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ADSORPTION STUDIES OF BASIC DYES ONTO TEAK (*TECTONA GRANDIS*) LEAF POWDER

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Abstract: In this study, the adsorption potential of Teak (Tectona grandis) leaf powder (TLP) to remove Methylene blue (MB) and Malachite Green (MG) dye molecules from aqueous solution was investigated. Batch experiments were conducted to evaluate the influence of operational parameters such as, pH (2−9), adsorbent dosage (1−7 g/L), contact time (15−150 minutes) and initial dye concentration (20−120 mg/L) at stirring speed of 150 rpm for the adsorption of MB and MG on TLP. Maximum removal efficiency of 98.4% and 95.1% was achieved for MB and MG dye, respectively. The experimental equilibrium data were analysed using Langmuir, Freundlich and Temkin isotherm models and it was found that, it fitted well to the Freundlich isotherm model. The surface structure and morphology of the adsorbent was characterized using scanning electron microscopy (SEM) and the presence of functional groups and its interaction with the dye molecules were analysed using Fourier transform infrared spectroscopy (FTIR). Based on the investigation, it has been demonstrated that the teak leaf powder has good potential for effective adsorption of methylene blue and malachite green dye.

Keywords: Adsorption, Tectona grandis, Methylene blue, Malachite green

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INTRODUCTION

Discharge of dyeing effluents into natural water bodies is of rising concern due to its adverse effects on the aquatic lives (Franca *et al.*, 2009). The production and usage of dye stuffs has increased in many folds in the past few decades. A wide range of industries, from textiles, leather, and paper to plastics use different dyes to colour their products and thus release substantial amounts of coloured wastewater, which is of both toxicological and aesthetical concern (Uddin *et al.*, 2009; Ahmad *et al.,* 2011). In textile industries, to manufacture one kg of finished product, an average of 150-200 litres of water are consumed out of which 125 litres is generated as wastewater (Dural *et al.*, 2011; Ponnusami *et al.*, 2010). Thus the daily discharge of coloured wastewater is enormously high in these industries.

Synthetic dyes being non-degradable, its concentration must be reduced to acceptable levels before being discharged into the environment (Chowdhury & Saha, 2012) and hence effective and economic treatment of the wastewater becomes a necessity. Several physicochemical treatment methods including electro-coagulation, flocculation, ion-exchange, adsorption, ultra-filtration, reverse osmosis had been employed for the treatment of dyeing effluents (Argun *et al.*, 2013). Most of these techniques lack the advantages of being economic and environment-friendly (Ahmad *et al.,* 2012). However, adsorption technique has proved to be an effective one and serves to be an alternative treatment technique for the removal of dye in wastewater streams (Nasuha *et al.*, 2010).

Adsorption using activated carbon has long been in practice for the removal of pollutants in wastewater, but its higher production cost and regeneration difficulties had made way to research on the use of abundantly available natural bio-materials as adsorbents (Kyzasa *et al.*, 2012). The potential of several low-cost agricultural waste materials have been studied for the removal of MB and MG dye in effluents. Few of them include, banana stalk (Hameed *et al.*, 2008), jackfruit peel waste (Hameed, 2009), oil palm trunk fiber (Hameed & El-Khaiary, 2008a), potato plant waste (Gupta *et al.*, 2011), coconut carp (Vieira *et al.*, 2009), peanut husk (Song *et al.*, 2011), and pineapple leaves powder (Wenga *et al.*, 2009).

Methylene blue (MB) is most commonly used in dying cotton, wood and stalk. The exposure to high levels of MB causes eye-burns, nausea, profuse sweating and methemoglobinemia (Rafatullah *et al.*, 2011). Malachite green (MG) is extensively used in textile industry for colouring the fabrics. It is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals. MG is also known to be a multi-organ toxin (Hameed & El-Khaiary, 2008b).

