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Sorption Removal of Methylene Blue Dye from Aqueous Solution by Powdered Yellow Flame Tree Flower (*Peltophorum pterocarpum*)

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Abstract: Present study involves the biosorptive removal study of methylene blue, a blue cationic thiazine dye using *Peltophorum pterocarpum*flowers (PPF). The effect of parameters on dye removal, such as contact time, pH, adsorbent, and adsorbate concentrations, were examined. The results demonstrated that the optimal experimental conditions for the adsorption were attained at pH 9 and contact time at 40 minutes. The equilibrium data of adsorption isotherms were well fitted to the Langmuir model with maximum adsorption efficiency of 71.9434 mg/g. The pseudo-second-order model could well fit the adsorption kinetics. These results demonstrate that the PPF biomaterial has the potential in effective sorptive elimination of MB dye from aqueous solutions.

Keywords: adsorption isotherm; kinetics; methylene blue dye; *Peltophorum pterocarpum* flowers.

1. Introduction

Methylene Blue (MB) is an aromatic heterocyclic cationic dye [1] that comes under the group of polymethine dyes with high water solubility [2-4]. The stable solution of MB at room temperature is used as a redox indicator [5]. The MB with molecular formula $C_{16}H_{18}N_3ClS$ has the chemical structure shown in figure 1. MB has a distinctive deep blue color depending on its chromophoric and auxochrome groups. The N-S conjugated system on the central aromatic heterocycle and the N-containing groups with lone pair of electrons on the benzene ring is the chromophore and auxochrome units, respectively, present in MB [6].

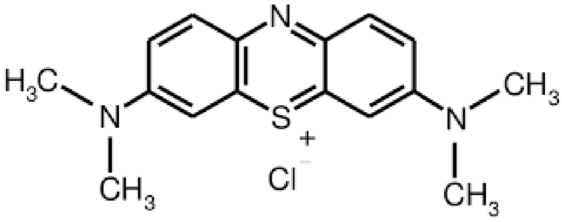

Figure 1. Chemical Structure of Methylene Blue dye.

MB gained interest with various properties and has various prospective applications in the biomedical, textile, clothing, paper, printing, paint, and food industries [7]. The excess use of MB in various industries causes a large amount of its release into water resources, raising concern about serious environmental problems that raise a health threat to human beings [8]. The substantial toxicity of MB is due to its toxic, carcinogenic, and non-biodegradable nature, leading to the environmental deterioration [9-14].

Hence, the management of wastewater that has MB dye before discharging impacts water quality. The most common approaches for dye removal are filtration, oxidation, adsorption, coagulation, Ion exchange, and biological and chemical precipitation [15-17]. However, adsorption is well established and widely used method for its advantages like simplicity of design, high efficiency, economics, and versatility [18]. One of the significant advantages of adsorption is its ability to remove the pollutants without decomposing the complex pollutant ascertaining the recovery of expensive pollutants even in bulk quantity. Many studies have been reported on producing inexpensive and potential adsorbents, and research is going on for deriving alternate adsorbents with an efficient adsorptive capacity [19-22]. Momcilic et al. [23] derived an adsorbent from pinecone for cationic dye removal. Mohammed et al. [24] utilized coconut fronds for the biosorptive removal of methylene blue.

The present study attempts to establish the efficiency of *Peltophorum pterocarpum* flowers (PPF), an abundant and inexpensive biosorbent for the removal of MB dye. PPF was evaluated for absorption performance, ascertaining process parameters such as pH, contact time, biosorbent concentration, and initial dye dosage. PPF flowers were chosen as biosorbent because they contain flavonoids (Kaempferol, quercitin), bergenin, phenolics, saponins, tannins, xanthoproteins, steroids, coumarins, carboxylic acids, and aliphatic alcohols, etc.[25].

2. Materials and Methods

2.1. Materials.

Peltophorum pterocarpum flowers were collected from BVRIT Hyderabad College located in Hyderabad, India. The reagents Methylene Blue, Sodium Chloride, and Hydrochloric acid were purchased from Merck. Double distilled water was utilized to prepare MB dye stock solutions.

