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Removal of methylene blue dye from aqueous solution by sorption onto leaves, flowers and bark of *Delonix regia*

Ghulam Shabir[1], Muhammad Afzal[1]*, Farooq Anwar[2], Zafar M.Khalid[1], Qaiser M.Khan[1], Muhammad Umar Khan[1], Zahid Iqbal Sajid[1]

[1]Soil and Environmental Biotechnology Division, National Institute for Biotechnology and Genetic Engineering (NIBGE), P.O. Box 577, Jhang Road Faisalabad, (PAKISTAN)
[2]Department of Chemistry, University of Sargodha, Sargodha-40100, (PAKISTAN)
E-mail: manibge@yahoo.com; afzal@nibge.org

Abstract : The contamination of water with dyes is one of the main problems all over the world. In recent years, concentrated efforts have been made to develop an efficient, cost-effective and environmentally friendly technology for the cleanup of water polluted with dyes. The current study was undertaken to assess the potential of leaves, flowers and bark of *Delonix regia* as adsorbent to clean up the water polluted with methylene blue dye. Different conditions, such as pH of aqueous solution, amount of adsorbent, agitation time and dye concentration, were optimized to get maximum removal of methylene blue from aqueous solution. The data obtained indicated that leaves performed better than flowers and bark as an adsorbent of methylene blue. The highest levels of removal of dye by leaves, flowers and bark were 92.2 %, 82.5 % and 69.2 %, respectively. Similarly, more COD reduction was observed by leaves than flowers and bark. The equilibrium data was best fitted with the Langmuir adsorption isotherm models. In particular, adsorption process was best depicted by pseudo second order kinetics. This is the first report that leaves, flowers and bark of *Delonix regia* were able to clean water polluted with methylene blue. Although different parts of *Delonix regia* showed potential to remove methylene blue from water, pH of water, amount of adsorbent, agitation time and dye concentration can affect the efficiency of adsorption of plant material.

Keywords : Methylene blue dye; *Delonix regia*; Leaves; Flowers; Bark; Adsorption.

INTRODUCTION

Dyes are frequently reported as contaminant in the effluent of textile, paper, plastic, food, leather, cosmetic and dye producing industries[1-3]. Dyes inhibit the penetration of light into water and consequently reduce photosynthetic activity in water bodies. Moreover, dyes showed persistence in the environment for a long period of time due to their non-biodegradable nature. Dyes can affect humans health due to their properties to cause allergy, dermatitis and cancer[4,5]. Synthetic dyes in particular methylene blue or their metabolites are toxic to the aquatic life and have shown carcinogenic, teratogenic and/or mutagenic effects[6,7]. Moreover, methylene blue uptake causes sickness, vomiting, mental confusion and methemoglobinemia[8,9]. Therefore, the removal of methylene blue from water is one of the hot topics in the field of environmental science and technology.

A number of conventional methods have been reported for the removal of dye from water[10-12]. However, these methods of dye removal are costly and cannot effectively be used to clean up the water contaminated with dyes[13,14]. Moreover, these methods require large amount of electrical energy and highly trained manpower[15-17]. Adsorption is considered as the best approach for the removal of dyes from water due to its simple operation and easy handling[18,19]. A number of plant based adsorbents, such as sawdust, corn cob, barley husk, rice hull and bagasse pith, showed potential to remove the dyes from water[20-22].

Delonix regia, belonging to the family *Caesalpiniaceae*, having notable range of medicinal and biological properties[23,24]. It has been used for the treatment of constipation, inflammation, arthritis, leucorrhoea and rheumatism[25]. However, the adsorption potential of leaves, flowers and bark of this valuable plant is rarely evaluated for the remediation of water polluted with dye. The aim of the present study was to explore the adsorption potential of leaves, flowers and bark of *Del*onix *regia* plant to clean water polluted with methylene blue. Moreover, different conditions, such as pH of water, dye concentration, agitation time and adsorbent dose, were optimized and adsorption isotherm and kinetics models were used to best describe the equilibrium adsorption data.

