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*Research Article*

# Removal of Methylene Blue from Aqueous Effluent Using Fixed Bed of Groundnut Shell Powder

**Sunil Kumar, V. Gunasekar, and V. Ponnusami**

*Department of Chemical Engineering, School of Chemical and Biotechnology, SASTRA University, Thirumalaisamudram 613 401, Tamil Nadu, Thanjavur, India*

Correspondence should be addressed to V. Ponnusami; vponnu@chem.sastra.edu

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Removal of methylene blue from aqueous solution using a low-cost adsorbent groundnut shell powder (GNSP) was studied using fixed bed. Bed service depth model and Thomas model were employed to study the adsorption kinetics and to predict break-through curves for the system. Both models fit the experimental data very well with very high $R^2$ values. Percentage color removal increased with increase in bed height. It was found that adsorption potential of GNSP was in the range of 0.238 to 0.272 kg/kg of adsorbent. These results show that the GNSP can be effectively used as low-cost alternate adsorbent for the removal of pollutants from aqueous streams.

## 1. Introduction

Dyes are widely used by several industries like plastics, textile, and paper, to color their final products [1]. Presence of dyes in industrial effluent poses serious threat to the environment. It interferes with the normal photosynthetic activities of aquatic life [2–4]. Majority of dyes are recalcitrant and usually take very long time for biodegradation. Moreover, it is reported that the intermediates formed during biodegradation of the dyes are more toxic than the original molecules. Photochemical oxidation can mineralize the compounds efficiently, but it is energy intensive and therefore not preferred for large-scale applications. Similarly, many other physicochemical techniques available for color removal are either costly or inefficient. Among them adsorption is proven to be one of the most efficient techniques [5, 6]. However, as cost of conventional adsorbents is too high, it is necessary to search for low cost adsorbents. Scientists are now exploring the possibilities of using low-cost agro wastes as alternate adsorbents. Agro wastes like rice husk [7–9], wheat husk [10, 11], saw dust of various trees [12–14], peels of fruits [15], seeds [16, 17], and leaves of various plants [18–22] have been studied recently. In this work, groundnut shell powder (GNSP) is used for the adsorption of methylene blue from aqueous effluent.

Groundnut shell is a byproduct of groundnut oil industry. It is a solid waste to be disposed off properly. If this material could be effectively used as an alternate adsorbent, then it can have double-fold advantage. In order to assess the adsorption potential of the GNSP, equilibrium studies were performed in batch mode. However, continuous adsorption is preferred over batch adsorption for large-scale applications owing to higher efficiency and effective utilisation of adsorbent capacity. Therefore, in this work fixed bed packed with GNSP was employed for adsorption of methylene blue from aqueous solution.

## 2. Materials and Methods

*2.1. Adsorbate.* Methylene blue (MB, chemical formula: C16H18N3SCl; FW: 320 g mol$^{-1}$, $\lambda_{\max} = 662$ nm, class: thiazine, CI classification number: 52015) was obtained from the Ranbaxy Laboratories Limited (India) and used without further purification. MB is not regarded as acutely toxic, but it can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while by ingestion through the mouth it produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis [23, 24]. Stock solutions were prepared as described in Ponnusami et al. [19]. Frequently in adsorption studies, MB is used as model dye for two reasons [18]: (i) MB is one of the commonly used commercial dye and (ii) MB is well known for its adsorption characteristics.

*2.2. Adsorbent.* The groundnut shell was first washed thoroughly with unpurified water to remove adhering foreign particles from the surface and then dried in solar light. Then it was dried in hot-air oven at 70°C for about 24 h. After drying, the adsorbent was crushed in ball mill and then size separated using sieve shaker. Particles of size BSS # −60 + 72 were collected and then stored in a plastic container for further use. Physical characteristics of the GNSP were determined, and results are summarized in Table 1. pH zero point charge ($pH_{zpc}$) of the adsorbent was determined by powder addition method [25].

Infrared spectrum of the sample was obtained using PerkinElmer spectrum RX I model Fourier transform infrared spectrometer by KBr pellet method in the range of 400 to 4000 $cm^{-1}$, with a resolution of 1 $cm^{-1}$. FT-IR spectrum is shown in Figure 1. The reported result is average of 20 scans. The deep absorption peak at 3398 $cm^{-1}$ corresponds to –OH stretching vibrations. Peak at 2929 $cm^{-1}$ corresponds to alkane stretching. Peaks at 1600 $cm^{-1}$ and 1363 $cm^{-1}$ indicate C=C stretching and $-CH_3$ bending vibration, respectively. As MB is a cationic dye, –OH functional groups on the surface of GNSP may increase the interaction between adsorbent and adsorbate and contribute for the adsorption of MB.