2.2. Batch experiments.

The PPF flowers were first washed properly with deionized water to remove dirt and water-soluble impurities. The PPF was dried, ground, and the powder was stored for further use. The experiment was carried out with these PPF without any chemical treatments. The batch experiments were conducted in 200ml bottles where 1-4g of biosorbent and 50 ml containing MB solution of 100-200mg/l. All the reagent bottles were shaken at 300 rpm at RT. The concentration of MB dye at frequent intervals was analyzed by UV-Visible Spectrophotometer at 660nm wavelength. The adsorption efficiency and amount of MB adsorbed by PPF at equilibrium were determined using Eqs. (1) and (2), respectively.

$$\text{Adsorption efficiency (\%)} = \frac{C0-Ce}{Ce} \times 100 \quad (1)$$

$$q_e = \frac{(C0-Ce)V}{m} \quad (2)$$

where C_0 is the initial concentration of MB dye, C_e is the equilibrium concentration of MB dye, respectively. V is the volume of the dye solution used for the experiment, m is the mass of sorbent used, and q_e (mg/g) is the amount of adsorbed MB at equilibrium.

3. Results and Discussion

3.1. Effect of pH.

The interdependence of adsorbent and adsorbate and the nature of a surface charge on the adsorbate affect the adsorption. Hence, the effect of pH on the adsorption was investigated over the range of 4-10(fig 2). The adsorption is less at low pH, ascribed to the repulsion between H^+ ions in the solution and positive surface charge on MB. With an increase in pH, there was a tendency for a good removal of MB owing to the increase in negative charge on the adsorbent that enhances the electrostatic force occurring amid the negative surface charge on the sorbent existing positive charge on MB dye. The MB removal rate became stable at pH 9; hence, the same pH was maintained for subsequent experiments.

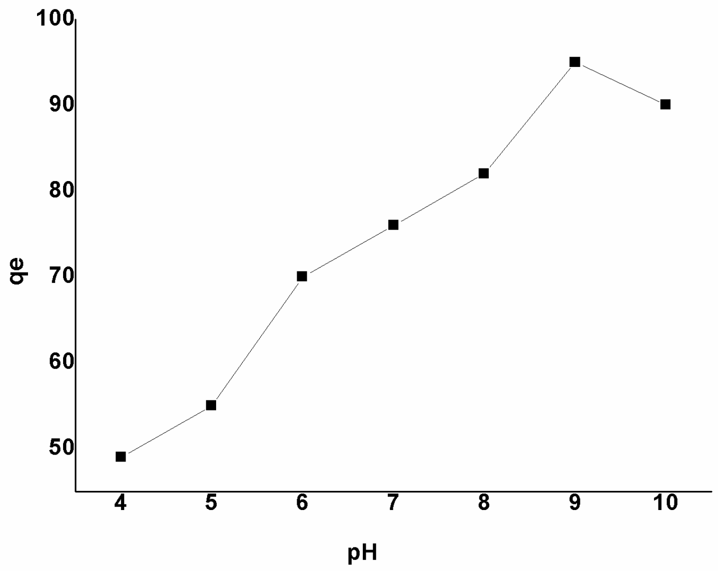

Figure 2. Variation of pH with adsorption maximum.

3.2. Effect of other variables with response surface and contour plots.

The contour, surface plots, and geometrical representations were utilized to interpret the system with multi-variants. To estimate MB sorption efficiency over independent variables, response surface and contour plots obtained by Origin software were represented in Fig 3-4. Fig.3 demonstrates the influence of PPF concentration on initial MB concentration for the reaction time of 40 minutes on MB dye sorption efficiency. The effect of MB dye and PPF concentration with sorption efficiency at a hold time 40 min exhibited that the sorption efficiency increased with a decrease in initial MB dye dosage and an increase in PPF concentration. The favorable increase in sorption efficiency is attributed to the increase in available surface area and the sorption sites on the increase in the adsorbent concentration. Fig.4 depicts the sorption efficiency for an initial MB dosage of 100 mg/l as a function of contact time and PPF concentration. It is observed that the MB adsorption efficiency reached88.35% when the contact time was 40 min and PPF concentration was 4 g/l. The biomaterials such as polyphenols, flavonoids etc., play a beneficial role in increased sorption efficiency.

