Research Article

Adsorptive removal of methylene blue dye from aqueous solution by limonia acidissima rind biomass

N Ramulu[1*], V Thirumurugan[2], R Rajajeyaganthan[3]

[1]T. U. K. Art's college, Karanthai, Thanjavur, Tamilnadu, INDIA.
[2]A.V. V. M. Sri Pushpam College, Poondi, Thanjavur, Tamilnadu, INDIA.
[3]Thanthai Hans Roever College of Arts and Science, Perambalur, Tamilnadu, INDIA.
Email: ramaravindh1967@gmail.com

Abstract

Adsorptive removal of Methylene blue from aqueous solution was studied by adsorption on Wood apple rind (WAR-*Limonia acidissima* rind) Wastes. Kinetics study was carried out to observe the effects of various process parameters. The results follow kinetics of pseudo second order rate equation for the removal of Methylene blue by WAR. The suitability of the WAR adsorbent for removal of Methylene blue from aqueous solution was tested by fitting the adsorption data with two isotherms, namely Freundlich and Langmuir isotherms. The characteristic parameters for each isotherm have been determined. The Langmuir equation represented the best fit for the experimental data of WAR in removal of Methylene blue than the Freundlich isotherm equation. It was observed that WAR adsorbent is suitable for removal of Methylene blue from aqueous solution.

Keywords: Biosorption, Isotherm, Kinetics, *Limonia acidissima*, Methylene blue.

[*]**Address for Correspondence:**
Dr. N. Ramulu, T. U. K. Arts College, Karanthai, Thanjavur, Tamilnadu, INDIA.
Email: ramaravindh1967@gmail.com

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INTRODUCTION

Wastewaters discharged from different industries such as the textile, leather tanning, paper production, food technology, hair colorings, etc. are usually polluted by dyes. Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling[1] Many dyes and their breakdown products may be toxic for living organisms[2]. Therefore decolorization of dyes is important before the discharge of effluent. Removal of dye has been attempted extensively using physico-chemical methods such as coagulation, ultra filtration, electro-chemical adsorption, photo oxidation, activated carbon adsorption etc.[3]. But these technologies are not efficient, satisfactory and also cost effective. Use of low cost, easily available biomaterials for the adsorption of dyes is practiced as an alternative method and several botanical, low cost materials have directly been used as an adsorbent for removal of dyes from wastewater.[4]. Several adsorbents have been reported in the literatures such as clay[5] Zeolite[6] fly ash[7], silica gel[8] chitosan[9] and algae[10]. Malachite Green is a basic, cationic, triphenyl methane dye. It has been extensively used in industries for dyeing leather, silk, wool, jute and in distilleries. It is used as a fungicide and antiseptic in aquaculture industries[11] regarding the adsorption of basic dyes from aqueous solution. The efficiency of the adsorption process mainly depends on the cost and removal capacity of adsorbents used. Now days, agricultural waste materials are receiving much more attention as adsorbents for the removal of dyes from waste water due to its low cost and good availability. In the present study, wood apple rind (WAR) has been used as adsorbent whose results showed good capacity of adsorption of Methylene blue in very short period of agitation. The *Limonia acidissima* (wood apple) is used medicinally as well as in making of sweet in India. Unemployed shell of fruit is waste which became the best application as the effective and inexpensive adsorbent.

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The study was carried out with isotherm as well as kinetic models, along with the thermodynamic study.

EXPERIMENTAL METHODS

Preparation of adsorbent

Preparation and characterization of adsorbent Wood apple rind (WAR) biomass were obtained from local fruit market and washed with tap water followed by double-distilled water. After thorough washing, WAR was cut into small pieces and dried under sunlight for 72 hours to remove moisture content present. The dried WAR pieces were washed repeatedly with hot water (70°C) to remove any soluble matter present and dried in oven at 85°C for 48 hours. The oven dried WAR was powdered and sieved through 100 mesh sieves and stored in airtight polyethylene bottles for sorption experiments. Un protonated WAR was used for sorption studies of Methylene blue.

Preparation of adsorbate

The Methylene blue dye was supplied by S.D. Fine Chem. Ltd. India. Stock solution of 0.1 g/dm^3 was prepared with deionized water. All working solutions used in study were prepared by appropriately diluting the stock solution to a pre-determined concentration.

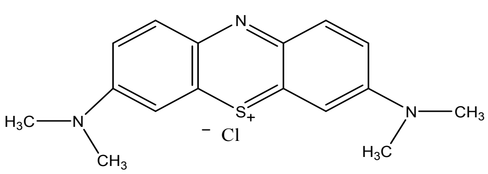

Figure 1: Chemical Structure of Methylene blue

Studies on pH

pH is considered as a very important parameter in adsorption process. Solution pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH in the adsorption of Methylene blue dye on WAR the pH from 4 to 10.

