

Adsorption of Methylene blue and Malachite Green in Aqueous Solution using Jack Fruit Leaf Ash as Low Cost Adsorbent

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Abstract— The adsorption of mixture of two basic dyes methylene blue and malachite green in aqueous solution onto jack fruit leaf ash in a batch system with respect to initial dye concentrations, pH, contact time, shaker speed and adsorbent doses was investigated. The pseudo-first-order and pseudo-second-order kinetics model were used to describe the kinetic data. The rate constants at different pH values (3-9.1) were evaluated. The experimental data fitted well with the pseudo-second-order kinetic model. Equilibrium isotherms were analyzed by Langmuir, Freundlich and Temkin isotherm models. Maximum adsorption capacity was 20.41mg/g was achieved by Langmuir isotherm model. Error analysis was done to find the best model that described the experimental data well and it was the Langmuir model. The result indicated that jack fruit leaf ash could be fruitfully employed as low cost adsorbent for the removal of mixture of two basic dyes MB and MG from the wastewater.

Keywords— adsorption, isotherm, jack fruit leaf ash, kinetic model, methylene blue, malachite green.

I. INTRODUCTION

The textile and other dye using industries consume large amount of water for its different operational phases. The use of huge water for their production purposes, it is inhabitable that they discharge a huge volume of wastewater which is rich in color. Due to more and more increasingly stringent restrictions, it is essential to eliminate dye contamination from wastewater before discharging to the open environment. There are various techniques such as adsorption, chemical oxidation, filtration, coagulation etc. have been used to remove dye pollutants from the wastewater. Among these different methods for the removal of colors, it has been well established that adsorption is the most useful and effective technique to remove dyes from the wastewater. The advantages of adopting this technique in wastewater treatment is because of its simple operation, higher

efficiency and ability to separate wide range of chemical compounds. The use of commercially available activated carbon is better choice but it involves huge cost, makes adsorption process infeasible. So in the recent years research is mainly focused on utilizing natural agricultural by products such as jack fruit leaf, neem leaf, rice husk, bagasse fly ash etc. available as abundant materials in rural Bengal. The use of such waste materials as low cost adsorbent is a typical attempt for this purpose. The basic dyes methylene blue and malachite green are one of the important and widely used dyes in textile and other dye using industries. In practice the wastewater from industries contain mixture of dyes. However, no literature is available since last 20 years to remove mixture of dyes from the wastewater. Both the dyes MB and MG are water soluble and very difficult to remove from the wastewater by simple removal technique. So the adsorptive removal of mixture of basic dyes using jack fruit leaf ash (JFLA) as low cost adsorbent is a typical attempt of the present work to solve the real life problem. The effects of adsorbent doses, contact time, pH, shaker speed and initial concentration of the solution dyes were investigated. The Langmuir, Freundlich and Temkin isotherms were used to fit the equilibrium data. Pseudo-first-order and Pseudo-second-order kinetic models were attempted.

II. MATERIAL AND METHODS

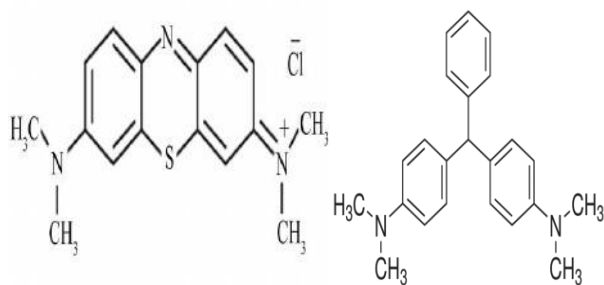
Adsorbent

The raw jack fruit leaf was collected locally in the Jadavpur University campus. The dry leaves washed with distilled water several times and dried for 8 hrs. in the woven. The dried leaves then put into the muffle furnace at 600⁰C to make it ash. The JFLA sieved through 300 μ sieve to eliminate the finer portion, and finally the adsorbent was prepared for the experiment.

Dyes

The dyes were collected from the local market of Kolkata and their chemical structure was illustrated in the figure 1.

Methylene Blue (MB) and Malachite Green (MG) are two cationic dyes. Two dyes of equal proportion was taken to prepare stock solution of 1000mg/L. The working solution was prepared by diluting the stock solution to give the appropriate concentrations.