In this paper, an attempt to elucidate the potential of teak (*Tectona grandis*) leaf powder for the adsorption of MB and MG has been carried out through batch scale studies. The effect of various parameters such as pH, adsorbent dose, contact time and initial dye concentration on the adsorption of dye was studied. The experimental data was further fitted to different isotherm models viz. Langmuir, Freundlich and Temkin models.

MATERIALS AND METHODS

Preparation of adsorbent

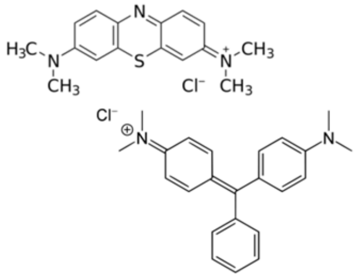
Teak leaves used in this study were collected from the University campus. The leaves were thoroughly washed in tap water several times to remove the dirt. The washed leaves were dried completely in a hot air oven at 80 ˚C for 48 hours. The dried leaves were then finely powdered using a domestic mixer and the powder was again washed with double- distilled water. It was again dried at 80 ˚C to ensure it is moisture free. The Teak leaves powder (TLP) was passed through 90µ sieve and stored in air tight container for further use.

Preparation of stock solution

Stock solution of 1000 mg/L was prepared by dissolving 1 gram of dye in 1 litre of double distilled water. The working solutions were prepared by diluting the stock solution with double distilled water to give the appropriate concentration of the working solutions. AR grade of methylene blue (Chemical formula: $C_{16}H_{18}N_3SCl$; FW: 319.86 g/mol; λ max: 665 nm) and malachite Green (Chemical formula: $C_{23}H_{25}N_2Cl$; FW: 365g/mol; λ max: 620 nm) dye were used without any further purification. The chemical structures of MB (Belala *et al.*, 2011) and MG (Chowdhury *et al.*, 2011) are presented in **Fig. 1a–b**, respectively.

Batch Adsorption Experiment

Adsorption experiments were carried out to investigate the effect of pH, adsorbent dosage, contact time and initial dye concentration on the adsorption of dyes on TLP by varying the parameter under study and keeping other parameters constant. The experiments were performed in 250 mL Erlenmeyer flasks with 100 ml working volume at 30˚C in an incubated orbital shaker at 150 rpm (REMI, CSI 24BL). The dye concentrations in the resulting solution were determined using UV-visible spectrophotometer (Cyberlab, USA) at wavelength of maximum absorption at 665 nm and 620 nm for methylene blue and malachite green respectively. The effect of pH was studied over a pH range of 2 to 10. The pH was adjusted using 0.1N H_2SO_4 and 0.1N NaOH. The effect of adsorbent dosage



(a) (b)

Fig. 1 Chemical structure of (a) MB and (b) MG dye was studied in the range of 1 to 7 g/L and effect of contact time for 15 to 150 minutes. Further, the effect of initial dye concentration was studied in the range of 20 to 120 mg/L.

The percentage removal of dye (%) and the adsorption capacity, q_e (mg/g) of TLP were calculated using **Eq. (1)** and **Eq. (2)**, respectively:

$$\% \, Removal = \frac{(C_i - C_f)}{C_i} * 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_f)\, V}{M} \qquad (2)$$

where, C_i and C_f are the initial and final dye concentration (mg/L) respectively, V is the volume (L) of the dye solution and M is the mass of the adsorbent (g).

Characterization of TLP

The surface morphology of the raw and dye loaded TLP was studied by employing scanning electron microscopy technique (JEOL, Japan). The samples were placed on stubs using double faced adhesive tape and images were captured with different magnifications. The FT-IR spectroscopy (AVATAR 330, Thermo Electron Corp., USA) was employed to determine the functional groups present in the adsorbent. FTIR was done for both raw and dye loaded TLP. The infrared spectrum of the adsorbent was recorded as KBr discs in the range of 4000−400 cm^{-1}.

