Decolorisation of Basic Textile Dye from Aqueous Solutions using a Biosorbent derived from *Thespesia populnea* used Biomass

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**Abstract:**

In the present study, the efficiency of a biosorbent derived from seeds of *Thespesia populnea* was investigated towards the removal of basic textile dye Methylene Blue from an aqueous solution. Adsorption studies were carried out in batch system. Influence of experimental parameters such as adsorbent dosage (0.1g/L-0.3g/L), pH (2-10) and initial dye concentration (50-130mg/L) on adsorption of dye onto biosorbent was investigated. Maximum uptake of dye was observed with 0.1g/L adsorbent dosage at pH 8.0. Equilibrium uptake of methylene blue dye by the adsorbent was analyzed by Langmuir and Freundlich isotherm models. The data fitted best with Freundlich model, suggesting that adsorption of the dye was by multilayer model on the surface of the adsorbent. Experimental results obtained support that the biosorbent used in the present study can be a suitable low cost alternate for the removal of basic textile dyes.

**1. Introduction:**

In this modern era, more than 1,00,000 varieties of dyes are commercially being produced in 7×10⁵ tons annually. Textile and associated industries are majorly (10% of total dye production) discharging the dyes into the environment through their effluents whereas, 2% of total dye production is being effluent discharged by manufacturing operations. Dyes are stable to light and reluctant towards oxidation. Even the existence of dye in small quantities can terminate the aesthetic nature and shows adverse, irreversible effects on the environment [1]. Dyes are objectionable pollutants and existence of dyes even in small quantities in water kills the aesthetics. Dyes have been known as toxic, teratogenic, carcinogenic, mutagenic and allergic. In concern to Indian industries, most of the carcinogenic agents such as naphthyl amine and benzidine based dyes were being used till 1992, which have been banned in USA and European countries since long time. Moreover, the chances of threats posed by dyes were more in India as most of the dyes being in use were devoid of carcinogenic screening due to financial constraints and expertise associated with carcinogenic assessment of dyes [2].

Dyes are recalcitrant towards light, water, oxidizing agents and other chemicals due to their complex structure [3]. A number of treatment techniques have been proposed for the removal of textile dyes from waste water, includes, photocatalytic, sonochemical and electrochemical degradation, ultrafiltration,
cation exchange membranes, Fenton-biological treatment and adsorption on to activated carbon. As most of the dyes used are being synthetic in nature, decolorization of dyes by adsorption on to economical and efficient solid support has been found advantageous [4]. Albeit, dyes adsorption on to activated carbon is proved to be the most efficient method of treating dye contaminated waters, it is not an economically viable method because of the cost of commercial activated carbon. In the recent years, extensive research has been carried out to exploit new, potential low cost adsorbent materials that could be an alternative to the activated carbon [3]. Such low adsorbents have been investigated includes, rice husk, cotton waste, teak wood bark [5], maize cob, bagasse pith [6], coir pith [7], palm fruit bunch [8], orange peel [9], banana pith [10], plum kernels [11], wheat straw, apple pomace [12], cassava peel [13], saw dust [14], castor seed shell [15], *Nymphaea rubra* [16], pineapple stem [4] and Pistachi hull [17] etc. However, low adsorption efficiencies were reported with the developed adsorbents. Therefore, there is a need to develop and exploit large number of economical and locally available adsorbents that would bring deduction in dye waste water treatment capital costs [3].

Among acidic, non-ionic and basic dyes, cationic dyes (basic) are found to be more toxic and even the dye degradation products are potential carcinogens [18]. A survey on aquatic toxicity of 46 dyes conducted over fish by American Dye Manufacturers Institute (ADMI) in 1971 has revealed that basic dyes are more toxic towards aquatic life due to their cationic nature [19, 20]. In the present investigation, experiments were carried out to explore a low cost adsorbent to remove basic (cationic) dyes from aqueous solutions.

