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Removal of Methylene Blue from Water Using *Calophyllum Inophyllum* Seed Husk Waste: Equilibrium and Kinetic Study

M. Saravanan*, Arumugam A. and Gautham B. Jegadeesan

School of Chemical & Biotechnology, SASTRA University, Thanjavur, India

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ABSTRACT

In the present study we have used seed husk of Calophyllum inophyllum plant, a low cost biomass and important agricultural waste, for the adsorption of methylene blue. Freundlich and Langmuir isotherms were used to describe equilibrium nature of adsorption. The maximum adsorption capacity for Calophyllum Inophyllum Seed Husk calculated from the Langmuir equations reaches to 500.44 mg g^{-1}. The kinetics of adsorption was examined using pseudo first-order, pseudo second-order models. The adsorption of methylene blue on seed husk followed pseudo second-order kinetics.

Keywords: Adsorption, *Calpohyllum inophyllum* seed husk, isotherm, kinetics, methylene blue.

INTRODUCTION

The annual wastewater discharged from textile industries is approximately 640 million m^3, which is approximately 75% of its annual consumption (from CSE India Webpage). It has been estimated that in Tirupur alone (a major textile hub in Tamilnadu, India) approximately 86 million litres per day of water was used for textile processing in 2000 [1]. Estimates from the Tamil Nadu Pollution Control Board suggest that approximately 21 million litres of wastewater is discharged into the Noyyal River Basin (the receiving water body in Tirupur) from the textile industry [2].Contamination of aqueous streams due to dyes emanated by textile and leather industries is a major environmental problem. Azo dyes, which contain one or more azo bonds, have been widely used in industries such as textiles, printing and leather and account for approximately 70% of all the dyes [3]. They are one of the largest groups of organic compounds that cause a serious threat to human beings because of their non-biodegradability and toxicity. Untreated effluent is usually discharged into the nearby rivers which cause serious damage to the aquatic life, impact water quality rendering the water unusable for drinking. Aquatic streams (e.g., rivers and lakes) in India are commonly used by local communities for drinking water and other household purposes. In addition, these streams also act as sinks for wastewater discharges from neighboring industries. Approximately 80% of domestic water supply in many industrialized and non-industrialized countries is returned as sewage and a significant fraction of that is discharged directly without treatment into receiving water bodies [1,2]. The contamination of the rivers and streams presents a clear and present danger to local communities. Therefore, it is of national interest to treat and reuse water and address water shortfalls.

Adsorption is a commonly used technique for dye removal, but is sometimes expensive due to the cost of the adsorbent. Therefore, there is a current need to search for alternative low cost adsorbents. Many researchers used various adsorbents like plant biomass, fruits and vegetable peels, rice husk etc. Adsorption is operative in most

natural physical, biological, and chemical systems and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification [5]. Methylene Blue MB, a basic dye was used as an adsorbate for the adsorption studies. It is a cationic dye. This dye has the molecular formula $C_{16}H_{18}N_3SCl$, CAS no 61-73-4 as per manufacture's information. The chemical structure of Methylene blue is as follows.Methylene blue (CI = 52015; chemical formula: $C_{16}H_{18}ClN_3S$; molecular weight = 319.86 g/mole; maximum wavelength = 662 nm) is known for its adsorption characteristics and widely used for adsorption studies [6]. In this present work, seed husk of *Calophyllum inophyllum*a low cost raw material is used as adsorbent to investigate the kinetic and equilibrium data of adsorption process.

MATERIALS AND METHODS

2.1 Materials

Seed husk of *Calophyllum inophyllum* were bought from a nearby oil extraction mill. Sodium hydroxide pellets (99%, Merck), ethanol (95%, Merck), hydrochloric acid (98%, Merck) were obtained from Merck Chemicals Pvt. Ltd. Methylene blue from Himedia laboratories Pvt. Ltd.

2.2 Preparation of seed husk from Calophyllum inophyllum

The seed cover was separated and grounded to fine powder. The sample of fine grounded seed husk was stored in air tight plastic cover in order to oppose any reaction to the raw material. The seed husk was repeatedly washed with deionized water to remove the impurities present in it. Then this raw material was dried by exposing it in the natural sunlight for the period of 24 h [7].