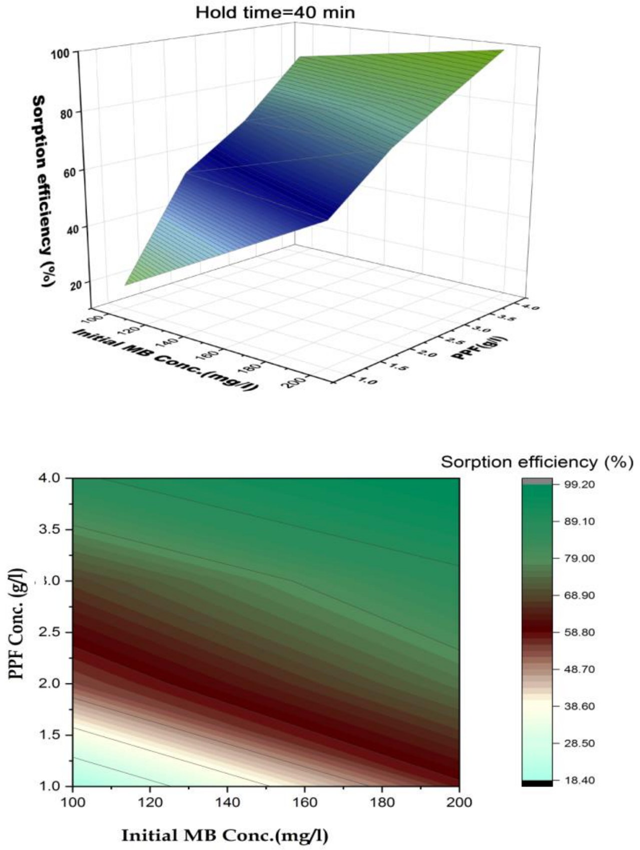

Figure 3. The response surface and contour plots of MB sorption efficiency (%) as a function of initial MB concentration (mg/L) and reaction time (min).

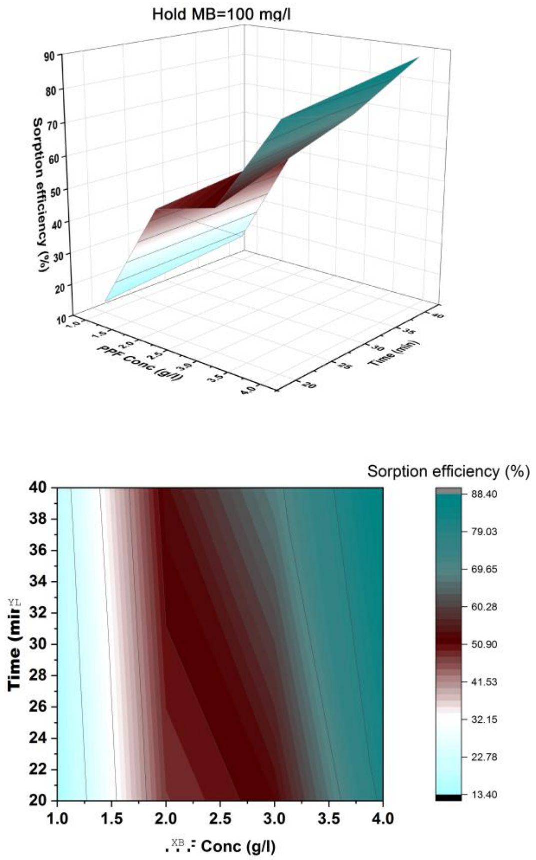

Figure 4. The response surface and contour plots of MB sorption efficiency (%) as a function of initial PPF concentration (g/L) and reaction time (min).

3.3. Effect of biosorption equilibrium.

Adsorption isotherm could be used to demonstrate the adsorption mechanism, and specific relation between the adsorbate equilibrium concentration and amount of adsorbed adsorbate at the surface, predict the maximum adsorption capacity of adsorbent and optimize the design of the adsorption system. The isotherms results of MB adsorption on PPF biosorbent at RT were analyzed utilizing three significant isotherms, including Langmuir (Fig 5), Freundlich (fig 6), and Temkin (fig 7); isotherm models are listed in Table1.

Table 1. Adsorption isotherm parameters of Methylene Blue dye on *Peltophorum pterocarpum* flowers for various models.

