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Research Article

ADSORPTION CAPACITIES OF LOW-COST ADSORBENT OF ACTIVATED CARBON *MERREMIA EMARGINATA* FOR REMOVAL OF METHYLENE BLUE

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ABSTRACT

In this research, the adsorption behavior of Methylene Blue dye from synthetic aqueous solution onto Activated Carbon *Merremia Emarginata* (ACME) was investigated. The effect of crucial parameters such as agitation time, pH, adsorbent dosage and other ionic concentration was studied. The equilibrium isotherm models, thermodynamic parameters and kinetic data have been evaluated. Adsorption equilibrium isotherms were expressed by Freundlich and Langmuir adsorption models and it was found that Langmuir adsorption model fits the experimental data better than Freundlich model. The adsorption can be best described by the pseudo second-order kinetic model. The objective of the present work suggests the ACME may be utilized as a low cost adsorbent for Methylene Blue dye removal from synthetic aqueous solution.

Keywords: Activated Carbon *Merremia Emarginata* (ACME), Methylene Bluedye (MB), Adsorption isotherm; Kinetics, Equilibrium models.

1. INTRODUCTION

Severe environmental pollution gets up as a result of the industrial accomplishments and technology expansion due to waste streams of dyes from several industries which are poured into rivers without treatment. Numerous dyes are used in various industries such as polymer, printing, paper and pulp, textile, and cosmetics to increase the aesthetics of their final products. Most of these dyes are hazardous due to their acute and chronic health effects, some being classified as carcinogenic. The removal of these dyes from aqueous solution has a significant responsiveness over the past decades to reduction their impact on the environment [1]. Several physical and chemical methods have been technologically advanced for the removal of organic dyes from aqueous solution [2, 3]. Physical methods, primarily adsorption on many supports were recognized to be a promising and in effect process to remove dyes from aqueous solution completely [4-6]. Activated carbon is the most widely used adsorbent and can be prepared by acid/thermal activation.

Now this study, we have reported workdesigned the possibility of using stem of a *Merremia Emarginata* plant as an adsorbent for the adsorption of organic dye such as Methylene Blue from synthetic aqueous solution. A study of the literature shows that no work has been done to *Merremia Emarginata* as an adsorbent.

2. MATERIAL AND METHODS

All chemicals used were of analytical quality and used as obtained.

2.1. Activated carbon

The *Merremia Emarginata* bio materials were collected from agriculture ground at district of Mayiladuthurai, then the stem was washed with distilled water several times to remove the dust and dirt and successively dried in a hot air oven at 110°C. After that, carbonization of biomaterial was done by adding w/v ratio of Conc. H_2SO_4 and the carbon was activated at >900°C for 6hrs using muffle furnace.

2.2. Batch Method

The batch process [7] was made active to evaluate the factors such as contact time, dose of activated carbon, initial pH of the solution and strength of other ion concentrations to remove MB dye onto activated carbon *Merremia Emerginata* (ACME). The after process of the residual solution was analyzed using UV-Visible spectrophotometer at 470 nm. The amount of adsorption and removal percentage at specific time t, can be determined using the following formulations,

$$q_t = V \times \frac{(C_0 - C_t)}{w} \quad (1)$$

$$\%\ Removal = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (2)$$

Where, q_t is the mass of adsorbed dye per unit mass of adsorbent (mg g^{-1}), V is the volume of the treated solution (mL), C_0 and C_t are the initial and actual concentration (g dm^{-3}) of dye at time, respectively 'w' is the mass of adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Primary factors of batch adsorption experiments

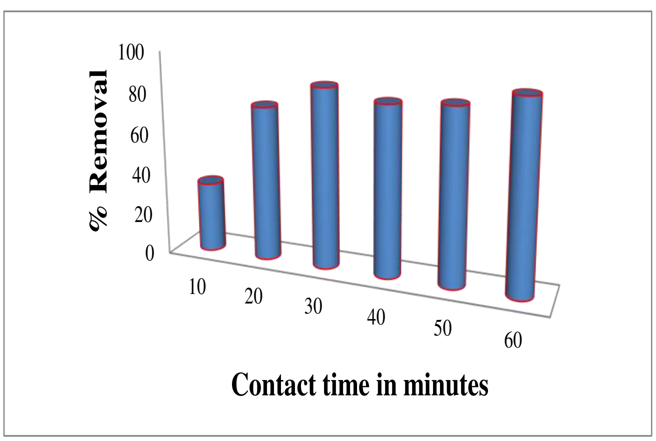
The function of conduct time [8] was estimated for adsorption of MB dye onto ACME, the results were as shown in fig.1 and the equilibrium data are given in Table 1. The fig. shows that the initial rise rate was rapid after the maximum absorption was completed in 30 min. The equilibrium reached in 50 min. therefore; an equilibrium period 60 min. was selected for all experiments.