*2.3. Batch Equilibrium Studies.* 100 mL of MB solution of desired concentration (0.02, 0.04, 0.06, 0.08, 0.1, 0.125, 0.15, and 0.2 $kg/m^3$) was taken in a 500 mL conical flask. 0.5 g of adsorbent was added to the solution, and the mixture was kept in an orbital shaker at constant temperature (303, 313, and 323 K) and 200 RPM for 24 h to ensure equilibrium. After 24 h samples were taken from each flask using a fine tip syringe to avoid carryover of solid particles. The samples were then centrifuged to collect clear supernatant solution. Concentration of MB was estimated using UV-Vis spectrophotometer, by measuring the optical density at 660 nm. Optical density was then converted into concentration units using calibration chart [18]. Though the $pH_{zpc}$ of the GNSP was found to be 7.5, for adsorption studies pH was maintained at 7 throughout this study to minimise the addition of chemicals.

Equilibrium data was analysed with most frequently used Langmuir isotherm [26] which is given by $q_e = q_{max} K_L C_e/(1 + K_L C_e)$. Here, $q_e$ is equilibrium solid-phase concentration of MB (kg/kg), $q_{max}$ is monolayer adsorption capacity of the adsorbent (kg/kg), $C_e$ is equilibrium liquid phase concentration of MB ($kg/m^3$), and $K_L$ is the Langmuir equilibrium constant ($m^3/kg$). The Langmuir isotherm parameters $K_L$ and $q_{max}$ were determined by nonlinear regression [27, 28] using Curve expert 1.40 (Microsoft corporation, 1993). Chi-square, defined as $\chi^2 = \sqrt{(q_e - q_{e,m})^2/q_{e,m}}$, was used as the error function while determining isotherm parameters by non-linear regress analysis [27]. Here, $q_{e,m}$ stands for the equilibrium solid phase concentration of MB (kg/kg) as predicted by the model.

Table 1: Physical and chemical properties of GNSP used in the experiments.

| Property | Value |
|---|---|
| Moisture content (%) | 4.2 |
| Volatile matter (%) | 63.7 |
| Ash (%) | 23.8 |
| Fixed carbon (%) | 8.3 |
| Bulk density ($kg/m^3$) | 380 |
| Average particle size, BSS # −60 + 72 ($\mu$m) | 231 |
| $pH_{zpc}$ | 7.5 |

*2.4. Column Experiments.* Bulk removal of MB onto GNSP was investigated using a packed bed of BSS # −60 + 72 size GNSP particles. Larger-size particles were chosen to reduce excessive pressure drop and to ensure plug flow. A 2 cm diameter glass column was used for this study. The column was fitted with five sampling ports located at regular intervals of 5 cm. At the bottom of the column, 2 cm high layer of glass beads (3 mm dia.) was used to ensure proper distribution of inlet flow. Dye solution (0.2 $kg/m^3$) was introduced at the bottom of the column in upward direction at a rate of 1 l/h using a peristaltic pump. Samples were collected at regular time intervals from the sampling points located at 5, 10, and 15 cm heights. Performance of the column operation is described by break-through curves. Break-through time and shapes of break-through curves are very important characteristics of the column for determining the operation and dynamic response of the bed.

Volume of effluent ($V_{eff}$) processed is calculated as:

$$V_{eff} = Q \times t_{total}, \quad (1)$$

where $Q$ = volumetric flow rate in l/h and $t_{total}$ is the service time of the column in h. Exhaustive time is taken as the service time ($t_{total}$) of the column for the purpose of calculating $V_{eff}, q_t, m_{total}$, and %$R$. Total amount of dye adsorbed in the column ($q_t$, kg) for a given feed concentration and flow rate is calculated using the formula

$$q_t = \frac{QC_0}{1000}\int_{t=0}^{t=t_{total}}\left(1 - \frac{C_t}{C_0}\right)dt, \quad (2)$$

where $C_0$ is initial concentration in $kg/m^3$ and $t$ is time in h. If the total amount of dye passed through the column is $m_{total}$ ($=QC_0 t_{total}/1000$), then percentage dye removed is calculated as

$$\text{Total percentage removal, } \%R = \frac{q_t}{m_{total}} \times 100 \quad (3)$$

*2.5. Bed Depth Service Time (BDST) Model.* Bed depth service time model [29] is a simple model that assumes a linear relationship between bed height and service time of a column.