2.3 Preparation of adsorbate

The stock solution of concentration 1000 ppm was prepared by dissolving 1g of dye in 1000ml of distilled water. The stock solution can be diluted to further to different working concentrations using distilled water the characteristic wavelength at lambda max 662 nm was observed using UV-Vis Spectrophotometer 169 (Systronics, Wavelength range: 320-990nm) [8].

2.4 Experimental Methods

0.1g of fine powder of inner layer of the raw material is taken in a 250 ml conical flask. Particle size which was enormously used in the studies was retained in the 72 mesh. It is shaken in the incubator at constant speed of 125 rotations per minute at constant room temperature. The readings were noted at different time intervals like 2, 5, 10, 20, 30, 60, 90and 120min.The dosage is also not varied at constant conditions. The equilibrium studies were carried out in an incubatory rotator shaker at 308K.The study was conducted using different concentrations ranging from 40-500ppm. 1g of adsorbent was added to 100ml of the aqueous dye solutions at corresponding working concentration. The dye solutions with adsorbent taken in conical flasks (250ml) were incubated at 308K in a incubated rotator shaker at 125 rpm. Samples were withdrawn after 2 hours, centrifuged concentration of the dye in the mixture after the adsorption was measured using spectrophotometer at λ_{max}=662nm .To ensure equilibrium state, samples were withdrawn after 24 h.

RESULTS AND DISCUSSION

3.1 Equilibrium Studies

As expected, the uptake of dyes on the biomass waste increased with increased dye concentration in the equilibrium studies. The increase was observed to be almost linear, indicating higher capacity of the dye. Isotherm describes the relationship between equilibrium concentrations of the adsorbate in aqueous and solid phase at a constant temperature. The most frequently used isotherm models applicable for single component systems are Langmuir and Freundlich. Langmuir isotherm model is the most widely used theoretical model to describe the equilibrium data. Langmuir theory assumes uniform energy distribution of the adsorption sites and is applicable for monolayer adsorption. The Langmuir isotherm parameter q_m (mg/g) represents monolayer adsorption capacity of the adsorbent. K_L (dm^3/mg) is the equilibrium constant, which indicates the affinity of binding sites. The linear form of the Langmuir isotherm model is described as:

$$\mathbf{C_e q_e} = \frac{1}{\mathbf{K_e q_m}} + \mathbf{C_e q_m} \qquad (1)$$

where K_L is the Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mg/g).

The Freundlich model assumes heterogeneous surface energydistribution. The model can be expressed as follows:

$$\mathbf{q_e = K_f\ C_e^{(1/n)}} \qquad (2)$$

K_f and n are indicators of adsorption capacity and adsorption intensity respectively. The value of Freundlich constant (n) should lie in the range of 1 to 10 for favourable adsorption. In order to choose the isotherm that best explains the equilibrium, linear regression method is widely used. Coefficient determination R^2 and non-linear error function $\chi 2$ are used to determine optimum values of the isotherm parameters [9].Both Langmuir and Freundlich isotherm were used to explain the equilibrium data for the adsorption of methylene blue MB on seed husk of *Callophyllum inophyllum.*

From the Figure 1, it was inferred that Freundlich modelexplains the adsorption of the dye methylene blue on the seed husk powder compared to Langmuir isotherm. Since the value of the regression factor for Freundlich isotherm is more than the Langmuir isotherm it is considered that the best fitting isotherm is Freundlich isotherm [10]. The Freundlich isotherm parameter, n also falls within the range 1 to 10 (1.54202), thus making the adsorption favourable (Table. 1).