RESULTS AND DISCUSSION

Characterization of TLP

SEM Analysis

Scanning Electron Microscopy (SEM) studies were performed to characterize the surface structure and morphology of the raw and dye loaded samples of TLP. **Figure 2** shows the SEM images of (a) raw TLP, (b) MB adsorbed TLP and (c) MG adsorbed TLP, respectively. From **Fig. 2a**, it can be noted that raw TLP has a heterogeneous surface with considerable number of pores and cavities that can provide suitable binding sites for the adsorption of dye. The MB and MG dyes

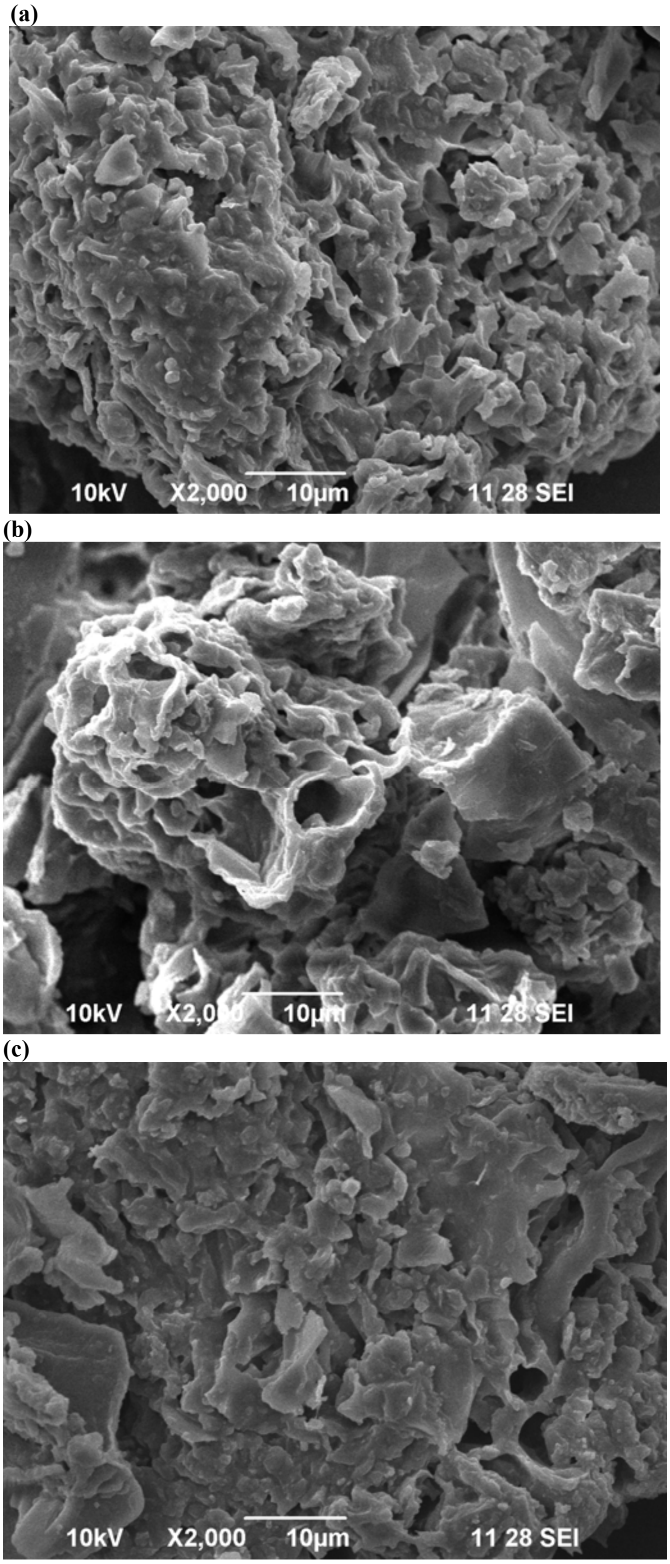


Fig. 2 SEM images of (a) Raw TLP, (b) Methylene blue adsorbed TLP and (c) Malachite green adsorbed TLP adsorbed into the pores of TLP are depicted in **Fig 2b** and **Fig 2c** respectively.

