Adsorptive Removal of Dye (Methylene Blue) Organic Pollutant from Water by Pine Tree Leaf Biomass Adsorbent

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Abstract: In this laboratory batch adsorption study, the raw pine tree leaf biomass solid waste adsorbent material was used for the removal of methylene blue (MB) dye from water at different physicochemical process conditions. The characteristics of adsorbents were determined for particle size, surface area, the existence of functional group identification, and the morphology of the adsorbent surface. The adsorption was performed at different process conditions, which include solution pH, dye concentrations, adsorbent doses, and temperature, respectively. In this study, it was found that MB dye adsorption increased with increases in solution pH and adsorbate MB dye concentration but decreased with adsorbent doses and temperature at fixed process conditions. The Langmuir isotherm model was best fitted with the experimental equilibrium data, with a higher linear regression coefficient ($R^2$) value of 99.9% among the two widely used Langmuir and Freundlich adsorption isotherm model equations. The maximum Langmuir monolayer adsorption capacity of raw pine leaf was found to be 36.88 mg/g, which was comparable with other reported adsorbent capacities towards methylene blue (MB) dye adsorption. The value of the separation factor, $R_L$, from the Langmuir isotherm model equation gives an indication of favorable adsorption. Thermodynamic parameters such as standard Gibbs free energy change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$), and standard entropy change ($\Delta S^0$) indicated that the methylene blue (MB) dye adsorption by pine tree leaf biomass was spontaneous and exothermic in nature and that the mechanism of adsorption was mainly physical adsorption. Finally, limitations and future studies are also discussed here. The outcome of this batch adsorption study may result in the valorization of locally available large pine tree leaf residue waste, which could be used in water purification.

Keywords: methylene blue dye adsorption; pine tree leaf biomass adsorbent; thermodynamics; equilibrium isotherm model

1. Introduction

Synthetic dyes are commonly used as coloring agents in different industries, such as the textile, food, paper, and cosmetic industries, for their products colours [1–3]. Interestingly, the textile industry is the largest consumer of synthetic dyes, utilizing about 56% of the total world dye production per year [4]. The discharge of untreated colour dye-bearing effluents from these industries into natural streams caused increased toxicity levels and chemical oxygen demand (COD), which had a significant derogatory effect on photosynthetic phenomena [4–6]. The dye-bearing effluents are toxic, and synthetic dyes are carcinogenic and take a long time to degrade [6]. The presence of the azo group (-N=N-) in synthetic dyes makes them non-biodegradable, toxic to life, and potential pollutants [6]. The cationic MB dye is most commonly used in various industries, such as textile and leather dyeing, medical applications, printing, and tannery industries [7]. Whereas anionic dyes are comparatively less toxic than cationic methylene blue (MB) dye. It was reported that approximately 15% of synthetic dye production per year has been lost during various industrial processes that commonly produce and handle organics that
Processes 2023, 11, 1877 2 of 16