EXPERIMENTAL

Preparation of adsorbents

Leaves, flowers and bark of *Delonix regia* collected from the University of Agriculture, Faisalabad (Pakistan) were dried and pulverized. Equal amounts of leaves, flowers and bark were soaked in equal volume of methanol in conical flasks and were kept in a shaker for eight hours. After filtration, the residues of leaves, flowers and bark were air dried at room temperature and then rinsed with distilled water to eliminate the surface-adhered material and water-soluble particles. Latter on material was dried at 104°C in an oven for 20 h, and sieved through 80 mesh size sieve. The obtained plant material was applied to remove methylene blue from water.

Experimental set up

The efficacy of the prepared adsorbents was evaluated at different agitation times, adsorbent dosages, dye concentrations and pH of dye solution. Experiments were performed by using required amount of adsorbent into 250 mL conical flasks containing 100 mL of methylene blue solution. The conical flasks were put in a shaker (100 rpm) at room temprature. After specified time, water samples were collected, and the amount of residual dye in water was examined at maximum wavelength (668 nm) of the dye. The dye adsorption concentration at equilibrium q_e (mg/g) was determined using following equation:

$$q_e = (C_o - C_e)V / W$$

where, C_o and C_e (mg L^{-1}) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used[26].

Determination of chemical oxygen demand

Before and after treatment of methylene blue solution with adsorbent, the chemical oxygen demand (COD) of the water was determined by using standard method[27].

RESULTS AND DISCUSSION

Effect of pH on adsorption of methylene blue

The pH of the water is considered one of the most important parameters that can affect adsorption efficiency of an adsorbent material. To determine the influence of pH on methylene blue adsorption onto leaves, flowers and bark, the experiments were performed by varying pH of aqueous solution of methylene blue from 2-10. Maximum removal of dye was attained at pH 7.0 with leaves and at pH 6.0 with both flowers and bark material (Figure 1). The highest levels of removal of dye by leaves, flowers and bark were 92.2 %, 82.5 % and 69.2 %, respectively. Upon decreasing the pH of the solution, the number of negatively charged adsorbent sites increased, that not favors the adsorption of the positively charged dye cations[4,28].

Effect of agitation time on adsorption of methylene blue

The effect of various agitation intervals on adsorption of methylene blue using leaves, flowers and bark materials is shown in Figure 2. The higher adsorption