Isotherm	Parameters
Langmuir	
Q_0 (mg/g)	71.9424
b(L/mg)	1.6626
R^2	0.98618
Freundlich	
K_f (mg/g(L/mg)$^{1/n}$)	11.0405
n	4.591
R^2	0.94109
Temkin	
b(L/mol)	100.385
A(L/g)	451
R^2	0.98696

Langmuir Model is applicable for the uptake of adsorbate with monolayer adsorption onto the homogeneous surface with a finite number of identical sites given by the following equation:

$$qe = Q0bCe/(1 + bCe) \quad (3)$$

Where Ce (mg/L) is the equilibrium concentration of MB and qe (mg/g) is the amount of adsorbed adsorbate per unit mass of adsorbent, respectively. Q_0 (mg/g) is the maximum adsorption capacity, b(L/mg) is the constant associated with an affinity of the bonding sites. The linearized Langmuir equation is presented as follows

$$\frac{Ce}{qe} = \frac{1}{Q0} Ce + \frac{1}{Q0b} \quad (4)$$

The Langmuir isotherm could be well fitted to the adsorption process, and the maximum adsorption capacity was observed to be 71.9424 mg/g.

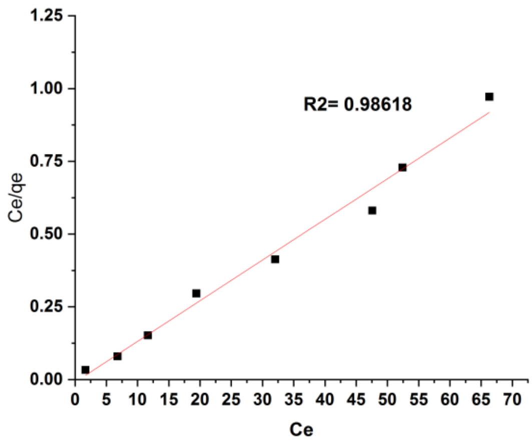

Figure 5. Linear plot of Langmuir isotherm of MB adsorption on PPF.

Freundlich isotherm assumes that multilayer adsorption occurs as more binding sites are occupied by adsorbates and can be represented as

$$Qe= K_f C_e^{1/n} \quad (5)$$

Where K_f (mg/g(L/mg) is the sorption capacity of the adsorbent and n indicates the favourability for the sorption process. Freundlich isotherm can be linearised as follows to determine the K_f and n values from the intercept and slope of the plot of log qe vs. log Ce.

$$\log qe = \log Kf + \frac{1}{n} \log Ce \quad (6)$$

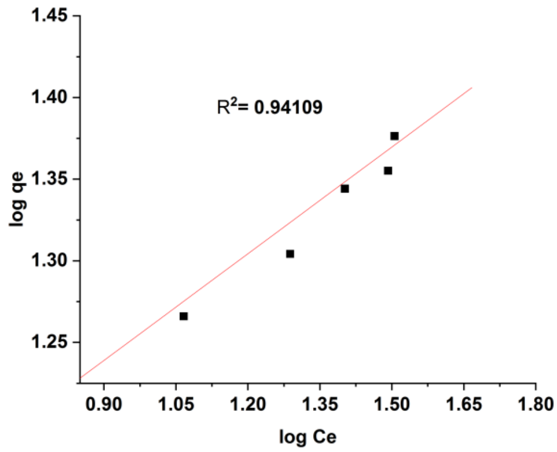

Figure 6. Linear plot of Freundlich isotherm of MB adsorption on PPF.

Temkin model explains the effect of the indirect interaction of adsorbate and adsorbent on adsorption isotherm. The Temkin isotherm has been generally represented in the following equation

$$qe = \frac{RT}{b} \ln ACe \quad (7)$$

And can be linearized as

$$qe = B\ln A + B\ln Ce \quad (8)$$

Where B=RT/b, b is the Temkin constant related to the heat of sorption, and A is the Temkin isotherm constant. R is the universal gas constant (8.314 J/molK), and T is the absolute temperature in Kelvin.