*Thespesia populnea* (*T. populnea*) is a large tree, habitat of coastal forests and tropical regions of India. In the present investigation, de-oiled seed (powder) biomass of *T. populnea* has been utilized as low cost adsorbent (biosorbent) material for the removal of basic textile dye from aqueous solutions. Adsorption experiments were carried out with Methylene blue (MB) as a model basic dye. The effect of biosorbent dosage, pH and initial dye concentration on adsorption of MB by *T. populnea* derived biomass was studied. Langmuir and Freundlich equilibrium isotherm models were also discussed.

2. Materials and Methods:

2.1 Chemicals:

MB (C16H18N3SCl, molecular weight 319.86 g/mol, $\lambda_{max}$ = 665 nm) was purchased from Balaji Chemicals Pvt Ltd, Chennai, India. NaOH and KOH of analytical grade were procured from Thermo Fisher Scientific India Pvt, Ltd. All the experiments were carried out with deionized water.

2.2 Preparation of Biosorbent:

Seeds of *T. populnea* were collected from the vicinity of Anna University, Chennai. The seeds were subjected to oven drying at 75°C until a constant weight of the seeds was recorded. The seeds were ground and sieved through 60 mesh to obtain fine homogenous particle size. The seed powdered was subjected to oil extraction by using Soxhlet apparatus with Hexane solvent. After repeated cycles of extraction, the seed powder was collected and oven dried at 80°C for 1hr to ensure the evaporation of Hexane solvent moisture in the biomass. As hexane is a highly volatile solvent and no other solvents have been used in oil extraction process, the dried biomass has been taken directly as biosorbent without any further treatments and purification.

2.3 Batch experimental studies:

Dye stock solution was prepared by dissolving appropriate quantity of MB dye in deionized water at a concentration of 1mg/mL, which was later diluted to obtain experimental dye solutions. Batch studies...
were performed using a rotary shaker (ORBITEK, model 400) at 150 rpm and 30°C as described elsewhere with slight modifications [21]. Set of Erlenmeyer flasks of 250mL capacity were taken with 100mL of experimental solutions. Appropriate quantity of biosorbent was added to each flask and the samples were taken at prefixed time intervals (0, 5, 10, 20, 30, 60, 90, 120, 150, 180, 210 and 270min) of incubation. Samples were centrifuged at 5000rpm for 15min and the absorption of supernatant was measured at a wavelength of 665nm (λ_{max}) using UV spectrophotometer (Hitachi, U3210, Japan).

The amount of dye adsorbed was calculated using the eq (1) [22],

\[ q = \frac{(C_0-C)}{R} \]  \hspace{1cm} (1)

Where, \( q \) is the amount of dye adsorbed per unit mass of adsorbent in mg/g, \( C \) is dye concentration after certain time of adsorption (mg/L), \( C_0 \) is initial dye concentration (mg/L) and \( R \) is the biosorbent dosage in g/L.

2.4 Adsorption parameter studies:

2.4.1 Biosorbent dosage. 100mL of 90mg/L concentrated dye solution was taken in to a set of 55 Erlenmeyer flasks and were added with different biosorbent dosages from 0.1g/L-0.3g/L. The flasks were maintained at 30°C and 150rpm in the rotary shaker. Absorbance was measured at regular intervals using UV spectrophotometer.

2.4.2 PH. Experimental solution of 90mg/L was dispersed into flasks and added with optimum quantity of the biosorbent obtained in the previous step. Effect of PH on adsorption was monitored in the range of 2-10 PH values. PH of the solution was altered by using 0.1N HCl and 0.1N NaOH solutions. Alterations in the PH were measured using digital PH meter. After respective intervals, the samples were taken out and absorbance was measured.

2.4.3 Initial dye concentration. The effect of initial dye concentration on adsorption process was studied with five different initial concentrations ranging from 50mg/L-130mg/L. Each flask was added with optimum biosorbent dosage, PH and maintained at 30°C, 150rpm in the shaker. The same procedure mentioned above has been followed to obtain the absorbance.

