase. RB5 dynamical adsorption data was fitted into linear and non-linear equations of pseudo-second order (PSO) (Equations 4 and 5) and intra-particle diffusion (IPD) (Equation 6) models. The possible adsorption process for RB5 once in contact with TSB adsorbent in solution: (i) movement of RB5 molecules from bulk solution to the external boundary film adjacent to TSB adsorbent; attachment of dye molecules to the binding sites of TSB which is a rapid step and may include the physical adsorption or chemical (whether weak or strong) and/or both; (iii) RB5 diffusivity into the inner sites of TSB.

PSO kinetic model (Ho et al., 1999) assumes adsorption over the complete contact time range expressed in differential form as under;

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (3)$$

Integrating Eq. 24 while applying boundary conditions ($t=0, q_t=0, t=t$ and $q_e = q_t$)

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (4)$$

Linearizing

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Intraparticle diffusion (IPD) model

$$q_t = K_{pi} t^{\frac{1}{2}} + C_i \quad (6)$$

The calculated values of kinetic model parameters, constants, and R^2 are listed in Table 2.

Isotherms analysis

To analyze the underlying adsorption mechanism, linear and nonlinear forms of Langmuir and Freundlich isotherms were fitted to equilibrium data collected by varying initial concentrations of BBY dye, i.e., 25, 50, 75, 100, and 200 mg/L.

Langmuir determines the chemisorptive interaction between adsorbate and adsorbent and indicates monolayer formation. Both linear (equation 3) and non-linear (equation 4) forms are given as:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}} \right) \frac{1}{C_e} + \frac{1}{q_{max}} \quad (7)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (8)$$

Where C_e represents the concentration at equilibrium (mg.g^{-1}), q_{max} denotes the maximum adsorption capacity of adsorbent (mg.g^{-1}) and K_L stands for the Langmuir constant, which is used to determine the maximum energy of adsorption related to the area occupied by the adsorbent.

The Freundlich isotherm was used to verify the nature of the multilayer adsorption of MG as well as the heterogeneity of the studied adsorbent. Linear (Equation 5) and non-linear (Equation 6) forms of this model are generally expressed as.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (9)$$

$$q_e = K_F C_e^{1/n} \quad (10)$$

Where, C_e represents the concentration at equilibrium, while q_e denotes the amount of adsorbate per unit mass of the adsorbent (mg.g^{-1}), K_F is the adsorption capacity and $1/n$ indicates the adsorption intensity. The error distribution, i.e., Chi-square (χ^2) error, between experimental and linear model predicted values q_{cal} were minimized by reducing the error function using solver add-in Microsoft Excel.

The chi-square (χ^2) error function equation used for this function is as follows:

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e \text{ exp}} - q_{e \text{ cal}})^2}{q_{e \text{ cal}}} \quad (11)$$

$$\text{Coefficient of determination } (R^2) = \frac{\sum (q_{t \text{ cal}} - \bar{q}_{t \text{ exp}})^2}{\sum (q_{t \text{ cal}} - \bar{q}_{t \text{ exp}})^2 + \sum (q_{t \text{ cal}} - q_{t \text{ exp}})^2} \quad (12)$$

Thermodynamic Analysis

The BBY adsorption by PSD with temperature was explained further by thermodynamic parameters, i.e., changes in Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH). To dimensionless equilibrium constant (K_d , L/g), K_d was multiplied by solution (water) density ($\rho_w \approx 1000 \text{ g/mL}$) (Tran). The above thermodynamic parameters were estimated using slope and intercept of Van't Hoff plot ($\ln K_d$ versus $1/T$) with the help of the following equations:

$$\ln K_d (\rho_w) = \frac{q_e}{R} \quad (13)$$

$$\ln K_d (\rho_w) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

Results and Discussion

Discussion on Dye Removal by PSD Adsorbent

The set of graphs provides a thorough examination of the PSD adsorbent's dye removal effectiveness and adsorption capacity across a range of circumstances, including pH, contact time, initial dye concentration, and adsorbent dose

Effect of Contact Time

Graph (a) shows the connection between adsorption capacity and dye removal effectiveness as well as contact time. Within the first 50 minutes, the dye clearance % rises quickly, suggesting a high initial adsorption rate since there are plenty of active sites. Following this time frame, the removal rate steadily declines and reaches about 35 % after 300 minutes. With most of the active sites occupied, this plateau indicates that the adsorption process has nearly reached equilibrium. Similarly, the adsorption capacity exhibits an initial rapid increase before stabilizing at approximately 15 mg/g, indicating the equilibrium state. A slow approach to equilibrium is typical of many adsorbents, after the initial fast adsorption phase (Yadav et al., 2022).