are toxic and harmful to life [8]. Wastewaters from dye production and application industries present an environmental problem because the color is visible even at low dye concentrations. Although methylene blue (MB) is less toxic to human health, it can cause eye irritation, skin irritation, vomiting, nausea, diarrhea, mental disorderness, etc. [7,9]. The selection of a suitable treatment method for dye removal becomes complicated due to their non-biodegradable stability toward light and oxidizing agents [10]. Over the years, several methods, such as membrane separation, including reverse osmosis, flocculation and coagulation, electrochemical processes, advance oxidation, adsorption and ion-exchange, precipitation, photocatalytic reduction, biological treatments etc., have been used for dye removal from wastewater. Among these separation techniques, adsorption, where the accumulation of adsorbate pollutants takes place on an adsorbent solid surface mainly by physical adsorption, is the most advantageous one. This is mainly because of its simple design, easy operation, cost effectiveness with alternative solid waste-based adsorbents, high efficiency of separation, biodegradability, and ability to treat dyes in a more concentrated form [3,6,7,9,11]. Currently, commercial activated carbon (CAC) adsorbents are commonly used in the adsorptive removal of organic/inorganic contaminants from water and treatment systems due to their high adsorptive separation efficiencies and highly stable porous structure. However, the high cost and regeneration issues of commercial activated carbon (CAC) remain challenging problems for engineers and scientists. Therefore, recently, numerous cost-effective and renewable but sustainable adsorbents, mainly agricultural biomass-based adsorbents, clay minerals, and other solid waste adsorbents, have been developed for the removal of dyes from wastewater. In this research direction, there are a number of recently reported batch experimental laboratory results in the successful removal of aqueous phase MB dye by various cost-effective and efficient biomass or other solid waste-based adsorbents. These include but are not limited to pine leaves [3], pine needle biomass [12], white pine sawdust [13], leaf residues of *Thymus numidicus*, *Origanum glandulosum*, and *Spindus mukorossi* [14], pine cones and pine leaves [15], pea waste [16], banana peel and avocado seed [17], sugarcane-saw dust composite [18], sugarcane bagasse, peanut hull, and orange peel [19], cashew nut shell [4], raw and modified plumeria alba (White frangiparm) [1], raw kaolin [20], kaolin [21], natural clay [22], and kaolinite [23]. Readers are encouraged to go through the review articles by Adegoke and Bello [2], Boakye et al., 2022 [6], and Afroza and Sen [24], where a large number of agricultural solid waste-based adsorbents, clay minerals, and industrial solid waste-based adsorbents are tabulated for the removal of aqueous phase dyes and other pollutants. From the compilation list of a large number of reported batch adsorption results at the solid/liquid interface by various reported review articles, the adsorption kinetics and equilibrium adsorption depend on many physicochemical process parameters, which include initial adsorbate concentration, adsorbent doses, solution pH, interaction between adsorbent and adsorbate, adsorbent characteristics, and temperature [2,6,24]. For example, Hock et al. [25] reported the results of batch adsorption kinetics and equilibrium studies for aqueous phase malachite green (MG) by banana peel adsorbents at different physico-chemical process parameters. The biosorption mechanism of MB from water onto white pine sawdust was identified, and the effectiveness of pine sawdust adsorbent in the removal of MB at different solution pH, adsorbent doses, initial dye concentrations, and solution temperatures was tested by Salazar-Rabago et al. [13]. Moreover, pine cones, pine leaves, and pine sawdust were successfully used as an effective biomass-based adsorbent in the removal of inorganics such as Cu (II) and Cr (IV), and various operating conditions were identified and optimized [15,26]. The batch dye adsorption results of methyl orange (MO) and methylene blue (MB) by treated pine leaf biomass were reported by Huynh et al. [3], and they obtained maximum adsorption capacities of the adsorbent of 140.85 mg/g and 136.99 mg/g for MB and MO, respectively. Boakye et al. [6] reviewed and critically discussed some of the commonly used bio-based materials, including agricultural biomass, as adsorbents in the removal of inorganics and organics in wastewater treatment. They have also highlighted some of the potential drawbacks of using these bio-based adsorbent materials for large-scale,
real-world wastewater treatment applications. Therefore, it is very critical to identify the various influential process parameters at solid/liquid adsorption and their optimum values through laboratory batch adsorption studies before selecting an adsorbent material for continuous column experiments with a real wastewater treatment system.

A literature review [3,24] showed that pine leaves have not been used much as an adsorbent to remove dyes from colored wastewater despite their abundance, availability, and pricelessness, hence this research work. Pine leaves are abundant in Australian forests and residential areas. Therefore, the aims of these laboratory synthetic wastewater-based batch adsorption studies are mainly threefold: (a) to select and test the effectiveness of pine leaf biomass as adsorbents for the removal of aqueous phase MB dye; (b) to identify the basic influential process parameters and their optimum values on dye adsorption kinetics and equilibrium adsorption characteristics; and (c) to determine the selected adsorbent’s capacity, its re-generation ability, and its adsorption mechanism. Finally, limitations and future studies have also been discussed here.

2. Materials and Methods

2.1. Adsorbent and Characterization

The biomass of pine tree leaves (Pinus radiata) was collected from the main campus of Curtin University, Bentley, and Perth, Australia. Initially, the collected pine leaf biomass was thoroughly washed with deionized water to remove sand, dirt, and other particles, and then oven dried at 70 °C for 24 h. The scales on the dried leaves were then removed and ground in a turbo blender and mixer. Pine leaf powder was analyzed by Malvern Hydro 2000S master Sizer, Malvern Instruments Ltd., Malvern, UK. The Spectrum 100 FT-IR Spectrometer was used to determine functional groups, and BET (Brunauer, Emmett, and Teller) surface area was also used to measure the surface area of the pine leaf powder. The surface morphology of adsorbent pine tree leaves was analyzed by scanning electron microscopy (SEM) EVO-40.

The point of zero charge (pH_{pzc}) of the pine tree leaf biomass adsorbent was determined by the salt addition method as per Touihri et al. [15].

