

---

# Removal of Methylene Blue from Aqueous Solution by Adsorption Using Tamarind Nut Carbon

Sweetlin Rajula Rubavathi<sup>1</sup>, Aroul Rosario<sup>1</sup> &  
Balakumar Subramanian

<sup>1</sup>Loyola College, Nungambakkam, Chennai-600034.

<sup>2</sup>PSN College of Engineering and Technology, Tirunelveli-627152, India D.

---

**Abstract:** *The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of activated carbon for the removal of dyes from waste water. Adsorbents prepared from tamarind nut carbon are used to remove the methylene blue from aqueous solution. The effect of various experimental parameters has been investigated using a batch adsorption technique to obtain information on treating effluents from the dye industry. The extent of dye removal increased with decrease in the initial concentration of the dye and also increased with increase in contact time and amount of adsorbent. Adsorption data were modeled using the Freundlich adsorption isotherm and first order kinetic equation Lagergren equation. The results of the present study will be helpful in the design of removal of methylene blue dye from various industries using tamarind nut carbon.*

**Keywords:** *Methylene blue, Tamarind nut carbon, Adsorption*

**Abbreviation:** *TNC-Tamarindnut carbon, MB-Methylene blue*

## Introduction

Waste water effluents from many industries, including paper, leather, textiles, rubber, plastics, printing, cosmetics, pharmaceuticals and food, contain several kinds of synthetic dyestuffs[1]. Colour stuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sun light penetration into the stream and affecting aquatic ecosystem [2]. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade[3]. Various physical, chemical and biological methods, including adsorption, biosorption, coagulation and flocculation, ozonation, oxidizing agents, ultra-Filtration, electrochemical, and membrane separation for the treatment of dye-bearing wastewater[4-7]. However these processes are costly and cannot effectively be used to treat the

wide range of dye waste water. In contrast, an adsorption technique is by far the most versatile and widely used. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But commercially available activated carbon is very expensive. Recently a large number of low-cost adsorbents have been utilized to develop cheaper and effective adsorbents to remove dyes from wastewater, including cucumber peels, durian leaf powder, watermelon seed hulls, grape pulp, chitosan kenaf core fibres etc[8-13]. The reported results showed that most of these readily available biosorbents possess high efficiency in removing dyes from aqueous solutions[14]. The present study is undertaken to evaluate the efficiency of a carbon adsorbent prepared from tamarind nut for the removal of methylene blue in aqueous solution. The adsorption study was carried out systematically involving various parameters such as initial concentration, adsorbent dose and contact time. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and mass-transfer models for the adsorption of methylene blue on to tamarind nut carbon.

## Dye solution preparation

For this study, methylene blue was used and it was obtained from S.D fine chemicals, Mumbai, India. Stock solutions were prepared by dissolving an accurately weighed quantity of the dye in 1L distilled water. The desired concentrations for batch adsorption tests were obtained by further dilution. Concentrations of the aqueous solutions of dye were monitored on UV-Visible spectrophotometer.

## Preparation of adsorbent

Tamarind nut (seeds) procured from the market washed with distilled water, dried and pulverized to 300-800µm particles. It was heated in the hot air oven at a temperature of 170°C for 24 hr. The carbonized material was cooled to room temperature.

### Adsorption experiment

The adsorption experiments were carried out in a batch process. The known weight of the adsorbent material was added to 50 ml of the dye solution with an initial concentration of 10mg/l to 200mg/l. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The samples were withdrawn from the shaker at the predetermined time intervals, and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 min. The solutions were then filtered through Whatman No.40 filter paper and the absorbance of the filtrate was determined using a UV-visible ELICO double beam spectrophotometer(model SL-164) at a maximum wavelength of 665nm. The percentage removal of the dye and the amount adsorbed (in  $\text{mg l}^{-1}$ ) were calculated using the following relationships,

$$\text{Percentage removal} = 100 \frac{C_o - C_f}{C_o}$$

$$\text{Amount adsorbed} = \frac{C_o - C_f}{m}$$

where  $C_o$  and  $C_f$  are the initial and final concentration (in  $\text{mg l}^{-1}$ ) of dye and  $m$  is the mass of the low-cost adsorbent (in  $\text{g l}^{-1}$ ). The effect of initial concentration; adsorbent dosage and contact time were investigated. Each experimental point is the average of three independent runs and all the results were reproducible with  $\pm 3\%$  error limit.

### Results and discussion

#### Effect of initial concentration

The influence of the initial concentration of MB in the solutions on the rate of adsorption on TNC was studied. The experiments were carried out at fixed adsorbent dose (500mg/100mL) in the test solution,  $29 \pm 1^\circ\text{C}$  room temperature, and at different initial concentrations of MB (10, 50, 100, 150 and 200mg/l). The relevant data are given in table-1. Table-1 reveal that the percent adsorption decreases with the increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of adsorbent increases with increase in dye concentration. It means that the adsorption is highly dependent on the initial concentration of dye [15]. This is because at lower concentration, the ratio of the initial number of dye molecule to the available surface area is low, subsequently; the fractional adsorption becomes independent of the initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence, the percentage removal of dye is dependent upon the initial concentration. This was similar to the one reported in literature [16].