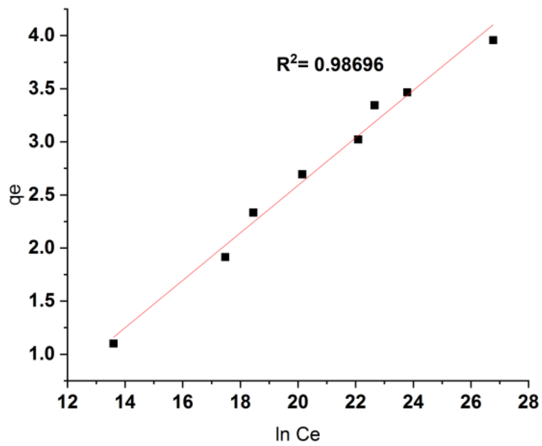

Figure 7. Linear plot of Temkin isotherm of MB adsorption on PPF.

3.4. Biosorption kinetics.

Figure 8 represents the effect of initial MB dye dosage on the rate of dye adsorption onto PPF. Due to the agglomeration of MB dye on the vacant sites, the dye concentration reduced as time progressed. The kinetic data were well suited to the pseudo-second order kinetic model to demonstrate MB dye adsorption on PPF.

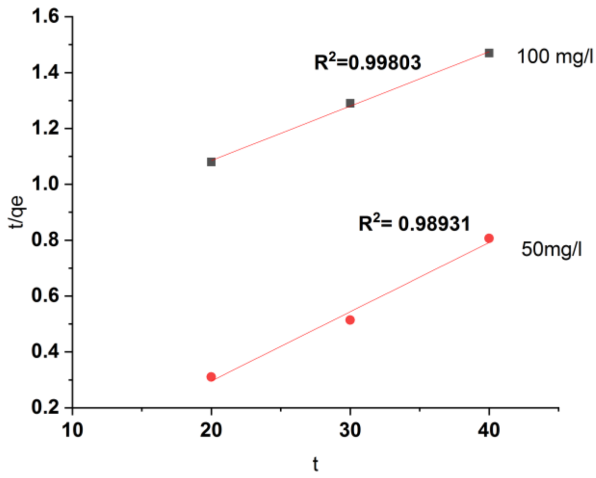

Figure 8. Pseudo second order adsorption kinetics of MB dye on PPF.

The rate constant of adsorption is calculated from the linear pseudo-second-order rate equation in the following form

$$\frac{t}{qt} = \frac{1}{\mathrm{k2qe2}} + \frac{1}{qe}t \qquad (9)$$

where q_e is the equilibrium capacity and k_2 is second-order kinetics, both are calculated from the slope and intercept of the graph plotted for t/q_t vs. t. The plots demonstrate that the pseudo-second-order kinetics favor the MB dye adsorption on PPF with correlation coefficients above 0.98(Table 2).

Table 2. Adsorption kinetic parameters of Methylene Blue dye on *Peltophorum pterocarpum* flowers for pseudo-second-order kinetics.

Initial MB concentration (mg/l)	k_2 (g/mg min)	q_e	R^2
100	$1.16x10^{-4}$	41.4937	0.98931
200	$2.6x10^{-4}$	51.2820	0.99902

3.5. Environmental Significance of this work.

Biosorption has been evolving in recent years as an effective multidimensional process [26]. It has been perceived as an alternate venerable wastewater treatment compared to other traditional methods. Biosorption removal of pollutants is significant for conserving the environment with a low-cost strategy. The eco-friendly techniques have come into keeping because of the various disadvantages of chemical adsorbents. As PPF flowers are abundant and eco-friendly, causing no damage to the environment can be assessed in terms of pollutant removal efficiency, and large-scale application of PPF as a low-cost adsorbent is possible.

4. Conclusions

The study of the ability of PPF as biosorbent for the removal of MB dye has been successfully carried out. Sorption of MB dye on PPF was illustrated in the batch adsorption method and obtained to be robustly reliant on sorbent dosage and initial concentration of MB dye. The optimum adsorption capacity was found to be 71.9434 mg/g and was obtained at room temperature within 40 minutes at pH 9. Adsorption of MB dye by PPF is well suited to Langmuir isotherm adsorption. The pseudo-second-order kinetic model concurred well with the dynamic data of MB dye on PPF sorbent.

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Conflicts of Interest

The authors declare no conflict of interest.

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