Methylene Blue Malachite Green
 Fig.1: Chemical structure of MB and MG

Batch adsorption experiments

All adsorption experiments were carried out by agitating the jack fruit leaf ash of required amount with 200 mL dye solution of different concentrations as required in a 250 mL bottle at constant room temperature in a shaker at 120 rpm except during varying shaker speed observation. The experiment was carried out for various JFLA dosage, initial concentrations, shaker speed and pH. At the end of the predetermined shaking time the samples were withdrawn and centrifuged at 5000 rpm for 10 minutes. The resulting supernatant was then analyzed using spectrophotometer.

The amount of adsorption at equilibrium, q_e (mg/g), was computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{m_s} \text{-----(1)}$$

where, C_0 and C_e are the initial and equilibrium solution concentrations (mg/L) respectively, V is the volume of the solution (L), and m_s is the weight of JFLA used (g). In the experiments of batch kinetic adsorption, 200 mL of the chosen desired concentration of the stock solution of two dyes in mixture (1:1) were placed in the measuring bottle of 250 mL together with 5 gm JFLA and agitated by shaker at room temperature (30°C) and at normal pH. At predicted intervals of times, samples were taken, and their concentrations were determined by spectrophotometer.

III. RESULTS AND DISCUSSION

3.1 Effect of adsorbent dosage

The effect of JFLA dosage on the amount of dyes adsorbed was investigated by containing 200mL of dye solution with initial concentration of each dyes 12.5mg/L, mixing equally (1:1) to make 25mg/L at room temperature 30°C at 120 rpm. Different amount of JFLA

(0.1 to 12 gm) for methylene blue and malachite green were applied. The result showed that when the adsorbent dosage increased from 0.1 gm to 5gm the removal of two dyes increased from 15.83 to 90.49% and then reached a plateau. It is reported that the larger adsorption surface caused higher adsorption of dyes. Therefore, for convenience the adsorbent dosage for the present study was selected as 5 gm as equilibrium dosage. The plot of dye removal (%) versus adsorbent dosage (g/L) is shown in the fig.2.

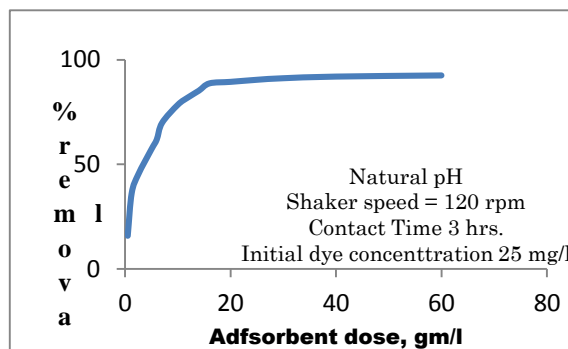


Fig.2: Effect of adsorbent dosage on adsorption onto JFLA

3.2 Effect of contact time

The effect of contact time for adsorption of mixed dye solution MB and MG onto JFLA was shown in the fig.3. The adsorbent dose was taken as 5gm, initial concentrations of mixed dye solution as 25mg/L, shaker speed as 120 rpm. The experiment was done for 6 hrs. It can be seen that the rate of adsorption under various fixed other operating conditions, the percentage removal increased rapidly for initial 10 to 165 mins and beyond that contact time no noticeable change in the percentage removal was observed. As the equilibrium time is also function of initial dye concentration, 165 min is sufficient to reach equilibrium study. The percentage removal at 165 min was noticed as 95.72%, and considered to be the optimal contact time for the adsorption study.

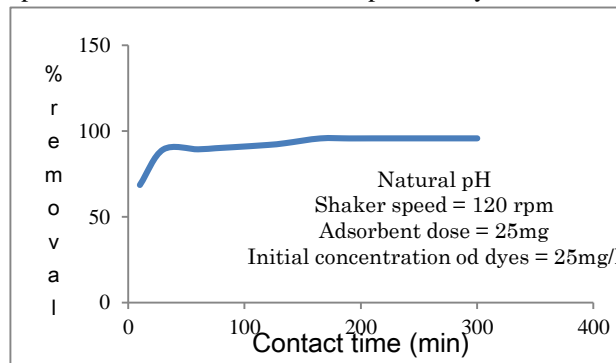


Fig.3: Effect of contact time on adsorption onto JFLA

3.3 Effect of initial dye concentrations

The influence of varying the initial concentrations of mixed dyes was assessed (Fig.4).The percentage removal

at initial concentration 25mg/L was 88.53% and that decreased to 58.25% at concentration of 150mg/L, under fixed other operating conditions. It can be concluded that the percentage removal is decreased by increasing the initial concentrations of dye mixture.

