

Comparative Adsorption Characteristics of Methylene Blue on Raw Leaves and Biochar of Guinea Grass (*Megathyrsus maximus*)

M. A.O.Y. Weeratunge

University of Peradeniya

M. D.N. Dinusha

University of Peradeniya

R. M.M.K. Karunathilaka

University of Peradeniya

Namal Priyantha

`namal.priyantha@yahoo.com`

University of Peradeniya

Research Article

Keywords: Adsorption, Guinea grass, Biochar, Kinetics, Methylene blue

Posted Date: October 30th, 2025

DOI: <https://doi.org/10.21203/rs.3.rs-7692254/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Comparative Adsorption Characteristics of Methylene Blue on Raw Leaves and Biochar of Guinea Grass (*Megathyrsus maximus*)

M.A.O.Y. Weeratunge^{1,2}, M.D.N. Dinusha^{1,2}, R.M.M.K. Karunathilaka^{1,2}, and

N. Priyantha^{2*}

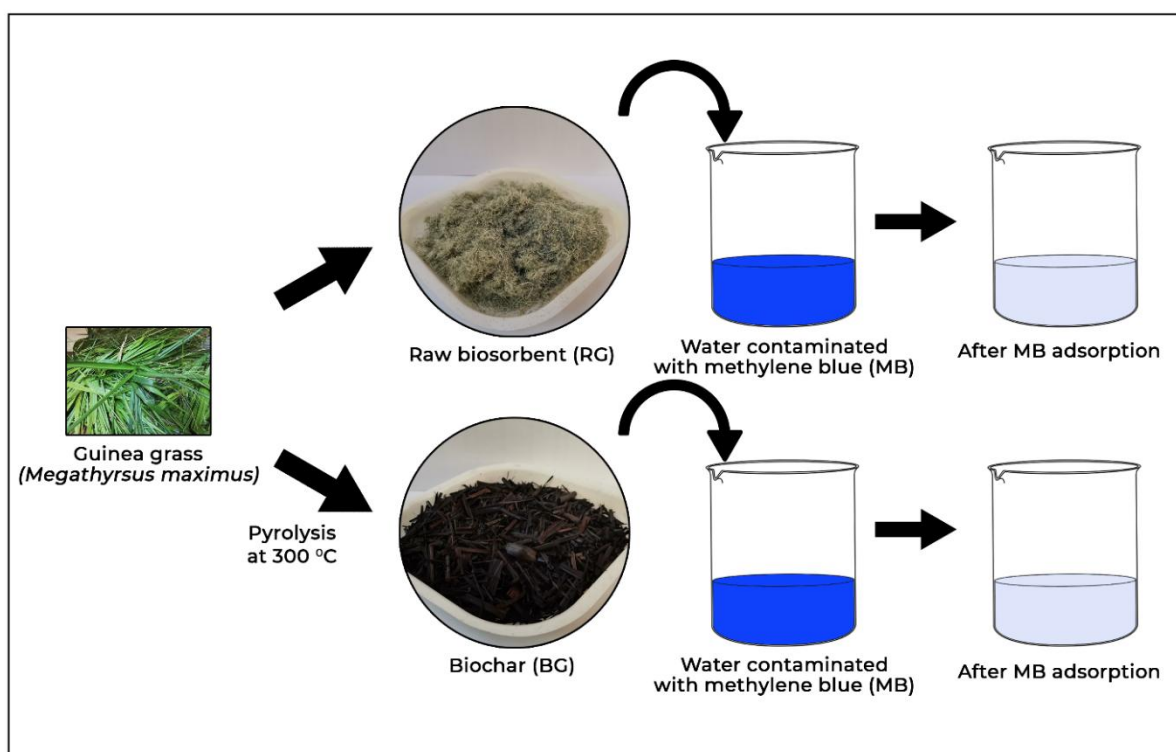
¹Department of Environmental and Industrial Sciences, University of Peradeniya, Peradeniya, Sri Lanka

²Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

*Corresponding author: Namal Priyantha, Department of Chemistry, Faculty of Science, University of Peradeniya, Peradeniya, 20400, Sri Lanka

Email address: namal.priyantha@yahoo.com

ORCID: 0000-0001-8625-8579



Abstract

Wastewater discharged from textile industries leads to severe impact on aquatic ecosystem and public health. Methylene blue (MB), commonly found in textile wastewater systems, would cause many health problems on humans and lead to undesirable ecological changes in the environment. Hence, removal of MB from contaminated water is a priority to safeguard the environment. This study thus aims to explore the practicability of utilizing both raw biosorbent and biochar of guinea grass (*Megathyrsus maximus*) for removal of MB cationic dye from synthetic contaminated water. The raw biosorbent and biochar were characterized by scanning electron microscopy and Fourier transform infrared spectroscopy. Effect of adsorbent dosage, shaking time, settling time and pH of the MB solution were investigated in batch experiments. Adsorption kinetics investigated under pre-equilibrium conditions leads to the validity of the pseudo second-order kinetics model according to linear regression analysis, which can be attributed to the presence of two or more functional groups involved in the adsorption process. Moreover, adsorption equilibrium data of both biosorbents show the validity of the Langmuir adsorption isotherm over the Freundlich isotherm according to the linearized relationships, indicating the monolayer adsorption of MB molecules. Both raw biosorbent and its biochar exhibit more than 95% removal of MB under the experimental conditions employed. Another desirable factor is that the raw biosorbent could easily be modified to further improve adsorption characteristics. Although both biosorbent types are cost-effective, ecofriendly and sustainable, it is more economical to use the raw biosorbent for the removal of MB from aqueous systems.

Keywords: Adsorption, Guinea grass, Biochar, Kinetics, Methylene blue

Introduction

Over the past few decades, the rapid growth of the global population and their demands have prompted the establishment and expansion of various industries, resulting in discharge of large volumes of pollutants into the environment including water bodies. Most industrial effluents contain heavy metals and toxic dyes, which would seriously affect human life and aquatic ecosystems [1]. Textile, paper and leather industries, in general, release large volumes of inorganic and organic synthetic dyes, and effective treatment of dye effluents may not be implemented in all industries, thereby polluting water bodies. Recent data indicate that nearly 100 thousand commercially dyed products with a total of 7×10^5 tons of dyestuff are produced annually, some of which have been discharged into the aquatic environment without proper treatment [2].

When dye effluents are discharged into the aquatic environment, it would block sunlight coming in, increase the color intensity of the receiving water and threaten the aquatic life [3]. Moreover, allergenic, mutagenic and carcinogenic properties of these dyes would cause harm to all living things, requiring effective treatment of dye effluents before releasing them into the environment [4,5]. Without adequate treatment, the release of colored wastewater can have

severe consequences on the environment, such as increasing toxicity by raising the chemical oxygen demand and the biological oxygen demand in water bodies [6]. In this respect, numerous wastewater treatment methods, including adsorption, chemical coagulation, chemical precipitation, ion exchange, liquid-liquid extraction, membrane filtration, oxidation and ozonation, have been employed depending on the composition of the effluent and the requirements to be fulfilled in disposing of [4,7,8]. Among these, adsorption is considered to be a promising approach due to its cost effectiveness, high efficiency and simplicity, and can be made eco-friendly as a vast range of natural materials is available as adsorbents to select from. *Artocarpus altilis* peel and core, *Artocarpus odoratissimus* leaves, banana peel, garlic peel, *Ipomoea aquatica* waste, pineapple leaf fiber, water lettuce and wood apple shell are some natural biosorbents reported for the removal of dyes [9-11]. Activated carbon is also widely used as an effective adsorbent for dye removal and has proven to have strong adsorption capacities for aqueous systems for a variety of organic and inorganic pollutants. However, the production process of activated carbon is costly, requires chemicals for the activation process and consumes energy [12]. Therefore, research is focused on environmentally friendly, cost-effective, and naturally available biosorbent materials and their modified forms as alternative to commercial activated carbon [12,13].