Effect of Initial Dye Concentration

Different starting dye concentrations (C_0) have an impact on dye removal and adsorption capability, as shown in Graph (b). As the concentration rises, the clearance % first rises and peaks at around 70 mg/L before slightly declining. This pattern implies that larger dye concentrations at first give a stronger mass transfer driving force, which improves adsorption. Saturation of the active sites causes the clearance efficiency to decrease at very high concentrations. As dye concentrations rise, on the other hand, the adsorption capacity increases and reaches a maximum of about 55 mg/g at 200 mg/L. While the effectiveness in terms of % removal declines at high dye concentrations, this suggests that the PSD adsorbent has a large capacity for dye uptake (Gupta et al., 2011).

(a) Effect of Adsorbent Dose

The adsorbent dose has an impact on both adsorption capacity and dye removal, as seen in graph (c). At 5 g/L, the dye removal percentage reaches a maximum of around 55% as it increases with the adsorbent dosage. The increased availability of adsorption sites with larger adsorbent amounts is the cause of this growth. Nevertheless, there is a trend toward a diminishing adsorption capacity (mg/g) as the adsorbent dose increases. According to this inverse connection, while the amount of adsorbents increases overall dye removal, the amount of dye absorbed per unit weight of the adsorbent decreases. This is probably because higher dosages of adsorbent particles aggregate, which reduces the surface area available for adsorption (Kara et al., 2007).

(b) Effect of pH

Graph (d) shows how pH affects adsorption capacity and the effectiveness of color removal. When the pH rises from acidic to alkaline, both metrics exhibit a noticeable decrease. The pH of 2 yields the maximum dye removal % and adsorption capacity, suggesting that acidic environments are the optimal conditions for the PSD adsorbent to function. Surface charges of the adsorbent and the dye's ionization state are responsible for the decline in performance at higher pH values. Adsorption efficiency is increased in acidic environments by the positive charge on the adsorbent surface, which increases the attraction of negatively charged dye molecules. Reduced dye adsorption occurs in alkaline settings due to electrostatic repulsion caused by the negative charge on the adsorbent surface (Yadav et al., 2022).

The PSD adsorbent exhibits efficacious dye removal properties, whereby its performance is contingent upon contact time, initial dye concentration, adsorbent dosage, and pH. Lower pH, higher starting dye concentration, proper contact time, and regulated adsorbent dosage are ideal for achieving maximum dye removal and adsorption capacity. These results offer insightful information for maximizing PSD adsorbent utilization in real-world dye removal applications.