The effect of dosage of activated carbon [9] was studied by varying the adsorbent dose like following 10, 25, 50, 100, 200 and 250mg to 50mL of solution. The percentage of adsorption increased with increases in the dosage of ACME, which is attributed to increased carbon surface area and the availability of more adsorption sites. The results obtained from this study are shown in fig. 2, which reveals that the direct and equilibrium capacities of MB dye are functions of the dosage of ACME and 25 mg was enough for each experiment.

Adsorption process was highly depending on the pH of treated solution; where the effect of pH [10] was predict using pH range of 3-9 for removal of MB dye from synthetic aqueous solution. The percentage removal increased around 40% to 91% whereas it decreased slowly after pH 6.8 that is pH_{zpc} (Zero point charge), as shown in fig. 4. The pH_{zpc} was one of the most reasonable characters for removal of dye, where the surface of ACME becomes electrically zero for the reason that maximum removal exist at pH 6.8.

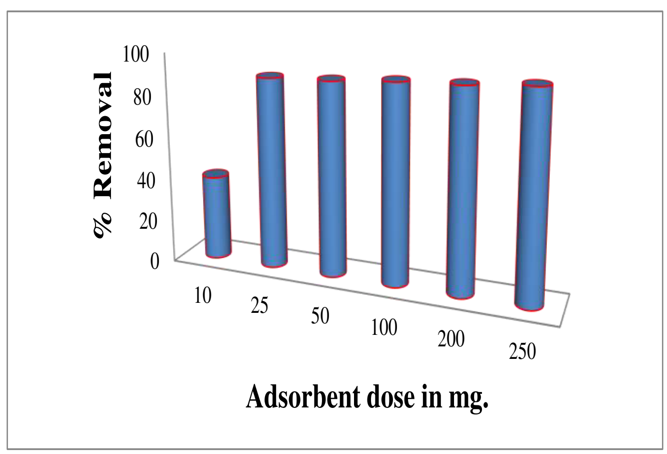
Table 1: Equilibrium parameters for the adsorption of MB onto ACME

C_0	Ce (Mg/L)				q_e (Mg/L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	2.688	2.526	2.156	2.150	44.625	44.948	45.687	45.700	89.250	89.895	91.374	91.400
50	6.988	6.452	5.935	4.839	86.025	87.095	88.130	90.322	86.025	87.095	88.130	90.322
75	12.944	11.720	10.213	9.462	124.111	126.560	129.575	131.075	82.741	84.374	86.383	87.384
100	18.858	17.245	16.358	15.344	162.285	165.509	167.283	169.311	81.142	82.755	83.642	84.656
125	27.950	26.980	26.385	24.818	194.100	196.039	197.230	200.364	77.640	78.416	78.892	80.145



[MB]=25mg/L; Temperature 30°C; Adsorbent dose=0.025g/50mL.

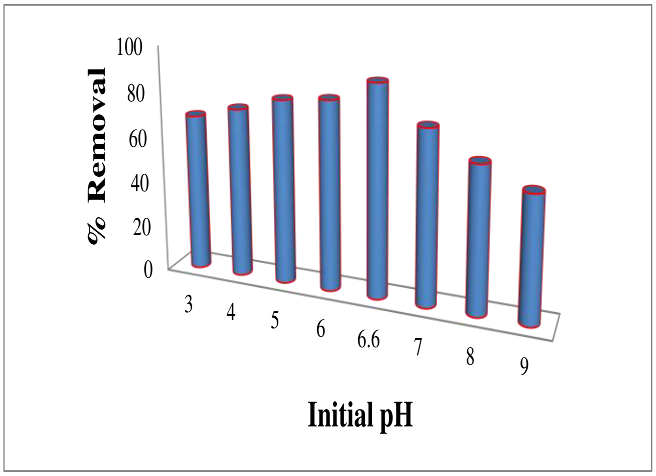
Fig. 1: Effect of Contact Time on the Removal of MB dye



[MB]=25mg/L; Temperature 30°C;Contact Time 60 min.