Methylene blue (MB), a cationic dye, is one of the most widely used synthetic dyes in the textiles, pharmaceutical, food and paper industries [14]. It is also commonly used in dyeing and finishing materials, and as a staining agent for the classification of microorganisms [15]. Consequently, there are many avenues through which water resources are contaminated with MB. Excessive exposure to MB poses health risks to both humans and aquatic life, potentially causing skin irritation of skin, mouth and throat, neurological issues, cardiovascular diseases and elevated blood pressure [2,3]. Owing to extensive industrial uses of MB and its health risks, search for cost-effective and sustainable methodologies to reduce the effects of MB through removing it from the environment has been widely focused. The biosorption approach for the removal of MB from water has become attractive [13,16], and further, mechanistic investigation and details of boundary layer effect of adsorption of MB on different surfaces have been reported [17,18]. Transfer of MB into thin polymer membranes of low diffusion coefficients has also been attempted [19]. Chemically modified adsorbent material synthesized from dried fibers of cotton for the removal of MB has recently been reported [20]. Nevertheless, fibrous biosorbents and their modified forms have not been much investigated for the removal of environmental pollutants.

Megathyrsus maximus (Guinea grass) is an invasive perennial weed species which causes negative impact on agriculture [21]. This plant is commonly available in tropical countries, and it can easily grow up to 2-3 m in height without proper control in larger areas of agricultural lands. On the other hand, biochar is classified as an effective biosorbent material due to its unique physicochemical properties, capable of adsorbing a wide range of pollutants from wastewater. Its high surface area, porous structure, cation exchange capacity and surface functional groups make it a highly suitable adsorbent for capturing contaminants, such as heavy metals, dyes and organic pollutants [22]. Nevertheless, comparative studies of raw biosorbents and their biochar have not been much elaborated.

In this context, the goal of this study was to investigate the use of guinea grass, a fibrous biosorbent, and its biochar as an eco-friendly and cost-effective novel biosorbent material for the removal of MB from aqueous solutions containing wastewater. Advantages and drawbacks of the raw biosorbent and its biochar were systematically investigated with reference to various experimental parameters and adsorption characteristics. The adsorbents were characterized by Fourier transform infra-red (FTIR) spectroscopy scanning electron microscopy (SEM) and X-ray fluorescence (XRF) spectroscopy. Batch adsorption experiments were carried out by optimizing adsorbent dosage, shaking time, settling time and solution pH. Investigation of the validity of adsorption isotherm and kinetics models were performed to provide a better understanding of the adsorption process. The chemical structure and the three-dimensional space-filling model of MB are given in Figure 1.

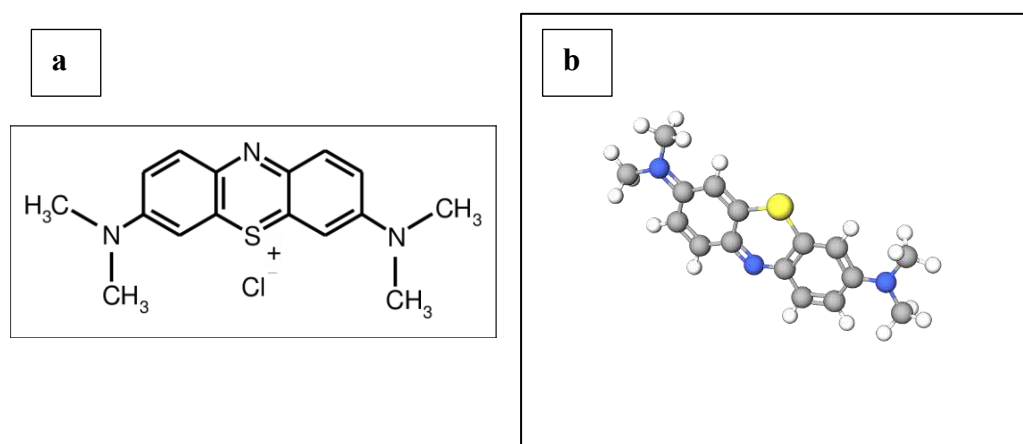


Figure 1: a) Chemical structure and b) space-filling model of MB [23].

Materials & Methods

Sample preparation

Raw leaves of Guinea grass (RG) biosorbent: Leaves of mature guinea grass were randomly collected from the premises of the University of Peradeniya, Sri Lanka, and cut into 1.0 – 2.0 cm in length. After washing cut pieces several times with tap water and deionized water to remove the soil and loosely bound particles, they were crushed for several minutes using laboratory blender. Crushed samples were washed again with deionized water until the supernatant became clear. Finally, samples were filtered and the residue was heated at 120 °C for 2.0 h to remove moisture, and then mixed well to form a homogeneous biosorbent sample.

Biochar preparation: A fraction of a dried guinea grass sample from the earlier preparation was placed on electric muffle furnace at 300 °C for 30 min to obtain its biochar (BG). This BG sample was washed several times with deionized water and heated up to 120 °C for 2.0 h to obtain a pure BG sample free of ash, which was stored in sealed containers until use to avoid moisture absorbance.

Chemicals and reagents

All chemical reagents used in this experiment were of analytical grade and used without further purification. MB [IUPAC name: 3,7-bis(dimethylamino)phenothiazin-5-ium chloride; chemical formula: $C_{16}H_{18}N_3SCl$; molar mass: $319.85 \text{ g mol}^{-1}$], also called methylthioninium chloride, was selected as the adsorbate in this study. A stock solution of 1000 mg L^{-1} MB solution was prepared by dissolving 1.000 g of MB powder in deionized water and diluted to 1.00 L with deionized water in a 1000.00 mL volumetric flask. MB solutions of concentrations of $10, 50, 100, 250, 500$ and 750 mg L^{-1} were prepared by diluting the stock MB solution with deionized water.

Instrumentation

The pH of MB solution was adjusted by adding $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ and/or $0.1 \text{ mol L}^{-1} \text{ NaOH}$ solutions using pH meter (ORION STAR A214). Absorbance measurements of MB solutions were recorded, in triplicate, using UV-Visible spectrophotometer (SHIMADZU UV-1800) at the characteristic λ_{max} of 658.0 nm , and the concentration of MB in each solution was determined based on a calibration curve constructed daily. The FTIR spectrophotometer (JASCO FTIR - 6700) was used for the identification of functional groups present in RG and BG adsorbents. SEM (ZEISS EVO LS 15) was used for morphological characterization of the biosorbent.

Adsorption experiments

All adsorption experiments were carried out, in triplicate, using 50.00 mL of 10 mg L^{-1} MB solution, and the contents were agitated on orbital shaker at a constant speed of 150 rpm , at ambient temperature. The effect of dosage of biosorbent was carried out by changing the mass of biosorbent from 0.025 g to 1.250 g ; the effect of shaking time was investigated using different shaking time periods from 5 to 60 min at the optimum biosorbent dosage; the effect of settling time was determined by shaking the samples for the optimum shaking time with the optimum biosorbent dosage, followed by allowing to settle for different time periods up to 60 min ; the effect of solution pH was carried out by adjusting the pH of MB solution from 2.0 to 12.0 with the optimum biosorbent dosage, using optimized shaking time and settling time. The amount of MB dye adsorbed on RG and BG at equilibrium was determined using Equation (1).

$$\text{Adsorption capacity } (q_e) = \frac{C_o - C_e}{m} v \quad (1)$$

where q_e (mg g^{-1}) is the amount of MB dye adsorbed by the biosorbent at equilibrium, C_o (mg L^{-1}) is the initial concentration of dye, C_e (mg L^{-1}) is the concentration of dye at equilibrium, v (L) is the volume dye solution and m (g) is the mass of the biosorbent material. The percentage of dye removal ($\%R$) was determined according to Equation (2).

$$\text{Percentage of dye removal } (\%R) = \left[\frac{C_o - C_e}{C_o} \right] \times 100 \quad (2)$$

Kinetics studies

Kinetics studies were conducted by mixing 10.000 g of each biosorbent with 1000.00 mL of 10.0 mg L⁻¹ MB solution with continuous stirring at ambient temperature. Initially, the supernatant was withdrawn at every 1 min time interval for the first 10 min, and thereafter, samples were withdrawn at 10 min time intervals up to 120 min. Then, the absorbances were recorded and the kinetics data obtained were fitted to linearized forms of pseudo first order (PFO) and pseudo second order (PSO) models.

