

Research Article

Evaluation of Methylene Blue Sorption onto Low-Cost Biosorbents: Equilibrium, Kinetics, and Thermodynamics

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This paper presents a study on batch sorption of methylene blue dye from aqueous solution onto *Ginkgo biloba* sorbent, a waste material produced during the Fall season in many parts of the world. Batch kinetics, equilibrium, and thermodynamic studies were conducted to evaluate the effect of contact time (0–150 min), sorbent dose (0.5–3.0 g/L), pH (2–11), temperature (30–50°C), initial MB concentration (10–30 mg/L), and particle size (177 μ m—590 μ m) on the methylene blue dye sorption. More than 99% removal of methylene blue was observed within 120 minutes. A Lagergren pseudo-first-order model, a pseudo-second-order model, and intraparticle diffusion models fitted well to the kinetics experimental data. Langmuir and Freundlich isotherm models also fitted well with the observed equilibrium data. Additionally, removal of methylene blue increased with increase in solution pH. Higher sorption capacity (~20 mg/g) was observed with smaller particle size (170 μ m) as compared to larger particle sizes (590 μ m). Thermodynamic parameters such as ΔG° , ΔH° , and ΔS° indicated that the sorption process was feasible, spontaneous, and endothermic in nature. The study shows that *Ginkgo biloba* leaves have the potential to be an efficient sorbent for the removal of methylene blue from surface water samples.

1. Introduction

Dyes are used in many industries such as paper, plastics, photography, ink, and textile. While these industries use dyes to color their final products, it also results in imparting color to water and wastewater [1-3]. Methylene blue (MB) has found extensive use in the coloring of textiles [3, 4]. It is also used as a staining agent in surgery and diagnostic examination. Other medical applications include treatments of methaemoglobinemia and cyanide poisoning [5, 6]. If dyeloaded wastewater is discharged directly to a municipal water treatment plant, it may break down to toxic carcinogenic products [1, 6]. The discharge of such colorant material in wastewater can lead to serious environmental (such as reduced penetration of sunlight into waters, retarded photosynthesis, inhibition of growth, and toxicity to aquatic biota) and health (allergic dermatitis, skin and eye irritation, mutagenic, and potentially carcinogenic)

problems and is a matter of concern for both toxicological and aesthetic reasons [1, 7-9]. The presence of even a small amount of dye can also impart undesirable color to water which affects the public perception of water quality [1, 8, 9]. Therefore, it is imperative to decontaminate dyes from wastewater to ensure safe environment.

Several methods have been reported for the sequestration of dyes from wastewater [10–14]. Physicochemical processes such as chemical coagulation, ion exchange, electrolysis, and activated carbon sorption are used to treat color in wastewater. However, these processes have high capital and operating costs [11–14]. This limitation has led to search for effective substitutes at a lower cost point. Among these, adsorption is a very effective and attractive technique with respect to cost, ease of use, and simplicity [1–3]. Several studies have reported the use of low-cost materials for dye removal [15, 16]. Various biosorbents such as *Carica papaya* [17], lotus leaf [18], olive stone [19], spent rice biomass [20], maize husk leaf [21], palm oil agrowaste [22], and pulverized marula seed husk [1] have been studied for sorption of methylene blue.

The biosorbent material used in this study is *Ginkgo biloba* leaves (GBLs). *Ginkgo biloba* is also considered as "living fossil" due to its age (>180 million years) [23]. *Ginkgo biloba* has been reported to be rich in many biologically active compounds (flavonoids, alkylphenols, carboxylic acids, terpene lactones, and polyprenols) which can make it a potential adsorbent for decontamination of environmental pollutants, and it has been used extensively in traditional Chinese medicine [24, 25].

In Virginia, USA, GBL is a locally available waste material in the form of fallen leaves during spring and summer season (April to September). Best management practices (BMP) currently used to manage this waste are collection and disposal through local county governments. The collection and disposal of GBL require resources and are considered an economic burden on cities and counties. Improper collection and disposal of these leaves may also clog local storm water and sewer distribution systems.

A preliminary study reported the application of GBL as a potential sorbent for dye removal [26]. However, no details on the kinetics, equilibrium, or thermodynamics were provided. The aim of this study is to investigate sorption potential of GBL as a potential biosorbent for the removal of methylene blue (MB) in aqueous solution. The natural sorbent is characterized, and sorption is quantified through a series of equilibrium and kinetics batch sorption experiments as a function of different system variables, including pH and temperature. Thermodynamic considerations are also identified.

2. Materials and Methods

2.1. Preparation of the Sorbent. GBLs were collected during the Fall (September–November, 2017) from the grounds of the University of Virginia in Charlottesville VA (USA). The leaves were washed using organic-free deionized water to remove any dirt and earth materials. The leaves were subsequently dried in an oven at $105^{\circ}C \pm 3^{\circ}C$ for 24 h. The dried leaves were crushed into powder using a mortar and pestle. Analytical sieves were used to fractionate the powder into various particle sizes. Particle sizes $\leq 590 \,\mu$ m were stored in a plastic bottle and used as biosorbent for the uptake of methylene blue (MB) dye from aqueous solution.

2.2. Ginkgo biloba (Sorbent) Characterization. Physical and chemical characterization of GBL powder was performed to investigate the mechanism of dye sorption. Carbon (C) and nitrogen (N) content of the GBL sorbent was analyzed using a Flash 2000 NC soil analyzer (Thermo Scientific (formerly Fisons/Carlo Erba)). For this analysis, GBL powder sample was dried at 60°C in an oven for 24–48 h. A sample of 20–25 mg of sorbent material was pulverized with mortar and pestle and used for analysis.

