Eco. Env. & Cons. 28 (December Suppl. Issue) : 2022; pp. (S425-S430)

ISSN 0971–765X

DOI No.: http://doi.org/10.53550/EEC.2022.v28i08s.064

Activated Carbon *Merremia emarginata* Adsorption Capacities of Low-cost Adsorbent for Removal of Methylene Blue

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(Received 17 July, 2022; Accepted 20 September, 2022)

ABSTRACT

The effectiveness of synthetic aqueous Methylene Blue dye adhering to Activated Carbon *Merremia emarginata* (ACME) was investigated in this study. The effects of important variables on the outcomes, such as agitation time, pH, adsorbent dosage, and other ionic concentration, were assessed. It has actually been done to evaluate the equilibrium isotherm models, thermodynamic variables, and kinetic data. Adsorption equilibrium isotherms were expressed using the Freundlich and Langmuir adsorption models, although it was found that the Langmuir model more accurately reflected the experimental results. The pseudo second-order kinetic model can also make the adsorption more understandable. The goal of the survey was to determine whether it was possible to remove Methylene Blue dye from synthetic aqueous solution utilising ACME as a cheap adsorbent.

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

Introduction

As a consequence of technological and industrial progress, there is a serious surge in environmental contamination from dye waste streams that are discharged into rivers without being treated. Several dyes are used in a range of industries, including polymer, printing, paper and pulp, textile, and cosmetics, to enhance the aesthetics of their finished products. Most of these colours are harmful due to their effects on both short- and long-term health; some have even been connected to cancer. The impact of these dyes on the environment has greatly decreased over the past few decades as a result of their removal from aqueous solutions (Aksu, 2005). Physical and chemical advancements have been made in the removal of organic dyes from aqueous solutions (Arivoli *et al.,* 2008). One physical method that has been shown to be efficient in completely eliminating colours from aqueous solutions is adsorption on a variety of substrates (Arthur *et al*., 2009; Demirbas *et al*., 2013). Activated carbon, which is created through acid/thermal activation, is the most common adsorbent. Using the stem of a *Merremia emarginata* plant as an adsorbent, research was done to test if an organic dye like methylene blue could be absorbed from a synthetic aqueous solution. A review of the literature revealed that

Merremia emarginata hasn't been investigated as an adsorbent.

Materials and Methods

Every chemical seems to be of analytical purity and administered exactly as it was obtained.

Activated carbon

The Mayiladuthurai district's agricultural fields were where the *Merremia emarginata* biomaterials were collected. To remove any last bits of dust and dirt, the stem was repeatedly cleansed with distilled water. After that, it was gradually dried in a hot air oven at 110 °C. After that, the carbon was activated in a muffle furnace at a temperature of >90 ^{0}C for 6 hours after the biomaterial was carbonised by adding a w/v ratio of condensed H_2SO_4.

Batch Method

The batch process (Duwiejuah *et al*., 2017) was engaged to evaluate factors such as contact time, activated carbon dose, starting solution pH, and strength of other ion concentrations to remove MB dye from activated carbon *Merremia emerginata* (ACME). The after-process of the residual solution was investigated with a UV-Visible spectrophotometer at 470 nm. The percentage of adsorption and removal at a specific time t can be estimated using the following formulae:

$$q_t = (C_o - C_e)\, V/M \quad .. (1)$$

$$\% \text{ Removal} = (C_o - C_t) \times 100/C_o \quad .. (2)$$

Where C_i and C_t are the initial and liquid phase concentrations of Metals/dyes ions at time 't' (mg L^{-1}) q is the amount of metals/dyes adsorbed on the adsorbent at any time (mg g^{-1}), M(g) the mass of the adsorbent sample used and V the volume of the metals/dyes solution.

Results and Discussion

Primary factors of batch adsorption Experiments

The function of conduct time (Hakan Demiral and Gül Gündüzoglu, 2010) was established for the adsorption of MB dye onto ACME; the results are shown in Fig. 1 and the equilibrium values are given in Table 1. The chart shows how the initial rate of increase was rapid following the achievement of the maximum absorption in 30 minutes. Because the equilibrium was reached in 50 minutes, a 60-minute equilibrium time was adopted for all trials. The effect of activated carbon dosage was investigated by varying the adsorbent dose, such as 10, 25, 50, 100, 200, and 250 mg to 50 mL of solution (Hema and Arivoli, 2007). The percentage of adsorption increased as the dosage of ACME was raised because more adsorption sites are available and there is more carbon surface area. The results of the study are shown in Figure 2, which shows how the dosage of ACME affects the direct and equilibrium properties of the MB dye and how 25 mg was adequate for each experiment. The pH range of the treated solution was crucial for the adsorption process and for the removal of MB dye from synthetic aqueous solution (3–9). The percentage elimination increased by around 40% to 91%, as shown in Fig. 4, but began to