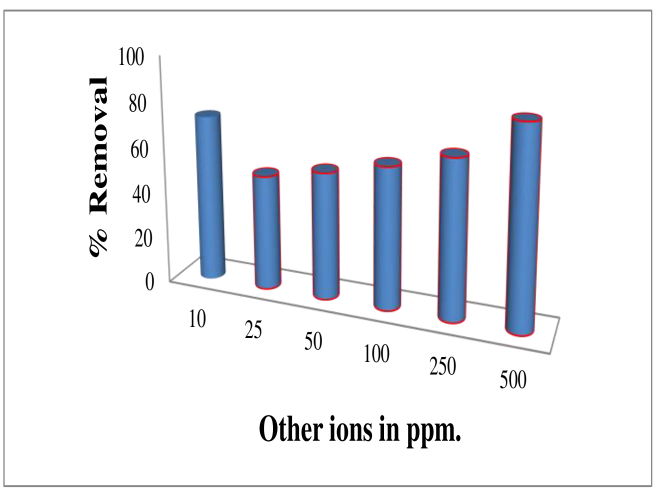
Fig. 2: Effect of Adsorbent dose on the Removal of MB dye

Contaminated water may contain various ions, so the effect of other ions [11] should be examined. Ion strength was studied using various concentrations of chloride ion solutions, where chloride ion were added to 50 mL of MB dye solutions and the content was stirred for 60 min at 30°C. The results shown in fig.4 reveal that the low concentration of the chloride ion does not affect the percentage of absorption of MB dye onto ACME, while the concentration of the chloride ion increases, while the absorption by competition at the available surface sites of the sorbent increases, the percentage absorption decreases.



[MB]=25mg/L; Temperature 30°C; Adsorbent dose= 0.025g /50mL.

Fig. 3: Effect of Initial pH on the Removal of MB dye



[MB]=25mg/L; Contact time=60 min.; Adsorbent dose= 0.025g /50mL.

Fig. 4: Effect of other ionic strength on the removal of MB dye

3.2. Adsorption isotherm models

The Freundlich model [12, 13] representing the surface diversity of adsorbent is described by the following equation,

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \quad (3)$$

Where, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log q_e and log C_e for the adsorption of MB were as shown fig. 5.

The Langmuir adsorption isotherm [14, 15] equation which is valid for monolayer adsorption on to a surface is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol/L), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and $C_e$for the adsorption of MBon to ACME it's shown in fig. 6. The correction coefficient (R^2) values confirm good agreement our experimental results the values of the monolayer capacity (q_m) and equilibrium constant $K_L$has been calculated above equation and these data was given in table 2. The dimensionless separation factor R_L is one of the essential properties of the Langmuir isothermal model, which is expressed following the mathematical equation.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Where, C_o (mg/L) is the highest initial concentration of adsorbent and K_L (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$ -Unfavorable adsorption
$0 < R_L < 1$ -Favorable adsorption
$R_L = 0$ -Irreversible adsorption
$R_L = 1$ -Linear adsorption

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table 3.

3.3. Thermodynamic treatment of the adsorption process

Thermodynamics [16, 17] parameters related to adsorption studies, the effective free energy change equation given by the following expression,

$$\Delta G^0 = -RT\ln K_0 \quad (6)$$

$$\ln K_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

Where, ΔG° is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin, R is the universal gas constant (8.314 J mol/K) and K_0 is the equilibrium constant for the ratio between C_{solid} is the solid phase concentration at equilibrium (mg/ L) and C_{liquid} is the liquid phase concentration at equilibrium (mg/L) in addition ΔH° is the standard heat change of sorption (kJ/mol),ΔS° is standard entropy change (kJ/mol). These values are calculated from the plot of ln K_0 against 1 / T and are shown in table 4.

This result indicates that the ΔG° values were negative at all temperatures which suggests that physisorption is very favorable for the absorption of MB dye. Positive values of ΔH° show the endodermic nature of the adsorption and it governs the possibility of physical absorption. This is because in the case of physical absorption, as the temperature of the system increases, the amount of MB absorption increases, which negates the possibility of chemical changes. The low ΔH° value depicts MB dye is physisorbed onto adsorbent ACME.