The surface morphology of the GBL sorbent was imaged using scanning electron microscopy (SEM, JEOL, JSM-5610,

Japan) after sputtering with gold. The chemical structures of GBL powders, sorbent, and dye-loaded sorbent were characterized by Fourier transform infrared spectroscopy (Thermo Scientific USA, Nicolet iS5) at wavelengths ranging from 4000 to 600 cm^{-1} .

2.3. Kinetics, Equilibrium, and Thermodynamic Studies. Batch sorption studies were carried out using 50 mL polypropylene centrifuge vials containing the DI water with various dye concentrations. Each solution was spiked with a predetermined sorbent dosage and placed in a temperaturecontrolled shaker at 150 rpm for 150 minutes. Kinetic studies were performed by varying the time from 30–180 minutes, at different GBL dosages (0.5–3.0 g/L), and at three different methylene blue concentrations (10, 20, and 30 mg/L). At predetermined time intervals, samples were taken out of the shaker, centrifuged at 250 rpm to remove the sorbent, and analyzed for residual methylene blue concentration.

Similarly, batch equilibrium studies were performed with GBL powder sorbent dosages from 0.5-2.5 g/L at 10 mg/L of initial methylene blue concentration. After shaking each batch experiments for 4 hours, samples were centrifuged at 250 rpm and analyzed for residual methylene blue concentration.

Thermodynamic studies were performed similar to equilibrium studies using various GBL sorbent dosages and different concentrations of MB (10, 20, and 30 mg/L) at different temperatures (303, 313, and 323°K). After 4 h, samples were taken out of the shaker, centrifuged at 250 rpm, and analyzed for residual methylene blue concentration.

2.4. Effect of Solution pH and GBL Particle Size. The effect of solution pH on the methylene blue removal was determined by varying the pH from 2–11 at three different methylene blue concentrations (10, 20, and 30 mg/L). Solution pH was adjusted to the desired value in the beginning of the experiment using 1 M HCl and 1 M NaOH. Effects of GBL particle size on the uptake of methylene blue was also investigated using different dosages of 177 μ m, 300 μ m, and 500 μ m particle sizes of GBL. Initial and final methylene blue concentrations were analyzed.

2.5. Matrix Effect on the Methylene Blue Dye Removal. The effect of sample matrix on MB removal was studied using spiked surface water samples collected from an open overflow water retention facility (Dell pond) located at University of Virginia in Charlottesville, VA. Prior to experimentation, Dell pond water was characterized for various physicochemical water quality parameters such as pH, dissolved oxygen (DO), temperature, and major anions and cations. Surface water pH, DO, and temperature were measured using Thermo Orion VersaStar pH meter. Anions and cations in Dell pond water were analyzed using a dual channel Dionex ICS5000⁺ ion chromatograph connected to an autosampler. The Dionex ICS5000+ system used a patented eluent generation (EG) technology. Stock solutions of the anions and cations were purchased from Thermo Fisher. Samples were prepared by filtering through $0.45^{\circ}\mu$ m Whatman syringe filters. Analytical blanks (Milli-Q water) and check standards were used at 10% for Quality Analysis/ Quality Control (QA/QC). Dell pond water was spiked with stock methylene blue (MB) dye solution to produce a dye concentration of 10 mg/L and then combined with different sorbent masses. All the experiments were conducted in triplicate and the mean values were reported.

2.6. Methylene Blue Determination. Methylene blue (MB) was purchased from Fisher Scientific (USA). A stock solution of 1000 mg/L was prepared and different dye concentrations (10 mg/L, 20 mg/L, and 30 mg/L) were made by serial dilution of stock solution using deionized water. Methylene blue concentrations were quantified using a UV Spectrophotometer (Hach DR 6000) at a wavelength of 663 nm. A quartz cuvette with path length of 1 cm was used for the methylene blue determination. All other chemicals and reagents used in the study were of analytical grade and purchased from Fisher Scientific USA. All the analyses were performed in triplicate and the mean was reported in each case. The sorption capacity of methylene blue from solution was calculated using the following equation:

$$q_e = \left(\frac{C_o - C_e}{W}\right)V,\tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of MB, respectively, V(L) is the volume of the solution, and W(g) is the mass of adsorbents used.

3. Results and Discussion

3.1. Biosorbent Characterization. Sorption of methylene blue dye depends on various sorbent characteristics such as carbon and nitrogen content, surface area, and pore size. The GBL sorbent had 47% carbon and 0.75% nitrogen. The SEM Micrographs of GBL samples were taken before and after dye sorption (Figures 1(a) and 1(b)). Figure 1(a) shows that GBL has irregular pore-like structures, whereas a more homogenous surface was observed after sorption (Figure 1(b)) which clearly indicated that the surface of GBL had adsorbed some of the dye molecules.