Isotherm studies

Equilibrium adsorption studies were carried out at ambient temperature by mixing 50.00 mL of MB solutions of different initial MB concentrations of 10, 50, 100, 250, 500, 750, 1000 mg L⁻¹ with 0.250 g of RG/BG for a period of 20 min at 150 rpm. After another 20 min settlement, the mixtures were filtered, and the absorbance of each filtrate was determined. Thereafter, the data obtained were plotted according to the linearized forms of the Langmuir and Freundlich isotherm models.

Results & Discussion

SEM characterization

SEM images shown in Figure 2 reveals distinct morphological changes in the leaves of *Megathyrus maximus* during pyrolysis at 300 °C. The RG presents a smoother surface with less porosity, whereas the resulting BG exhibits a significantly increased number of pores. This structural transformation results from the thermal degradation of organic matter, which enhances the surface area and the number of available adsorption sites. However, it is difficult to come to a conclusion from SEM images alone, as there would be structural changes of the adsorbent surface that would occur during pyrolysis.

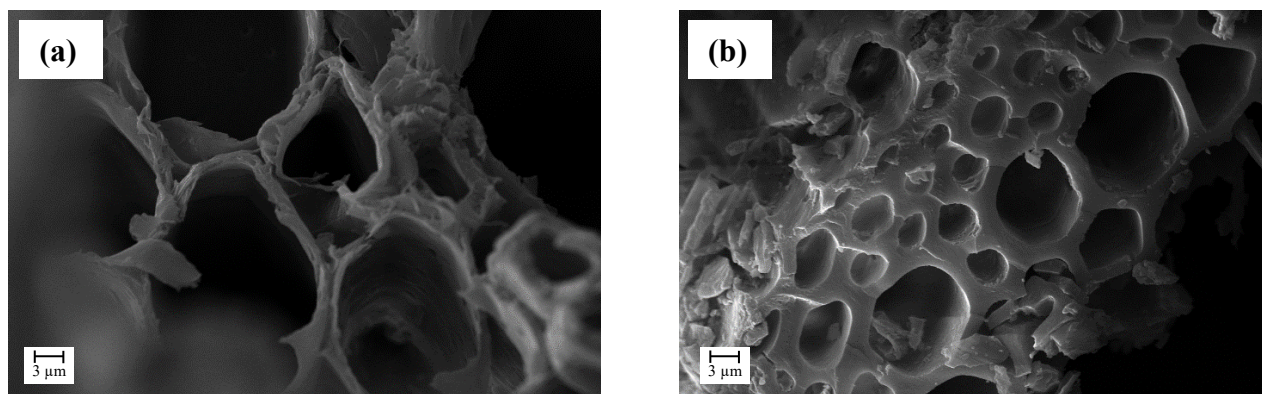


Figure 2: SEM images (5000× magnification) of surface morphology of (a) RG and (b) BG.

FTIR characterization

FTIR spectra (Figures 3 and 4) of RG and BG of *Megathyrus maximus* provide valuable insight into the functional groups involved in MB adsorption. Before adsorption, RG has shown prominent bands at 3290 cm^{-1} (-OH stretching), 1632 cm^{-1} ($\text{C}=\text{C}$ stretching) and 1320 cm^{-1} (C-N stretching). After MB adsorption, these bands have shifted to 3300 cm^{-1} , 1620 cm^{-1} and 1315 cm^{-1} , respectively, with the appearance of a new band at 892 cm^{-1} , corresponding to C-S stretching. On the other hand, BG has shown bands at 3155 cm^{-1} (-OH stretching), 1635 cm^{-1} ($\text{C}=\text{C}$ stretching), and 1365 cm^{-1} (C-N stretching) before its exposure to MB. After adsorption, these bands have shifted to 3045 cm^{-1} , 1620 cm^{-1} and 1311 cm^{-1} , respectively, and an additional new band appears at 945 cm^{-1} indicating C-S stretching (Table 1). These changes highlight the strong interaction between *Megathyrus maximus* biosorbents (RG and BG) and MB, involving hydrogen bonding, π - π interaction, and electrostatic attraction with complexation as main adsorption modes. Higher changes in band positions in FTIR spectra after MB adsorption observed for BG (Figure 4 and Table 1) as compared to those in Figure 3 align with the increased surface activity after pyrolysis are indicative of stronger adsorption by BG although it would be difficult to comment on equilibrium and kinetics aspects specifically from FTIR results [24,25].

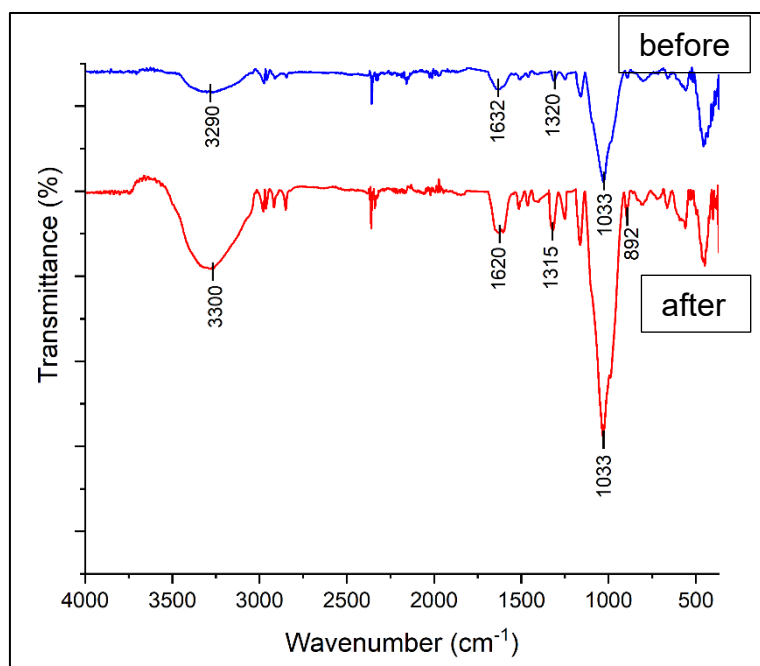


Figure 3: FTIR spectra of RG before and after MB adsorption.

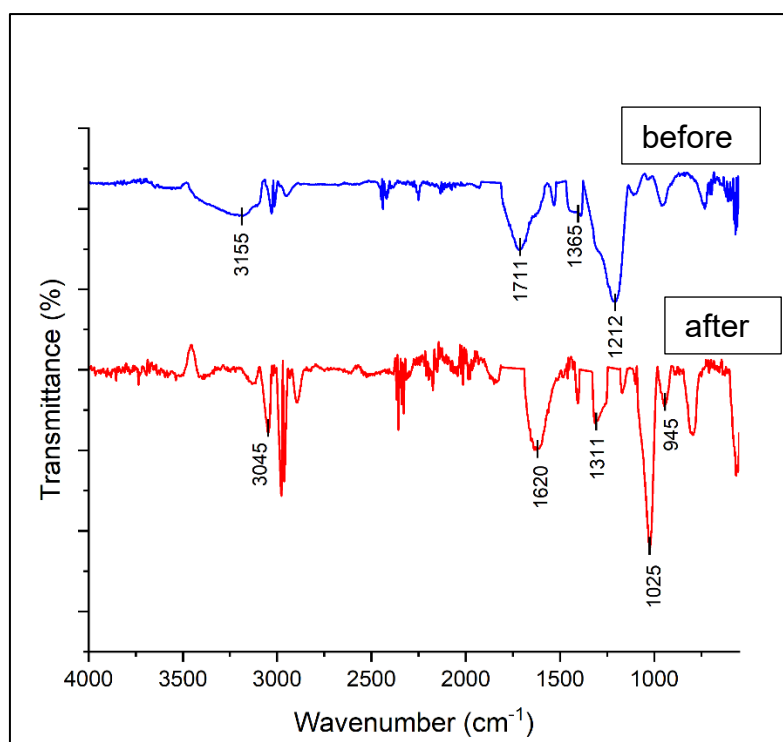


Figure 4: FTIR spectra of BG before and after MB adsorption.