2.2. Chemicals

All chemicals used were of analytical grade. The ethylene blue (MB) was procured from Sigma-Aldrich Pty. Ltd., Castle Hill, NSW, Australia, and was of 99.99% purity. It was used to produce synthetic color waste dye solutions. A stock solution of 1000 mg/L of MB was prepared by dissolving the appropriate amount of dye powder in 1 L of deionized water. The working solutions of various concentrations were prepared by dilution method. The acidic or basic solution pH was adjusted either by addition of 0.1 M HCl or 0.1 M NaOH solutions, respectively, and it was measured by Orien pH meter. All sample bottles and glassware were cleaned, rinsed with deionized water, and oven-dried before use in experimental run. Methylene blue (MB) dye concentration was measured by SP-8001 UV/VI spectrophotometer in Japan. The dye concentration was measured using UV/visible spectrometer at a λ_{max} = 664 nm. A previously known calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance–concentration profile that was used to determine the unknown dye concentration.

2.3. Adsorption

2.3.1. Adsorption Kinetic Experiment

Batch adsorption experiments were carried out with a 40 mL volume of MB dye solution mixture of known concentration and fixed amount of adsorbent doses in a series of 250 mL conical flasks that were shaken in a constant-temperature orbital shaker at 150 rpm speed at a temperature of 30 °C for a period of 3 h. At predetermined time interval, the bottles were withdrawn from the shaker and then centrifuged, and finally, residual methylene blue (MB) dye solution concentration at a particular time was determined from
supernatant by a UV spectrophotometer. The same experimental procedure was followed by varying dye concentration, solution pH, adsorbent doses, and temperature.

The amount of dye adsorbed per unit gram of adsorbent, \( q_t \) (mg/g), at time \( t \) was calculated by the following Equation (1):

\[
q_t = \frac{(C_o - C_t)V}{m},
\]

and the dye removal efficiency, i.e., % of adsorption, was calculated as

\[
\% \text{ Adsorption} = \frac{(C_o - C_t)}{C_o} \times 100,
\]

where \( C_t \) is the dye concentration measured at time (t), \( C_o \) is the initial dye concentration in ppm (mg/L), \( m \) is adsorbent mass in grams (g), and \( V \) is the reaction mixture volume (L). Experimental runs were conducted in replicates, hence the inclusion of error bars in all figures. Error bar based on standard deviations with custom-specified trial runs.

2.3.2. Equilibrium Adsorption Isotherm Experiments

Adsorption isotherm experiments were performed with 40 mL of reaction mixture of dye concentration ranges of 20, 30, 40, 50, 60, and 70 mg/L and 20 mg of adsorbent pine tree leaf biomass powder in a series of 250 mL conical flasks shaken in a constant temperature shaker for a period of 3 h (more than the equilibrium time). All other experimental conditions remained constant. After equilibrium, the reaction mixture was centrifuged, and the residual methylene blue (MB) dye concentrations were measured from the supernatant solution. The dye amount adsorbed at equilibrium, \( q_e \) (mg/g), and % of adsorption were measured using Equations (1) and (2).

3. Adsorption Theory

3.1. Adsorption Isotherm

The two traditional isotherm models, Freundlich (1906) [27] and Langmuir (1918) [28], were selected to determine the adsorbent’s effectiveness and to find possible adsorptive reaction mechanisms at the solid/liquid interface.

The most common but old practice is to apply the following linearized Freundlich model equation to the experimental isotherm adsorption data [29,30] and to determine the Freundlich adsorption isotherm model parameters based on the multilayer adsorption mechanism [29,30]:

\[
\ln q_e = \ln k_f + \frac{1}{n} (\ln C_e)
\]

where \( C_e \) is the residual equilibrium methylene blue (MB) dye concentration in ppm (mg/L) and \( q_e \) (mg/g) is the amount of dye adsorbed per unit mass of adsorbent at equilibrium time (mg/g). The slope and intercept of a linear plot between \( \ln q_e \) and \( \ln C_e \) will give the value of the Freundlich constant, \( n \), rate of adsorption, and intercept \( K_f \), is capacity, respectively [29], whereas Langmuir model describes the monolayer adsorption on the active sites of the adsorbent [6,24]. As per old practice, the following linearized Langmuir-1 model equation can be applied to the experimental isotherm data, which is as follows [7,29,30]:

\[
\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m},
\]

where \( q_m \) (maximum monolayer adsorption capacity of selected adsorbent in mg/g and Langmuir constant \( K_a \) (L/mg)) are determined from the slope and intercept of the linear plot between \( C_e/q_e \) and \( C_e \).
A further analysis of the Langmuir equation can be made based on the dimensionless equilibrium parameter $R_L$, also known as the separation factor, given by Equation (5) [31]:

$$R_L = \frac{1}{1 + K_a C_0},$$

(5)

where $K_a$ is the Langmuir model constant obtained from linear fitting of the Langmuir plot and $C_0$ is the initial adsorbate dye concentration (mg/L). When $R_L$ values at different initial dye concentrations lie in the range of $0 < R_L < 1$, this indicates favorable adsorption [32].