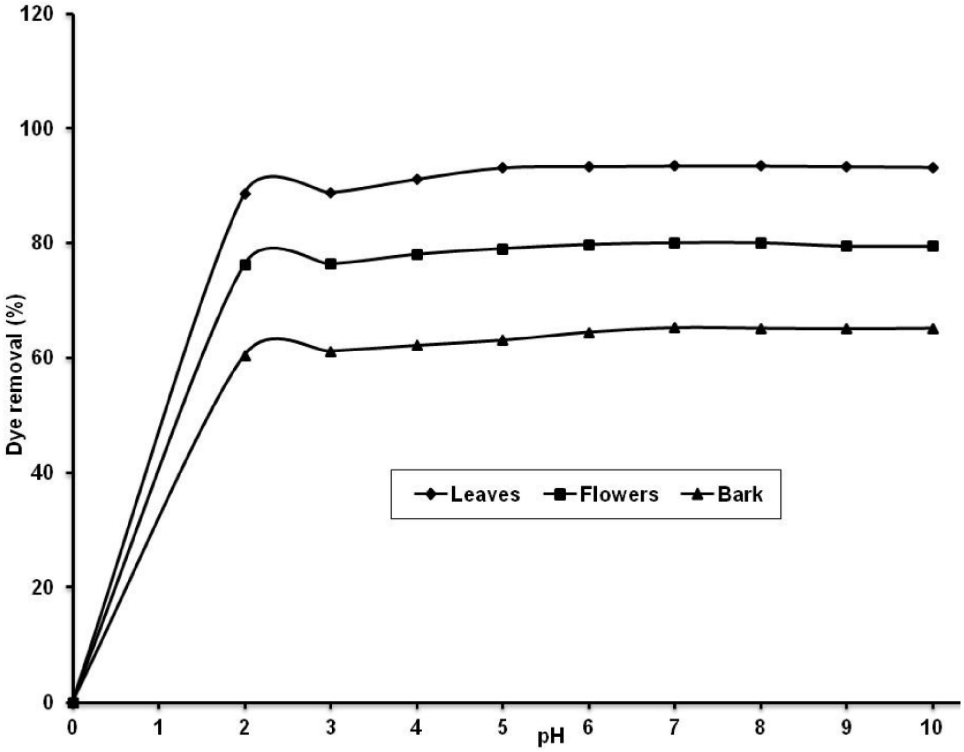

Figure 1 : Effect of pH on dye removal by leaves, flowers and bark of *Delonix regia* (initial dye concentration = 100 mg L^{-1}; adsorbent dose = 0.4 %; agitation time = 2 h). Values are means of triplicate determinations.

level was attained when the agitation time was 15, 30 and 45 minutes for leaves, flowers and bark, respectively. The maximum removal (97.1%) of dye form aqueous media was obtained using leaves as adsorbent. In case of flowers and bark as adsorbent material the maximum removal of dye was 86.9 % and 79.8 %, respectively. These results indicated that leaves were more effective for the removal of dye from water in comparatively less time. This might be due to the available of more adsorption sites in leaves material as compare to flowers and bark. With increase in contact time, the adsorption rate declined to a constant level. It might be due to that all existing sites were engaged and no more active sites were present for the attachment of remaining dye molecules on adsorbent surface. Recently, Anwar et al[29] reported that initially large numbers of unoccupied surface sites were present for adsorption process, and after some time remaining sites were not occupied due to repulsive forces between the solute molecules on the solid and bulk phase solution. The equilibrium was achieved rapidly within 15 min at the studied concentration of dye by using leaves as adsorbent. However, in case of flowers and bark the equilibrium was achieved in about 30 and 45 min, respectively. Initially in the dye adsorption process molecules have to first encounter the surrounding layer and then it has to diffuse from boundary layer film onto adsorbent surface[30].

Effect of adsorbent dose on adsorption of methylene blue

To study the influence of adsorbent dose on the removal of dye from aqueous solution, different amounts of material of leaves, flowers and bark ranging from 0.2 to 1.0% (wt/vol) were used. The maximum removal of dye from water was achieved at adsorbent dose of 0.4% for leaves and 0.6% for flowers and bark (Figure 3). However, further increase in adsorbent dose decreased removal of dye from water. Similarly, in another study removal of dye form water decreased as the amount of adsorbent increased[31].

Effect of initial dye concentration on adsorption of methylene blue

The influence of initial methylene blue concentration on its adsorption onto leaves, flowers and bark was studied at 50, 100, 150, 200 and 250 mg L^{-1} of methylene blue. Maximum dye removal was achieved by leaves at 100 mg L^{-1} of dye concentration. However, flowers and bark showed maximum dye removal