Studies on biosorbent dosage

Adsorbent dosage is an important parameter studied while conducting batch mode studies. The effect of adsorbent dosage on removal of Methylene blue dye was studied by varying adsorbent dosage of WAR. From results it was found that adsorption increases with increase in adsorption dosage and is highly dependent on adsorbent concentration. The point of saturation for dosage was fixed based on colour removal. For higher dosage, the colour removal cannot be measured using colorimeter. The point of saturation for WAR was found 0.08g of with 96% of removal efficiency for Methylene Blue. Based on the results, the 0.05 g of WAR was used in the adsorption study of Methylene Blue.

Studies on time

Contact time plays an important role in affecting efficiency of adsorption. In order to optimize the contact time for the maximum uptake of dyes, contact time were varied. The adsorption of Methylene blue by WAR is in single phase and there was rapid adsorption of Methylene blue dye within 30 min**.**

RESULT AND DISCUSSION

Fourier Transform Infrared Spectroscopy analysis

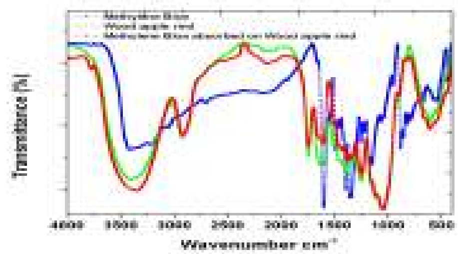

Figure 2: *FTIR* Spectrum for adsorption of Methylene blue by WAR

The FTIR spectrum of the WAR as shown the various functional group with respect to their peak value. Peak at 3408.75 and 2921.67 cm^{-1} indicates the functional group OH and C-H respectively. The peak value at 1737.92 confirm the functional group C=O.

UV Studies

The maximum wavelength (λ_{max}) corresponding to 250 nm, 285 nm and 500 to 700 nm are the characteristic absorption of Methylene blue dye. The concentration of Methylene blue in Methylene blue aqueous solution after treatment with WAR, the concentration starts to decrease with increasing dose. For dosage of 0.05g of WAR, and for stirring 30 minutes, the (λ_{max}) of Methylene blue completely disappeared which indicates the efficient adsorption of Methylene by WAR.

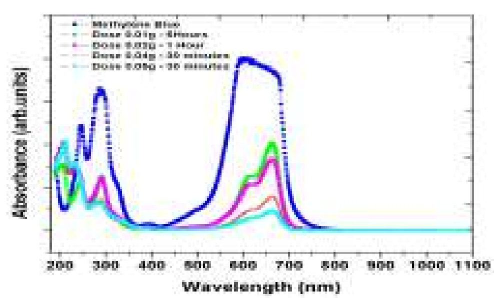

Figure 3: UV Spectrum for adsorption of Methylene blue by WAR

Effect of pH

The effect of pH in the adsorption of Methylene blue dye on WAR was determined by varying the pH from 4 to 8 (Table.1) The experimental data showed that the percentage of dye removal increases with increase in pH up to 8 for removal of Methylene blue by WAR.

Table 1: Effect of pH on removal of Methylene blue by WAR

Sr. No	Dose(g)	ph	Time (min)	In. con of dye solution (mg/20 ml)	final. con. of dye solution (mg/20 ml)	removal of mb %
1	0.01	4	60	5	3.00	40.00
2	0.01	5	60	5	2.60	48.00
3	0.01	6	60	5	2.60	48.00
4	0.01	7	60	5	2.60	48.00
5	0.01	8	60	5	2.46	50.80

Effect of adsorbent dosage

Adsorbent dosage is an important parameter studied while conducting batch mode studies. The effect of adsorbent dosage on removal of Methylene blue dye was studied by varying adsorbent dosage of WAR. From results it was found that adsorption increases with increase in adsorption dosage and is highly dependent on adsorbent concentration. The point of saturation for dosage was fixed based on colour removal. For higher dosage, the colour removal cannot be measured using colorimeter. The point of saturation for WAR was found 0.08g of (Table.2) with 96% of removal efficiency for Methylene Blue (Figure.4)