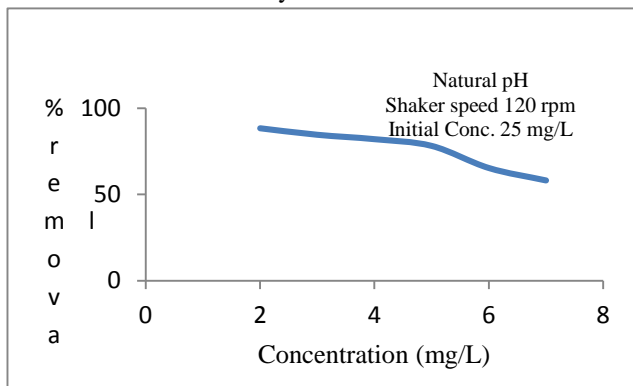


Fig.4: Effect of initial dye concentration on adsorption onto JFLA

3.4 Effect of shaker speed

The effect of shaker speed on the percentage removal of dye mixture was studied (fig. 5) under the various other fixed operating conditions. It can be seen that percentage removal increased initially 96.28 to 98.46 as the shaker speed increased from 30 to 120 rpm and beyond that it reached a constant value.

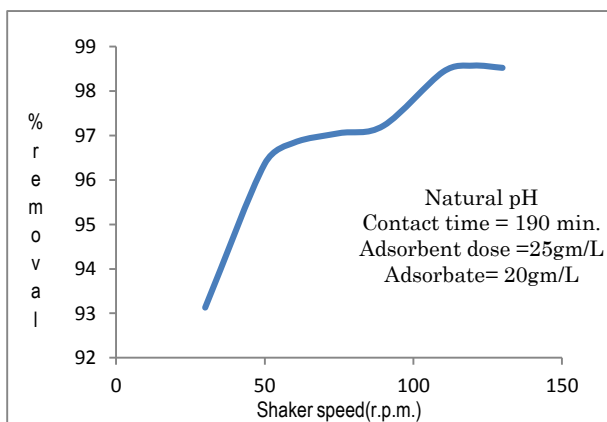


Fig.5: Effect of shaker speed on adsorption onto JFLA

3.5 Effect of pH of the initial solution of dyes

The effect of initial pH on the adsorption of mixed dyes MB and MG onto JFLA is shown in the figure 6. As these two are cationic dyes, adsorbed onto the JFLA effectively at higher pH. The removal efficiency increased from 94.87 to 99.18 % as the pH of the solution increased from 3.0 to 9.1.

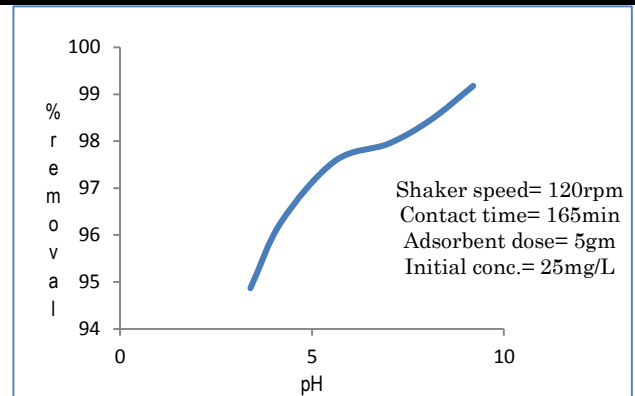


Fig.6: Effect of initial pH on adsorption onto JFLA

3.6 Adsorption kinetics

The mechanism of solute sorption onto a sorbent can be expressed by different kinetic models. To explore the fast and effective model the different parameters of adsorption mechanism such as chemical reaction, diffusion control and mass transfer to be evaluated by these kinetic model equations.

3.6.1 Pseudo-first-order equation

Pseudo-first-order equation is generally represented as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \text{ --- (1)}$$

where q_e is the amount of dye adsorbed at equilibrium, q_t the amount of dye adsorbed at time t and k_1 is the equilibrium rate constant of pseudo-first-order kinetics.

Integrating the equation (1), applying boundary condition $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, it becomes

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \text{ --- (2)}$$

From the straight line plots of $\log(q_e - q_t)$ versus t for the adsorption of mixture of two dyes MB and MG onto JFLA at different pH (3.0 to 9.1), the rate parameters were evaluated. Values of K_1 , q_e and correlation coefficient (R^2) were given in the Table-1.

3.6.2 Pseudo-second-order equation

The Ho and Makay's pseudo-second-order chemisorption kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \text{ --- (3)}$$

where, q_e and q_t are the amount of dye adsorbed at equilibrium and any time t respectively. K_2 is the rate constant of pseudo-second-order model.

