

# Adsorption of methylene blue and amaranth on to tamarind pod shells

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## Abstract

The present study, agricultural waste tamarind (*Tamarindus indica*) pod shells were used for the adsorption of dyes like methylene blue and amaranth. The operating variables studied were initial concentration, initial solution pH, adsorbent dosage and contact time. Experimental equilibrium data were fitted to Freundlich and Langmuir isotherms. The kinetics of methylene blue and amaranth onto tamarind pod shells was found to follow a pseudo first order kinetics. The maximum adsorption of amaranth and methylene blue are 65.04 and 60.11 mg/g of the adsorbent respectively. The fourier transformed infrared spectroscopy reveals that -OH, -COOH, C=O and C-O groups are involved in the adsorption process. The optimum pH for the adsorption of amaranth is 2 and methylene blue, a cationic dye shows maximum adsorption in the pH range 6-12. Characterisation of the tamarind pod shells showed that the relative percentage of protein is very less making it an excellent adsorbent for the removal of dyes from wastewater effluents.

**Keywords:** Dye adsorption, methylene blue, amaranth, tamarind pod shells, fourier transform infrared spectroscopy, desorption studies.

## Introduction

In developing countries like India, industries cannot afford to use conventional wastewater treatment chemicals like alum, ferric chloride, polymer flocculants and coal based activated carbon as they are not cost-effective. An inexpensive and more easily available adsorbent would make the removal of pollutants an

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economically viable alternative. Agricultural wastes like tamarind pod shells are discarded in the agricultural sector in India. Disposal of agricultural by-products is currently a major economic and ecological issue, and the conversion of by-products to adsorbents, represents a possible alternative.

Dyes are used extensively in industries including textiles, paper and leather. The effluents emanating from these industries are often highly coloured, and the disposal of their wastes into the environment can be extremely undesirable. Once in the environment, they may show toxic and genotoxic effects toward organisms (Yesilada et al. 2003). Dyes are usually of synthetic origin, with complex aromatic molecular structures, making them very stable and difficult to biodegrade (Aksu 2005). In particular, printing and dyeing unit wastewaters contain several types of coloring

Several research works has been performed to search for efficient and low-cost materials to remove methylene blue and other basic dyes from aqueous solution, including rice husk (Vadivelan and Kumar 2005) beech sawdust (Batzias and Sidiras 2004), agro-industry wastes (Garg et al. 2004) and activated carbon from date pits (Abdulkarim et al. 2002). However, as the adsorption capacities of the above adsorbents are not large, new adsorbents are still under development.

The main focus of this study was to evaluate the biosorption capacity of a novel, low cost, and renewable biomass, tamarind pod shells for the removal of Methylene blue and Amaranth as model compounds for anionic and cationic dyes. In a tropical country like India, tamarind pod shell is found in plenty and is discarded as waste, as they have very less calorific value. The effects of pH, contact time, initial dye concentration and biomass dosage on the biosorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit the experimental data.

## Materials and Methods

### *Biomass and dye solution preparation*

The tamarind pod shells (TH) were collected from dehulling unit and were washed extensively in running tap water to remove dirt

and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husks were oven dried at 105°C for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size.

Methylene blue and amaranth has been used in this study as model molecules for cationic and anionic dyes. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water to give a concentration of 1000 mg/L and diluting when necessary. Initial pH was adjusted by adding dilute solutions of HCl or NaOH.

#### Batch adsorption experiments

Batch adsorption studies were conducted in a routine manner. The 250 ml flasks containing 100 ml of the dye solution was contacted with the predetermined amount of the biosorbent at equilibrium time. The flasks were agitated at a 120 rpm constant shaking rate to ensure that equilibrium is achieved. The dye solution was separated from the biosorbent using Whatman No.1 filter paper.

Adsorption uptake values were determined as the difference between the initial dye concentration and the one in the supernatant. All the experiments were carried out in duplicates and the average values were used for further calculations.

#### Analysis of the dyes

The concentration of the unadsorbed amaranth and methylene in the biosorption medium was measured colorimetrically using a spectrophotometer. The absorbance of the colour was read at 665 and 520 nm for methylene blue and amaranth respectively.