The FTIR spectra of GBL before and after dye sorption are shown in Figures 2(a) and 2(b). The spectrum range of FTIR was collected between 4000 and 600 cm⁻¹. The broad band at around 2919 cm⁻¹ corresponds to C-H stretching vibrations of methyl group [27, 28]. The peak at 1717 cm⁻¹ can be attributed to C=O stretching vibration of a carbonyl group (carboxyl (-COOH) and ethyl (-COOR) groups). The peak at 1635.18 cm⁻¹ is attributed to N-H stretching vibration of a primary amine. Observed peak at 1238 is attributed to -C-O-C stretching vibration of ether. Strong peaks were observed at 1102 and 1024 cm⁻¹ which are attributed to C-O stretching vibration of carboxylate groups. Between 600 and 1300 cm⁻¹, sorption bands are associated with the dye overlap with the spectra of GBL. Thus, these areas were difficult to distinguish after the dye sorption. Additionally, the absorption between 1600 and 1450 cm⁻¹ are typical C—C ring stretches. However, we can see the difference between the spectra in the 1600 and 1450 cm⁻¹ range, likely from the presence and shifting of peaks at the surface of GBL. This shift in peak suggests possible interaction between MB with the functional groups of the GBL [29, 30].

3.2. Effect of Contact Time: Batch Kinetics Study. The timedependent sorption of methylene blue (MB) onto GBL powder is shown in Figure 3. Uptake appears to be most rapid in the first 30 minutes with a near-equilibrium condition reached within about 100 min. At 0.5 g/L, 1.25 g/L, and 2.5 g/L sorbent doses, more than 89%, 90%, and 91% MB removal, respectively, was achieved in the first 30 minutes. The initial speed of MB removal could be attributed to more vacant sites being available in the beginning of sorption process. However, with lapse in time, a greater number of vacant sites become saturated with MB dye resulting in slower kinetics eventually resulting in equilibrium. After 150 minutes, no statistically significant difference in MB dye removal was observed regardless of sorbent dose. A Similar observation on MB dye removal has been reported on cotton stalk, neem leaf powder, and banana leaf powder [31, 32]. However, these studies have reported removal efficiencies at either high sorbent doses (2 to 10 g/L) or longer contact time (>120 minutes).

The rate-determining step and the kinetics of the sorption process were determined by the rate of dye removal as a function of time using various kinetic models. The expression of the pseudo-first-order model is shown in the following equation [33]:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \left(\frac{k_{\rm ad}}{2.303}\right)t,\tag{2}$$

where q_e and q_t (both in mg/g) are the amount of MB sorbed per unit mass of GB at equilibrium, *t* represents time, and k_{ad} is the rate constant (min⁻¹). Values of k_{ad} and q_e were calculated from the slopes and intercepts of the plots of log $(q_e - q_t)$ versus *t* for different sorbent doses (Figure 4). It can be seen from Figure 4 that the sorption data fit well to Lagergren kinetics model with $R^2 \ge 0.93$ for the three sorbent doses studied.

A nonlinear relationship is expected when pore diffusion limits the sorption process between the sorption rate and initial dye concentration. However, change in the sorption rate is expected to be proportional to the concentration if the sorption is strictly a surface sorption [24]. Transport of MB can be aided from the solution to the pores of GBL through stirring which usually occurs in batch experiment. The possibility of such intraparticle diffusion was tested with our dataset (Figure 5) using the following equation [34]:

$$q = K_p \cdot t^{1/2},\tag{3}$$

where $K_p (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2})$ is the intraparticle diffusion rate constant and *t* is time.



FIGURE 1: SEM micrograph of (a) GBL sorbent and (b) MB loaded GB sorbent with more homogenous surface.



FIGURE 2: FT-IR plot of GBL before (a) and after (b) dye sorption.



FIGURE 3: Percent dye removal as a function of time for GB sorbent in water at 20°C for different sorbent doses.



FIGURE 4: First-order rate kinetics for the sorption of methylene blue (MB) onto *Ginkgo biloba* leaf (GBL) powder.



FIGURE 5: Intraparticle diffusion curve for the MB removal onto *Ginkgo biloba* leaf powder.

The amount of MB sorbed per unit mass of GBL at time t (q_t) was plotted as a function of the square root of time $(t^{0.5})$. Linear plots were determined (Figure 5) which imply that intraparticle diffusion is involved in the rate-limiting step. K_p values obtained from the slopes of the plots were 0.5102, 0.0992, and 0.0467 mg·g⁻¹·min^{-1/2} at sorbent doses of 0.5 g/L, 1.25 g/L, and 2.5 g/L, respectively. The plots did not pass through the origin indicating a complex reaction mechanism of MB removal on GBL. From the plots, it is believed that both surface adsorption and intraparticle diffusion contribute to the rate determining step [30, 31, 35]. As per Weber and Morris [34], intraparticle plot between q_t vs. $t^{0.5}$ usually shows two or more intersecting lines depending on the exact sorption mechanism involved, with the initial part of the curve representing surface adsorption followed by latter part of intraparticle diffusion. No clear identification of two such distinct parts was observed in the present study indicating that both these processes were indistinguishable. Thus, it can be inferred from Figure 5 that the intraparticle diffusion was a dominating sorption process at early times.

The pseudo-second-order kinetic model (equation (4)) was also used to analyze the experimental data:

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

The plot of t/q_t versus "t" would give a linear relationship if the reaction conforms to the model; q_e and k_2 can be determined from the slope and intercept, respectively [36]. Based on the linearized coefficients from the kinetic plots, the pseudo-second-order kinetic model (Figure 6) best described the kinetics of the adsorption process.