Table.1 Effect of various parameters on the removal of MB.

Adsorption System	Percentage of Dye removal
<b>Initial dye concentration(mg/l)</b>	
10	99.99
50	98.14
100	97.70
150	84.00
200	80.10
<b>Adsorbent dosage(g/L)</b>	
1.25	81.00
3.0	82.50
4.0	89.00
5.0	97.00
10.	98.99
<b>Contact time(min)</b>	
5	89.1
15	92.5
25	95
35	96.3
45	97.7
55	97.7

#### Effect of adsorbent dosage

The adsorption of MB on TNC was studied by changing the quantity of adsorbent (1.25-10g/L) in the test solution while keeping the initial dye concentration (150g/L), temperature ( $29 \pm 1^\circ\text{C}$ ) constant. As shown in table-1, the percentage removal of MB increased with the increase in adsorbent dosage. Increase in the adsorption with adsorbent dosage can be attributed to increased surface area and availability of more adsorption sites [17]. This was similar to the one observed earlier [18].

#### Effect of contact time

In the adsorption system contact time plays a vital role irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of MB by TNC the adsorption experiments were carried out at different contact time (5-55min) at constant initial concentration of dye (100mg/l) with a fixed dose of adsorbent (500mg/100mL). It is found that the removal of MB increases with increase in contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of MB on the available adsorption sites on adsorbent material [19]. The results show that equilibrium time required for the adsorption of MB on TNC is 45 minutes. The percentage removal of dye on

TNC at 45 minutes of contact time reveals that TNC has maximum removal efficiency of 97.7%. The relevant data are given in Table-1.

**Adsorption isotherm**

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent for different pollutants. Equilibrium data can be analyzed using commonly known adsorption isotherm, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Freundlich equation[20], which is given by,

$$Q_e = K_f C_e^{1/n}$$

Where  $K_f$  and  $n$  are the Freundlich constants that indicate adsorption capacity and adsorption intensity respectively.

The linearized form of Freundlich isotherm can be written as

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

The value of  $K_f$  and  $n$  can be calculated by plotting  $\ln q_e$  versus  $\ln C_e$ . Figure-1 shows the Freundlich curves for MB adsorption on TNC. The isotherm constants and correlation coefficients are shown in Table-2

It has been stated that Mckay etal [21] that magnitude of the exponent  $n$  gives an indication of the favorability and capacity of the adsorbent/adsorbate system. Values of  $n > 1$  represents favorable adsorption condition. In this case the observed exponent is  $1 < n < 10$  showing beneficial adsorption [22].

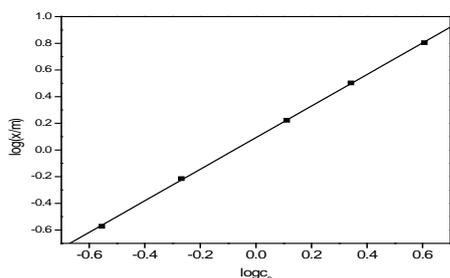


Figure 1: Freundlich adsorption isotherm for the adsorption of MB on TNC

**Table.2 Equilibrium constants for MB onto TNC**

Freundlich isotherm parameters		
K	N	R
3.6846	8.3857	0.9999

**Adsorption kinetics**

In order to study the rate constant for MB-TNC system, the well known Lagergren first order rate equation was employed. The first order rate equation is  $\log (q_e - q_t) = \log q_e - (K_{ad}/2.303) t$  Where  $q_e$  and  $q_t$  (both in  $mg\ g^{-1}$ ) are the amounts of MB adsorbed at equilibrium time and at any time  $t$  respectively. The straight -line plot of  $\log (q_e - q_t)$  vs.  $t$  (Fig-2) indicates the validity of Lagergren equation for the present system and explained that the process follows the first order kinetics. The values of  $K_{ad}$  calculated from the slope of the plots, was  $0.0055\ min^{-1}$  for TNC at  $500\ mg/100\ mL$  dosage.

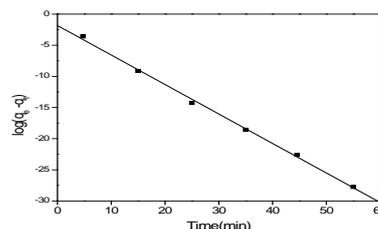


Figure 2: Lagergren plot for the adsorption of MB ON TNC

**Intra-particle diffusion study**

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in a intra-particle diffusion plot. Besides adsorption at the outer surface of the adsorbent there is also a possibility of intra-particle diffusion of dye molecule from bulk of the outer surface into the pores of TNC. This possibility was exposed by plotting the amount of dye adsorbed against square root of time,  $t^{0.5}$ . According to Weber and Morris[23], an