3.2. Thermodynamic Study

Thermodynamic parameters such as Gibb’s free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$), and change in entropy ($\Delta S^0$) for the adsorption of dye on pine leaves have been determined by using the following equations [30]:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

(6)

and

$$\log \left( \frac{1000 \, q_e}{C_e} \right) = \frac{\Delta S^0}{2.303R} - \frac{-\Delta H^0}{2.303RT},$$

(7)

where $q_e$ is the amount of dye adsorbed per unit mass of pine leaves (mg/g), $C_e$ is the equilibrium concentration (mg/L), $T$ is the temperature in K, and $R$ is the gas constant (8.314 J/mol K).

4. Results and Discussion


Pine leaves are mostly composed of cellulose and lignin, whose components serve as active sites for dye adsorption. The FTIR spectrum of pine leaves before and after adsorption is shown in Figure 1. Many peaks were found in the spectra that account for the binding of the cationic dye methylene blue (MB). The peaks at 3331.5 cm$^{-1}$ represent O–H extending vibrations, and the spectra bands observed at 2917.7 cm$^{-1}$ signpost vibrations of CH$_n$, mostly due to C–CH$_2$ and C–CH bonds. The peak at 1733.3 cm$^{-1}$ describes C=O and the vibration of C=C. The peaks of 1030.4 cm$^{-1}$ are likely assigned to the -C–C– stretching.

In Figure 1, after MB sorption, the majority of peaks disappeared or shifted. After the adsorption, the shifting of specific peaks from their original positions (before adsorption) and also changes in intensity indicated the surface functional group’s participation in the adsorption of the MB dye molecule by electrostatic forces of attraction and/or by weak Van der Waals interactions [3].

Figure 2a,b show the SEM of raw pine leaf powder to analyze the surface morphology of the adsorbent before and after dye adsorption. From Figure 2a, it is indicated that the surface of adsorbent pine leaves had a rough and course morphology with a less porous structure. However, from Figure 2b, the surface morphology of the adsorbent indicates the surface accumulation of the adsorbate MB dye molecule with some changes in morphology and porosity after adsorption.

The particle size is also a very important characteristic because it can affect the surface area, which has an effect on the adsorption process. The particle size distribution was determined by using the Malvern Master Sizer 2000S with the Hydro 2000S (A) Sampler along with the Master Sizer 2000 software to interpret the findings, which are presented in Figure 3. The volume-weighted mean particle size of 167.46 µm and the surface-weighted mean particle size of 52.09 µm were found for a specific surface area of 0.115 m$^2$/g (Figure 3).
Figure 1. FTIR spectra of pine leaf powder biomass before and after MB adsorption.

Figure 2. (a) SEM of raw pine leaves before adsorption, magnification x 300 and (b) SEM of pine leaves after adsorption, magnification x 1000.
4.2. Studies on Adsorptive Methylene Blue (MB) Removal by Pine Tree Leaf Biomass at Different Physicochemical Process Conditions

4.2.1. Effect of Solution pH

The amount of contaminant adsorption by the selected adsorbent strongly depends on solution pH [3,7,24]. The variation of solution pH facilitates the degree of ionization of the adsorbate molecule and the adsorbent surface functional groups, and hence changes in adsorption capacity [31]. Basically, adsorbent surface charges vary with the solution pH, which affects the rate of adsorption [31]. The pH at the point of zero surface charge (pHpzc) of the adsorbent is very important in adsorption. For pH < pHpzc, the adsorbent surface becomes positive in charge due to protonation and hence favors anionic adsorption. Where pH > pHpzc, the surface charge of the adsorbent is predominately negative, and hence strong cationic adsorption takes place. The pHpzc of the pine tree leaf adsorbent was determined to be 4.9. A similar pHpzc value of 4.4 for pine leaves and 6.6 for pine cones was reported by Touihri et al. [15]. Figure 4 shows the effect of initial solution pH (ranges from 3–9) on MB dye adsorption amount (qt (mg/g) at equilibrium for a 10 mg/L adsorbate dye concentration. All other experimental conditions remained constant. From Figure 4, it was found that pine leaf absorbent significantly increased the dye adsorption amount, qt (mg/g), from 10.85 mg/g at a solution pH of 3 to 18.47 mg/g at a solution pH of 6, and thereafter very slowly increased the amount of adsorption from pH 6 to 9 (18.86 mg/g). The corresponding methylene blue (MB) dye percentage removal efficiencies increased from 54.25% to 94.33% in the same solution pH range of 3 to 9, for which a plot is not presented here. The pH-dependent adsorption performance of methylene blue dye should be explained based on the pKa value of the adsorbate and the pHpzc of the adsorbent. The pKa of methylene blue is 3.8, and therefore, at pH values higher than 3.8, the predominant methylene blue species in solutions are cationic [12]. Basically, at higher solution pH, particularly when pH > pHpzc, the pine leaf biomass exhibits a negative surface charge owing to the deprotonation of phenolic and carboxylic surface groups, which favors the adsorption of cationic methylene blue (MB) due to strong electrostatic attraction forces [12,33]. In water, methylene blue, a base dye, decomposes into MB⁺ ions, and the lower the medium pH value (greater concentration of H⁺ ions in the solution), the lower dye adsorption takes place due to the presence of competitive adsorption between MB⁺ and H⁺ ions in solution [3,34]. Further pHpzc values of pine leaves also support these results. Similar trends in pH effects on methylene blue (MB) dye batch adsorption results are also being reported by other researchers for other systems under similar experimental conditions [8,12,30,35,36].
Processes 2023, 11, x FOR PEER REVIEW... 1 0
Amount Adsorption, qt (mg/g)