3.3. Batch Equilibrium Studies. Batch equilibrium studies were performed to ascertain the conditions for the uptake of MB by GBL. To relate the adsorbate concentration in the bulk solution to the adsorbed amount at the interface, the equilibrium data obtained were fitted to linear Freundlich and Langmuir sorption isotherms. The plots for these are shown in Figures 7 and 8, respectively. The Freundlich equation is shown in the following equation:

$$\log q_e = \log K + \frac{1}{n} \log C_e,\tag{5}$$

where q_e (mg/g) is the adsorption density, C_e is the equilibrium MB concentration in solution (mg/L), and K and n are the constants representing the adsorption capacity (mg/g) and intensity of the adsorbent, respectively [37]. The plot between log q_e and log C_e (Figure 7) was linear with a correlation coefficient greater than 0.97. The values of 1/n and K were determined from the slope and the intercept of the plot, respectively (Table 1).

Equation (6) shows the Langmuir isotherm used to quantify adsorption capacity [38]:

$$\frac{1}{q_e} = \frac{1}{b \cdot q \cdot C_e} + \frac{1}{q_m},\tag{6}$$

where C_e and q_e are equilibrium solute concentration (mg/L) and equilibrium sorption capacity (mg/g). Langmuir



FIGURE 6: Pseudo-second-order kinetics for the sorption of methylene blue (MB) onto Ginkgo biloba leaf (GBL) powder.



FIGURE 7: Freundlich isotherm plot for the sorption of methylene blue onto *Ginkgo biloba* leaves: (a) nonlinear form; (b) linear form (temperature: 303°K and 323 K; MB concentration: 30 mg/L).



FIGURE 8: Langmuir sorption isotherm for the sorption of methylene blue onto *Ginkgo biloba* leaves (temperature: 303°K and 323 K; MB concentration: 30 mg/L).

constants q_m and b represent sorption capacity (mg/g) and energy of sorption (L/mg), respectively. A linear plot was also obtained (Figure 8) and the values of b and q_m calculated from the slope and intercept, respectively, are reported in Table 1.

The following equation shows the separation factor (R_L) that can also be used to express the shape of an isotherm [39]:

$$R_L = \frac{1}{1 + bC_o},\tag{7}$$

where C_o is the initial MB concentration (mg/L) and *b* is the Langmuir constant (L/mg). $R_L > 1$ implies an unfavorable monolayer adsorption process, and $R_L = 1$ indicates a linear process. The process is favorable when $0 < R_L < 1$ and irreversible when $R_L = 0$. R_L values between 0 and 1 were obtained in this study at various dye concentrations and temperatures (Table 1), indicating a favorable sorption process. Table 2 shows the maximum monolayer adsorption of MB on GBL, which was higher than those reported for sun flower seed husk and orange waste but was lower than those reported for date palm leaves and *Platanus orientalis* leaves. It is noteworthy to indicate that this comparison did not take into consideration the differences in the experimental conditions of the reported sorption studies.

Freundlich isotherm Langmuir isotherm R_L Temperature (°K) MB dye concentration (mg/L) R^2 R^2 K b n q_m 303 0.27 0.99 45.45 0.23 0.93 0.13 30 5.67 323 30 9.59 0.28 0.99 48.07 0.33 0.98 0.09

TABLE 1: Freundlich and Langmuir adsorption isotherm parameters.

TABLE 2: Comparisons of the maximum monolayer adsorption of MB onto various unmodified plant-based adsorbents.

Adsorbent	$q_m (\mathrm{mg/g})$	References
Sunflower seed husk (<i>Helianthus annuus</i>)	23.20	[40]
Citrus fruit peel	25.5	[41]
Spent rice	8.13	[20]
Orange waste	30.3	[42]
Date palm leaves	58.1	[43]
Platanus orientalis leaves	114.94	[44]
Durian skin	7.23	[45]
Coconut leaves	112.35	[46]
Typha stem and leaves	126.6	[47]
Marula seed husk	33	[1]
Ginkgo biloba leaves	48.07	This study

3.4. Thermodynamic Studies. The feasibility of the sorption process was determined by the thermodynamics experiments performed at various temperatures. On average, the uptake of MB decreased with increased temperature in this study. According to thermodynamics, Gibb's free energy change is also related to the enthalpy change (Δ H°) and entropy change (Δ S°) at constant temperature by the following equations [48]:

$$\Delta G^{\circ} = -2.303 RT \log KD, \qquad (8)$$

$$\mathrm{KD} = \frac{q_e}{C_e},\tag{9}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}, \qquad (10)$$

$$\ln \text{KD} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT},$$
(11)

where K_D is the equilibrium constant. The plot of $\ln K_D$ versus (1/T) is linear (Figure 9) and the change in enthalpy (ΔH°) and entropy (ΔS°) was calculated from the slope and intercept, respectively, and the values obtained are presented in Table 3.

The change in Gibb's energy was negative implying that the sorption process was spontaneous. Generally, a value of ΔG° in the range of 0 and -20 kJ/mol is consistent with electrostatic interaction between sorption sites and the adsorbate (physical adsorption) while a more negative ΔG° value (\sim -80 to -400 kJ/mol) indicates that chemisorption plays a major role in the sorption process [49]. The positive ΔH° value (47.625 kJ·mol⁻¹) confirmed that the sorption process is endothermic and of physical nature, while the positive value of ΔS° (164.8 J·mol⁻¹·K⁻¹) reflects the affinity of MB toward sorbent. Similar observations have been reported by other authors for sorbents including palm kernel, cotton waste, cotton dust, tree fern, and *Ficus carica* activated carbon [50–53].



FIGURE 9: Thermodynamic parameters for the sorption of methylene blue onto *Ginkgo biloba* leaves.

TABLE 3: Thermodynamic parameters for the sorption of MB ontoGBL.