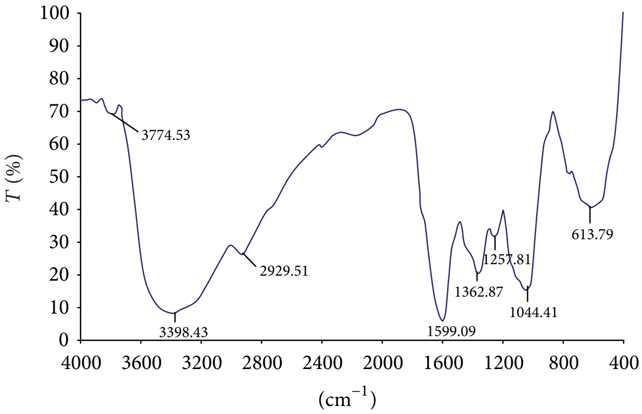


Figure 1: FTIR of groundnut shell powder.

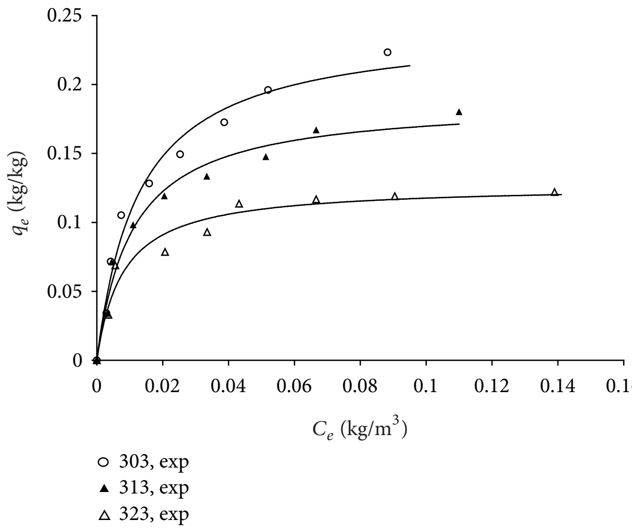


Figure 2: Equilibrium studies on adsorption of MB onto GNSP. (RPM = 200, $T$ = 303, 313, and 323 K, adsorbent = 0.5 kg/m$^3$, pH = 7).

The equation can be expressed as:

$$t_b = \frac{N_0 Z_0}{C_0 U_0} + \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_B} - 1\right), \tag{4}$$

where $t_b$, $N_0$, $Z_0$, $C_0$, $U_0$, $K_a$, and $C_b$ are break-through time (h), bed capacity (kg/m$^3$), bed height (m), initial dye concentration (kg/m$^3$), superficial velocity through bed (m/h), kinetic constant (m$^3$/kg h), and break-through concentration (kg/m$^3$), respectively. In spite of ignoring the intra-particle mass transfer resistance and external film resistance, the model fits many packed bed adsorption systems well and provides information ($N_0$ and $K_a$) useful for scale up of given adsorption system [24].

*2.6. The Thomas Model.* Prediction of concentration–time profile and maximum adsorption capacity is important for satisfactory design of a column adsorption. The Thomas model [18, 24] is one of the most general and widely used models to describe packed bed adsorption. It assumes (i) Langmuir's isotherm, (ii) no axial dispersion, and (iii) second-order adsorption kinetics. Linear form of the model is given by the equation [29, 30]:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_{\mathrm{Th}} q_0 X}{Q} - \frac{K_{\mathrm{Th}} C_0}{Q} V_{\mathrm{eff}}. \tag{5}$$

The kinetic parameters $K_{\mathrm{Th}}$(m$^3$kg$^{-1}$h$^{-1}$) and $q_0$ (kg/kg) were determined from the slope and intercept of the plot of $\ln(C_0/C_b - 1)$ versus $t$ at a given flow rate.

## 3. Results and Discussion

*3.1. Batch Equilibrium Studies.* Equilibrium curves are shown in Figure 2. Langmuir's isotherm parameters determined by non-linear regression are given in Table 2. High $R^2$ values (≈1) indicate the goodness of fit. The values of Langmuir's monolayer adsorption capacities, shown in Table 2, indicate the efficiency of GNSP as an alternate adsorbent.

Table 2: Langmuir 's isotherm parameters for the adsorption of MB onto GNSP.

| Parameter | 303 K | 313 K | 323 K |
|---|---|---|---|
| $K_L$ (m$^3$/kg) | 78.23 | 93.16 | 126.13 |
| $q_m$ (kg/kg) | 0.242 | 0.188 | 0.127 |
| $R^2$ | 0.989 | 0.990 | 0.978 |
| $\chi^2$ | 0.63 | 0.37 | 0.08 |

*3.2. Column Studies*

*3.2.1. Bed-Depth Service Time (BDST).* Effect of bed depth was studied at a constant initial dye concentration of 0.2 kg/m$^3$. Samples were drawn from various heights of the column. Figure 3 shows the break-through curve for the adsorption of MB using a fixed bed of GNSP. Break-through concentration was fixed as 10% of initial concentration (that is 0.02 kg/m$^3$). Break-through time increased with increase in bed height in consistent with the theory. Values of $N_0$ and $K_a$ are found to be 77.99 kg/m$^3$ and 0.45 m$^3$ kg$^{-1}$ h$^{-1}$, respectively. Percentage color removal was calculated be 67, 77, and 79, respectively, for bed heights 5, 10, and 15 cm. Percentage color removal increases with increase in bed height as utilisation of bed improves with increase in bed height [24].