Table 1: Band positions observed for functional groups present in RG and BG before and after interaction with MB.

Identification	Position of the band / cm^{-1}			
	RG		BG	
	Before	After	Before	After
O – H (carboxylic acid group)	3290	3300	3155	3045
C = H	1632	1620	1635	1620
C – N	1320	1315	1365	1311
C – S		892		945

Optimization of experimental parameters

Optimization of experimental parameters is a key step in adsorption research to determine under which conditions the adsorbate – adsorbent interactions lead to the most efficient removal. Further, by studying the effect of each parameter within a broad range of its magnitude is indicative of how the extent of removal changes with the changes in each parameter. Optimum conditions will also be important to extend laboratory studies to large-scale operations.

Biosorbent dosage

The effect of dosage of RG and BG on the extent of MB dye removal investigated by changing the dosage of each biosorbent from (0.025 ± 0.001) g to (1.250 ± 0.001) g results in

increased values from 61.49% to 99.95% and from 16.19% to 95.82% for RG and BG, respectively [Figure 5(a)]. During the optimization of biosorbent dosage, other parameters, namely, shaking time, settling time, initial pH of MB solution and initial concentration of MB, were kept constant. According to the variation of the extent of MB removal with biosorbent dosage, the optimum dosage can be taken as 0.250 g. In general, the extent of removal of MB is less with BG when compared to RG probably due to the loss of some organic functionalities containing hetero atoms which would easily interact with positively charged methylene blue molecules.

Shaking time

Shaking time is a crucial parameter in adsorption processes, because saturation of the active sites of the adsorbent material upon the adsorption of adsorbate species depends on shaking time. Also, shaking time controls the establishment of the equilibrium. Figure 5(b) indicates the extent of removal of MB by BG and RG for a range of shaking time periods determined at the optimum biosorbent dosage of (0.250 ± 0.001) g. When the shaking time was increased from 0 to 60 min, the extent of removal was increased from 70.80 % to 98.60 % and from 88.78 % to 99.65 % for BG and RG, respectively. Functional groups present in the raw biosorbent provides sufficient condition for biosorption to be more effective leading to more than 90% removal even for short time periods of less than 10 min. Based on the observed variation of the extent of removal for both biosorbent types, the optimum shaking time was selected to be 20 min beyond which the extent of removal remained unchanged.

Settling time

Another important parameter in adsorption processes is the establishment of the settling time required for adsorption equilibrium to be reached. Therefore, the effect of settling time was determined using previously determined optimum biosorbent dosage of (0.250 ± 0.001) g and optimum shaking time of 20 min while other parameters such as initial MB concentration and initial pH of MB solution were kept constant. Figure 5(c) illustrates that the extent of removal of MB by both BG and RG for varying settling time periods from 5 min to 60 min is not significantly changed. Although settling time does not affect the removal, 20 min was selected as the optimum settling time to assure the establishment of equilibrium. Similar observations have been reported for cationic dyes in biosorption investigation [26].

Although functional groups present in the raw biosorbent (RG) provides sufficient condition for biosorption to be more effective, a larger number of pores present in the BG provides the condition for stronger adsorption of MB. Consequently, both RG and BG are capable of adsorbing MB on their surfaces through different modes leading to more than 90% removal at equilibrium under the conditions employed. Initial lower extent of removal of MB by BG can be attributes to the lack of functional groups for trapping adsorbate molecules.

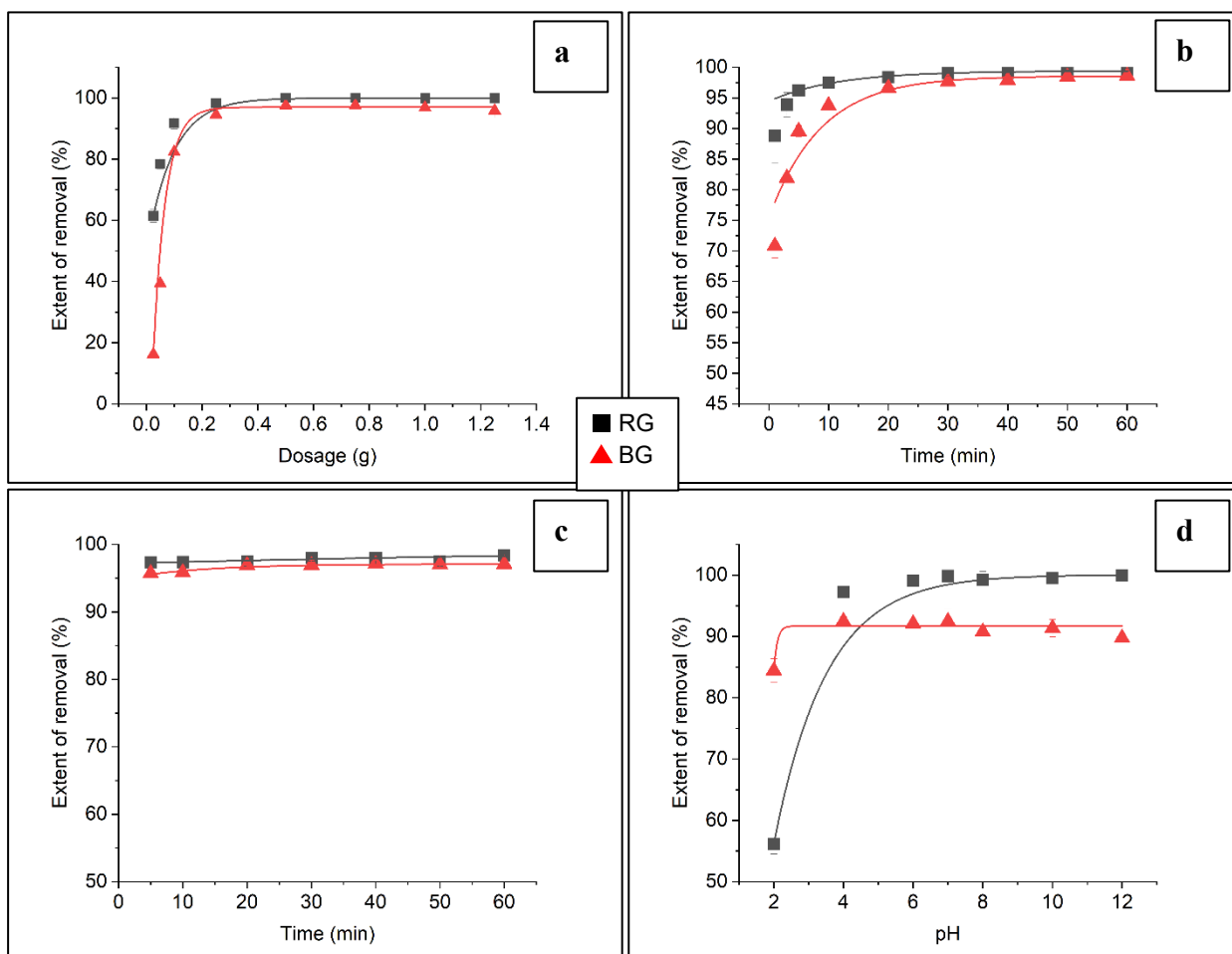


Figure 5: Variation of the extent of removal of MB by RG and BG with experimental parameters. (a) mass of biosorbent (b) shaking time (c) settling time and (d) solution pH.

Solution pH

Solution pH could be the most essential and critical parameter that significantly impact the adsorption process because it affects the chemistry of the adsorbate – adsorbent system due to various processes, such as protonation, ionization and precipitation. As the pH of the solution affects the surface nature of the adsorbent, it could alter adsorption characteristics as well. Although a quantitative relationship between the extent of removal of an adsorbate and the solution pH is not easily formulated, experimental observation of the extent of

removal of the adsorbate within a broad pH range makes it possible to determine an optimum value giving due consideration to the chemistry of the system.