Temperature (K)	ΔG° (J/mol·K)	ΔH° (J/mol·K)	ΔS° (J/mol·K)
303	-5.149	47.625	164.808
313	-8.300		
323	-9.308		
333	-10.601		

3.5. Effect of Solution pH on MB Removal. In order to determine the optimum pH for the sorption of MB by GBL powder, the removal of MB as a function of hydrogen ion concentration was studied. MB sorption was monitored for 24 h. From Figure 10, it is evident that maximum adsorption (98–100%) was achieved in the pH range of 4–12 for initial MB concentrations. Similar trend has been reported for MB sorption onto yellow passion fruit peel [54], Posidonia oceanica (L Fibers) [55], and duckweed [56].

The equilibrium concentration (C_e) was found to increase with increased solution pH to about 4.0 after which percent removal becomes constant. This effect of pH could be explained using speciation diagram of MB adopted from other studies [57]. As per the speciation diagram, MB can be present in aqueous solution as the cationic species (MB⁺) and undissociated molecules (MB⁰). Above pH 6.0, only MB⁺ species are observed in the solution, whereas below pH 3.0, MB is only predominantly in its undissociated form (MB^0) . At higher pH (>5.0), the surface of GBL particles get negatively charged, which enhances the sorption of the positively charged cationic dye (MB⁺) through electrostatic forces of attraction. Other researchers have reported similar effects of the solution pH on the sorption of cationic dyes [53, 57, 58]. Salazar et al. [57] further reported that at $pH > pH_{PZC}$, MB was adsorbed on natural sawdust even though the surface charge was neutral, indicating that MB was adsorbed by other mechanisms than electrostatic attraction.



FIGURE 10: Effect of solution pH on the sorption of MB onto GBL.

3.6. Effect of Particle Size on Dye Removal. As evident from Figure 11, higher sorption capacity (q_e) was observed at smaller GBL particle size. Sorption capacity decreased from 19.81 to 16.31 mg/g as size increased from 177 μ m to 590 μ m at a sorbent dose of 0.5 g/L. The impact of particle size on sorption capacity becomes less significant with sorbent dose increase from 0.5 g/L to 2.5 g/L. Lower particle sizes provide higher surface area for the sorption of dye molecules, thus providing higher sorption efficiency/capacity. However, as sorbent dose increased from 0.5 g/L to 2.5 g/L, mean sorption capacity decreased by 80% for the 177 μ m particle size. At higher sorbent doses (2.5 g/L), the low sorption capacities at all particle sizes could be attributed to the limiting concentration of dye molecules while many sorption sites remained unfilled.

Similar impacts of particle size on the removal efficiency and sorption capacities are reported by others on various sorbent materials such as clay [59], tree fern [51], dried sea grape [60], chitosan [61], and *Prunus amygdalus* L [62]. Although smaller particle size shows higher removal efficiencies and sorption capacities, many operational and handling issues limit their use in practical applications. Some of these major issues with smaller particles are greater head losses, clogging, and pump damage. Therefore, careful selection of sorbent particle size is warranted for all practical applications.

3.7. Matrix Effect on MB Sorption. Dell pond at University of Virginia is a water overflow retention facility used for controlling flow during high rainfall/snow events. Dell pond was characterized for various physical and chemical water quality parameters such as pH (7.3), conductivity (217.1 μ S/m), dissolved oxygen (10.8 mg/L), temperature (8°C), and TOC (1.0 mg/L). Various anions and cations present in Dell pond were sulphate (5.5 mg/L), chloride (22 mg/L), potassium (4.0 mg/L), sodium (30 mg/L), calcium (15.8 mg/L), and magnesium (3.8 mg/L). This pond water was spiked with stock dye solution to make a concentration of 10 mg/L.



FIGURE 11: MB sorption capacity as a function of particle size.



FIGURE 12: Matrix effect: comparative plot of Milli-Q and Dell pond water sample.

As can be seen in Figure 12(a), no significant difference was observed in sorption capacity between laboratory (Lab) and surface water samples. Also, a similar trend between sorption capacity and dye removal at different concentrations was observed with Milli-Q spiked lab studies as well (Figure 12(b)).

4. Conclusions

The adsorption of methylene blue from aqueous solution onto GBL has been studied. Adsorption experiments were carried out as a function of contact time, adsorbent dosage, temperature, solution pH, particle size, and dye concentration. The adsorption experiments indicated that GBL powder of 177–590 μ m was effective in removing methylene blue dye from aqueous solutions. Removal effectiveness decreased with an increase in initial dye concentration in the solution and increased with an increase in sorbent dosage. The adsorption data fit well to the Freundlich and Langmuir sorption isotherm models. The rates of sorption were found to conform to Lagergren-first-order and pseudo-secondorder kinetics. Solution pH plays a major role in the sorption of dye as solution with pH of over 5.5 yielded more than 98% dye removal. The results also indicated that with increased temperature, the adsorption increased which indicated an endothermic process. Methylene blue dye removal in surface water revealed similar sorption capacities to those observed under laboratory. This indicates that GBL sorbent could be employed for sorption of dye from actual surface water. Utilizing Ginkgo biloba leaves (GBLs), an inexpensive and easily available material, for dye removal may not only solve a critical water pollution issue but also mitigate a potential waste management issue, thus benefiting local economy and environment.