3.4. Kinetic models

Pseudo-second-order [18] equations can be used assuming that the measured concentrations are equal to surface concentrations. The mathematical form of pseudo second order equation becomes,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (8)$$

Where, q_t (mgg^{-1}) is the amount of adsorbed dyes on the adsorbent at time t, q_e the equilibrium sorption uptake and k_2, (min^{-1}) is the rate constant of pseudo-second-order adsorption. The plot t/q_tagainst t gives a straightforward line says second order kinetic model is applicable then q_e and k_2 are determined from the slope and intercept of the plot, respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values shown in table 5.

Table 2: Freundlich and Langmuir isotherm parameter for the adsorption of MB onto ACME

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f(mg/g) (L/mg)$^{1/n}$	24.359	25.870	29.974	31.672
	n_f	1.5749	1.5750	1.6659	1.6570
	R^2	0.9972	0.9930	0.9892	0.9769
Langmuir	q_m(mg/g)	312.07	311.28	290.61	292.05
	K_L (L/mg)	0.0565	0.0627	0.0801	0.0885
	R^2	0.9822	0.9911	0.9934	0.9986

Table 3: Dimensionless separation Factor (R_l) for the adsorption of MB onto ACME

(C_0)	Dimensionless Separation Factor(R_L)			
	30°C	40°C	50°C	60°C
25	0.4144	0.3895	0.3331	0.3113
50	0.2614	0.2418	0.1999	0.1843
75	0.1909	0.1753	0.1427	0.1309
100	0.1503	0.1375	0.1110	0.1015
125	0.1240	0.1131	0.0908	0.0829

Table 4: Thermodynamic parameter for the adsorption of MB onto ACME

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
25	-5331.9	-5687.6	-6338.1	-6543.6	7.709	43.034
50	-4578.2	-4968.8	-5383.7	-6183.8	11.1963	51.808
75	-3948.4	-4388.2	-4961.3	-5358.0	10.62126	48.067
100	-3676.1	-4081.2	-4382.1	-4728.3	6.80141	34.649
125	-3135.9	-3357.1	-3540.5	-3863.3	4.00919	23.533

The Elovich model [19] equation is commonly expressed as,

$$q_t = \frac{1}{\beta} ln\,(\alpha\beta) + \frac{1}{\beta} lnt \qquad (9)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g/mg) during any one experiment. If MB adsorption fits with the Elovich model, a plot of $q_t$vs.ln (t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β) ln (αβ). The Elovich model parameters α, β, and correlation coefficient (R^2) are summarized in table 5. This model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the ASCC adsorbent.

The kinetic data were further analyzed using the intra-particle diffusion model [20] based on the following equation.

$$log\,R = log\,K_{id} + \alpha\,log\,t \qquad (10)$$

Where, k_{id} is the intra-particle diffusion rate constant and its related to the thickness of the boundary layer. According to above equation a plot of log R versus log t gives a straight line that indicates the adsorption mechanism follows the intra-particle diffusion process and the evidence of correlation co-efficient values are close to unity (R^2→1).