## Results and Discussion

#### Characterisation of tamarind husk

The carbon, hydrogen and nitrogen content of the husk showed very low percentage of nitrogen (0.94%) in comparison to the carbon quantities (46.01%). This indicates that few nitrogen containing compounds are involved in the adsorption of dyes. A relatively larger percentage of hydrogen (6.14%) in comparison to nitrogen compounds indicates that carbon-hydrogen groups might be available for adsorption of metals and dyes. The relatively low percentage of nitrogen shows that very less percentage of protein might be present in the husks. This is advantageous over protein rich adsorbents since proteinous materials are likely to putrefy under moist conditions

The FT-IR spectra of the tamarind husk in the range of 400-4000  $\text{cm}^{-1}$  were taken in order to obtain information on the nature of functional groups on the husk and dye interaction. It exhibits absorption bands at 3430, 2924, 1654 and 1030  $\text{cm}^{-1}$ , which indicate the presence of -OH, -COOH, C=O and C-O groups respectively.

#### The effect of initial pH

Initial pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the dyes: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the adsorption availability of the dyes. The effect of initial pH on the biosorption of methylene blue and amaranth is presented in Figure 1 a and b. Methylene blue, a cationic dye

showed maximum adsorption in the pH range 6-10. Therefore, the best pH range for adsorption of MB was from 6.0 to 10.0. This result could be explained considering the electrostatic interaction between the surface of the biosorbent, negatively charged, mainly due to  $\text{COO}^-$  species, since the  $\text{pK}_a$  values of carboxylic acids range from 3.8 to 5.0 (Roberts and Caserio, 1977), with the cationic dye MB. At lower pH a possible protonation of  $\text{COO}^-$  occurs, precluding the electrostatic attraction with the MB dye, decreasing the adsorbate uptake. Thus, at pH values ranging from 6.0 to 10.0, the carboxylic groups are available to adsorb the positively charged dye, increasing the removal of MB from aqueous solution. The maximum removal of the anionic dye amaranth occurred at pH 2 for the different dye concentrations 10, 20 and 50 mg/L. The percent removal decreased with increase in initial pH. Similar results for methylene blue (Kumar et al. 2005; Bhattacharyya and Sharma 2005; Kavitha and Namasivayam 2005; Rahman and Saad 2003) and amaranth (Mittal et al. 2005; Gong et al. 2005) were reported.

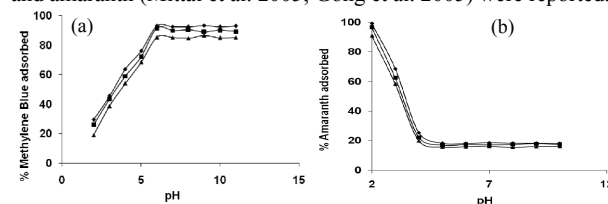


Figure 1a & b: Effect of pH on the methylene blue and amaranth adsorption respectively by tamarind pod shells (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

#### Effect of adsorbent dosage

The biosorption of methylene blue and amaranth was studied at various biosorbent concentrations ranging from 0.5 to 5 mg/L. The percentage removal of the dye increased with increase in the sorbent dosage (Fig 2 a and b). The results revealed that the colour removal was increased up to adsorbent dosage of  $1 \text{ g l}^{-1}$  and  $3 \text{ g l}^{-1}$  for methylene blue and amaranth respectively and then it remained almost constant. Increase in the percentage of dye removal with adsorbent dosage could be attributed to an increased in the adsorbent surface area, which increased the availability of more adsorption sites. In the further experiments the adsorbent dosage was fixed at  $1 \text{ g l}^{-1}$  for adsorption of methylene blue and at  $3 \text{ g l}^{-1}$  for amaranth.

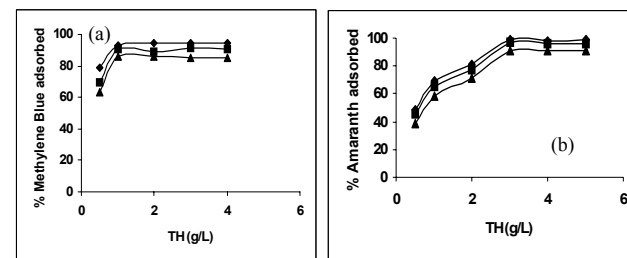


Figure 2a & b: Effect of adsorbent dosage on the methylene blue and amaranth adsorption respectively by tamarind pod shells (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

#### Effect of contact time

The uptake of methylene blue and amaranth by tamarind husk increased with the increase in contact time and it remained constant after an equilibrium time as shown in Figure 3 a and b.