Nomenclature

- *b*: Langmuir constant $(l \cdot mg^{-1})$
- *C*: Methylene blue concentration in solution $(mg \cdot l^{-1})$
- C_e : Equilibrium methylene blue concentration in solution (mg·l⁻¹)
- *C_t*: Methylene blue concentration in solution at time *t* (mg·l⁻¹)
- *E*: Free energy of adsorption $(kJ \cdot mol^{-1})$
- ΔG° : Gibb's free energy change (kJ·mol⁻¹)
- ΔH° : Enthalpy change (kJ·mol⁻¹)
- K_{ad} : Adsorption rate constant (h⁻¹)
- *K*: Freundlich constant ($mg \cdot g^{-1}$)
- K_p : Intraparticle diffusion coefficient (mg·g⁻¹·h^{-1/2})
- K_0 : Equilibrium constant
- *m*: Mass of the adsorbent (g)
- *M*: Mass of the adsorbent per unit volume of particle-free adsorbate solution $(g \cdot l^{-1})$
- *n*: Freundlich constant (dimensionless)
- *q*: Adsorbed phase concentration $(mg \cdot g^{-1})$
- q_e : Amount of solute uptake per unit mass of adsorbent at equilibrium (mg·g⁻¹)
- q_m : Langmuir isotherm constant (mg·g⁻¹)
- \hat{R} : Gas constant (kJ·mol⁻¹·K⁻¹)
- $\Delta S:$ Entropy change (kJ mol⁻¹)
- *t*: Time (minutes)
- *T*: Temperature (°C and/or °K)
- *x*: Amount of methylene blue adsorbed in solid phase (mg)
- M: Methylene blue
- GBL: Ginkgo biloba leaf.

Data Availability

Major data used to support the findings of this study are included within the article. Other data can be made available upon request from the corresponding author.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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References

- J. N. Edokpayi, S. S. Ndlovu, and J. O. Odiyo, "Characterization of pulverized marula seed husk and its potential for the sequestration of methylene blue from aqueous solution," *BMC Chemistry*, vol. 13, p. 10, 2019.
- [2] V. Katheresan, J. Kansedo, and S. Y. Lau, "Efficiency of various recent wastewater dye removal methods: a review," *Journal of Environmental Chemical Engineering*, vol. 6, no. 4, pp. 4676–4697, 2018.
- [3] F. Silva, L. Nascimento, M. Brito, K. da Silva, W. Paschoal, and R. Fujiyama, "Biosorption of methylene blue dye using natural biosorbents made from weeds," *Materials*, vol. 12, no. 15, p. 2486, 2019.
- [4] D. A. Yaseen and M. Scholz, "Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review," *International Journal of Environmental Science and Technology*, vol. 16, no. 2, pp. 1193–1226, 2019.
- [5] S. Rangabhashiyam and P. Balasubramanian, "Adsorption behaviors of hazardous methylene blue and hexavalent chromium on novel materials derived from *Pterospermum acerifolium* shells," *Journal of Molecular Liquids*, vol. 254, pp. 433–445, 2018.
- [6] S. Shakoor and A. Nasar, "Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 66, pp. 154–163, 2016.
- [7] P. S. Kumar, S. Ramalingam, and K. Sathishkumar, "Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent," *Korean Journal of Chemical Engineering*, vol. 28, no. 1, pp. 149–155, 2011.
- [8] S. Aoudj, A. Khelifa, N. Drouiche, M. Hecini, and H. Hamitouche, "Electrocoagulation process applied to wastewater containing dyes from textile industry," *Chemical Engineering and Processing: Process Intensification*, vol. 49, no. 11, pp. 1176–1182, 2010.
- [9] S. I. Siddiqui, G. Rathi, and S. A. Chaudhry, "Acid washed black cumin seed powder preparation for adsorption of methylene blue dye from aqueous solution: thermodynamic, kinetic and isotherm studies," *Journal of Molecular Liquids*, vol. 264, pp. 275–284, 2018.
- [10] L. Lin, Y. Lin, C. Li, D. Wu, and H. Kong, "Synthesis of zeolite/ hydrous metal oxide composites from coal fly ash as efficient adsorbents for removal of methylene blue from water,"

International Journal of Mineral Processing, vol. 148, pp. 32–40, 2016.