The effect of solution pH on the adsorption of MB from its aqueous solution by RG and BG investigated within the pH range from 2.0 to 12.0, shown in Figure 5(d), clearly indicates that solution pH plays an important role in the removal of MB, where at low pH levels, adsorption was very low for both biosorbents. When the pH increases from a low value of 2.0, a significant increase in the extent of removal of MB has resulted in; from 58.0% to 97.4% by RG and from 84.7% to 96.8% by BC. After pH 4.0 and 5.0, the extent of removal of MB is not much affected from the pH for RG and BG respectively, which leads to consider that the solution pH of 5.6, ambient value of MB solution, can be taken the optimum. Many biosorption studies of MB have been performed at its ambient pH [27].

In acidic solutions, H_3O^+ ions contained in the MB solution promote the protonation of the surface functional groups of BG as well as RG, increasing its positive surface charge [4]. Therefore, the lower adsorption rate was observed due to the competitive interaction between the MB molecules and the H_3O^+ ions for the same adsorption sites, together with creating a repulsion between the positively charged surface of and MB molecules [25]. On the other hand, at higher pH, increased OH^- concentration promotes the deprotonation of the surface of biosorbent material resulting in an increased negative surface charge. As a result, the adsorption of positively charged MB molecules is favored, leading to higher removal percentages [1].

Table 2 summarizes the values of optimum experimental parameters for the most efficient removal of MB. Such conditions could be used in subsequent experiments.

Table 2: Optimized parameters for MB removal by both BC and RG.

Parameter	Magnitude of optimized parameter
Biosorbent dosage	0.250 g
Shaking time	20 min
Settling time	20 min
pH	5.60 (ambient)

Adsorption kinetics

Kinetics studies are important to determine the rate of the adsorption process and to understand the mechanism of adsorption and also to extend laboratory findings to large-scale industrial applications. It can be argued that during early times of MB – biosorbent interaction, well before the equilibrium is established, the activity of adsorbate molecules is assumed to be relatively large, and hence pseudo-order condition can be applied on the adsorbate. If there is any concentration dependent rate of adsorption, it should therefore be due to activity changes of the adsorbent surface.

The rate equation of the pseudo-first-order kinetics model is expressed as,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where q_e (mmol g⁻¹) is the equilibrium adsorption capacity, q_t (mmol g⁻¹) is the adsorption capacity at time t (min) and k_1 is the rate constant of pseudo-first-order adsorption (s⁻¹ or min⁻¹). The values of q_e and k_1 can be determined by the intercept and the slope of the plot of $\log(q_e - q_t)$ vs. t , respectively [11,28].

The rate equation of the pseudo-second-order kinetics model is expressed as,

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

where k_2 (g mmol⁻¹ min⁻¹) is the rate constant of pseudo-second-order adsorption [11,28]. Kinetics plots and their regression coefficients obtained for MB adsorption within the early stage of up to 5 min are shown in Figure 6 and Table 3. Accordingly, adsorption kinetics data, having high values of regression coefficient, better fit the pseudo second-order model. Therefore, the rate constants obtained from this model are more reliable for further interpretation (Table 3).

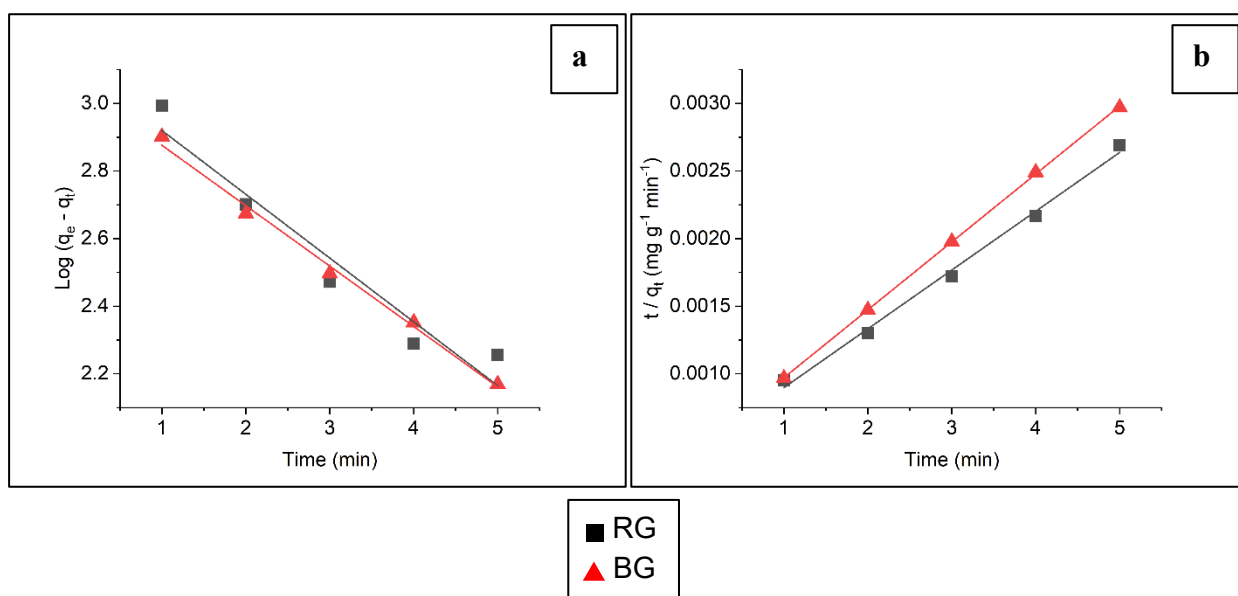


Figure 6: Fitting adsorption data of MB on RG and BG to kinetics models
(a) Pseudo first-order model (b) Pseudo second-order model. (concentration of MB: 10 mg L⁻¹, mass of RG: 0.250 g, mas of BG: 0.250 g)

Table 3: Kinetics parameters determined for the adsorption of MB onto BG and RG.

Kinetics model	Parameter	RG	BG
Pseudo-first-order	k_1 (min ⁻¹)	4.35×10^{-1}	4.12×10^{-1}
	R^2	0.9369	0.9942
Pseudo-second-order	k_2 (g mg ⁻¹ min ⁻¹)	4.08×10^{-1}	5.39×10^{-1}
	R^2	0.9948	0.9998

As the time period used for kinetics analysis is up to 5 min, it can be assumed that the rate law is controlled by the activity of the adsorbent. It can also be assumed that MB molecules

are adsorbed through chemisorption on the surface of biosorbents and that two distinct types of attractions are possible to govern the kinetics [29,30]. This behavior is valid for both RG and BG biosorbents.

Adsorption isotherms

Isotherm models are essential to explain adsorbent-adsorbate interactions, adsorptive capacity of the adsorbent, and the mechanism of the adsorption process [31]. In order to further understand the interaction of MB dye with BG and RG, adsorption isotherm studies were carried out under previously determined optimum conditions with initial MB dye concentrations ranging from 10.0 to 1000.0 mg L⁻¹. Various isotherm models can be employed to fit the experimental data and evaluate the applicability of these isotherm models for MB dye adsorption [12]. This study mainly focused on the Langmuir and the Freundlich isotherm models to predict the type of adsorption [32,33]. Their equations, both linear and non-linear forms are shown in Table 4, where C_e is the equilibrium concentration of the MB dye, q_e is the amount of MB dye adsorbed (mg g⁻¹), q_{max} is the maximum adsorption capacity, K_L (L mg⁻¹) is the Langmuir constant, K_F (L mg⁻¹) is the Freundlich constant, and n is the Freundlich parameter, which is related to the adsorption intensity of adsorbent [10].

Table 4: Linearized forms and parameters selected for the investigation of different isotherm models.