FTIR Analysis

The FTIR spectra of raw, MB and MG dye loaded TLP are presented in **Fig. 3(a)**, **3(b)** and **3(c)**, respectively.

The spectrum of the adsorbent showed a number of absorption peaks which indicated its complex nature. From the **Fig. 3(a)**, the peaks at 3275.13 cm^{-1} and 2924.09 cm^{-1} indicates the presence of –OH group.

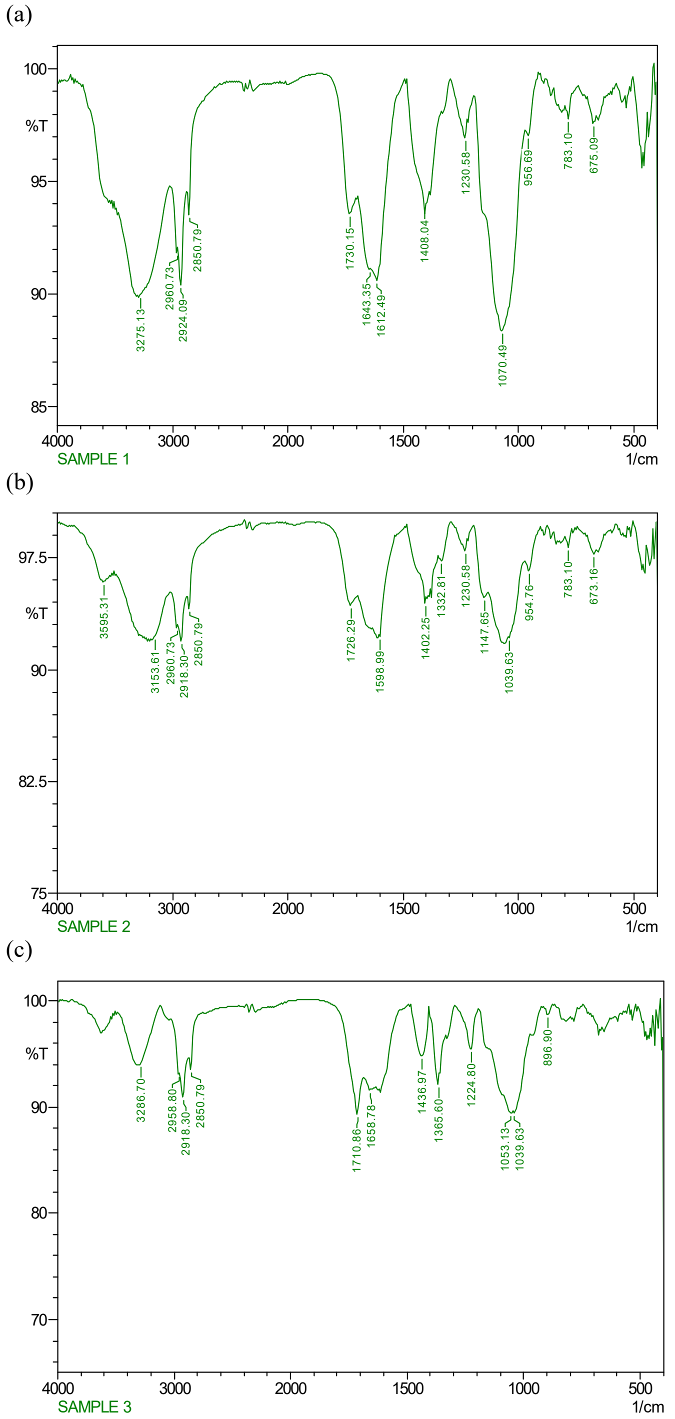


Fig. 3 FTIR spectra of (a) Raw TLP, (b) Methylene blue adsorbed TLP and (c) Malachite green adsorbed TLP.