- [11] A. Bhatnagar and M. Sillanpää, "Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-a review," *Chemical Engineering Journal*, vol. 157, no. 2, pp. 277–296, 2010.
- [12] S. Chen, J. Zhang, C. Zhang, Q. Yue, Y. Li, and C. Li, "Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from *Phragmites australis*," *Desalination*, vol. 252, no. 1–3, pp. 149–156, 2010.
- [13] H. Patel and R. T. Vashi, "Removal of Congo red dye from its aqueous solution using natural coagulants," *Journal of Saudi Chemical Society*, vol. 16, no. 2, pp. 131–136, 2012.
- [14] P. V. Nidheesh and T. S. A. Singh, "Arsenic removal by electrocoagulation process: recent trends and removal mechanism," *Chemosphere*, vol. 181, pp. 418–432, 2017.
- [15] D. Lin, F. Wu, Y. Hu et al., "Adsorption of dye by waste black tea powder: parameters, kinetic, equilibrium, and thermodynamic studies," *Journal of Chemistry*, vol. 2020, Article ID 5431046, 13 pages, 2020.
- [16] T. Lee, S. Wang, Z. Huang et al., "Tea stem as a sorbent for removal of methylene blue from aqueous phase," *Advances in Materials Science and Engineering*, vol. 2019, Article ID 9723763, 15 pages, 2019.
- [17] S. Rangabhashiyam, S. Lata, and P. Balasubramanian, "Biosorption characteristics of methylene blue and malachite green from simulated wastewater onto *Carica papaya* wood biosorbent," *Surfaces and Interfaces*, vol. 10, pp. 197–215, 2018.
- [18] X. Han, W. Wang, and X. Ma, "Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf," *Chemical Engineering Journal*, vol. 171, no. 1, pp. 1–8, 2011.
- [19] A. B. Albadarin and C. Mangwandi, "Mechanisms of alizarin red S and methylene blue biosorption onto olive stone byproduct: isotherm study in single and binary systems," *Journal* of Environmental Management, vol. 164, pp. 86–93, 2015.
- [20] M. S. U. Rehman, I. Kim, and J.-I. Han, "Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass," *Carbohydrate Polymers*, vol. 90, no. 3, pp. 1314–1322, 2012.
- [21] A. A. Jalil, S. Triwahyono, M. R. Yaakob et al., "Utilization of bivalve shell-treated *Zea mays* L. (maize) husk leaf as a lowcost biosorbent for enhanced adsorption of malachite green," *Bioresource Technology*, vol. 120, pp. 218–224, 2012.
- [22] B. Shanmugarajah, I. M. Chew, N. M. Mubarak, T. S. Choong, C. Yoo, and K. Tan, "Valorization of palm oil agro-waste into cellulose biosorbents for highly effective textile effluent remediation," *Journal of Cleaner Production*, vol. 210, pp. 697–709, 2019.
- [23] C.-W. Zhang, C.-Z. Wang, and R. Tao, "Analysis on the physicochemical properties of *Ginkgo biloba* leaves after enzymolysis based ultrasound extraction and soxhlet extraction," *Molecules*, vol. 21, no. 1, p. 97, 2016.
- [24] T. A. Van Beek and P. Montoro, "Chemical analysis and quality control of *Ginkgo biloba* leaves, extracts, and phytopharmaceuticals," *Journal of Chromatography A*, vol. 1216, no. 11, pp. 2002–2032, 2009.
- [25] T. A. Van Beek, "Chemical analysis of *Ginkgo biloba* leaves and extracts," *Journal of Chromatography A*, vol. 967, no. 1, pp. 21–55, 2002.
- [26] J. X. Mu, M. J. Shi, X. Y. Wu, and J. Y. Li, "Adsorptive removal of methylene blue by ginkgo leaf powder," *Applied Mechanics and Materials*, vol. 130–134, pp. 829–832, 2012.

- [27] Y. Huang, Y. Hu, L. Chen et al., "Selective biosorption of thorium (IV) from aqueous solutions by Ginkgo leaf," *PLoS One*, vol. 13, p. 3, 2018.
- [28] J. Edokpayi, J. Odiyo, E. Popoola, O. Alayande, and T. Msagati, "Synthesis and characterization of biopolymeric chitosan derived from land snail shells and its potential for Pb2₊ removal from aqueous solution," *Materials*, vol. 8, no. 12, pp. 8630–8640, 2015.
- [29] J. Liang, J. Xia, and J. Long, "Biosorption of methylene blue by nonliving biomass of the brown macroalga Sargassum hemiphyllum," Water Science and Technology, vol. 76, no. 6, pp. 1574–1583, 2017.
- [30] K. Bhattacharyya and A. Sharma, "Kinetics and thermodynamics of methylene blue adsorption on neem () leaf powder," *Dyes and Pigments*, vol. 65, no. 1, pp. 51–59, 2005.
- [31] R. R. Krishni, K. Y. Foo, and B. H. Hameed, "Adsorptive removal of methylene blue using the natural adsorbent-banana leaves," *Desalination and Water Treatment*, vol. 52, no. 31–33, pp. 6104–6112, 2014.
- [32] H. Deng, J. Lu, G. Li, G. Zhang, and X. Wang, "Adsorption of methylene blue on adsorbent materials produced from cotton stalk," *Chemical Engineering Journal*, vol. 172, no. 1, pp. 326–334, 2011.
- [33] S. K. Lagergren, "About the theory of so-called adsorption of soluble substances," *Kungliga Svenska Vetenskapsakademiens Handlingar*, vol. 24, pp. 1–39, 1898.
- [34] W. J. Weber and J. C. Morris, "Kinetics of adsorption on carbon from solution," *American Society of Civil Engineers*, vol. 89, pp. 31-60, 1963.
- [35] T. S. Singh and K. K. Pant, "Equilibrium, kinetics and thermodynamic studies for adsorption of as (III) on activated alumina," *Separation and Purification Technology*, vol. 36, no. 2, pp. 139–147, 2004.
- [36] Y. S. Ho and G. McKay, "Kinetic model for lead (II) sorption on to peat," Adsorption Science & Technology, vol. 16, no. 4, pp. 243–255, 1998.
- [37] H. Freundlich, "Über die adsorption in Lösungen," Zeitschrift für Physikalische Chemie, vol. 57U, pp. 385–470, 1907.
- [38] I. Langmuir, "The constitution and fundamental properties of solids and liquids: part I solids," *Journal of the American Chemical Society*, vol. 38, no. 11, pp. 2221–2295, 1916.
- [39] K. R. Hall, L. C. Eagleton, A. Acrivos, and T. Vermeulen, "Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions," *Industrial & Engineering Chemistry Fundamentals*, vol. 5, no. 2, pp. 212–223, 1966.
- [40] S. T. Ong, P. S. Keng, S. L. Lee, M. H. Leong, and Y. T. Hung, "Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*)," *International Journal of Physical Sciences*, vol. 5, pp. 1270–1276, 2010.
- [41] S. Dutta, A. Bhattacharyya, A. Ganguly, S. Gupta, and S. Basu, "Application of response surface methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of methylene blue," *Desalination*, vol. 275, no. 1–3, pp. 26–36, 2011.
- [42] S. Irem, Q. Mahmood Khan, E. Islam et al., "Enhanced removal of reactive navy blue dye using powdered orange waste," *Ecological Engineering*, vol. 58, pp. 399–405, 2013.
- [43] M. Gouamid, M. R. Ouahrani, and M. B. Bensaci, "Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm leaves," *Energy Procedia*, vol. 36, pp. 898–907, 2013.
- [44] M. Peydayesh and A. Rahbar-Kelishami, "Adsorption of methylene blue onto *Platanus orientalis* leaf powder: kinetic, equilibrium and thermodynamic studies," *Journal of Industrial and Engineering Chemistry*, vol. 21, pp. 1014–1019, 2015.