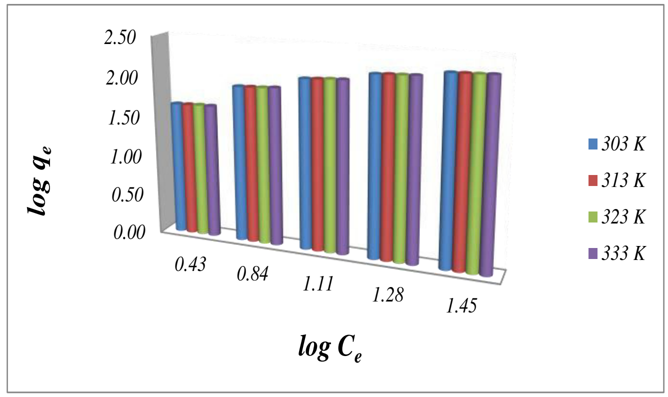


Fig. 5: Freundlich adsorption isotherm for the removal of MB dye

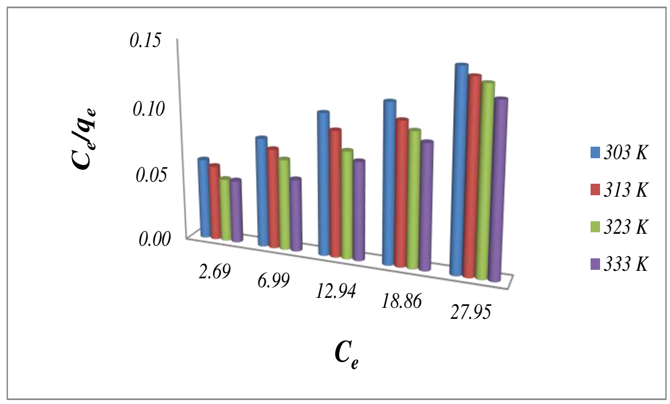


Fig. 6: Langmuir adsorption isotherm for the removal of MB dye

Table 5: The kinetic parameters for adsorption of MBonto ACME

C_0	Temp°C	Pseudo second order				Elovich model			Intra-particle diffusion		
		q_e	k_2	R^2	H	α	β	R^2	α	K_{id}	R^2
25	30	49.8820	2.36E-03	0.9930	5.8749	4.3E+01	1.34E-01	0.9592	0.1934	39.6354	0.9741
	40	49.7334	2.61E-03	0.9940	6.4545	6.1E+01	1.42E-01	0.9592	0.1786	42.4661	0.9731
	50	49.5020	3.31E-03	0.9959	8.1202	1.8E+02	1.66E-01	0.9592	0.1466	49.3470	0.9708
	60	49.4991	3.33E-03	0.9959	8.1550	1.8E+02	1.67E-01	0.9592	0.1460	49.4739	0.9708
50	30	92.7192	1.75E-03	0.9928	15.0421	4.4E+02	9.32E-02	0.9058	0.1389	47.4515	0.9230
	40	93.3452	1.93E-03	0.9950	16.8234	7.0E+02	9.75E-02	0.9288	0.1300	50.0893	0.9431
	50	94.9842	2.15E-03	0.9979	19.3559	8.3E+02	9.64E-02	0.9510	0.1282	52.1250	0.9565
	60	94.7850	2.46E-03	0.9948	22.0690	4.9E+03	1.19E-01	0.8810	0.1014	58.2567	0.8960
75	30	130.2464	1.84E-03	0.9954	31.2644	1.4E+04	9.29E-02	0.8541	0.0935	55.1216	0.8674
	40	133.9396	2.01E-03	0.9986	36.0520	9.5E+03	8.54E-02	0.9402	0.0988	56.2292	0.9447
	50	138.1682	1.71E-03	0.9988	32.7088	3.0E+03	7.33E-02	0.9677	0.1137	54.2235	0.9720
	60	137.5430	2.44E-03	1.0000	46.2274	1.7E+04	8.63E-02	0.9889	0.0942	59.8641	0.9859
100	30	171.4084	1.82E-03	0.9998	53.5707	8.6E+03	6.33E-02	0.9734	0.1040	53.6531	0.9704
	40	174.6058	1.71E-03	1.0000	52.1237	8.3E+03	6.21E-02	0.9905	0.1044	54.3652	0.9869
	50	176.0450	1.82E-03	1.0000	56.4344	1.2E+04	6.37E-02	0.9820	0.1005	55.9460	0.9776
	60	178.1228	1.82E-03	1.0000	57.7017	1.4E+04	6.37E-02	0.9835	0.0991	56.9461	0.9797
125	30	204.0452	1.08E-03	0.9937	44.9637	8.5E+03	5.41E-02	0.8589	0.1037	49.4465	0.8756
	40	206.2853	1.06E-03	0.9939	45.1226	8.1E+03	5.32E-02	0.8635	0.1043	49.8426	0.8801
	50	206.7506	1.13E-03	0.9944	48.4469	1.5E+04	5.64E-02	0.8563	0.0974	51.6271	0.8720
	60	210.4413	1.04E-03	0.9930	46.1522	9.1E+03	5.27E-02	0.8425	0.1031	51.0868	0.8597

4. CONCLUSION

Batch adsorption technique was conducted on the removal of MB dye onto ACME from aqueous solution. The removal efficiency was associated with primary parameters such as contact time, dose of activated carbon, initial solution pH, and strength of other ion concentration. Adsorption data fitted well with the Freundlich and Langmuir models however, Langmuir isotherm displayed a better fitting model than Freundlich isotherm because of the higher correlation coefficient that the former exhibited, thus, indicating to the applicability of monolayer coverage of the dye on the surface of adsorbent. Activated Carbon *Merremia Emarginata* (ACME) potentially provide a less expensive raw material and a highly effective adsorbent for water treatment.

Conflict of Interest

None declared.

5. REFERENCES

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