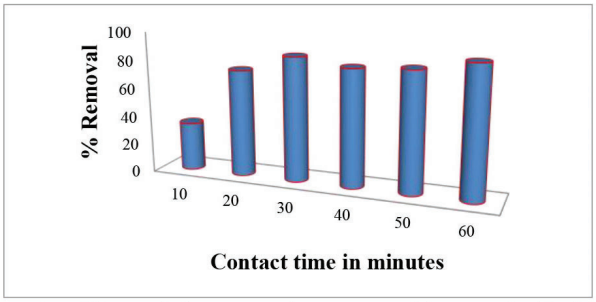

Fig. 1. Effect of Contact Time on the Removal of MB dye [MB] = 25 mg/l; Temperature 30 °C; Adsorbent dose=0.025 g/50 ml

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	2.15	44.625	44.948	45.687	45.7	89.25	89.895	91.374	91.4
50	6.988	6.452	5.935	4.839	86.025	87.095	88.13	90.322	86.025	87.095	88.13	90.322
75	12.944	11.72	10.213	9.462	124.111	126.56	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	27.95	26.98	26.385	24.818	194.1	196.039	197.23	200.364	77.64	78.416	78.892	80.145

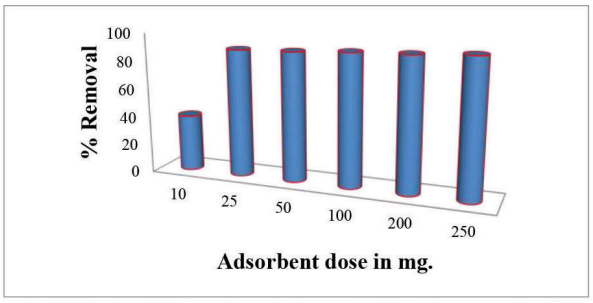

Fig. 2. Effect of Adsorbent dose on the Removal of MB dye
[MB]=25 mg/l; Temperature 30 °C; Contact Time 60 min.

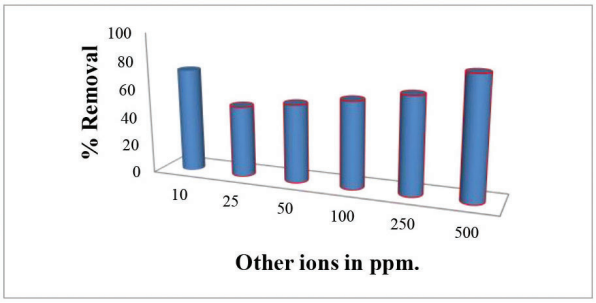

Fig. 4. Effect of other ionic strength on the removal of MB dye
[MB]=25mg/l; Contact time=60 min.; Adsorbent dose=0.025g/50 ml.

decline at pH 6.6, or pH zpc (Zero point charge). The pHzpc was one of the most sensible parameters for dye removal, when the surface of ACME becomes electrically zero, because maximum dye removal occurs at pH 6.6. Since contaminated water may contain a range of ions, it is crucial to consider how other ions may affect the situation (Jayajothi *et al.*, 2021). By adding various amounts of chloride ions to 50 ml of MB dye solutions and stirring the mixture for 60 minutes at 30 °C, the ion strength was examined. The results in Fig. 4 show that the low concentration of the chloride ion has no effect on the percentage of MB dye absorption onto ACME, but that as the concentration of the chloride ion rises, competition at the available surface sites of the sorbent increases and the percentage absorption decreases.

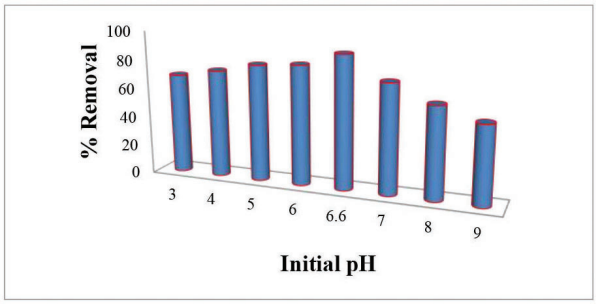

Fig. 3. Effect of Initial pH on the Removal of MB dye
[MB]=25 mg/l; Temperature 30 °C; Adsorbent dose=0.025 g/50 ml.