Table 1:The equilibrium parameters were obtained by non-linear regression analysis

Langmuir Isotherm		Freundlich Isotherm	
K_L	0.133 (L/g)	K_F	58.14(mg/g)(L/g)$^{1/n}$
q_m	500.44(mg/g)	n	1.628
R^2	90.7	R^2	96.9

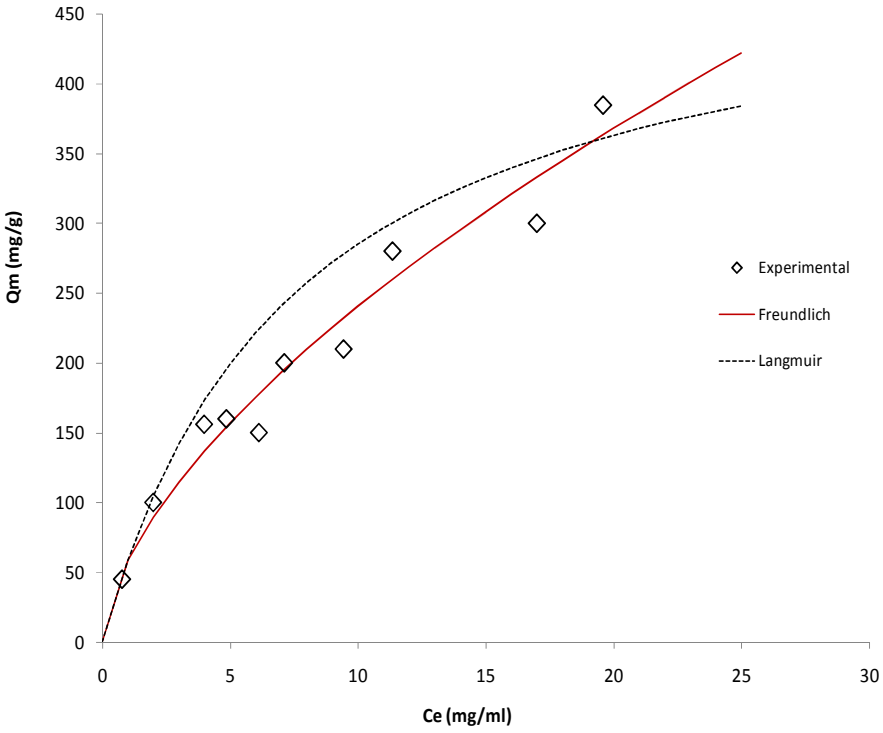

Figure 1: Equilibrium data isotherm curves

3.2 Batch Kinetic studies

The initial dye concentration was varied from 40-1000 ppm and its effect on adsorption was studied. The pseudo first order kinetic model has been widely used to predict dye adsorption kinetics [11]. The pseudo first order rate expression suggested originally by Lagergren based on solid capacity is expressed as follows.

$$\log (\mathbf{q_e} - \mathbf{q_t}) = \log \mathbf{q_e} - \mathbf{K_1 t} \quad (3)$$

Values of q_e and K_1can be obtained from the slope and intercept of the plot log (q_e−q_t) versus t/2.303.Pseudo-second order model is expressed by the equation.

$$\frac{\mathbf{t}}{\mathbf{q_t}} = \frac{1}{\mathbf{K_2 q_e^2}} + \mathbf{K_2 t} \quad (4)$$

Values of q_e and K_2can be obtained from the slope and intercept of the plot t/q_t versus t [12].Both the pseudo first order and pseudo second equations were used to fit the kinetic data (Figure.2).From the values of the regression factor we can conclude that the pseudo second order equation (R^2=0.996) is best fit for the adsorption kinetics.