The percent dye removal at equilibrium time decreased with increase in dye concentration, although the amount of dye removed increased with increase in initial dye concentration. It is clear that the percentage removal of dyes depends on the initial concentration

of the dye. The time taken to attain equilibrium for 10, 20, 50 and 100 mg/l amaranth solutions was 40-50 minutes and the time required for methylene blue adsorption is 60 minutes for 10 and 20 ppm solutions and for 50 and 100 ppm solutions, the equilibrium time increased to 70 and 80 minutes respectively.

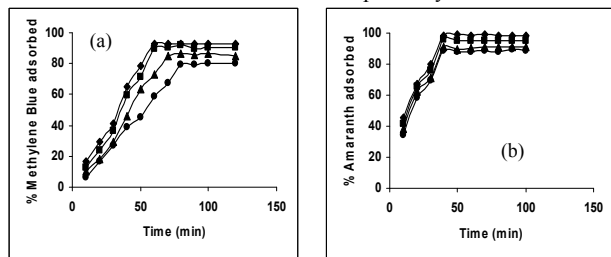


Figure 3 a and b: Effect of contact time on the methylene blue and amaranth adsorption respectively by tamarind pod shells (◆ 10 mg/L □ 20 mg/L ▲ 50 mg/L ● 100mg/L)

**Kinetic Studies**

The kinetic data were treated with the following Lagergren’s pseudo-first-order rate equation:

$$\log_{10} (q_e - q) = \log_{10} q_e - K_{ad} * (t / 2.303) \dots\dots\dots(1)$$

where q and q<sub>e</sub> are amounts of adsorbate adsorbed (mg/g) at time, t (min) and at equilibrium, respectively, K<sub>ad</sub> is the rate constant of adsorption (l/min). The linear plots of log<sub>10</sub> (q<sub>e</sub>-q) vs t for the dyes were studied at different concentration shows the applicability of the above equation. Values of K<sub>ad</sub> were calculated from the slope of the linear plots. The rate constant for the dyes generally decreased with increase in adsorbate concentration. The high values of correlation coefficient showed that the data conformed well to the pseudo-first-order rate kinetic model.

**Isotherm Modelling**

In order to optimize the design of a sorption system to remove dyes from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves. The isotherms data were analyzed using two of the most commonly used equilibrium models, Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) isotherm models (Fig). The mathematical expressions are given by Equations 2 and 3, respectively, as follows:

$$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \dots\dots\dots (2)$$

$$q = K_f C_{eq}^{1/n} \dots\dots\dots (3)$$

The calculated isotherm constants given in Table 1 were evaluated from the linear plots represented by Equations 4 and 5, respectively for Langmuir and Freundlich isotherms.

$$\frac{C_{eq}}{q} = \frac{1}{q_{max} b} + \frac{C_{eq}}{q_{max}} \dots\dots\dots (4)$$

$$\ln q = \ln K_f + (1/n) \ln C_{eq} \dots\dots\dots (5)$$

The best-fit equilibrium model was determined based on the linear squared regression correlation coefficient R<sup>2</sup>. From Table 1, it was observed that the equilibrium sorption data were very well represented by Langmuir isotherms followed by the Freundlich model with high correlation coefficients. Hence, the best fit of equilibrium data in Langmuir isotherm expressions confirm the

monolayer coverage process of methylene blue and amaranth by tamarind husk. Furthermore, the value of Freundlich exponent n in the range of 1–10, indicates a favourable adsorption (Ho and McKay 1998). Also, high adsorption capacity indicates the strong electrostatic force of attraction between dye molecules and biosorbent binding-sites (Kaewsarn and Yu 2001). The comparison of results of this work with the others found in the literature showed that tamarind husk has a significantly high adsorption capacity for binding the dyes (Table 2).