Figure 4. The changes in methylene blue (MB) dye adsorption amount at equilibrium by pine tree leaf biomass powder with the variation of solution pH. Experimental conditions: adsorbent dose = 20 mg; volume of reaction mixture solution = 40 mL; initial dye concentration = 10 mg/L; temperature = 30 °C; shaker speed = 120 rpm; time = 3 h.

4.2.2. Effect of Initial Adsorbate MB Dye Concentration

The amount of dye adsorption, $q_t$ (mg/g), by pine leaf biomass increases with the variations of the initial dye concentration, which are shown in Figure 5. All experimental runs were conducted with methylene blue dye concentrations of 5, 10, 20, 30, and 40 mg/L, respectively, whereas a reverse trend on percentage dye adsorption was observed with the dye concentration for which Figure 6 is presented here. The other experimental conditions remained constant. One of the objectives was to test the adsorptive removal effectiveness of raw pine leaf biomass adsorbent within the low adsorbate methylene blue (MB) dye concentration ranges, and hence an experimental design has been set up accordingly. From Figure 5, it was found that with the increase in initial dye concentration from 5 to 40 mg/L, the amount of dye adsorption at equilibrium increased from 9.43 mg/g to 38.98 mg/g, but the percentage dye removal decreased from 94.34% to 48.72% with the same initial methylene blue (MB) dye concentration ranges and with the same experimental conditions (Figure 6). This is because the increase in initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and solid phases. The initial fast adsorption rate was due to the large initial availability of the adsorbent’s active sites and simultaneously to the large initial mass transfer concentration driving force between bulk phase adsorbate solute and the adsorbent surface. For a fixed adsorbent dose in a fixed volume of reaction mixture, the limited available adsorption sites may play a major role in the lower percentage of dye adsorption rate at higher initial dye concentration ranges [3,30]. The increase in initial concentration also enhances the interaction between the adsorbent and dye molecules. Therefore, an increase in initial dye concentration leads to an increase in the amount of dye adsorption due to a higher mass transfer driving force. This similar trend in the amount of dye adsorption and the percentage removal of dye was previously reported by many other researchers [1–3,19,37].
was a decrease in dye adsorption amount from 25.93 to 9.37 mg/g with the increase of (MB) dye variation was found with the increase of the same adsorbent doses from 0.01 to 0.04 g, for which the results are presented in Figure 8. The division of mass transfer flux or concentration driving force between bulk solute concentration and adsorbent

The influences of initial methylene blue (MB) dye concentration load on the amount of dye adsorption at equilibrium with mass of adsorbent pine tree leaves biomass = 20 mg; volume of reaction mixture = 40 mL; temperature = 30 °C; pH = 5.18; shaker speed = 150 rpm; time = 3 h.

Figure 5

Effect of methylene blue (MB) concentration on the percentage removal of methylene blue (MB) dye by pine leaf powder at equilibrium with adsorbent dose = 20 mg; volume of reaction mixture solution = 40 mL; temperature = 30 °C; pH = 5.18; shaker speed = 150 rpm; reaction time = 3 h.