The peak at 1612.49 cm^{-1} is attributed to –NH stretching and the peak at 1070.49 cm $^{-1}$ is due to the stretching vibrations of the C-O bond. In the **Fig. 3(b)**, the downshift of wave number from 3275.13 cm^{-1} to 3153.61 cm^{-1} shows that –OH group is involved in the adsorption of Methylene blue. The downshift of wave number from1612.49 cm^{-1} to 1598.99 cm^{-1} is attributed to –NH stretching. The down shift of wave number from 1070.49 cm^{-1} to 1039.63 cm^{-1} indicates that C-O is involved in MB adsorption. In the **Fig. 3(c)**, the upshift of wave number from 3275.13 cm^{-1} to 3286.70 cm^{-1} shows that –OH group is involved in the adsorption of Malachite green. The downshift of wave number from 1730.15 cm^{-1} to 1710.86 cm^{-1} indicated the involvement of C = O bond in the adsorption of MG. The down shift of wave number from 1070.49 cm^{-1} to 1053.13 cm^{-1} is due to the stretching vibrations of C-O bond in MG adsorption (Pavia *et al.*, 2004).

Effect of solution pH

The effect of solution pH was studied in the range of 2−10 in 100 ml of 100 mg/L initial dye concentration with adsorbent dose of 0.3 g/100 ml for 90 minutes at 150 rpm and 30°C. It was observed from the study that, the percentage removal of dye increases with increase in pH for both the dyes (**Fig. 4**)

From **Fig. 4**, it can be noted that the percentage dye removal increases with increase in pH till pH 8 for MB and pH 7 for MG and later becomes constant. At low pH, the relatively higher concentration of H^{+} ions will compete effectively with the dye cations for the adsorption sites and hinder their adsorption. However, as the pH increases, the H^{+} ion concentration decreases which paves way for the adsorption of MB and MG increases. Maximum removal was attained at pH 8 and pH 7 for MB and MG respectively and hence was taken as the optimum for all further experiments. Similar results have been found in literature (Hameed, 2009; Chowdhury *et al.*, 2011).

Effect of Contact Time

The effect of contact time was studied in the range of 15-150 minutes in 100 mg/L initial dye concentration with an adsorbent dose of 0.3 g/100 ml for both the dyes at their respective optimum pH. From **Fig 5**, it can be observed that the maximum percentage removal was achieved at 120 minutes and 90 minutes for MB and MG respectively after which the removal almost reached a constant. Hence, an equilibrium time of 120 minutes for MB and 90 minutes for MG were considered for all further studies.

Effect of Adsorbent Dose

The effect of adsorbent dose was studied in the range of 0.1 to 0.7 g/100 ml in 100mg/L initial dye concentration at their respective optimum pH and equilibrium time for both the dyes. It can be noted from **Fig. 6** that, the removal percentage increases with increase in adsorbent dose and reaches a constant at 0.5 for MB and 0.3 for MG after which, the removal almost remained a constant. This could be due to the reason that, with increasing adsorbent dose, more number of adsorption sites becomes available allowing more dye molecules to adhere to it, but as the sites becomes saturated after its maximum adsorption capacity, the percentage removal reaches a constant (Ahmad *et al.*, 2009). Hence, 0.5 and 0.3 g/100 ml are taken as optimum adsorbent dose for MB and MG respectively.

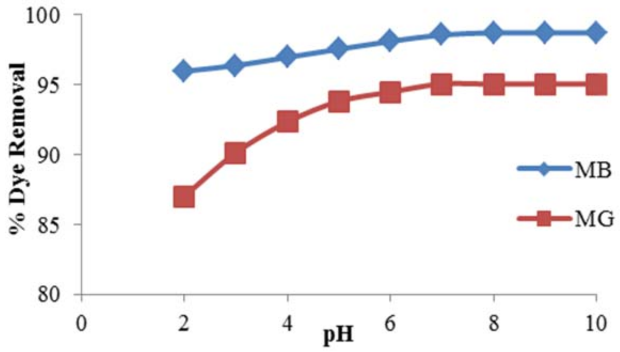


Fig. 4 Effect of pH on the adsorption of MB and MG on TLP.