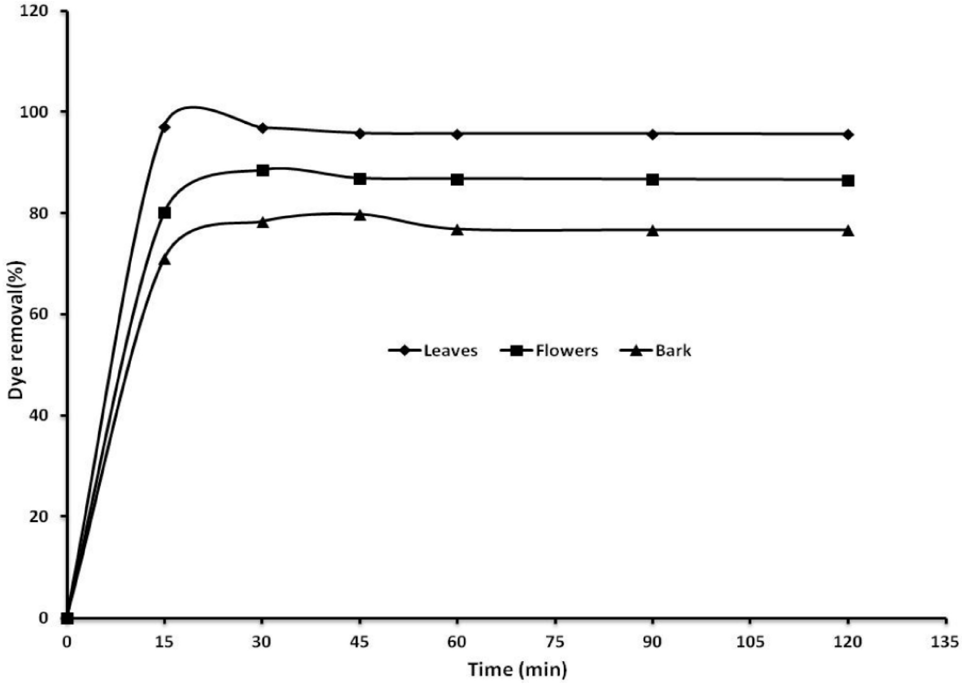

Figure 2 : Effect of agitation time on dye removal by leaves, flowers and bark of *Delonix regia* (adsorbent dose = 0.4%; pH= 7.0). Values are means of triplicate determinations.

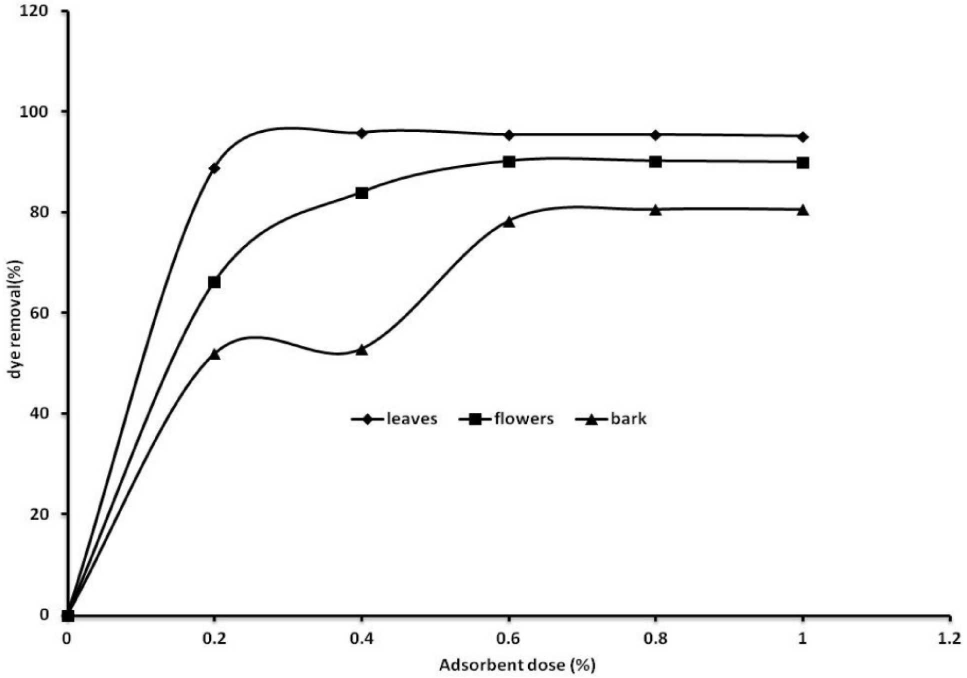

Figure 3 : Effect of adsorbent dosage on dye removal by leaves, flowers and bark of *Delonix regia* (adsorbent dose = 0.4 %; pH= 7.0). Values are means of triplicate determinations.

at 150 mg L^{-1} dye solution. As the initial amount of dye in the water enhanced, adsorption efficiency of leaves, flowers and bark decreased (Figure 4).

COD reduction

The COD removal from the methylene blue solution by leaves, flowers and bark material was evaluated at 100 mg L^{-1} of dye concentration; adsorbent dose 0.4% and pH 7.0. The reduction in COD was 75.8%, 61.7% and 48.7% by using leaves, flowers and bark adsorbents, respectively (Figure 5).