Intra-particle diffusion coefficient  $K_p$  is defined by the equation

$$Q = K_p t^{0.5}$$

where  $Q$  (in  $mg\ g^{-1}$ ) is the amount of MB adsorbed at any time  $t$  and  $K$  ( $mg\ g^{-1}\ min$ ) is the intra-particle diffusion rate constant. The shape of the  $q$  versus  $t^{0.5}$  plot is curved (fig.3) at a small time limit which might be due to mass transfer effect[24]. There are two separate regions in the curves. The initial curved portion reflects film or boundary layer diffusion effect and the linear portion to the Intra-particle diffusion effect[25]. The values of  $K_p$  were obtained from the slope of the straight lines, and was  $1.765\ mg\ g^{-1}$

Figure-3 shows that intra-particle diffusion is slow and rate determining step. The linear portions of the curves (fig.3) do not pass through the origin. This indicates that mechanism of dye removal on TNC is complex and both, the surface adsorption as well as Intra-particle diffusion contribute to the rate determining step[26].

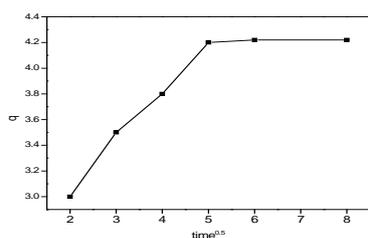


Figure 3: Intra particle diffusion effect for the adsorption of MB on TNC.

### Conclusion

In this study, the adsorption of MB from aqueous solution was investigated using TNC as an adsorbent. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial dye concentration, contact time and adsorbent dosage. The results show that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of MB. Equilibrium data fitted very well in a Freundlich isotherm equation. Adsorption Kinetics obey Lagergren first-order kinetics model. This study proved that TNC is an attractive option for dye removal from industrial effluents.

### References

1. Safiul Azhar, S., Ghaniey Liew, A., Suhardy, D. *Am. J. of App. Sci.* 2(11), 2005, 1499-1503.
2. Yamin Yasin, Mohd Zobir Hussein and Faujan Hj Ahmad *The Malaysian Journal of Analytical Sciences*, Vol 11, No 11, 2007, 400-406
3. Sekaran G, Shanmugasundaram K.A, Mariappan. M and Raghavan K. V, *Indian J chem. Technol*, 2, 1995, 311.
4. Yao, Z., Wang, L., Qi, J. *Clean Soil Air and Water*, 37(8), 2009, 642.
5. El- latif, MA, Ibrahim. AM, El-Kady. M, *J. Am. Sci*, 6(6), 2010, 267.
6. Ghaedi M, Hassanzadeh A, Kokhan. S N, *J. Chem. Eng. Data*, 56(5), 2011, 2511.
7. Vimonses, V., Lei, S., Jin, B., Chow, C W K, *Saint. C, Chem. Eng. J.* 148, 2009, 354.
8. Akkaya. G, Guzel. F, *Chem. Eng. Commum*, 201(4), 2014, 557.
9. Ahmad. A, Rafatullah. M, Sulaiman O, J. *Hazar. Mater*, 170(1), 2009, 357.
10. Hussin. Z M, Talib. N, Hussin. NM, *Am. J. Environ. Eng.* 5(3A), 2015, 38.
11. Saygili. H, Akkaya Saygili. G, Guzel. F, *Asia. Pac. J. Chem. Eng.* 9(2), 2014, 214.
12. Thakur VK, Thakur M K, *ACS Sustain Chem Eng.* 2(12), 2014, 2637.
13. Jeminat. O, Jose Santos, Zahangir, *Int. J. Chem.* 7, 2016, 333.
14. Vakili M, Rafatullah. M, Salamatina. B, *Carbohydr. Polym.* 113, 2014, 115.
15. Kannan. N and Karupaswamy. K., *Indian J. Env. Prot* 18, 1998, 683-686.
16. Stephan Inabaraj. K, Selvarani and Sulochana. N *J. Sci. Ind. Res.* 61, 2002, 971 – 978.
17. Mahri. A. H, Makki. A and Eslami. A – *Am. J. of App. Sci.* 1(4), 2004 321 – 326.
18. Salim. R Al-Subu MM and Qashoa. S J. *Environ. Sci. Health A* 29, 1994 2087-2114.
19. Low K. S. and Lee C.K. *Pertanica, J. Sci. Technol.*, 1990. 24, 199045.
20. Ira. N. Levine, *Physical Chemistry*, Fifth edition.
21. G. McKay, J. A. Stephen and K. Y. H. Khayer *Chem. Technology, Biotech.* 45(291-302) (1989)
22. G. A. nnadurai, *Indian. J. Env., Port* 20, 2000, 731-737.
23. Weber, W. J. Morris, J. C. J. *Division, American Society of Chemical Engineers* 89 1963, 31
24. Vadivelan v, Vasanthkumar K. *J. Colloid Interf. Sci.* 286, 2005, 91.
25. Weber W. J. *Principle and application of water chemistry*, edited by Faust S. D and Hunter J. V. Wiley, New York, 1967.
26. Namasivayam .C and Kanchana. N *Chemosphere*, 21, 1992, 1691.