*3.2.2. The Thomas Model.* The Thomas model plot is shown in Figure 4. The model parameters $K_{\mathrm{Th}}$ and $q_0$ are presented in Table 3. High $R^2$ values obtained indicate that Thomas model fits the experimental data well for this system. Comparison of experimental and predicted break-through curves is shown in Figure 3. The values of $K_{\mathrm{Th}}$ decreased with increase in bed height. Values of $q_0$ predicted by the Thomas model were in the range of 0.272, 0.238, and 0.241 kg/kg. These

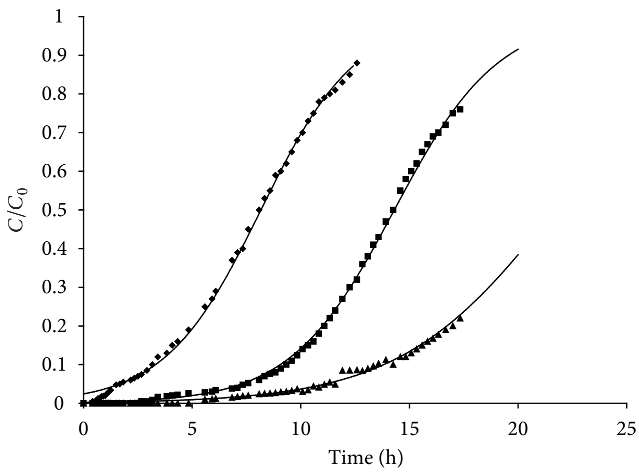


Figure 3: Break-through curves for MB adsorption onto GNSP at different bed heights. Flow rate = 1 l/h, initial dye concentration = 0.2 kg/m$^3$, pH = 7.

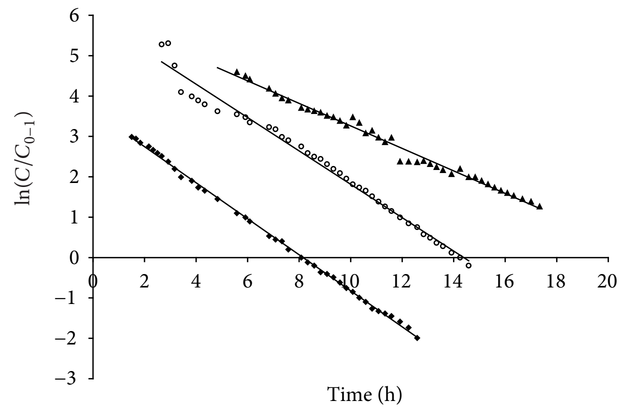


Figure 4: The Thomas model curve for MB adsorption onto GNSP at different bed heights. Flow rate = 1 l/h, initial dye concentration = 0.2 kg/m$^3$, pH = 7.

Table 3: The Thomas model parameters.

| Bed height (cm) | $q_0$ (kg/kg) | $K_{TH}$ (m$^3$/kg h) | $R^2$ |
|---|---|---|---|
| 5 | 0.272 | 2.262 | 0.99 |
| 10 | 0.238 | 2.091 | 0.99 |
| 15 | 0.241 | 1.395 | 0.99 |

are comparable with the actual values 0.253, 0.228, and 0.231 kg/kg as calculated using (2). This shows that the prediction of the Thomas model is close enough to the actual values. The difference seen here is largely due to the deviation of the Thomas model during the initial period. It is seen that the height of the bed did not show any definite effect on $q_0$. This suggests plug flow conditions prevailed in the column and the axial dispersion was negligible. This is comparable to other low-cost adsorbents reported in the literature [24]. This indicates that the GNSP has good adsorption potential and it can be employed as an alternate adsorbent.

## 4. Conclusion

Continuous removal of methylene blue from aqueous solution was studied using a fixed bed packed with of groundnut shell powder. Up to 80% color removal was possible with the fixed bed. Thomas model could satisfactorily predict the adsorption break-through curve. Adsorption capacity of the bed was found to be in the range of 0.238 to 0.272 kg/kg. These results demonstrate that groundnut shell powder possesses good adsorption capacity and can be effectively used as a low cost alternate adsorbent for the removal of pollutants like methylene blue from industrial effluents.

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