Table 2: Effect of adsorbent dosage on removal of Methylene blue by WAR

Sr. No	Dose (g)	p^h	Time (min)	In. con of dye solution(mg/20 ml)	final. con of dye solution (mg/20 ml)	removal of mb %
1	0.01	8	60	5	2.46	50.8
2	0.02	8	60	5	2.18	56.4
3	0.03	8	60	5	1.64	67.2
4	0.04	8	60	5	1.19	76.2
5	0.05	8	60	5	0.737	85.2
6	0.06	8	60	5	0.792	84.1
7	0.07	8	60	5	0.341	93.1
8	0.08	8	60	5	0.200	96.0

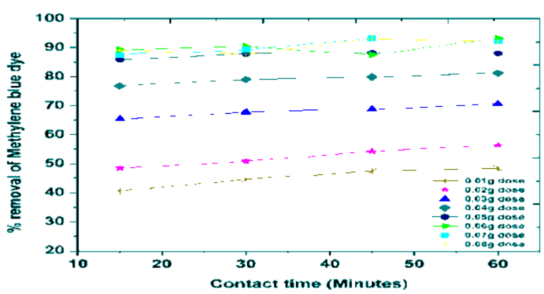

Figure 4: Effect of adsorbent dosage on removal of Methylene blue by WAR

Effect of time

Contact time plays an important role in affecting efficiency of adsorption. In order to optimize the contact time for the maximum uptake of dyes, contact time were varied. Result shows that the adsorption of Methylene blue by WAR is in single phase and there was rapid adsorption of Methylene blue dye within 30 minutes. (Figure.5)

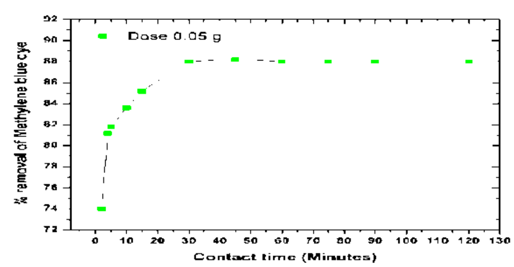

Figure 5: Effect of time on removal of Methylene blue by WAR

Adsorption isotherm

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. If a quantity, q is absorbed by an adsorbent at the steady state equilibrium concentration, c and then the function q(c) describes the adsorption isotherm. The most widely accepted surface adsorption models for single solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid – phase concentration was tested with these models. For this analysis, different initial concentration of dye aqueous solution is taken and its final concentration is measured and tabulated in the Table 3**.**

Table 3: Adsorption Isotherm for the adsorption of Methylene blue by WAR

Time (min)	Initial concentration (g/ 20 ml)					
	0.004 (g/ 20 ml)	0.005 (g/ 20 ml)	0.006 (g/ 20 ml)	0.007 (g/ 20 ml)	0.008 (g/ 20 ml)	0.009 (g/ 20ml)
	Final concentration (g/20 ml)					
5	0.00068	0.00102	0.00156	0.00204	0.00218	0.00260
10	0.00060	0.00091	0.00147	0.00193	0.00204	0.00243
15	0.0005	0.00074	0.00130	0.00193	0.00193	0.00243

Langmuir isotherm

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption on the surface without transmigration of adsorbate in the plane of the surface. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The values of V_m and 1/bVm are calculated by plotting C_e/q_e versus C_e (Figure.6 Table. 4.). The influence of isotherm shape on "favorable" or "unfavorable" adsorption has been considered. In present experiment the R^2 value was found to 0.9578 (Table.6) which clearly indicate the adsorption was favorable. The plot of C_e/q_e versus C_e for the adsorption of Methylene blue on WAR at constant temperature shows the linear forms of Langmuir isotherm. The 1/bVm (intercept) and $1/V_m$ (slope) obtained from this plot are given in Table.4.

Table 4: Langmuir adsorption Isotherm for the adsorption of Methylene blue by WAR

Ce	Qe	Ce/qe
0.00056	0.00138	0.407
0.00065	0.00174	0.374
0.00125	0.00190	0.658
0.00184	0.00230	0.800
0.00193	0.00243	0.795
0.00229	0.00268	0.853

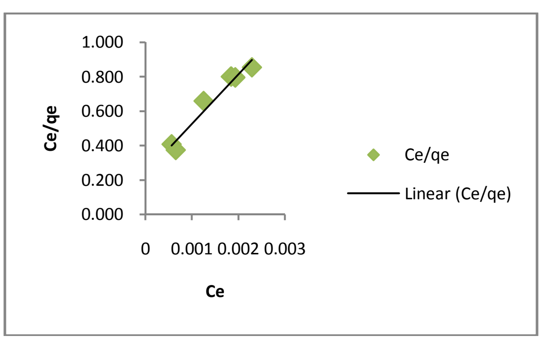

Figure 6: Langmuir adsorption Isotherm for the adsorption of Methylene blue by WAR