Adsorption isotherm models

The Freundlich model representing the surface diversity of adsorbent is described by the following equation,

$$\log q_e = \log K_f + 1/n_f \log c_e \quad .. (3)$$

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. 2.

The Langmuir adsorption isotherm (Li *et al.*, 2010) equation which is valid for monolayer adsorption on to a surface is given below:

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad .. (4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e ($molL^{-1}$), qm (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. Figure 2 depicts the graphs created between Ce/qe and Ce for the adsorption of MB on to ACME

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	25.87	29.974	31.672
	n	1.5749	1.575	1.6659	1.657
	R^2	0.9972	0.993	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

(b). The values of the correction coefficient (R2) values show that our experimental findings and the values of the monolayer capacity (qm) and equilibrium constant KL are in good agreement. These data are shown in Table 2. One of the fundamental characteristics of the Langmuir isothermal model, which is stated by the following mathematical equation, is the dimensionless separation factor RL.

$$R_L = 1/1+K_L C_0 \quad .. (5)$$

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.

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	0.39	0.333	0.311
50	0.2614	0.242	0.2	0.184
75	0.1909	0.175	0.143	0.131
100	0.1503	0.138	0.111	0.102
125	0.124	0.113	0.091	0.083

Thermodynamic treatment of the adsorption process

Thermodynamics (Moaaz, K., *et al.* 2020) parameters related to adsorption studies, the effective free energy change equation given by the following expression,

$$\Delta G° = -RT\ln K_0 \quad .. (6)$$

$$\ln K_0 = \Delta S°/R - \Delta H°/RT \quad .. (7)$$

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), ΔΔS° 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 5. This finding suggests that physisorption is highly advantageous for the absorption of MB dye because the G° values were negative at all temperatures, according to the results. Positive values of H° indicate that the adsorption is endodermic, and they control whether physical absorption is possible. This is due to the fact that in the case of physical absorption, the amount of MB absorption increases as the system's temperature rises, eliminating the potential of chemical modifications. The low H° value shows that the MB dye has physically sorbed onto the adsorbent ACME.

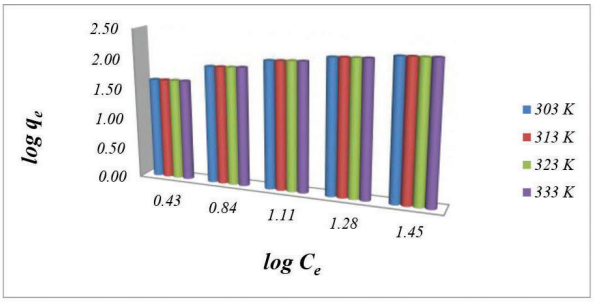

Fig. 3.2 (a) Freundlich adsorption isotherm for the removal of MB dye

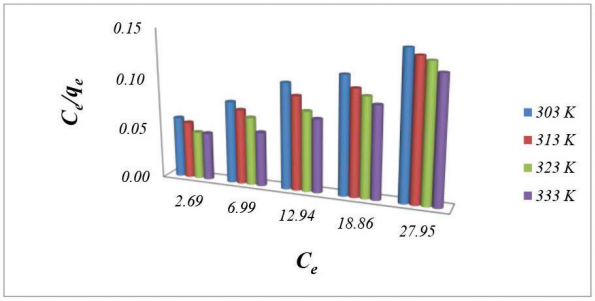

Fig. 3.2 (b) Langmuir adsorption isotherm for the removal of MB dye

Kinetic models

Pseudo-second-order (Soltzberg *et al*., 2017) equations can be used assuming that the measured concentrations are equal to surface concentrations. The mathematical form of pseudo second order equation becomes,

$$t/q_t = 1/k_2.q_e^2 + t/q_e \quad .. (6)$$

Where, qt (mgg^{-1}) is the amount of adsorbed dyes on the adsorbent at time t, q_e the equilibrium sorp-

tion uptake and k_2, (min-1) is the rate constant of pseudo-second order adsorption. The plot t/qt against t gives a straightforward line says second order kinetic model is applicable then qe 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 Tables 3-4.