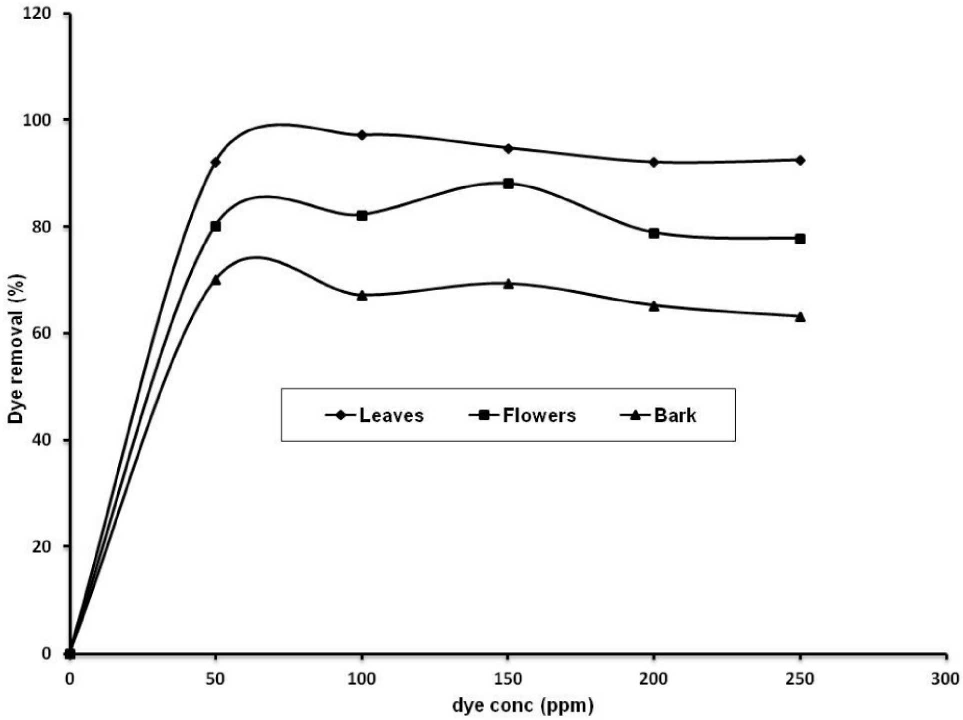

Figure 4 : Effect of methylene blue concentration on its removal by leaves, flowers and bark of *Delonix regia* (adsorbent dose = 0.4 %; pH= 7.0). Values are means of triplicate determinations.

Analysis of data using adsorption models

To fit the equilibrium adsorption data, the five mainly adsorption isotherm models were employed, which included the Langmuir, Freundlich, Florry-Huggins, Temkin and Dubinin-Radushkevich models.

Langmuir isotherm model

The Langmuir isotherm model presumes monolayer coverage of adsorbate on a homogeneous surface of adsorbent. It is usually adapted for specific homogeneous sites within the adsorbents. The Langmuir isotherm is described by the following linear equation[32].

$$\frac{C_e}{q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m} \qquad (1)$$

Where C_e (mg L^{-1}) is the amount of dye at equilibrium, q_e (mg g^{-1}) indicates the quantity of adsorbate adsorbed per unit mass of adsorbent, whereas X_m and K_L are the Langmuir constants associated to adsorption capability and rate of adsorption, respectively.

The corresponding parameters of Langmuir isotherms for methylene blue adsorption onto leaves, flowers and bark were shown in TABLE 1. The 'X_m' values were 90.91, 129.87 and 117.65 mg g^{-1} for leaves, flowers and bark, respectively. The values of 'K_L' for methylene blue were 0.073, 0.0104, and 0.0054 L g^{-1} for leaves, flowers and bark adsorbents, respectively. The 'K_L' is adsorption equilibrium constant linked to apparent energy of adsorption. The correlation coefficient value (R^2) is impending to one, clearly indicating that Langmuir isotherm holds good to show adsorption of methylene blue dye on leaves, flowers and bark. The data signified the homogeneous distribution of active site onto the adsorbent surface.