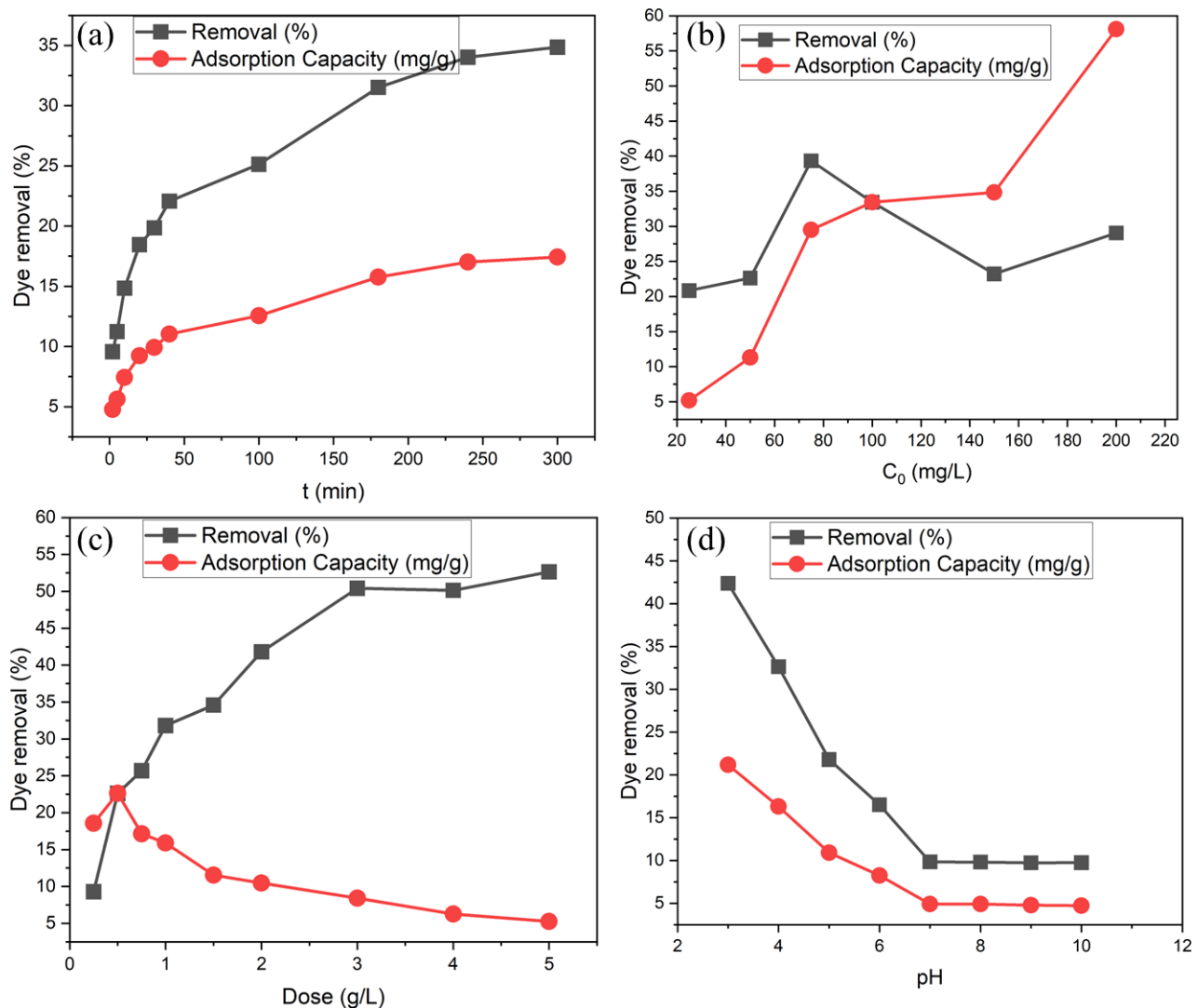


Figure 1. Evaluation of the prepared bio-adsorbent with BBY dye under different parameters
 (a) Effect of time (b) Effect of initial dye concentration (c) Effect of dose of the adsorbent
 (d) Effect of pH

Effect of Temperature

Figure 2. (a) illustrates the connection between temperature (T), adsorption capacity, and dye removal efficiency. At 30 °C, the proportion of dye removed climbs to around 22 %; at 50 °C, it reaches about 30 %. This temperature increase is consistent. This pattern suggests that higher temperatures improve the adsorption process. This is probably because the dye molecules have more kinetic energy, which makes it easier for them to move and interact with the adsorbent surface. Higher temperatures may also cause the adsorbent's pores to enlarge, creating more active sites for the adsorption of dyes. Additionally, there is a positive association between temperature and adsorption capacity, which increases from roughly 15 mg/g at 30 °C to 25 mg/g at 50 °C. This improvement shows that the adsorption process is endothermic, meaning that the dye molecules and PSD adsorbent interact better at higher temperatures (Senthil Kumar et al., 2014).

Effect of Particle Size

Particle size has an impact on both adsorption capacity and dye removal efficiency, as shown in Figure 2. (b). The dye removal percentage increases dramatically as the particle size drops from 400 μm to 100 μm , reaching a maximum of approximately 55 % at the smallest particle size. The reason behind this increase is that smaller particles have more surface area available for adsorption, which means that there are more active sites for dye molecules to stick.

In a similar vein, the adsorption capacity increases marginally as the particle size decreases, going from roughly 15 mg/g at 400 μm to about 25 mg/g at 100 μm . By improving the surface area-to-volume ratio, the adsorbent may absorb more dye molecules per unit weight because of the reduced particle size.

Higher temperatures and smaller particle sizes show enhanced dye removal efficiency and adsorption capacity of the PSD adsorbent. While the rise in smaller particle sizes emphasizes the significance of surface area in adsorption efficiency, the temperature-dependent increase in adsorption points to an endothermic adsorption process. These results highlight the possibility of maximizing PSD adsorbent performance in dye removal applications by improving adsorption conditions, such as temperature control and particle size reduction (Kara et al., 2007).