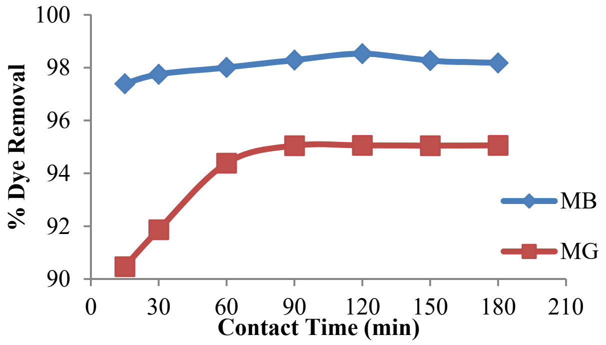


Fig. 5 Effect of contact time on the adsorption of MB and MG on TLP.

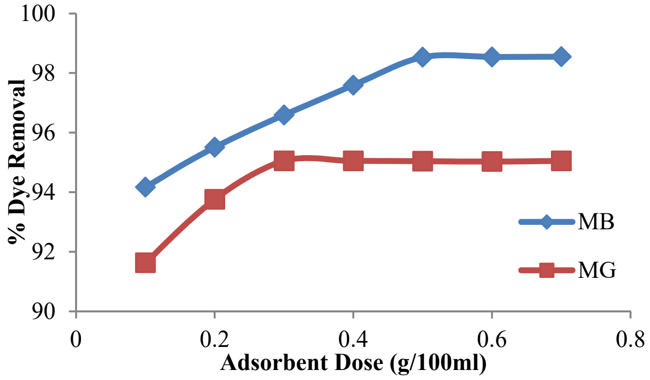


Fig. 6 Effect of adsorbent dose on the adsorption of MB and MG on TLP.

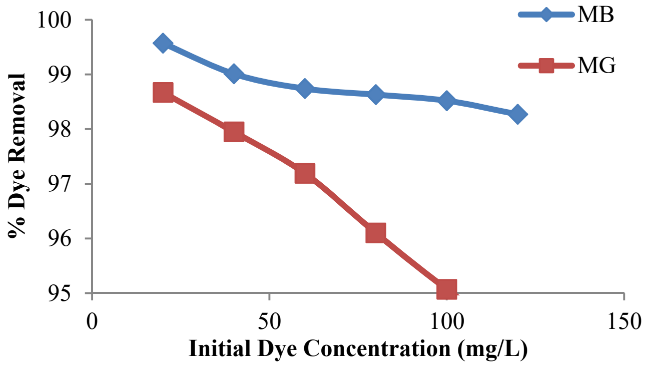


Fig. 7 Effect of initial dye concentration on the adsorption of MB and MG on TLP.

Effect of Initial dye concentration

The effect of initial dye concentration was studied in the range of 25−120 mg/L for both the dyes at their optimum pH, adsorbent dose and equilibrium time. It can be noted from **Fig. 7** that, with increase in initial dye concentration, the percentage removal decreases. This can be due to the fact that, the adsorbent has a limiting number of adsorption sites, which becomes saturated at a particular concentration. Similar trend has been reported in Ling *et al.* (2013).

Adsorption Isotherms

The equilibrium data of MB and MG dye adsorption on TLP was fitted with three isotherm models namely, Langmuir, Freundlich and Temkin. It is important to study the adsorption isotherm for the design of the adsorption system. The conformity between experimental values and model predicted values was expressed by the correlation coefficient (R^2). Models with R^2 value close to unity is considered more appropriate to represent the experimental data.