Freundlich isotherm model

The Freundlich isotherm model was used to determine the adsorption strength of the adsorbate on the adsorbent surface. The Freundlich isotherm is illustrated by following equation[33].

$$\log q_e = \frac{1}{n} \log C_e + \log k \qquad (2)$$

Where q_e is the concentration of dye adsorbed at equilibrium (mg g^{-1}) and C_e represents the equilibrium concentration of the dye. *K* and *n* are Freundlich constants, *n* indicates how favorable the adsorption process is, and *K* (mg g^{-1} (L mg^{-1}) $1/n$) is the adsorption capability of the adsorbent. The $1/n$ is slope ranged between 0

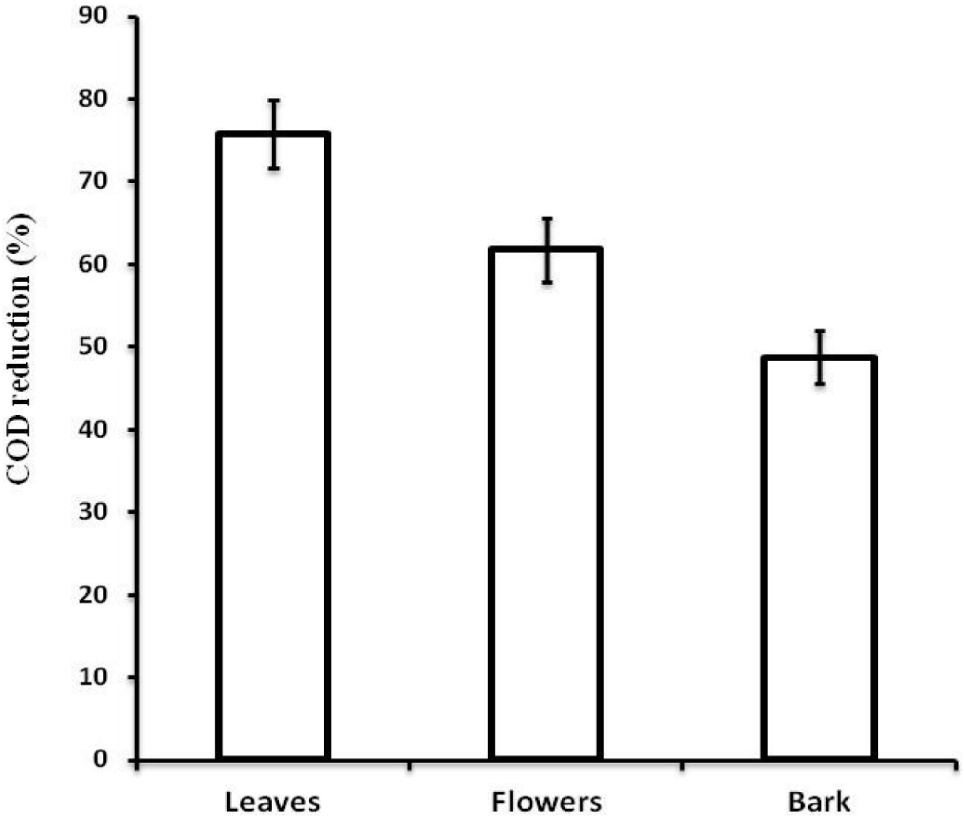

Figure 5 : Effect of different biosorbents on COD reduction in aqueous solution of methylene blue (dye concentration 100 mg L^{-1}; adsorbent dose 0.4%; pH = 7.0; agitation time 3h). Values are means of triplicate determinations.

and 1 and showed adsorption intensity.

For all the isotherms studied, the isotherm constants and the correlation coefficients R^2 are shown in TABLE 1. The *K* values were 15.070, 2.832 and 1.395 L g^{-1} for leaves, flowers and bark, respectively. The values of '*n*' for methylene blue adsorption were, 2.721, 1.467 and 1.384 for leaves, flowers and bark, respectively, indicating the adsorption strength of these plant materials.

The Florry–Huggins isotherm model

To find out the level of surface coverage characteristic of the adsorbate on the adsorbent, the Florry–Huggins isotherm model was used. Florry-Huggins linearized equation is represented as.

$$\log\frac{\theta}{C_o} = \log K_{FH} + n\log(1-\theta) \tag{3}$$

Where *n* is number of adsorbate molecules approaching adsorbent, K_{FH} is equilibrium constant, C_o is initial adsorbate concentration and $\theta = (1 - C_e / C_o)$ is limit of surface coverage. A lesser value of '*n*' designates lower number of sorbate molecules whereas a greater value of '*n*' is indication of higher number of sorbate molecules residing in active sites of sorbent. K_{FH} represents efficiency of biomass and a higher value of K_{FH} indicates most efficient adsorbent.