Figure 6

4.2.3. Effect of Pine Leaf Biomass Adsorbent Doses

Here, methylene blue (MB) dye adsorption kinetics were carried out by changing adsorbent amounts of 0.01, 0.02, 0.03, and 0.04 g for a reaction volume of 0.04 L, and the results are presented in Figure 7. Other experimental conditions remained constant, with initial dye concentration \(C_0\) = 10 mg/L, solution pH = 5.18, and temperature \(T\) = 30 °C, respectively. The selection of these ranges of adsorbent doses was based on activated carbon doses applied in spent textile dyeing wastewater treatment operations [38]. There was a decrease in dye adsorption amount from 25.93 to 9.37 mg/g with the increase of adsorbent dosages from 0.01 to 0.04 g at the end of the 3 h reaction time (Figure 7), whereas an increasing trend (from 64.86% to 93.66%) of percentage removal of methylene blue (MB) dye variation was found with the increase of the same adsorbent doses from 0.01 to 0.04 g, for which the results are presented in Figure 8. The division of mass transfer flux or concentration driving force between bulk solute concentration and adsorbent
surface [33,39] may be the main reason for the reduction of dye amount per unit gram of adsorbent weight, $q_t$ (mg/g), with the increase in adsorbent dose [33,39]. Further, with the increase in adsorbent doses, there may be an increase in adsorbent particle size due to more agglomerations and hence fewer active sites for adsorption, and therefore the adsorption of methylene blue (MB) decreased (Figure 7). A similar trend of results was reported by many researchers for different systems [1,2,12].

![Figure 7](image_url)

**Figure 7.** Variation of adsorbent pine tree leaf biomass dosages on methylene blue (MB) dye adsorption at equilibrium with volume of reaction mixture dye solution = 40 mL; initial dye concentration = 10 mg/L; pH = 5.18; temperature = 30 °C; shaker speed = 150 rpm; reaction time = 3 h.

![Figure 8](image_url)

**Figure 8.** Variation of adsorbent pine tree leaf biomass dosages on percentage removal of methylene blue (MB) dye at equilibrium with volume of reaction mixture dye solution = 40 mL; initial dye concentration = 10 mg/L; pH = 5.18; temperature = 30 °C; shaker speed = 150 rpm; time = 3 h.

4.2.4. Temperature Effect and Thermodynamic Behavior of MB Dye Adsorption

The exothermic or endothermic nature of the adsorption reaction depends on the temperature effect in batch adsorption studies, and hence different thermodynamic parameters are estimated here at various temperatures. Therefore, batch adsorption studies on MB dye removal by pine leaf biomass were conducted at three different temperatures of 30, 40, and 60 °C using 0.02 g of pine leaf adsorbents and 40 mL of the 10 mg/L methylene blue solution.
(MB) dye solution at a pH of 5.18. Figure 9 shows the solution temperature effect on MB dye adsorption by pine tree leaf biomass. From Figure 9, it was found that there is a very slight decrease in dye adsorption amount from 16.95 mg/g to 16.15 mg/g with the increase in temperature, which indicates the adsorption is mildly exothermic in nature but more or less independent of temperature. This small decrease in adsorption may be due to the slight desorption of adsorbed MB molecules from the adsorbent surface with the increase in temperature-induced kinetic energy of MB dye molecules [1,2,7].

![Figure 9. Variation of solution temperature on methylene blue (MB) dye adsorption on pine tree leaf biomass at equilibrium with adsorbent dose = 20 mg; volume of dye solution = 40 mL; solution pH = 5.18; dye concentration = 10 mg/L; shaker speed = 150 rpm; time = 3 h.](image)

The values of Gibb’s free energy changes ($\Delta G^\circ$) have been calculated by knowing the values of the enthalpy of adsorption ($\Delta H^\circ$) changes and the entropy of adsorption ($\Delta S^\circ$) changes, which are obtained from the slope and intercept of the Van’t Hoff plot of log ($q_e$/$C_e$) versus 1/$T$ as per Equation (7). All these thermodynamic parameters are tabulated in Table 1. The negative values of $\Delta H^\circ$ and $\Delta G^\circ$ indicate (Table 1) at all temperatures that the adsorption processes are spontaneous and exothermic in nature [2,3,12,30]. Further, the negative value of $\Delta G^\circ$ indicates the adsorption of methylene blue dye at the solid/liquid interface is highly favorable [2]. When 20 kJ/mol < $\Delta H^\circ$ < 80 kJ/mol, the nature of adsorption is predominately physical adsorption [2]. The positive values of $\Delta S^\circ$ indicate disorder and randomness of dye adsorption at the solid/liquid interface.