Table 1: Sorption isotherm constants and coefficients of determination for adsorption of dyes by Tamarind pod shells

	Langmuir equation			Freundlich equation		
	q <sub>max</sub> (mg/g)	b (l/mg)	R <sup>2</sup>	K <sub>F</sub> (mg/g)	n	R <sup>2</sup>
Amaranth	65.04	0.01	0.97	2.58	1.74	0.99
Methylene Blue	60.11	0.012	0.98	2.02	1.53	0.96

Table 2: Comparison of adsorbent capacities of low cost adsorbents

Adsorbent	Adsorbate	q <sub>max</sub> (mg/g)	References
Coir pith and carbon	Congo Red	6.72	Namasivayam and Kavitha, 2002
Spent brewery	Acid Orange 7	30.5	Silva <i>et al.</i> , 2004
Rice husk	Methylene Blue	40.6	Vadivelan and Kumar, 2005
Powdered peanut hull	Amaranth	14.90	Gong <i>et al.</i> , 2005
	Sunset Yellow	13.99	
	Fast Green	15.60	
	FCF		
Bagasse fly ash	Orange G	18.8	Mall <i>et al.</i> , 2006
	Methyl Violet	26.2	
Tamarind pod shells	Methylene Blue	60.11	This study
	Amaranth	65.04	

**Desorption studies**

Both incineration and land disposal represent possible options for final disposition of spent adsorbent material. However, both methods directly or indirectly pollute the environment. If regeneration of dyes from the spent adsorbent were possible then it would not only protect the environment but also help recycle the adsorbate and adsorbent and hence contribute to the economy of wastewater treatment.

Desorption experiments were carried out at different pH values. Desorption of the dyes with water was not significant. If the adsorption is by physical bonding then the loosely bound solute can be easily desorbed with distilled water in most of the cases (Agarwal *et al.*, 2006). Hence, physical adsorption is ruled out. Among the dyes, the percentage of amaranth desorbed was the highest with increase in pH. About 46.32% of the dye was desorbed from tamarind husk. The percentage of methylene blue desorbed did not exceed 2.45%. (Figure 4)

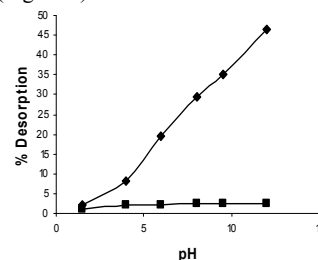
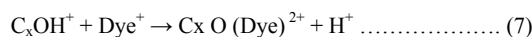
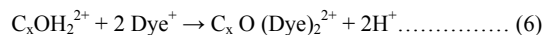


Figure 4: Effect of pH on desorption of methylene blue (■) and amaranth (●) by tamarind pod shells

### Mechanism of adsorption of dyes

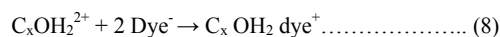
Based on the results obtained, the mechanism of adsorption of methylene blue and amaranth is discussed below.

Adsorption of methylene blue: The mechanism of methylene blue adsorption by tamarind pod shells is depicted below.



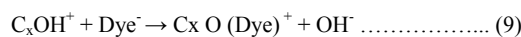
Adsorption of amaranth: When dye anions (amaranth) are introduced in the system containing adsorbents, they may be adsorbed onto the positively charged surface in two ways (Sharma and Forster, 1994):

The first way:



This reaction does not account for the change in pH of the solution after dye adsorption compared to the blank i.e. in the absence of dye anion.

The second way:



This accounts for the increase in pH of the solution after dye adsorption.

### Conclusion

The results of the present investigation show that tamarind pod shells is an effective adsorbent for the removal of methylene blue and amaranth dyes from aqueous solutions, and its adsorption capacity is quite comparable to the other adsorbents reported in literature. Tamarind pod shells were selected for studying adsorption due to its availability in India, as well as to assess the possibility of utilising an agricultural waste for dye removal. The results show that initial dye concentrations, pH and adsorbent dose highly affect the dye uptake capacity of adsorbents. The equilibrium has been analyzed using Freundlich and Langmuir adsorption isotherms. The kinetics of adsorption followed a pseudo first order rate reaction. The calculated isotherm constants were used to compare the adsorptive capacities of adsorbents for dye removal. Thus the use of tamarind pod shells as an adsorbent can be viewed as an effective waste management strategy.

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