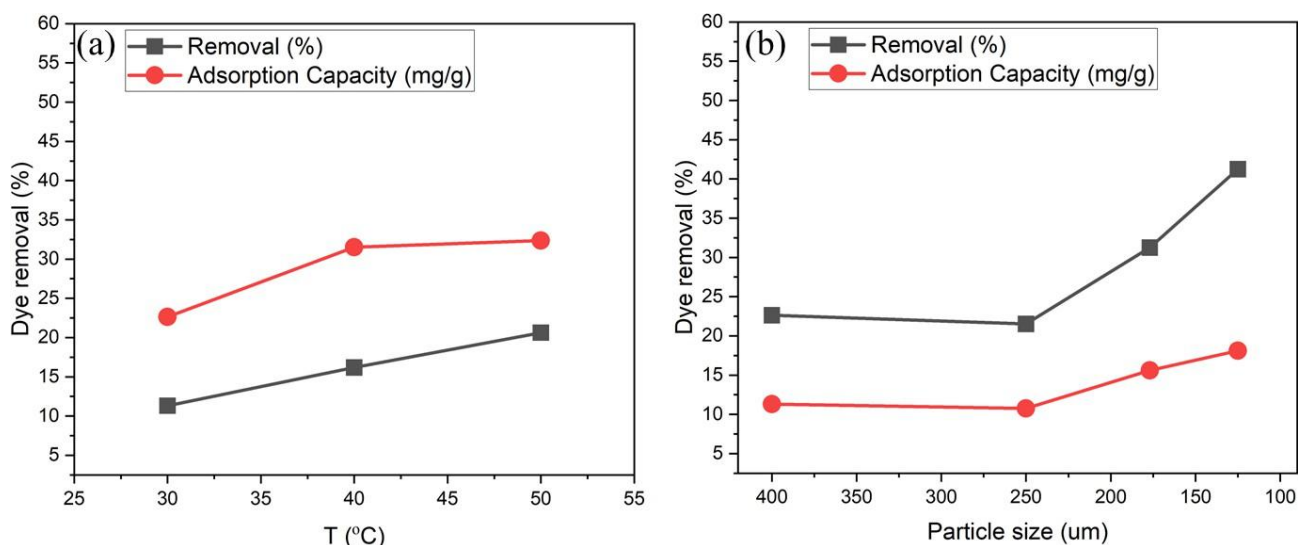


Figure 2. Evaluation of the prepared bio-adsorbent with BBY dye under different parameters
(a) Effect of Temperature (b) Effect of particle size of the PSD adsorbent

Kinetic models

Intraparticle diffusion (IPD) and pseudo-second order (PSO) kinetic models were employed to kinetics experimental data for the investigation of the rate of adsorption of dye on the adsorbent. These models have been extensively applied to explain the adsorption mechanism of pollutants from wastewater. The IPD model accounts for the pore and surface diffusion mechanisms which are greatly influenced by the porosity and the nature of the contaminant transport pathway.

In this (equation 6), I (mg g^{-1}) is the intercept and k_{diff} is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). The values of q_t were found to be linearly correlated with values of $t^{1/2}$ and the rate constant k_p was directly evaluated from the slope of the regression line. The linear form of the Pseudo second-order kinetic model can be expressed as:

Here in this equation, $5 q_e$ represents the equilibrium amount of the adsorbate absorbed in mg/g of the adsorbent, q_t denotes the quantity adsorbed in mg/g of the adsorbate at time t , and k_2 (min^{-1}) stands for the pseudo-second-order rate constant. IPD and PSO order plots are shown in figure 3a and 3b respectively. It can be seen from figure 3a that at a dye concentration of 30 mg/L , the model showed a poor fit with a correlation coefficient (R^2) of 0.6899. In contrast, at 100 mg/L , a higher R^2 value of 0.9048 was observed, suggesting a more significant role of intraparticle diffusion in the adsorption mechanism at higher dye concentrations similarly figure 3b depicts that when dye concentration is 30 mg/L , the Pseudo-second order model exhibited a R^2 value of 0.9741, and at 100 mg/L , R^2 value of 0.9809. Compared to the intraparticle diffusion model, the Pseudo-second order model demonstrates a better fit for the adsorption process at both concentrations, indicating that the adsorption kinetics are more accurately described by the Pseudo-second order mode.