Langmuir Isotherm

The Langmuir isotherm assumes that sorption occurs at specific homogeneous sites in the adsorbent and the adsorption capacity of the adsorbent is finite. The linear form of Langmuir equation **(Eq. 3)** is represented as (Langmuir, 1918):

$$\frac{Ce}{q_e} = \frac{1}{Kl.Qm} + \frac{Ce}{Qm} \tag{3}$$

where, q_e is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of metal ion in the solution (mg/L), Q_m is the monolayer adsorption capacity (mg/g) and K_l is a constant related to the free energy of adsorption. The plot of of C_e/q_e versus C_e for both MB and MG adsorption are presented in **Fig. 8a–b** respectively. It can be noted from the figure that the R^2 value for MB and MG dye are obtained as 0.8693 and 0.9787, respectively.

Freundlich Isotherm

The Freundlich isotherm is an empirical equation which assumes that, the adsorption process takes place on heterogeneous surface and adsorption capacity is related to the concentration of dye at equilibrium. The linear form of Freundlich equation **(Eq. 4)** is represented as (Hameed, 2011):

$$ln\, q_e = lnK_f + \frac{1}{n} lnC_e \tag{4}$$

where, K_f is a constant which indicates the relative adsorption capacity of the adsorbent (mg/g) and *n* is an empirical parameter that indicates the intensity of

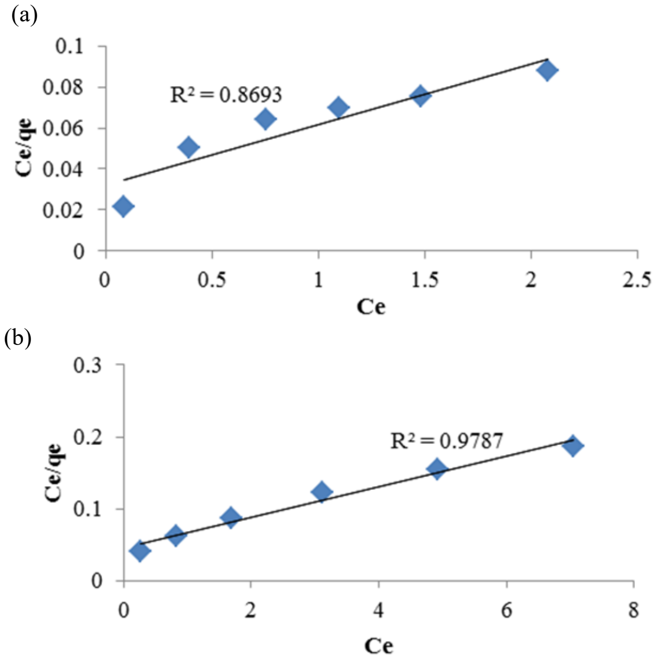


Fig. 8 Langmuir isotherm plots of (a) MB and (b) MG adsorption on TLP.

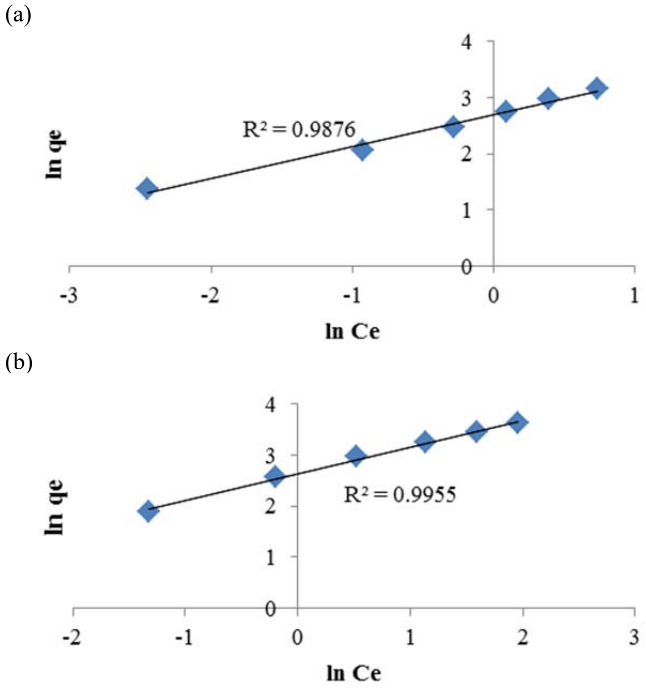


Fig 9. Freundlch isotherm plots of (a) MB and (b) MG adsorption on TLP.