Table 1. Analysis of various thermodynamic characteristics parameters at three different solution temperatures during methylene blue (MB) dye adsorption by pine tree leaf biomass.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$-13.9794$</td>
<td>$-13.4869$</td>
<td>0.001626</td>
</tr>
<tr>
<td>40</td>
<td>$-13.4386$</td>
<td>$-12.9298$</td>
<td>0.001626</td>
</tr>
<tr>
<td>60</td>
<td>$-13.5687$</td>
<td>$-13.0274$</td>
<td>0.001626</td>
</tr>
</tbody>
</table>

4.3. Mechanism of Adsorption and Isotherm Studies

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Two commonly used isotherm equations, such as the Langmuir and Freundlich adsorption isotherms, were studied here. Equilibrium MB dye adsorption experiments were conducted with different dye concentrations of 10, 20, 30, 40, 50, 60, and 70 mg/L for a period of more than 3 h. The other experimental parameters were adsorbent dose = 20 mg, solution
pH = 5.94, temperature = 30 °C, rpm = 150, and time = 3 h. Equilibrium/isotherm studies are always required to determine the effectiveness of a selected adsorbent in terms of its maximum adsorption capacity and the mechanism of the adsorption reaction. The most common and traditional approach is the linear fitting of Freundlich isotherm and Langmuir isotherm models. Equations (3) and (4) with the experimental isotherm results to determine the model parameters. Therefore, the linear fittings of the Freundlich adsorption isotherm model with the experimental isotherm data for pine tree leaves as an adsorbent are presented in Figure 10 with a linear correlation coefficient (R²) of 0.8438. From Figure 10, Freundlich constants K_f (adsorption capacity) and rate of adsorption, n, were found to be 0.57 L/mg for the methylene blue (MB)–pine tree leaf biomass system. The obtained pine tree leaf biomass adsorbent's maximum monolayer adsorption capacity of the selected adsorbent for this study, q_m (mg/g), was obtained as 36.88 mg/g, and the Langmuir constant, K_a, was found to be 0.57 L/mg for the methylene blue (MB)–pine tree leaf biomass system. The obtained linear regression coefficients (R²) values of 0.9989 strongly indicate that the Langmuir isotherm model fits better than the Freundlich model within the current experimental conditions.

Similarly, a linear plot of the Langmuir isotherm model equation as per Equation (4) was plotted between Ce/qe vs. Ce, which is presented in Figure 11. The very high fitted linear regression coefficients (R²) values of 0.9989 strongly indicate that the Langmuir model fits better than the Freundlich model within the current experimental conditions. The maximum monolayer adsorption capacity of the selected adsorbent for this study, q_m (mg/g), was obtained as 36.88 mg/g, and the Langmuir constant, K_a, was found to be 0.57 L/mg for the methylene blue (MB)–pine tree leaf biomass system. The obtained dimensionless separation factor (R_L) using Equation (5) at different initial dye concentrations was 0.128, 0.0685, 0.0467, 0.0355, 0.0286, and 0.0239, which confirmed the favorable adsorption of MB dye onto pine leaf biomass adsorbents as all lie in the range of 0 to 1. Similar results were also reported by many researchers on methylene blue (MB) dye removal by various adsorbents [2,3,12,24,30,37,41]. The fitted Langmuir isotherm model with a high value of the linear regression coefficient (R² = 0.9989) indicated monolayer coverage of methylene blue onto the pine tree leaf biomass adsorbent surface, which is predominately physical adsorption in nature. The obtained pine tree leaf biomass adsorbent’s capacity towards methylene blue (MB) dye adsorption was very much comparable with other reported adsorbents under more or less similar experimental conditions, which are presented in Table 2.

![Figure 10](image-url)  
**Figure 10.** Linear fittings of Freundlich adsorption isotherm model with the experimental isotherm data under specified process conditions.
Table 2. Comparison of maximum adsorption capacities of other reported agricultural biomass-based adsorbents with the current selected pine tree leaf biomass adsorbent for the removal of MB dye from water.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum Adsorption Capacity, $q_m$ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Various agricultural crop residues</td>
<td>21.1–46.1</td>
<td>Solih et al., 2023 [17]</td>
</tr>
<tr>
<td>Various leaf residues</td>
<td>24.2–41</td>
<td>Youcefi et al., 2021 [14]</td>
</tr>
<tr>
<td>Plumeria biomass</td>
<td>45.45</td>
<td>Deka et al., 2023 [1]</td>
</tr>
<tr>
<td>Sugar scum-sawdust</td>
<td>66.72</td>
<td>Chikri et al., 2021 [18]</td>
</tr>
<tr>
<td>Saragassum latitoliu biorefinery waste</td>
<td>8.54</td>
<td>Fawzy and Gomma, 2021 [42]</td>
</tr>
<tr>
<td>Magnetic chitosan</td>
<td>60.4</td>
<td>Auta et al., 2014 [43]</td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>25.25</td>
<td>Bulut et al., 2015 [5]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>40.588</td>
<td>Vadivelan and kumar, 2005  [39]</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>99</td>
<td>Oladoja et al., 2008 [44]</td>
</tr>
<tr>
<td>Caster seed shell</td>
<td>158.73</td>
<td>Oladoja et al., 2008 [44]</td>
</tr>
<tr>
<td>Yellow passion fruit</td>
<td>44.7</td>
<td>Pavan et al., 2008 [45]</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>41.3</td>
<td>Ferrero, 2007 [46]</td>
</tr>
<tr>
<td>Orange peel</td>
<td>20.5</td>
<td>Annadurai et al., 2002 [47]</td>
</tr>
<tr>
<td>Raw pine leaf biomass</td>
<td>36.88</td>
<td>Current study</td>
</tr>
</tbody>
</table>