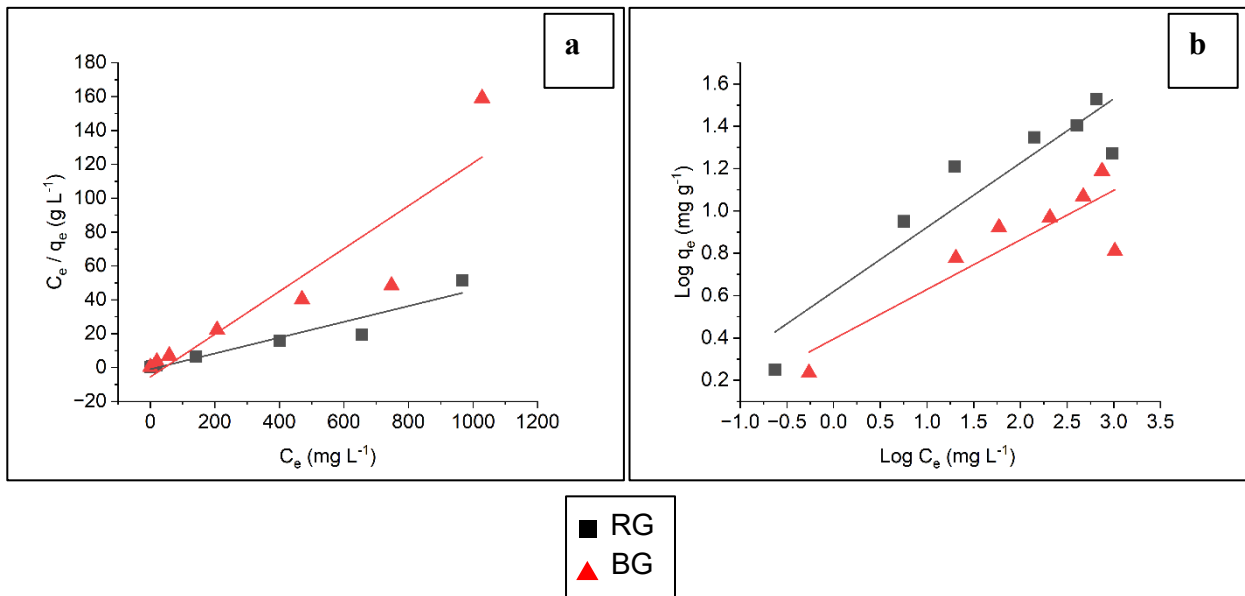
Isotherm model	Non-linear	Linear	Plot
Langmuir	$q_e = \frac{K_L q_{max} C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	$\frac{C_e}{q_e}$ vs C_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \frac{1}{n} \log C_e + \log K_F$	$\log q_e$ vs $\log C_e$

The Langmuir isotherm model is one of the most popular models used in many adsorption systems. This model assumes a constant adsorption energy and describes monolayer adsorption on a uniform surface. It is characterized by strong interactions between the adsorbate and the surface, resulting in a mono-layer adsorption of adsorbate molecules adhering to the surface, without the formation of multi-layer adsorption. The Freundlich isotherm model is used to describe the adsorption of a heterogeneous system, and the adsorption capacity is dependent on the concentration of molecules at equilibrium [35, 36].

It is predicted that RG and BG being fibrous in nature, lead to monolayer adsorption fulfilling the Langmuir adsorption isotherm. This is convinced by observing a good fit of adsorption data on the linearized Langmuir model with higher regression coefficients (R^2) when compared to the R^2 values determined for the Freundlich isotherm model (Table 5).

Table 5: Parameters of isotherm models for adsorption of MB with BG and RG at 298 K.

Model	Parameter	RG	BG
Langmuir	q_{max} (mg g ⁻¹)	21.44	7.91
	K_L (L mg ⁻¹)	2.17×10^{-3}	2.85×10^{-3}
	R^2	0.9168	0.8311
Freundlich	K_F (mg g ⁻¹)	4.15	2.48
	n	3.29	4.27
	R^2	0.8608	0.7710

**Figure 7:** Fitting adsorption data of MB by RG and BG to isotherm models
(a) Langmuir isotherm model (b) Freundlich isotherm model.

Adsorption mechanism

The adsorption of MB with RG or BG is subjected to a combination of electrostatic interactions, ion exchange and physical adsorption behavior [35]. According to the results summarized in Tables 3 and 5, although the rate constant of adsorption of MB on BG is higher than that on RG, the adsorption capacity of MB on RG is higher than that on BG. Higher rate constant of BG reflects fast adsorption process with MB, which can be attributed to the presence of more active pore sites in BG. As many sites of BG are expected to be available on the outer layer, MB molecules are attached to these pores quickly to establish

equilibrium [37]. On the other hand, the higher adsorption capacity of RG reflects the total number of MB molecules that can be adsorbed at equilibrium. RG contains more functional groups available in lignin, cellulose and hemicellulose, promoting the interaction with MB molecules. During the pyrolysis process, many of these function groups are lost contributing to the decrease in the adsorption capacity. Figure 8 shows different types of interactions, such as electrostatic interactions, hydrogen bonding and π - π transitions, with BG. As the MB molecule has approximate dimensions of $1.7 \text{ nm} \times 0.76 \text{ nm} \times 0.33 \text{ nm}$, and as the hydrated radii of main group elements present such as K^+ , Mg^{2+} and Ca^{2+} are larger than or equal to 0.33 nm , it is possible to have ion-exchange to limited extent through sideways of MB molecules [38-41]. Additionally, transfer of MB molecules to mesopores and micropores of the biosorbent is also possible.

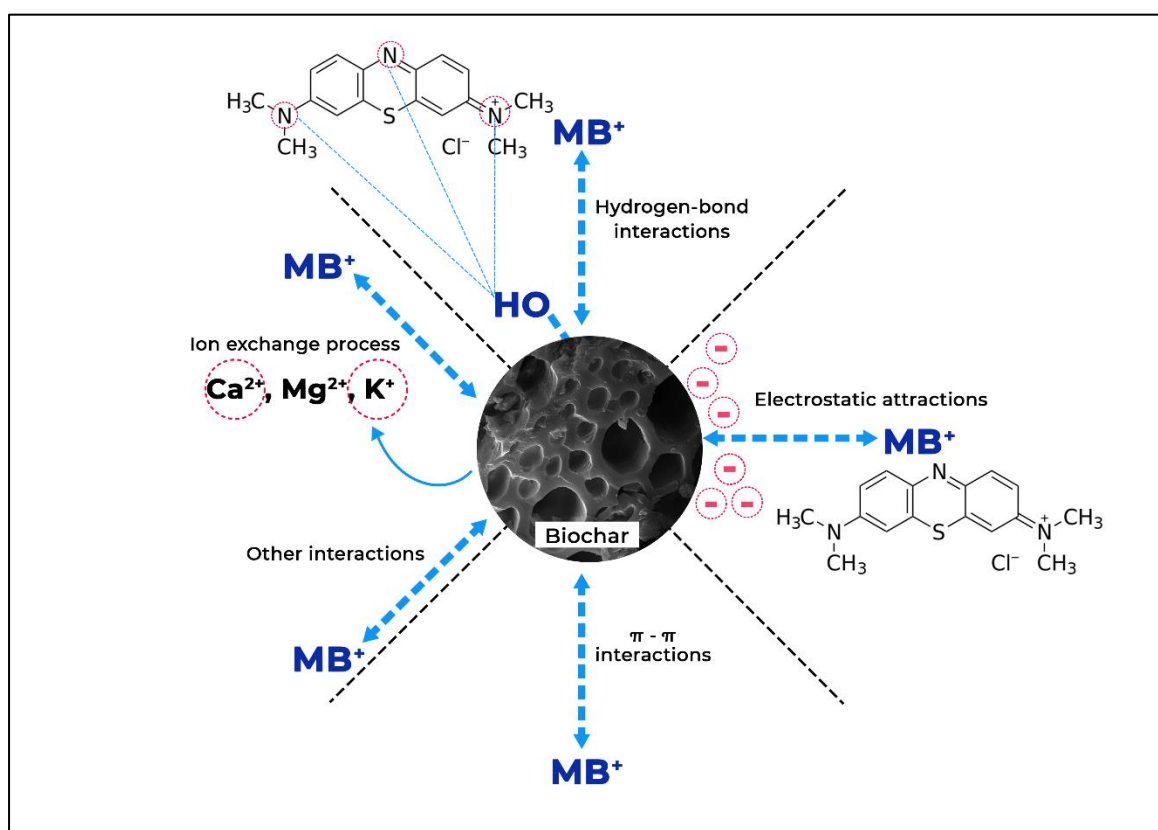


Figure 8: Possible interactions of the MB–BG system.