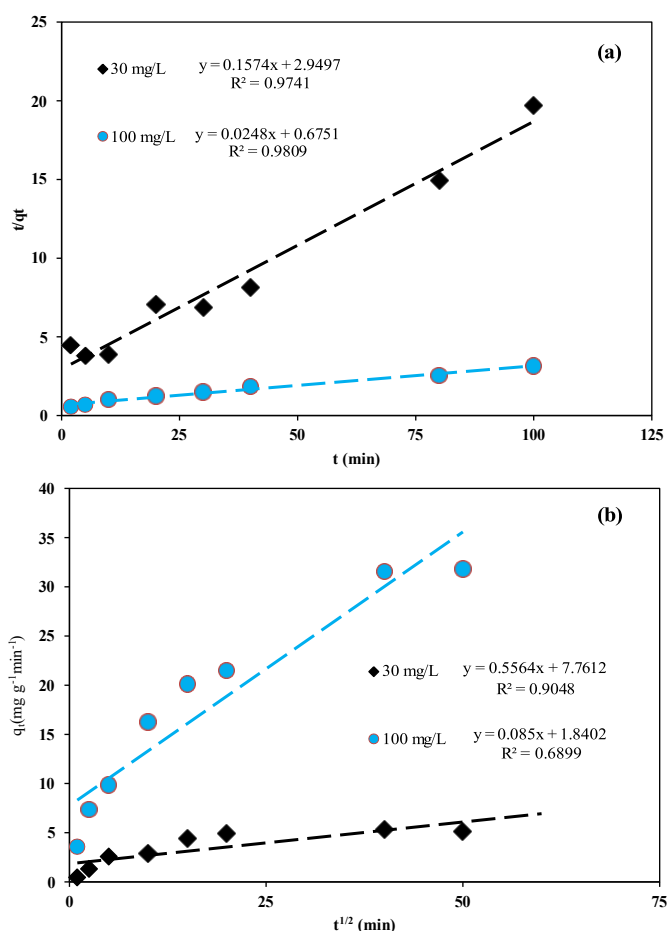


Figure 3. Kinetic modeling of the dye adsorption on PSD adsorbent (a) intraparticle diffusion model and (b) Pseudo second order kinetic model. Comparison of linear and Nonlinear fitting of IPD and PSO model

The kinetic parameters for BBY adsorption onto PSD adsorbent biomass were analyzed using both linear and nonlinear fitting for the PSO and IPD models. The linearized form of both models is provided in equation 6 and equation 5. The nonlinear form of the PSO model is as follows:

When using the linear form, experimental adsorption kinetics must be converted to a linear format for linear least-squares regression to estimate model parameters. It has been noted that changing non-linear equations to linear forms can unintentionally change how errors are measured in the model parameters. The kinetic parameters obtained from the linear and nonlinear fittings (figures 4a and 4b) are listed in table 1. It can be seen from table 1 that nonlinear fitting for the PSO model indicated better agreement with experimental data, evidenced by its lower χ^2 value (0.31 and 0.83 for 30 and 100 mg/L) and higher accuracy in q_e cal. values compared to linear fitting. The R^2 values were high for both fittings, indicating good fitness. In the case of the IPD model, nonlinear fitting demonstrated higher performance with higher R^2 values (0.9877 and 0.9802 for 30 and 100 mg/L respectively) and lower χ^2 values, suggesting that nonlinear fitting provides a more accurate representation of the BBY removal kinetics. Thus, nonlinear fitting is the better approach for both models based on these parameters. As evidenced by figure 4 and figure 5, q nonlinear is closer to q experimental these results demonstrate that non-linear fitting will be more appropriate than linear fitting to obtain the kinetic parameters.

Table 1.
Non-linear kinetic model parameters for BBY adsorption onto PSD adsorbent biomass

Kinetic models	Parameters	Initial MG Dye Concentration (mg/L)			
		Linear analysis		Nonlinear analysis	
		30	100	30	100
	$q_{e\text{ exp}}$ (mg/g)	5.35	31.38	5.35	31.38
PSO	$q_{e\text{ cal}}$ (mg/g)	6.35	40.32	6.62	39.77
	k_2 (g/m.min)	0.008	0.0009	0.0075	0.0009
	χ^2	0.32	0.89	0.31	0.83
	R^2	0.9741	0.9809		
IPD	I	1.84	7.76	2	5.2
	K_{diff} (mg/g.min)	0.04	0.28	0.2	2.33
	χ^2	11.62	50.42	10.64	10.33
	R^2	0.6899	0.9048	0.9877	0.9802