Values of *n* obtained in this study were not very close with experimental *q* values (TABLE 1). Greater values of 'n' in case of leaves material revealed that this material was more proficient than flowers and bark material for dye elimination. Values of K_{FH} showed that leaves were more efficient than flowers and bark. These results revealed that Florry–Huggins isotherm plot is not favorable to show the sorption. However, values of correlation coefficients as 0.9829 in case of leaves showed a linear relationship between Florry-Huggins isotherm models and leaves adsorbent.

Temkin isotherm model

Temkin isotherm plot evaluates the adsorption ability of sorbent for sorbate. When evaluated with respect to coefficient of determination (R^2), Temkin isotherm model indicated to be favorable for fitness to the experimental data.

Temkin isotherm equation can be illustrated as[34]

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \qquad (4)$$

Where *R* is universal gas constant (KJ mol^{-1} K^{-1}), *T* is temperature (K), K_T (dm^3 g^{-1}) is isotherm sorption potential and b_T (KJ mol^{-1}) is heat of sorption.

Values of K_T (dm^3 g^{-1}) for leaves biomass showed that model favors the experimental data of leaves biomass. Order of b_T values was in coincide with the experimental data because heat of sorption of the molecules declines linearly with coverage due to sorbate and sorbent interactions and lower values of b_T for leaves biomass revealed this biosorbent is more favorable (TABLE 1).

Dubinin-Radushkevich isotherm model

The Dubinin-Radushkevich model explains the unique porosity of the biomass and apparent energy of adsorption. The equation for Dubinin-Radushkevich isotherm is as below[35].

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e) \qquad (5)$$

Where B_D is free energy of sorption per mole of sorbate, *R* is universal gas constant (KJ mol^{-1} K^{-1}), T is temperature (K), C_e is equilibrium dye concentration (mg L^{-1}) and q_D is Dubinin-Radushkevich constant indicating the sorption ability of adsorbent.

The 'B_D' for the biomass towards the dye were less than unity showing that sorption of dye by leaves, flowers and bark material was significant (TABLE 1). The *q*D and R^2 values acquired from isotherm data supported the fitness of model to leaves, flowers and bark adsorbents.

Kinetic modeling

In this study, pseudo-first-order and pseudo-second-order kinetics have been used to explain sorption rate. Linearized form of pseudo-first-order equation can be written as.

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}\, t}{2.303} \qquad (6)$$

and linearized pseudo-second-order equation is

$$\frac{t}{q} = \frac{1}{k_{2,ads}\, q_e^{2}} + \frac{t}{q_t} \qquad (7)$$

Where q_e and q_t indicate adsorption capacity values at equilibrium and time t, respectively. $k_{1,ads}$ and $k_{2,ads}$ represent pseudo-first-order and pseudo-second-order rate constants. These values can be calculated from slope and intercept. A higher value of R^2 for pseudo-second-order model than pseudo-first-order kinetic model suggestes pseudo-second-order kinetic model is favorable to explain sorption rate.

The kinetics of dye adsorption onto leaves, flowers and bark of *Delonix regia* were studied by applying

TABLE 1 : A comparison of different equilibrium models to explain sorption behavior of *Delonix regia* leaves, flowers and bark adsorbents

Equilibrium models	Parameters	Adsorbents		
		Leave	Flower	Bark
Langmuir isotherm model	K_L (dm^3 g^{-1})	0.073	0.0104	0.0054
	X_m (mg g^{-1})	90.91	129.87	117.65
	R^2	0.9852	0.9902	0.9923
Freundlich isotherm model	n	2.721	1.467	1.384
	K (dm^3 g^{-1})	15.07	2.832	1.395
	R^2	0.973	0.9831	0.988
Florry-Huggins isotherm model	n	0.8735	3.1734	50.246
	K_{FH}	5.198×10^{-5}	3.45×10^{-5}	2.069×10^{-5}
	R^2	0.9829	0.9149	0.9324
Temkin isotherm model	b_T (kj mol^{-1})	167.89	99.93	117.19
	K_T (dm^3 g^{-1})	3.418	0.01009	0.00266
	R^2	0.9811	0.9714	0.9686
Dubinin-Radushkevich isotherm model	B_D (mol^2 $kj^{2\ -1}$)	0.00055	0.0038	0.0065
	q_D (mg g^{-1})	67.98	74.55	61.26
	R^2	0.8915	0.9271	0.9263