Conclusion

The present study demonstrates the potential of both RG and BG as effective adsorbents for the removal of MB from aqueous solution. Due to the wide availability of guinea grass, it can easily be collected and used for the remediation of wastewater contaminated with toxic dyes. The adsorption isotherm for the interaction of MB with both biosorbent types fit with the Langmuir isotherm model having high R^2 values, indicating that MB dye molecules are preferentially adsorbed as a monolayer at ambient temperature, possibly due to their fibrous nature. The attractive adsorption capacities of both BG (7.91 mg g^{-1}) and RG (21.44 mg g^{-1}) according to the Langmuir isotherm model provide evidence for their potential application

in real-time wastewater treatment, preferably, after further optimization steps under dynamic conditions. In addition, adsorption of MB on both BG and RG follow pseudo-second order kinetics with high correlation coefficients. Although BG shows lower adsorption capacity, it is recommended for long-term applications due to higher stability; on the other hand, RG is recommended for short-term, suit for more efficient removal of MB. Overall, the emerging results of this study conclusively demonstrate that guinea grass is an eco-friendly, low-cost and sustainable biosorbent material for wastewater treatment. Large-scale practical applications would require detailed studies under dynamic conditions followed by prototype experiments.

Abbreviations

RG – Raw leaves of guinea grass

BG – Biochar of guinea grass

MB – Methylene blue

Acknowledgments

Special appreciation for the immense support provided by the Department of Chemistry, Faculty of Science, University of Peradeniya, Sri Lanka.

Data Availability Statement

The data that supports this study will be shared upon reasonable request to the corresponding author; Namal Priyantha. (namal.priyantha@sci.pdn.ac.lk).

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Declaration of Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Author Contributions

Author N. Priyantha contributed to the conceptualization of the study, funding acquisition, investigation and supervision. Data curation, data analysis, and writing the original draft of the manuscript were done by M.A.O.Y. Weeratunge M.D.N. Dinusha, R.M.M.K. Karunathilaka. Both authors contributed to reviewing and editing of the manuscript.

Consent to publish

Not applicable.

Consent to participate

Not applicable. This research did not involve any human or animal subjects.

Ethics declaration

Not applicable.

References

- [1] Chieng, H. I., Lim, L. B. L., & Priyantha, N. (2014). Enhancing adsorption capacity of toxic malachite green dye through chemically modified breadnut peel: equilibrium, thermodynamics, kinetics and regeneration studies. *Environmental Technology*, 36(1), 86–97. <https://doi.org/10.1080/09593330.2014.938124>
- [2] Hamad, H. N., & Idrus, S. (2022). Recent developments in the application of bio-waste-derived adsorbents for the removal of methylene blue from wastewater: A Review. *Polymers*, 14(4), 783–822. <https://doi.org/10.3390/polym14040783>
- [3] Rajendran, J., Panneerselvam, A., Ramasamy, S., & Palanisamy, P. (2024). Methylene blue and methyl orange removal from wastewater by magnetic adsorbent based on activated carbon synthesised from watermelon shell. *Desalination and Water Treatment*, 317, 100040. <https://doi.org/10.1016/j.dwt.2024.100040>
- [4] Filho, S., Silva, V. C., Silva, P. F., Cartaxo, J. M., Rodrigues, A. M., Menezes, R. R., & Neves, G. A. (2023). Isothermal and kinetic studies for the removal of malachite green and congo red dyes using wastes from mining and processing perlite in different particle sizes as sustainable adsorbents. *Sustainability*, 15(21), 15562–15581. <https://doi.org/10.3390/su152115562>
- [5] Priyantha, N., Lim, L. B. L., D. T. B. Tennakoon, D. T. B., Liaw, E. T. Z., , Chieng, H. I., & Liyandeniya, A. B. (2018). Biosorption of cationic dyes on breadfruit (*Artocarpus altilis*) peel and core. *Applied Water Science*, 8(1), 37–48. <https://doi.org/10.1007/s13201-018-0648-3>
- [6] Ng, S. N. M., Idrus, S., Ahsan, A., Marzuki, T. N. T. M., & Mahat, S. B. (2021). Treatment of wastewater from a food and beverage industry using conventional wastewater treatment integrated with membrane bioreactor system: a pilot-scale case study. *Membranes*, 11(6), 456–473. <https://doi.org/10.3390/membranes11060456>
- [7] Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials*, 177(1-3), 70–80. <https://doi.org/10.1016/j.jhazmat.2009.12.047>
- [8] Ghaedi, M., Nasab, A. G., Khodadoust, S., Rajabi, M., & Azizian, S. (2014). Application of activated carbon as adsorbents for efficient removal of methylene blue: Kinetics and equilibrium study. *Journal of Industrial and Engineering Chemistry*, 20(4), 2317–2324. <https://doi.org/10.1016/j.jiec.2013.10.007>
- [9] Lim, L. B. L., Priyantha, N., Chan, C. M., Matassan, D., Chieng, H. I., & Kooh, M. R. K. (2015). Investigation of the sorption characteristics of water lettuce (WL) as a potential low-cost biosorbent for the removal of methyl violet 2B. *Desalination and Water Treatment*, 57(18), 8319–8329. <https://doi.org/10.1080/19443994.2015.1017740>
- [10] Zaidi, N. A. H. M., Lim, L. B. L., Priyantha, N., & Usman, A. (2018). *Artocarpus odoratissimus* leaves as an eco-friendly adsorbent for the removal of toxic

Rhodamine B dye in aqueous solution: Equilibrium isotherm, kinetics, thermodynamics and regeneration studies. *Arabian Journal for Science and Engineering*, 43(11), 6011–6020. <https://doi.org/10.1007/s13369-018-3228-9>

- [11] Lu, Y. C., Priyantha, N., Lim, L. B. L., & Suklueng, M. (2020). Toxic yellow cow dung powder (Auramine O dye) removal via *Ipomoea aquatica* waste. *Desalination and Water Treatment*, 181, 422–435. <https://doi.org/10.5004/dwt.2020.25118>
- [12] Dawood, S., Sen, T. K., & Phan, C. (2016). Adsorption removal of methylene blue (MB) dye from aqueous solution by bio-char prepared from *Eucalyptus sheathiana* bark: kinetic, equilibrium, mechanism, thermodynamic and process design. *Desalination and Water Treatment*, 57(59), 28964–28980. <https://doi.org/10.1080/19443994.2016.1188732>
- [13] Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, 99, 19–33. <https://doi.org/10.1016/j.chemosphere.2013.10.071>
- [14] Oladoye, P. O., Ajiboye, T. O., Omotola, E. O., & Oyewola, O. J. (2022). Methylene blue dye: Toxicity and potential elimination technology from wastewater. *Results in Engineering*, 16, 100678. <https://doi.org/10.1016/j.rineng.2022.100678>
- [15] Fito, J., Abrham, S., & Angassa, K. (2020). Adsorption of methylene blue from textile industrial wastewater onto activated carbon of *Parthenium hysterophorus*. *International Journal of Environmental Research*, (14)5, 501–511 <https://doi.org/10.1007/s41742-020-00273-2>
- [16] Silva, F., Nascimento, L., Brito, M., da Silva, K., Paschoal, W., & Fujiyama, R. (2019). Biosorption of methylene blue dye using natural biosorbents made from weeds. *Materials*, 12(15), 2486–2502. <https://doi.org/10.3390/ma12152486>
- [17] Parvin, S., Rahman, Md. W., Saha, I., Alam, Md. J., & Khan, Md. M. R. (2019). Coconut tree bark as a potential low-cost adsorbent for the removal of methylene blue from wastewater. *Desalination and Water Treatment*, 146, 385–392. <https://doi.org/10.5004/dwt.2019.23598>
- [18] Dharmarathna, S. P., & Priyantha, N. (2024). Investigation of boundary layer effect of intra-particle diffusion on methylene blue adsorption on activated carbon. *Energy Nexus*, 14, 100294. <https://doi.org/10.1016/j.nexus.2024.100294>
- [19] Mohammad, N., & Atassi, Y. (2020). Adsorption of methylene blue onto electrospun nanofibrous membranes of polylactic acid and polyacrylonitrile coated with chloride doped polyaniline. *Scientific Reports*, 10(1). <https://doi.org/10.1038/s41598-020-69825-y>
- [20] Melese, H., & Tsade, H. (2024). Cellulose based adsorbent for cationic methylene blue dye removal. *Discover Applied Sciences*, 6(2), 46–61. <https://doi.org/10.1007/s42452-024-05653-3>