The Elovich model (Vijayakumaran *et al.* 2009) equation is commonly expressed as,

$$q_t = 1/\beta \ln \alpha\beta + 1/\beta \ln t \quad .. (7)$$

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 qtvs. 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 (R2) are summarized in Table 3-4. 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 intraparticle diffusion model (Xin-jiang *et al.*, 2011) based on the following equation.

$$\text{Log } R = \log_{\text{Kid}} + \alpha \log t \quad .. (8)$$

Where, kid 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 coefficient values are close to unity (R2→1).

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

(C_0)	ΔG°				ΔH°	ΔS°	Ea	S*
	30°C	40°C	50°C	60°C				
25	-5331.9	-5687.6	-6338.1	-6543.6	7.709	43.034	6970.3	0.00676
50	-4578.2	-4968.8	-5383.7	-6183.8	11.1963	51.808	9877.61	0.00285
75	-3948.4	-4388.2	-4961.3	-5358	10.62126	48.067	9046.67	0.00477
100	-3676.1	-4081.2	-4382.1	-4728.3	6.80141	34.649	5641.86	0.02
125	-3135.9	-3357.1	-3540.5	-3863.3	4.00919	23.533	3162.62	0.064

Table 5. The kinetic parameters for adsorption of MB onto ACME

C_0	Temp °C	Pseudo second order				Elovich model			Intra-particle diffusion		
		q_e	k_2	R^2	H	a	b	R^2	C	K_{id}	R^2
25	30	49.882	0.00236	0.993	5.8749	43	0.134	0.9592	0.1934	39.6354	0.9741
	40	49.7334	0.00261	0.994	6.4545	61	0.142	0.9592	0.1786	42.4661	0.9731
	50	49.502	0.00331	0.9959	8.1202	180	0.166	0.9592	0.1466	49.347	0.9708
	60	49.4991	0.00333	0.9959	8.155	180	0.167	0.9592	0.146	49.4739	0.9708
50	30	92.7192	0.00175	0.9928	15.0421	440	0.0932	0.9058	0.1389	47.4515	0.923
	40	93.3452	0.00193	0.995	16.8234	700	0.0975	0.9288	0.13	50.0893	0.9431
	50	94.9842	0.00215	0.9979	19.3559	830	0.0964	0.951	0.1282	52.125	0.9565
	60	94.785	0.00246	0.9948	22.069	4900	0.119	0.881	0.1014	58.2567	0.896
75	30	130.246	0.00184	0.9954	31.2644	14000	0.0929	0.8541	0.0935	55.1216	0.8674
	40	133.94	0.00201	0.9986	36.052	9500	0.0854	0.9402	0.0988	56.2292	0.9447
	50	138.168	0.00171	0.9988	32.7088	3000	0.0733	0.9677	0.1137	54.2235	0.972
	60	137.543	0.00244	1	46.2274	17000	0.0863	0.9889	0.0942	59.8641	0.9859
100	30	171.408	0.00182	0.9998	53.5707	8600	0.0633	0.9734	0.104	53.6531	0.9704
	40	174.606	0.00171	1	52.1237	8300	0.0621	0.9905	0.1044	54.3652	0.9869
	50	176.045	0.00182	1	56.4344	12000	0.0637	0.982	0.1005	55.946	0.9776
	60	178.123	0.00182	1	57.7017	14000	0.0637	0.9835	0.0991	56.9461	0.9797
125	30	204.045	0.00108	0.9937	44.9637	8500	0.0541	0.8589	0.1037	49.4465	0.8756
	40	206.285	0.00106	0.9939	45.1226	8100	0.0532	0.8635	0.1043	49.8426	0.8801
	50	206.751	0.00113	0.9944	48.4469	15000	0.0564	0.8563	0.0974	51.6271	0.872
	60	210.441	0.00104	0.993	46.1522	9100	0.0527	0.8425	0.1031	51.0868	0.8597

Conclusion

A batch adsorption technique was used to remove MB dye from an aqueous solution onto ACME. The removal efficiency was influenced by the contact time, amount of activated carbon, pH of the starting solution, and intensity of other ion concentration. Both the Freundlich and Langmuir models could accurately predict the adsorption data, however the Langmuir isotherm performed significantly better than the Freundlich isotherm due to its higher correlation coefficient, demonstrating the usefulness of dye monolayer coverage on the adsorbent surface. Activated Carbon *Merremia emarginata* (ACME) may provide a less expensive raw material and a very effective adsorbent for the treatment of water.

Acknowledgement

I am extremely grateful to the Principal and personnel of the Chemistry Department at Poompuhar College in Melaiyur, Tamil Nadu, India, for allowing me to carry out the experimental part there.

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