- [45] S. M. Anisuzzaman, C. G. Joseph, D. Krishnaiah, A. Bono, and L. C. Ooi, "Parametric and adsorption kinetic studies of methylene blue removal from simulated textile water using durian (*Durio zibethinus* murray) skin," *Water Science and Technology*, vol. 72, no. 6, pp. 896–907, 2015.
- [46] A. H. Jawad, R. A. Rashid, R. M. A. Mahmuod, M. A. M. Ishak, N. N. Kasim, and K. Ismail, "Adsorption of methylene blue onto coconut (*Cocos nucifera*) leaf: optimization, isotherm and kinetic studies," *Desalination and Water Treatment*, vol. 57, no. 19, pp. 8839–8853, 2016.
- [47] R. Sánchez-Orozco, M. Martínez-Juan, J. García-Sánchez, and F. Ureña-Núñez, "Removal of methylene blue from aqueous solution using typha stems and leaves," *BioResources*, vol. 13, no. 1, pp. 1696–1710, 2018.
- [48] V. Hoff, "Studies in dynamic chemistry," 1884, https://www. nobelprize.org/prizes/chemistry/1901/hoff/biographical/.
- [49] C.-H. Weng, Y.-T. Lin, and T.-W. Tzeng, "Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder," *Journal of Hazardous Materials*, vol. 170, no. 1, pp. 417–424, 2009.
- [50] M. Ertaş, B. Acemioğlu, M. H. Alma, and M. Usta, "Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust," *Journal of Hazardous Materials*, vol. 183, pp. 421–427, 2010.
- [51] Y.-S. Ho, T.-H. Chiang, and Y.-M. Hsueh, "Removal of basic dye from aqueous solution using tree fern as a biosorbent," *Process Biochemistry*, vol. 40, no. 1, pp. 119–124, 2005.
- [52] G. O. El-Sayed, "Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber," *Desalination*, vol. 272, no. 1–3, pp. 225–232, 2011.
- [53] D. Pathania, S. Sharma, and P. Singh, "Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast," *Arabian Journal of Chemistry*, vol. 10, pp. S1445–S1451, 2017.
- [54] F. A. Pavan, A. C. Mazzocato, and Y. Gushikem, "Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent," *Bioresource Technology*, vol. 99, no. 8, pp. 3162–3165, 2008.
- [55] M. C. Ncibi, B. Mahjoub, and M. Seffen, "Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres," *Journal of Hazardous Materials*, vol. 139, no. 2, pp. 280–285, 2007.
- [56] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, and E. S. Upatham, "Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*)," *Environmental Pollution*, vol. 125, no. 3, pp. 385–392, 2003.
- [57] J. J. Salazar-Rabago, R. Leyva-Ramos, J. Rivera-Utrilla, R. Ocampo-Perez, and F. J. Cerino-Cordova, "Biosorption mechanism of methylene blue from aqueous solution onto white pine (*Pinus durangensis*) sawdust: effect of operating conditions," *Sustainable Environment Research*, vol. 27, no. 1, pp. 32–40, 2017.
- [58] L. B. L. Lim, N. Priyantha, D. T. B. Tennakoon, H. I. Chieng, M. K. Dahri, and M. Suklueng, "Breadnut peel as a highly effective low-cost biosorbent for methylene blue: equilibrium, thermodynamic and kinetic studies," *Arabian Journal of Chemistry*, vol. 10, pp. S3216–S3228, 2017.
- [59] G. Mahdavinia, A. Baghban, S. Zorofi, and A. Massoudi, "Kappa-carrageenan: biopolymer-based nanocomposite hydrogel and adsorption of methylene blue cationic dye from water," *Journal of Materials and Environmental Science*, vol. 5, no. 2, pp. 330–337, 2014.
- [60] P. Pimol, M. Khanidtha, and P. Prasert, "Influence of particle size and salinity on adsorption of basic dyes by agricultural

- vironmental Sciences, vol. 20, no. 6, pp. 760–768, 2008.
 [61] Y. C. Wong, Y. S. Szeto, W. H. Cheung, and G. McKay, "Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan," *Adsorption*, vol. 14, no. 1, pp. 11–20, 2008.
- [62] F. Deniz, "Adsorption properties of low-cost biomaterial derived from *Prunus amygdalus* L. for dye removal from water," *The Scientific World Journal*, vol. 2013, Article ID 961671, 8 pages, 2013.