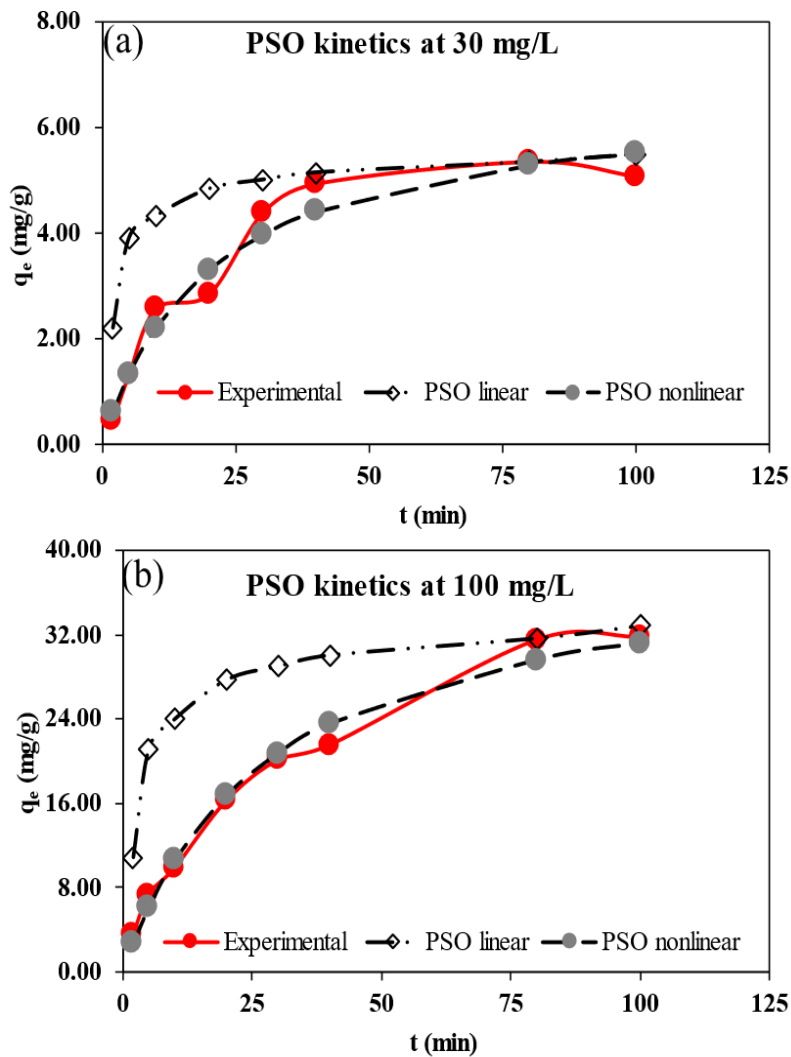


Figure 4. Comparison of predicted linear and nonlinear fitting of PSO under different initial dye concentrations, with experimental values (a) PSO kinetic modeling of 30 mg/L and (b) PSO kinetic modeling at 100 mg/L

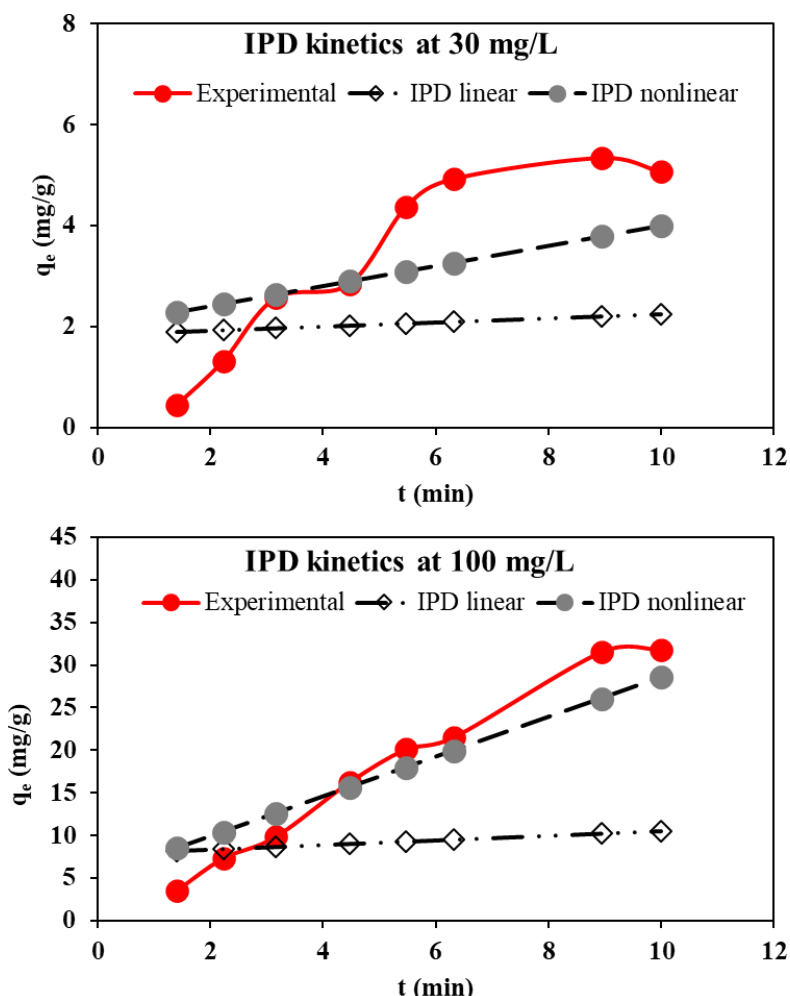


Figure 5. Comparison of predicted linear and nonlinear fitting of IPD under different initial dye concentrations, with experimental values (a) IPD kinetic modeling of 30 mg/L and (b) IPD kinetic modeling at 100 mg/L

Thermodynamic Analysis

The effect of different temperatures on adsorbent was studied and removal of BBY is displayed in Figure. 6a. The temperature varied at 300, 305, 310, 315 320, and 325. K The removal of BBY onto the adsorbent did not increase with a rise in temperature from the thermodynamic parameters including a change in enthalpy (ΔH) and entropy (ΔS) were computed using the Van't Hoff equation as under:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

Change in Gibbs free energy (ΔG) was determined using the equation. 16.