Freundlich isotherm

The Freundlich isotherm equation was employed for the adsorption of Methylene blue dye on the adsorbent. Linear plots of log q_e versus log C_e shows that the adsorption of Methylene blue dye obeys the Freundlich adsorption isotherm (Figure.7, Table.5). The values of K_f and n are given in Table.7. The intensity of adsorption is an indication of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption. However, the multilayer adsorption of Methylene blue through the percolation process may be possible. The values of N are more than one, indicating the physisorption is not more favourable. (Table.7) .As per the regression factor of experimental values, the results indicate that there is better fitting of Langmuir isotherm model than the Freundlich isotherm for adsorption of Methylene blue.

Table 5: Freundlich adsorption Isotherm for the adsorption of Methylene blue by WAR

Ce	Qe	log Ce	log q_e
0.00056	0.00138	-3.2518	-2.8613
0.00065	0.00174	-3.1870	-2.7594
0.00125	0.00190	-2.9030	-2.7212
0.00184	0.00230	-2.7351	-2.6328
0.00193	0.00243	-2.7144	-2.6147
0.00229	0.00268	-2.6401	-2.5712

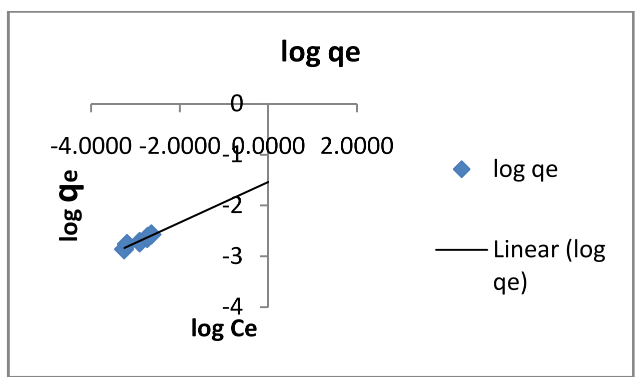

Figure 7: Freundlich adsorption Isotherm for the adsorption of Methylene blue by WAR

Table 6: Langmuir constant for the adsorption of Methylene blue by WAR

V_m (mg/g)	$1/bV_m$(1/mg)	R^2
0.00347 mode	0.239577	0.95780

Table 7: Freundlich constant for the adsorption of Methylene blue by WAR

K_f	N	R^2
0.0290	2.51	0.9254

Kinetic modeling

The plot of log(q_e-q_t) versus t (Figure.7) and the plot of t/q_t versus t (Figure. 8) for Methylene blue adsorption by WAR were plotted from the data obtained in kinetics studies (Table: 8 and 9).

Table 8: Pseudo First order model for the adsorption of Methylene blue by WAR

Sr. No	Time (min)	p^h	Dose(g)	In.con of dye solution (mg/ 20 ml)	Final.con of dye solution (mg/ 20 ml)	q_e	q_t	ln (q_e-q_t)
1	2	8	0.05	5	1.3	88.1	74.00	2.64617
2	4	8	0.05	5	0.94	88.1	81.80	1.84055
3	5	8	0.05	5	0.91	88.1	81.20	1.93152
4	10	8	0.05	5	0.82	88.1	83.60	1.50408
5	15	8	0.05	5	0.74	88.1	85.20	1.06471
6	30	8	0.05	5	0.6	88.1	88.00	-2.30259

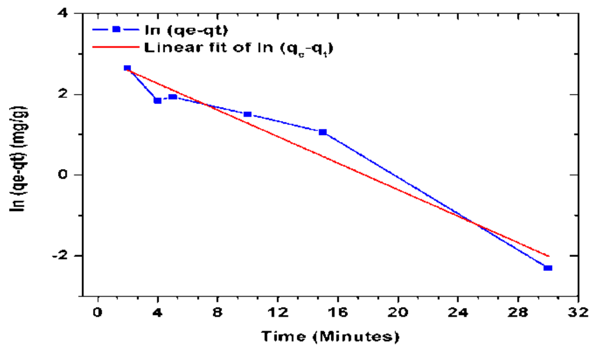

Figure 8: Pseudo first order model for the adsorption of Methylene blue byWAR

Table 9: Pseudo Second order model for the adsorption of Methylene blue by WAR

Sr. No	Time	pH	Dose(g)	In.con of dye solution(mg/20 ml)	final. con. of dye solution (mg/20 ml)	qt	t/qt
1	2	8	0.05	5	1.3	74.00	0.02703
2	4	8	0.05	5	0.94	81.80	0.04890
3	5	8	0.05	5	0.91	81.20	0.06158
4	10	8	0.05	5	0.82	83.60	0.11962
5	15	8	0.05	5	0.74	85.20	0.17606
6	30	8	0.05	5	0.6	88.00	0.34091