- [21] Karunarathna, K. H. T., Chandana, E. P. S., & Rajawatta, K. M. W. (2022). Preliminary Study of Guinea Grass (*Megathyrsus maximus*) Biochar as a Phosphorus Source. *Proceedings: 19th Academic Sessions – 2022, University of Ruhuna, Matara, Sri Lanka*, p10.
- [22] Pandey, D., Daverey, A., Dutta, K., Yata, V. K., & Arunachalam, K. (2022). Valorization of waste pine needle biomass into biosorbents for the removal of methylene blue dye from water: Kinetics, equilibrium and thermodynamics study. *Environmental Technology & Innovation*, 25, 102200. <https://doi.org/10.1016/j.eti.2021.102200>
- [23] Khan, I., Saeed, K., Zekker, I., Zhang, B., Hendi, A. H., Ahmad, A., Ahmad, S., Zada, N., Ahmad, H., Shah, L. A., Shah, T., & Khan, I. (2022). Review on Methylene Blue: Its properties, uses, toxicity and photodegradation. *Water*, 14(2), 242. <https://doi.org/10.3390/w14020242>
- [24] Khalid, F. E., Zakaria, N. N., Azmi, A. A., Shaharuddin, N. A., Sabri, S., Khalil, K. A., Gomez-Fuentes, C., Zulkharnain, A., Lim, S., & Ahmad, S. A. (2023). Guinea grass (*Megathyrsus maximus*) fibres as sorbent in diesel bioremediation. *Sustainability*, 15(5), 3904–3921. <https://doi.org/10.3390/su15053904>
- [25] Balogun, A. O., Adeleke, A. A., Ikubanni, P. P., Adegoke, S. O., Alayat, A. M., & McDonald, A. G. (2021). Study on combustion characteristics and thermodynamic parameters of thermal degradation of guinea grass (*Megathyrsus maximus*) in N₂-pyrolytic and oxidative atmospheres. *Sustainability*, 14(1), 112–133. <https://doi.org/10.3390/su14010112>
- [26] Corda, N. C., & Kini, M. S. (2018b). A Review on Adsorption of Cationic Dyes using Activated Carbon. *MATEC Web of Conferences*, 144, 02022. <https://doi.org/10.1051/mateconf/201814402022>
- [27] Farch, S., Yahoum, M. M., Toumi, S., Tahraoui, H., Lefnaoui, S., Kebir, M., Zamouche, M., Amrane, A., Zhang, J., Hadadi, A., & Mouni, L. (2023). Application of walnut shell biowaste as an inexpensive adsorbent for methylene blue dye: Isotherms, kinetics, thermodynamics, and modeling. *Separations*, 10(1), 60–79. <https://doi.org/10.3390/separations10010060>
- [28] Rathnayaka, R. M. H., Priyantha, N., & Gunathilake, W. S. S. (2024). Removal of trivalent and hexavalent chromium from aqueous solution using fiber of *Agave americana* plant and its modified forms. *Colloids and Surfaces C: Environmental Aspects*, 2, 100029. <https://doi.org/10.1016/j.colsuc.2024.100029>
- [29] Peng, X., Huang, D., Odoom-Wubah, T., Fu, D., Huang, J., & Qin, Q. (2014). Adsorption of anionic and cationic dyes on ferromagnetic ordered mesoporous carbon from aqueous solution: Equilibrium, thermodynamic and kinetics. *Journal of Colloid and Interface Science*, 430, 272–282. <https://doi.org/10.1016/j.jcis.2014.05.035>

- [30] Lim, L. B. L., Priyantha, N., Kamaludin, I. F., Zaidi, N. A. H. M., & Samaraweera, A. P. G. M. V. (2021). Adsorption of crystal violet dye with cellulose derived from bitter gourd waste. *Desalination and Water Treatment*, 217, 431–441. <https://doi.org/10.5004/dwt.2021.26917>
- [31] Xing, X., Alharbi, N. S., Ren, X., & Chen, C. (2022). A comprehensive review on emerging natural and tailored materials for chromium-contaminated water treatment and environmental remediation. *Journal of Environmental Chemical Engineering*, 10(2), 107325. <https://doi.org/10.1016/j.jece.2022.107325>
- [32] Chieng, H.I., Priyantha, N., & Linda, L. B. L. (2015). Effective adsorption of toxic brilliant green from aqueous solution using peat of Brunei Darussalam: isotherms, thermodynamics, kinetics and regeneration studies. *RSC Advances*, 5(44), 34603–34615. <https://doi.org/10.1039/c5ra01572c>
- [33] Wu, W., Li, P., Wang, M., Liu, H., Zhao, X., Wu, C., & Ren, J. (2023). Comprehensive evaluation of polyaniline-doped lignosulfonate in adsorbing dye and heavy metal ions. *International Journal of Molecular Sciences*, 25(1), 133–149. <https://doi.org/10.3390/ijms25010133>
- [34] Buhani, Istikomah, Suharso, Sumadi, Sutarto, Alghamdi, H. M., & Elwakeel, K. Z. (2023). Cationic surfactant-modified *Tetraselmis* sp. for the removal of organic dyes from aqueous solution. *Molecules*, 28(23), 7839–7855. <https://doi.org/10.3390/molecules28237839>
- [35] Fan, S., Wang, Y., Wang, Z., Tang, J., Tang, J., & Li, X. (2017). Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: Adsorption kinetics, equilibrium, thermodynamics and mechanism. *Journal of Environmental Chemical Engineering*, 5(1), 601–611. <https://doi.org/10.1016/j.jece.2016.12.019>
- [36] Chieng, H. I., Zehra, T., Lim, L. B. L., Priyantha, N., & Tennakoon, D. T. B. (2014). Sorption characteristics of peat of Brunei Darussalam IV: equilibrium, thermodynamics and kinetics of adsorption of methylene blue and malachite green dyes from aqueous solution. *Environmental Earth Sciences*, 72(7), 2263–2277. <https://doi.org/10.1007/s12665-014-3135-7>
- [37] Ariannezhad, M., Habibi, D., Heydari, S., & Khorramabadi, V. (2021). The nano-magnetite-loaded 2-mercaptobenzoxazole as an adsorbent for the selective removal of the Pb^{2+} , Ni^{2+} and Cd^{2+} ions from aqueous solutions. *Korean Journal of Chemical Engineering*, 38(7), 1510–1521. <https://doi.org/10.1007/s11814-021-0792-6>
- [38] Ozer, D., Dursun, G., & Ozer, A. (2007). Methylene blue adsorption from aqueous solution by dehydrated peanut hull. *Journal of Hazardous Materials*, 144(1-2), 171–179. <https://doi.org/10.1016/j.jhazmat.2006.09.092>
- [39] Jia, Z., & Wang, Y. (2015). Covalently crosslinked graphene oxide membranes by esterification reactions for ions separation. *Journal of Materials Chemistry A*, 3(8), 4405–4412. <https://doi.org/10.1039/c4ta06193d>

- [40] Arias, M., Lopez, E., Nunez, A., Rubinos, D., Soto, B., Barral, M. T., & Diaz-Fierros, F. (1999). Adsorption of methylene blue by red mud, an oxide-rich byproduct of bauxite refining. *Effect of Mineral-Organic-Microorganism Interactions on Soil and Freshwater Environments*, 361–365. https://doi.org/10.1007/978-1-4615-4683-2_39
- [41] Moldenhauer, H., Diaz-Franulic, I., Gonzalez-Nilo, F., & Naranjo, D. (2016). Effective pore size and radius of capture for K^+ ions in K^+ channels. *Scientific Reports*, 6(1). <https://doi.org/10.1038/srep19893>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Highlights6.docx](#)
- [Graphicalabstract1.docx](#)