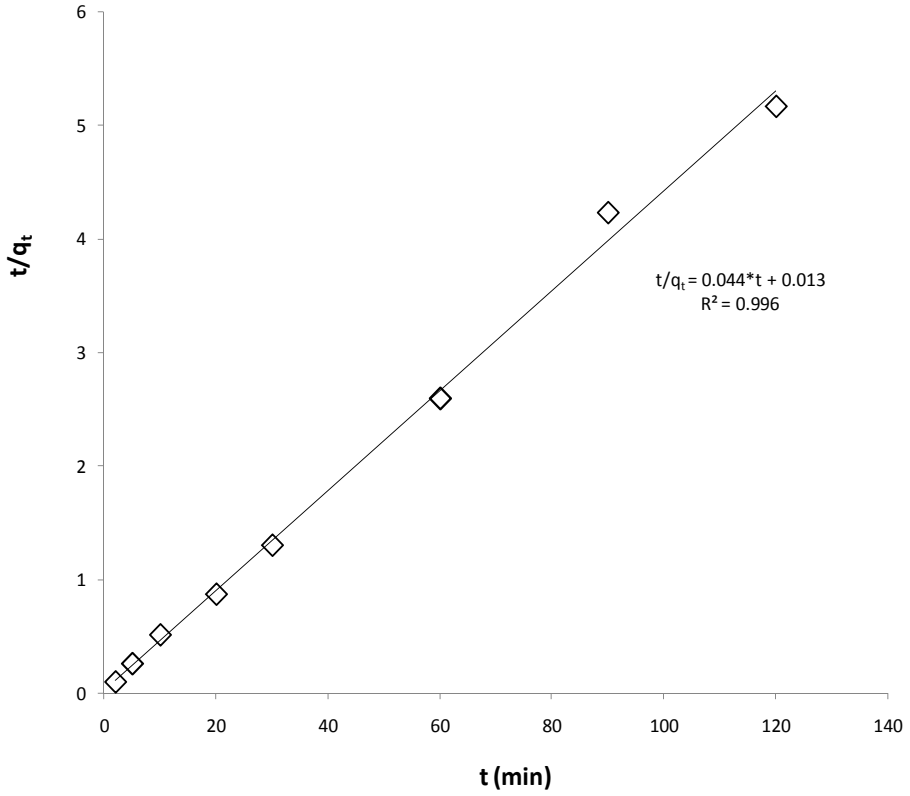

Figure 3: Pseudo second order plots of adsorption of lipase on seed husk of Callophyllum inophyllum

CONCLUSION

Decolourisation of dyes from industrial effluents is one of the important areas of concern in waste water treatment. In this study, dye decolorization was investigated using seed husk of *Callophyllum inophyllum*.Biosorption data were modeled using Langmuir and Freundlich adsorption isotherms. The results showed that equilibrium was reached within 120 min. Equilibrium data of the biosorption process fitted very well to the Freundlich adsorption

isotherms (R^2=0.969). Kinetic study reveals that that the adsorption of methylene blue onto *Callophyllum inophyllum* seed husk follows second-order kinetics.

REFERENCES

[1] Hossein Azarpira, Yousef Mahdavi, DavoudBalarak, *Der Pharma Chemica*, **2013**, 5(3), 141-155.
[2] Yan Zhang, Fan Gao, BridgidWanjala, Zhiyang Li, George Cernigliaro, Zhiyong Gu, *Appl Catal B-Environ*,**2016**, 199, 504-513.
[3] Muhammad Safdar, Yasmeen Junejo, Aamna Balouch, *J Ind Eng Chem*,**2015**, 31, 216-222.
[4] Rachita Mehta, Menka Surana, *Der Pharma Chemica*, **2012**, 4 (1):311-319
[5] A Arumugam, V Ponnusami , *Braz J Chem Eng*, **2013**, 30, 477 - 486.
[6] David Wiedmer, Einar Sagstuen, Ken Welch, Håvard J. Haugen, Hanna Tiainen, *Appl Catal B-Environ* , **2016**, 198, 9-15.
[7] A Arumugam, V Ponnusami , *Biomass Conv Bior*, **2014**, 4 (1), 35-41.
[8] A Arumugam, V Ponnusami , *Indian J Chem Techn*,**2013**, 20, 101-105.
[9] Davoud Balarak, Hossein Azarpira, Ferdos Kord Mostafapour, *Der Pharma Chemica*, **2016**, 8(10):114-121.
[10] Silvia Priscila Dias Monte Blanco, Fabiano Bisinella Scheufele, Aparecido Nivaldo Módenes, Fernando R. Espinoza-Quiñones, Pricila Marin, Alexander Dimitrov Kroumov, Carlos Eduardo Borba, *Chem Eng J*,**2017**,307, 466-475.
[11] Ran Bu, Feifei Chen, Jie Li, Wei Li, Feng Yang, *Colloid Surface A*, **2016**, 511, 312-319.
[12] Ganna Darmograi, Bénédicte Prelot, Amine Geneste, Louis-Charles De Menorval, Jerzy Zajac, *Colloid Surface A*,**2016**, 508, 240-250.