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The thermodynamic parameters in Table 2 for BBY elimination using BD adsorbent give information about the nature of the adsorption process. The negative values of enthalpy change (ΔH) and entropy change (ΔS) indicate that the process is exothermic. The positive Gibbs free energy change (ΔG) values indicate non-spontaneous adsorption at increased temperatures. The positive ΔG values also indicate that the adsorption process is not thermodynamically favorable under the current conditions.

Table 2.
Thermodynamics parameters calculated for BBY adsorption onto PSD adsorbent

ΔH (kJ/mol)	ΔS (J/mol.k)	ΔG (kJ/mol)			R^2
		303.1 5 K	313.1 5 K	323.1 5 K	
35.69	0.17	-14.34	-15.17	-15.99	0.9972

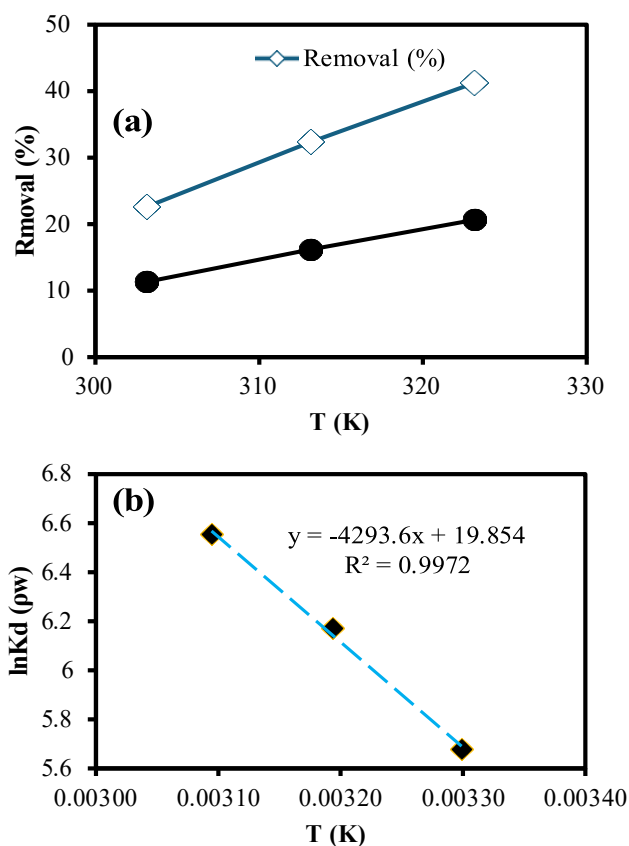


Figure 6. Effect of process parameters on BBY dye adsorption
a) Temperature, b) Van't Hoff plot

Adsorption Isotherms

By fitting the adsorption experimental data to different isotherm models, we can identify the most appropriate model that describes the adsorption behavior and gain an understanding of the driving forces behind the process. The equilibrium data of BBY on adsorbent was evaluated using linearized and nonlinearized forms of Freundlich and Langmuir isotherm models.

Here, KL represents the Langmuir isotherm constant, C_e is the adsorbate's concentration (mg/L), and Linear (equation 8) and non-linear forms of Freundlich isotherm are generally expressed as.

Here K_F is the adsorption capacity (mg/g), adsorption intensity is represented by $1/n$, q_e is the adsorbate uptake (mg/g), and C_e is the equilibrium concentration of dye in solution (mg/L). Table 3 displays all estimated parameters of linear and nonlinear fitting of Langmuir and Freundlich Isotherm models. The Langmuir model's linear fitting had a higher R^2 value of 0.9373 but a lower χ^2 value compared to its nonlinear fitting, which had a lower R^2 of 0.6154 but a higher χ^2 value. Similarly, the Freundlich model's nonlinear fitting showed higher R^2 and lower χ^2 values than its linear fitting. Overall, nonlinear fitting produced a better fit for both models.