5. Limitations and Future Work

To reduce secondary pollution and waste production, to know the mechanism of adsorption, and to make the process more cost-effective, separation, regeneration, and reuse of loaded adsorbents are essential steps in developing an effective adsorbent material for water treatment. For the regeneration of adsorbent, either heat treatment or chemical solvent treatments such as inorganic/organic acid treatment, base, ethanol, ace-
tone, etc. are normally carried out in adsorbent regeneration operations for further use in industrial situations.

In this present study, quick desorption of a methylene blue (MB)-loaded adsorbent, pine leaf biomass, was conducted using desorbing solvents such as water and strong inorganic nitric acid (HNO₃). Therefore, after reaching adsorption equilibrium, the methylene blue (MB)-loaded pine leaf biomass adsorbed were separated from solution by centrifugation and then oven dried at 50 °C overnight. The dried dye-loaded adsorbent was then added to 50 mL of selected desorbing solvents in an Erlenmeyer flask. The whole sample mixture was agitated for 3.5 h and then filtered. The desorbed methylene blue (MB) concentration was measured. Here, two different eluting solvents were chosen, i.e., water and 0.1M HNO₃. From these desorption experiments with strong nitric acid (HNO₃) having a pH value of 1.0, the maximum desorption efficiency of MB dye was found to be 47.21%, whereas for water desorbing solvent it was only 8.35% recovery. However, the detailed desorption process has to be optimized with the various desorbing solvent selection and heating options for future study before applying to a real-field wastewater treatment system. So far, we have not conducted any kind of reusability test or performance evaluation with this partially regenerated adsorbent. As desorption efficiency is not good, it seems that further detailed desorption studies with various options need to be tested in future studies. One advantage here is that pine leaf biomass is an agricultural solid waste, is locally available with a solid waste management problem, and is available at almost wholesale prices; therefore, regeneration of adsorbent may not be an important operation here. Further, the main objectives of this batch adsorption study with synthetic dye-bearing effluent are to determine the effectiveness of this pine tree leaf biomass as an adsorbent to give a partial solution to the agricultural solid waste management problem and to identify the basic influential process parameters and their optimum values on dye adsorption kinetics and equilibrium adsorption characteristics for future continuous column experimental designs with real dye-bearing wastewater effluents.

6. Conclusions

In this work, raw pine tree leaf biomass was successfully used in the removal of the color pollutant methylene blue (MB) dye from synthetic wastewater. Here the adsorbent, pine tree leaves, was characterized by the Malvern particle size analyzer, FTIR, and SEM. From these laboratory batch adsorption results, the various influential process parameters on adsorption characteristics have been identified, and their optimum values have also been determined.

The Langmuir isotherm model fitted better than the Freundlich isotherm model with the experimental data, and the obtained Langmuir maximum monolayer adsorbent capacity was 36.88 mg/g, which was comparable with many other adsorbent capacities towards methylene blue dye adsorption. The value of the separation factor, R_L, from the Langmuir equation gave an indication of a favorable adsorption reaction. From thermodynamic analysis, the negative values of ΔH° and ΔG° indicated that the adsorption processes were spontaneous and exothermic in nature, but dominant physical adsorption was mainly governed by weak van der Waals and electrostatic forces of attraction. Regeneration by desorption study, reusability, and limitations of this present study have been discussed here. Finally, by utilizing these large, locally available, priceless agricultural solid waste pine tree leaf residues as an alternative adsorbent in the removal of organics/inorganics from wastewater, we may find a solution to water pollution and a partial solution to agricultural solid waste management problems for which further large-scale continuous adsorption operations are required.

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Conflicts of Interest: The author declares no conflict of interest.

References


39. Vadivelan, V.; Kumar, K.V. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.* 2005, 286, 90–100. [CrossRef]


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