Integrating the equation (3) we get

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

From the plot of t/q_t versus t , under different pH values the constant were evaluated and was given in the Table-1.

Table 1: Constants of pseudo-first-order and pseudo-second-order model

pseudo-first-order model			pseudo-second-order model		
K ₁	q _e	R ²	K ₂	q _e	R ²
0.037	1.49	0.629	0.474	1.58	0.999

From the above table, adsorption kinetics of dye mixture was studied and the rates of sorption were found to be confirmed to pseudo-second-order kinetics with good correlation coefficient value.

3.7 Adsorption isotherm

Design optimization of an adsorption system for the adsorption of adsorbate appropriate correlation for the equilibrium curve is very important. Langmuir, Freundlich and Temkin isotherm were tested in the present investigation.

3.7.1 Langmuir isotherm

In this theory the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The equation can be written as

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \text{----- (5)}$$

where, q_e is the amount of dye adsorbed onto JFLA at equilibrium concentration of solution dyes, K_L the equilibrium constant and Q_m is the maximum adsorption capacity.

The linear form of the equation (5) is

$$\frac{1}{q_e} = \frac{1}{Q_m} + \left(\frac{1}{Q_m K_L}\right) \frac{1}{C_e} \text{----- (6)}$$

The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L, defined by

$$R_L = \frac{1}{1 + K_L C_0} \text{----- (7)}$$

Where, k_L is the Langmuir constant and C₀ is the initial solution of the mixture of two dyes, R_L value indicates the type of isotherm to be irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1) or unfavourable (R_L>1).

The isotherm constants were determined from the linear plot of 1/q_e versus 1/C_e (Figure-7) and the isotherm data fitted well with Langmuir equation (R²= 0.994). The values of different parameters are given in the Table2.

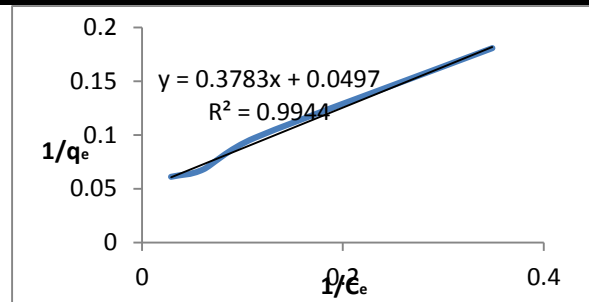


Fig.7: Langmuir isotherm equation

Table.2: Langmuir constants

q _m (mg/g)	K _L (L/mg)	R ²
20.41	0.13	0.994

3.7.2 Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Freundlich isotherm can be expressed as

$$q_e = K_F C_e^{\frac{1}{n}} \text{----- (8)}$$

Where, K_F is the adsorption capacity at unit concentration and 1/n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n=0), favourable (0 < 1/n < 1) or unfavourable (1/n > 1).

To examine the acceptance of the model with respect to the experimental data, the plot of log C_e versus log q_e plotted.

From the Figure 8 Freundlich constants K_F and 1/n were evaluated and are given in the Table-3.

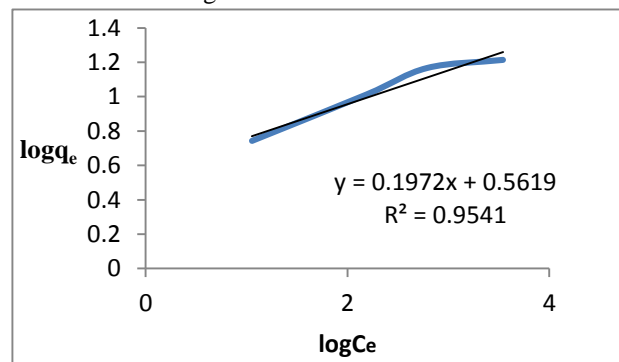


Fig. 8: Freundlich isotherm equation

Table.3: Freundlich constants

K _F (L/mg)	1/n	R ²
3.639	0.197	0.954

3.7.3 Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent-adsorbate interactions. This model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than

logarithmic change. The mathematical expression for the model is given as

$$q_e = \frac{RT}{b} \ln C_e \quad \text{----- (9)}$$

The linearized form of the equation is given as

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad \text{----- (10)}$$

where, r= gas constant (8.314 J/mol/K), T= Temperature in 'K' and B₁= RT/b.

From the plot of q_e versus log C_e (Fig. 9) the isotherm constants were evaluated and are given in the Table-4.