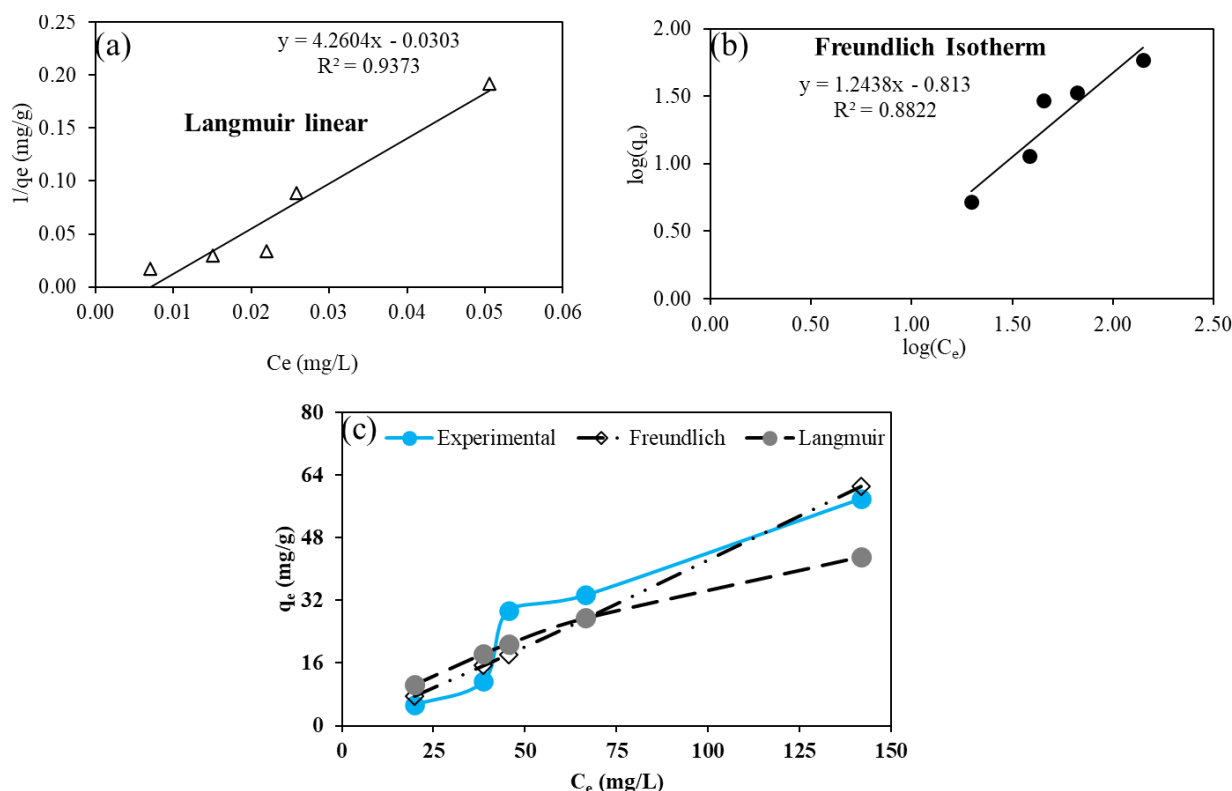


Figure 7. Isotherms Analysis (a) Langmuir isotherm analysis (b) Freundlich isotherm analysis (c) comparison of Experimental and Freundlich and Langmuir isotherm

Table 3.
Comparison of Isotherm Parameters: Linear vs. Non-Linear Fitting for the removal BBY dye by PSD biomass adsorbent

Isotherms	Parameters	Values	
		Linear fitting	Non-linear fitting
Langmuir	q_{exp}	58.12	
	q_{max}	33.00	86.62
	R^2	0.9373	0.6154
	χ^2	72.21	25.82
Freundlich	K_f	6.50	0.31
	n	0.80	0.94
	R^2	0.88	0.9005
	χ^2	17.32	7.98

Conclusion

This study aimed to explore the adsorption behavior of BBY dye on the surface of a powdered PSD biomass sample. Dye adsorption efficiency was optimized through the treatment of PSD biomass with dye solution under different working parameters such as equilibrium time, initial dye concentration, adsorbent dose, temperature, pH, and under different particle sizes of the biomass sample. The maximum dye adsorption efficiency was found to be around 50-60 % under different working conditions. This study shows that the non-linear forms of the PSO and IPD kinetic models were superior to the linear forms. Similarly, the Freundlich model's nonlinear fitting showed higher R^2 and lower χ^2 values than its linear fitting. The thermodynamic analysis reveals that the adsorption of BBY onto the PSD adsorbent is an exothermic process, and the positive Gibbs free

energy values suggest that the adsorption is non-spontaneous and thermodynamically unfavorable at the studied temperatures.

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