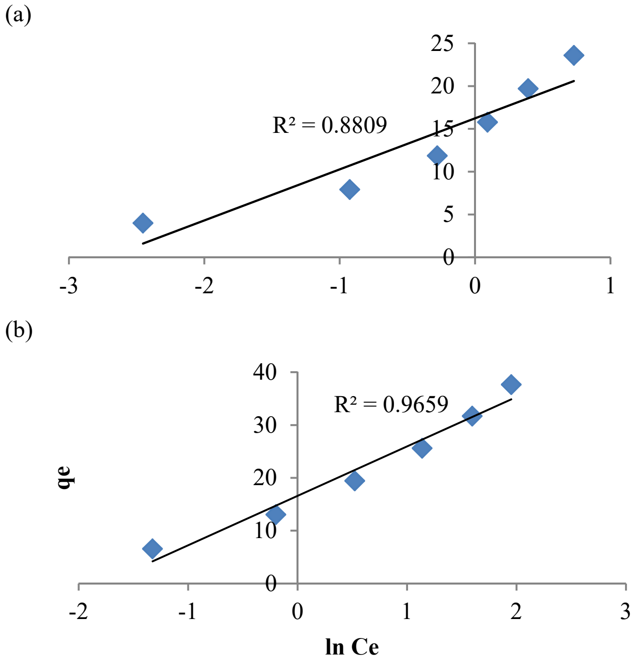


Fig. 10 Temkin isotherm plots of (a) MB and (b) MG adsorption on TLP

adsorption. The plots of ln q_e versus ln C_e for MB and MG adsorption on TLP is presented in **Fig. 9a** and **Fig. 9b** respectively. From the figure, it can be noted that the correlation coefficient value (R^2) obtained for MB and MG are 0.9876 and 0.9955, respectively, which suggests that the adsorption process can be more favourably described by Freundlich isotherm model.

Temkin Isotherm

The equilibrium data was further applied to Temkin isotherm model. The model assumes that a factor explicitly takes into account the adsorbing species-adsorbent interactions. It is generally expressed **(Eq. 5)** as (Nethaji *et al.*, 2010):

$$q_e = B_T lnA_T + B_T \ln C_e \qquad (5)$$

where, B_T is related to the heat of adsorption and A_T corresponds to the maximum binding energy. The plots of q_e versus ln C_e is presented in **Fig. 10**.

It can be seen from figure that R^2 values for the adsorption of MB and MG are 0.8809 and 0.9659, which is comparatively less than the other two models studies and hence the model becomes inapplicable.

CONCLUSION

Teak leaves powder was used as an adsorbent for the removal of Methylene blue and Malachite Green dye from aqueous solution. The characterization studies with SEM and FTIR indicated the presence of sufficient pores and functional groups on TLP, which can aid the adsorption process. Maximum removal efficiency of 98.4% and 95% was achieved for MB and MG dye, respectively. The study reveals that the experimental parameters including, pH, adsorbent dose, contact time and initial dye concentration have a greater influence on the adsorption of dye on TLP. The equilibrium data were analysed using the Langmuir, Freundlich and Temkin isotherm models. The experimental data suitably fits the Freundlich isotherm model which indicates heterogenous surface binding of the dye on TLP. Hence, it can be concluded that, teak leaves powder can be effectively used an adsorbent for the removal of basic dyes in industrial effluents.

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