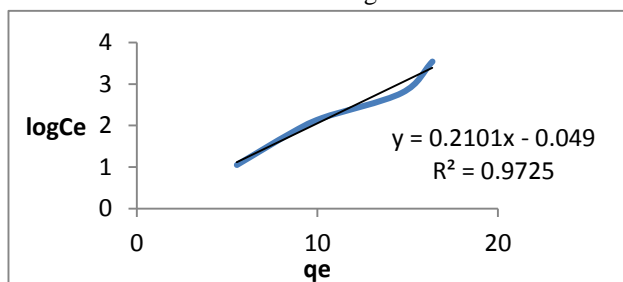


Fig. 9: Temkin isotherm equation

Table.3: Temkin constants

K _T (L/mg)	B ₁	R ²
0.097	0.021	0.972

3.8 Statistical analysis

The statistical analysis is employed in the present work due to inherent bias resulting from linearization. Five different error functions (Table-4) for statistical analysis were carried out to find the optimum isotherm model which best fitted with the data obtained from the experimental run. The another type of statistical analysis named chi-square (X²) test was also carried out to explore the significance of the effects of the parameters on present investigation of mixed dye removal and the residual concentrations of dye mixture at equilibrium.

Table.4: Different error functions

Statistical analysis	Formulae
Sum of the squares of the errors (SSE)	$\sum_{i=1}^n (q_{e\text{ cal}} - q_{e\text{ meas}})_i^2$
Sum of the absolute error (SAE)	$\sum_{i=1}^n \left \frac{(q_{e\text{ meas}} - q_{e\text{ cal}})}{q_{e\text{ meas}}} \right _i$
Average relative error (ARE)	$\frac{100}{n} \sum_{i=1}^n \left \frac{(q_{e\text{ meas}} - q_{e\text{ cal}})}{q_{e\text{ meas}}} \right _i$
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e\text{ meas}} - q_{e\text{ cal}})}{q_{e\text{ meas}}} \right]_i$

Marquardt's standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left\{ \frac{(q_{e\text{ meas}} - q_{e\text{ cal}})}{q_{e\text{ meas}}} \right\}_i^2}$
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3.8.1 Selection of best isotherm model

Since each of the error function produces a different set of isotherm parameters, it is difficult to identify directly an optimum set. Thus to find the best model a normalization of each parameter was employed. In the normalization processes first each error function was selected in turn and the results for each parameter set were determined. The normalized values of each isotherm against error analysis are given in the Table-5.

Table.5: Error analysis of isotherm equations

Isotherm	Error analysis				
	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	0.282	0.56	0.30	0.50	15.0
Freundlich	4.8	4.04	50	19.0	89.1
Temkin	22.7	9.03	95.8	191.2	270.2

The values from the Table clearly showed that Langmuir equation was best followed the equilibrium data, same as predicted by coefficient of regression (R²) value.

In order to avoid such uncertainty in claiming a specific isotherm model, it is thus imperative to carry out a more normalized error analysis as elucidated earlier in the form of chi-square test. The calculated values of chi-square test under various isotherm models are given in the Table -6. It can be seen that the adsorption of the two dyes in mixed solution follows Langmuir isotherm very well.

Table.6: Chi-square test value for different isotherms

Isotherm model	X ² value
Langmuir	0.0001
Freundlich	1.73
Temkin	9.27

Feasibility of adsorption isotherm is necessary for characterizing the adsorption beyond determining the optimum isotherm. In order to check the feasibility for adsorption for the adsorbent, JFLA onto mixed dyes in solution a dimensionless constant R_L was determined as given in the Table-7.

Table.7: Feasibility study for the adsorption of JFLA

Adsorbent	R _L	Remarks
JFLA	0.23	As 0 < R _L < 1 adsorption is favourable

IV. CONCLUSION

Equilibrium and kinetic studies were done for the adsorption of mixture of two basic dyes methylene blue and malachite green onto jack fruit leaf ash. The biosorbent exhibited high sorption capacities towards the mixture of two dyes. The kinetic studies of dye mixture on JFLA were performed based on pseudo-first-order and pseudo-second-order rate mechanism. The data indicate that the adsorption kinetics followed pseudo-second-order rate expression at the pH values of 3.0 to 9.1. The equilibrium data using Langmuir, Freundlich and Temkin isotherms and the characteristic parameters for each isotherm have been determined. The results showed that the experimental results were correlated reasonably well by Langmuir adsorption model. Error analysis was conducted and established Langmuir model more appropriate over the other two models. Results of the adsorption showed that jack fruit leaf ash can effectively used as a biosorbents for the removal of model cationic dyes methylene blue and malachite green from the mixture of aqueous solution.

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