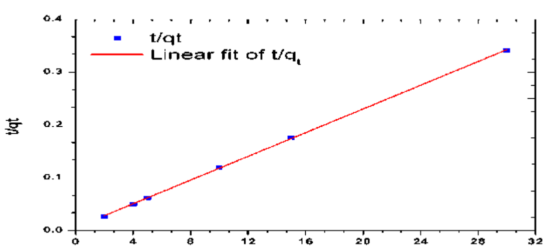

Figure 8: Pseudo second order model for the adsorption of Methylene blue by WAR

The R^2 value (Table. 10) of all the pseudo second order kinetics were very close to value of 1 so, the adsorption of Methylene blue by WAR follow pseudo second order kinetics.

Table 10: Kinetic parameters for the adsorption of Methylene blue by WAR

Sr. No	Adsorbent and dye	q_e (mg/g)	Pseudo first order		Pseudo second order	
			$k_1 x 10^{-3}$ (min^{-1})	R^2	$K_2 x 10^{-3}$ (min^{-1})	R^2
3	WAR and MB	88.1	0.025862	0.94	0.02280	0.99

CONCLUSION

Adsorption studies were carried out for adsorption of Methylene blue by WAR. The optimum pH is 8 for adsorption of Methylene blue by WAR. By increasing the dose of WAR and stirring time, adsorption increases for Methylene blue. For Methylene blue, the dosage of 0.05 g of WAR, the adsorption increases but at 30 min of stirring, adsorption of Methylene blue by WAR was saturated by reaching the maximum percentage of removal of ~ 88 % and after 30 min there is no more adsorption of Methylene blue by increasing the time. Adsorption process of Methylene blue by WAR follows second order kinetics. Adsorption processes of Methylene blue by WAR follow Langmuir adsorption. From the FTIR data, adsorption of Methylene blue by WAR was chemisorptions. From UV, there was considering decrease in color intensity. These studies indicate WAR can be used for adsorption of Methylene blue dye.

REFERENCE

1. B.H. Hameed, M.I. El-Khaiaryb, Journal of Hazardous Materials, (2008), 159, 574–579.
2. Kannan N. and Sundaram M, Kinetics and mechanism of removal of Methylene Blue by adsorption on carbons : a comparative study. Dyes and Pigments (2001)1(1), 25-40.
3. K.G. Bhattacharyya, A. Sharma, Azadirach indica,-Leaf powder as an effective biosorbent for dyes. Journal of Environmental Management. (2004), 71, 217-229.
4. Jayaraj R. Chandramohan M. Martin Deva Prasath and Khan T. H . Malachite Green dye removal using seaweed Enteromorpha. J. Chem . (2011)8 (2): 649-656.
5. Tehrani-Bagha, A.R., Nikkar, H., Mahmoodi, N.M., Markazi, M., Menger, F.M., The sorption of cationic dyes onto kaolin:kinetic, isotherm and thermodynamic studies. Desalination (2011),266, 274–280,
6. Han, R., Zhang, J., Han, P., Wang, Y., Zhao, Z., Tang, M., Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, Journal of Chemical Enginnering.(2008), 145, 496–504.
7. Rastogi, K., Sahu, J.N., Meikap, B.C., Biswas, M.N., Removal of methylene blue from wastewater using fly ash as an adsorbent by hydrocyclone. Journal of Hazardous Material,(2008), 158, 531- 540.
8. Kushwaha, A.K., Gupta, N., Chattopadhyaya, M.C., Enhanced adsorption of malachite green dye on chemically modified silica gel. Journal of Chemical and Pharmachutical Research.,(2010), 2 (6), 34–45.
9. Mahmoodi, N.M., Salehi, R., Arami, M., Bahrami, H., Dye removal from colored textile wastewater using chitosan in binary systems. Desalination,(2011), 267, 64–72.
10. Ncibi, M.C., Ben Hamissa, A.M., Fathallah, A., Kortas, M.H.,Baklouti, T., Mahjoub, B., Seffen, M., Biosorptive uptake of methylene blue using Mediterranean green alga Enteromorpha spp. J. Hazardous Material. (2009), 170, 1050–1055.
11. Zhang J. L. Y. and Zhang C. Adsorption of Malachite Green from aqueous solution onto carbon prepared from Arundodonax root. Journal Hazardous Material, (2008) 150(3): 774-782.

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