TABLE 2 : A comparison of different kinetic models to explain sorption rate of leaves, flowers and bark adsorbents

Sorbent dose	Kinetic model	Parameters	Adsorbents		
			Flowers	Leaves	Bark
0.2 g	Pseudo 1st Order Kinetic model	$K_{1,ads}$ (min^{-1})	0.0269	0.0578	0.0532
		q_e (mg g^{-1})	146.68	308.88	203.28
		R^2	0.8922	0.9869	0.8714
	Pseudo 2nd Order Kinetic model	$K_{2,ads}$ (g mg^{-1} min^{-1})	0.0002	0.000232	0.00031
		q_e (mg g^{-1})	238.09	312.5	188.68
		R^2	0.992	0.9892	0.9903
0.4 g	Pseudo 1st Order Kinetic model	$K_{1,ads}$ (min^{-1})	0.058	0.0568	0.0688
		q_e (mg g^{-1})	120.50	70.29	60.21
		R^2	0.84	0.9034	0.7536
	Pseudo 2nd Order Kinetic model	$K_{2,ads}$ (g mg^{-1} min^{-1})	0.00082	0.001427	0.0025
		q_e (mg g^{-1})	142.85	153.85	86.21
		R^2	0.9979	0.9988	0.999
0.6 g	Pseudo 1st Order Kinetic model	$K_{1,ads}$ (min^{-1})	0.0373	0.03846	0.0472
		q_e (mg g^{-1})	19.78	13.69	12.03
		R^2	0.9969	0.9951	0.8296
	Pseudo 2nd Order Kinetic model	$K_{2,ads}$ (g mg^{-1} min^{-1})	0.0038	0.005976	0.0064
		q_e (mg g^{-1})	91.74	101.01	83.33
		R^2	0.9999	1.000	0.9998
0.8 g	Pseudo 1st Order Kinetic model	$K_{1,ads}$ (min^{-1})	0.0658	0.0433	0.038
		q_e (mg g^{-1})	23.44	7.577	2.44
		R^2	0.9405	0.9858	0.9484
	Pseudo 2nd Order Kinetic model	$K_{2,ads}$ (g mg^{-1} min^{-1})	0.00629	0.0127	0.0341
		q_e (mg g^{-1})	71.94	75.76	63.29
		R^2	0.9997	1.000	1.000
1.0 g	Pseudo 1st Order Kinetic model	$K_{1,ads}$ (min^{-1})	0.0522	0.0688	0.0428
		q_e (mg g^{-1})	11.91	13.34	9.02
		R^2	0.894	0.9655	0.9549
	Pseudo 2nd Order Kinetic model	$K_{2,ads}$ (g mg^{-1} min^{-1})	0.00974	0.0136	0.00999
		q_e (mg g^{-1})	59.17	62.11	56.18
		R^2	0.9999	1.000	1.000

the pseudo-first and second order kinetic models. The values for rate constants $K_{1,ads}$ (min^{-1}), q_e (mg g^{-1}) and correlation coefficients are represented in TABLE 2. The data indicated a good acquiescence with the pseudo-second order model with correlation coefficient greater than 0.998 and the predicted values of *qe* nearly coincide the experimental values thus indicating the goodness of the plot.

CONCLUSION

It was concluded that leaves of *Delonix regia* were found to be more efficient adsorbent for the elimination of methylene blue dye from water than flowers and bark. Leaves of *Delonix regia* can be explored on industrial scale for the treatment of wastewater containing methylene blue dye. However, pH of effluent, amount of adsorbent, agitation time and dye concentration should be optimized to get maximum removal of dye from effluent.

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