2.5 Equilibrium isotherm modeling:

2.5.1 Langmuir model. Langmuir isotherm model was proposed on the hypothesis that, i) Adsorption occurs by monolayer, ii) adsorption sites are uniformly energetic and iii) lateral interactions are forbidden among adsorbed molecules [23]. The fundamental concept is that, adsorption occurs at homogenous sites and if once a site on adsorbent is occupied by the adsorbate molecule, there will not be any further adsorption at the respective site [22].The mathematical expression of Langmuir model is given by the eq (2),

\[ q_{eq} = \frac{Q^0bC_{eq}}{1+bC_{eq}} \]  \hspace{1cm} (2)

Where, \( q_{eq} \) is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), \( C_{eq} \) represents the equilibrium concentration of dye (mg/L), \( Q^0 \) is the maximum amount of dye adsorbed by monolayer interaction and \( b \) is the affinity (Langmuir) constant (L/mg) [16].

2.5.2 Freundlich model. Freundlich model proposes that adsorption sites on the adsorbent are heterogeneously energized and the adsorption occurs only at sites of different energies. Energy of
adsorption is a dependent factor of surface coverage [24]. Freundlich heterogeneous model of adsorption is represented as,

\[ q_{eq} = K_F C_{eq}^{1/n} \]

(3)

Where, \( q_{eq} \) and \( C_{eq} \) give the usual meanings as stated above, \( K_F \) represents the Freundlich constant and \( n \) is the heterogeneity factor whereas, \( 1/n \) gives intensity of adsorption [22].

2.6 Biosorbent morphology studies:

Surface morphology of biosorbent before and after adsorption was performed using Scanning Electron Microscopy (SEM, JEOL JSM-6360)

3. Results and Discussion:

3.1 Surface analysis by SEM:

SEM micrographs of \( T.populnea \) derived biosorbent are shown in Figure 1 (a & b). It is clear that the surface of biosorbent used was rough before subjecting to dye adsorption (a), whereas, the surface became smooth after adsorption of dye by the biosorbent (b).

![SEM micrographs of T.populnea derived biosorbent before (a) and after (b) adsorption](image)

Figure 1. SEM micrographs of \( T.populnea \) derived biosorbent before (a) and after (b) adsorption

3.2 Effect of Adsorption parameters on Adsorption:

3.2.1 Effect of Biosorbent dosage. A plot drawn between amount of dye adsorbed at equilibrium (\( q_{eq} \)) and biosorbent dosage (Figure 2) shows that equilibrium adsorption of dye on to adsorbent varies with the amount of biosorbent supplied. From the figure it is observable that, at low adsorbent dosage the dye adsorption was high and with increase in adsorbent dosage, the dye adsorption has decreased. Among the different biosorbent dosages tested (0.1g/L, 0.15g/L, 0.2g/L, 0.25g/L and 0.3g/L), the amount of dye adsorbed by the sorbent dosage of 0.1g/L was 43.1mg/g. While, with increase in biosorbent dosage to 0.3g/L, the dye adsorption decreased to 37mg/g. As the amount of dye adsorbed recorded was high at 0.1mg/L sorbent dosage, it was considered as optimum biosorbent dosage for further experiments. The reduction in adsorption with dosage could be due to that, at higher adsorbent concentrations, superficial adsorption of dye is rapid, thus leaving a very low concentrated dye solution. Also, it is obvious that a fixed mass of adsorbent can adsorb only a fixed amount of dye. Hence, higher the adsorbent, larger the amount of dye sorbed by the fixed mass of adsorbent. However, the declination in amount of dye adsorbed (\( q_{eq} \)) at high adsorbent dosages is due to the spilt in the concentration gradient of dye between the solution and dye adsorbed on the surface of adsorbent. Therefore, with increase in adsorbent dosage, the quantity of dye sorbed onto the unit weight of adsorbent decreases, leading to reduced dye uptake.
values [25]. Similar trend was observed with rubber seed shell [26] and phoenix tree leaves [27] as adsorbent towards MB adsorption.

Figure 2. Effect of biosorbent dosage on adsorption

3.2.2 Effect of $P^H$. The influence of $P^H$ on the adsorption phenomena was studied by varying the initial $P^H$ of the experimental dye solutions of 90mg/L concentration from 2-10. The effect of $P^H$ on dye adsorbed at equilibrium ($q_{eq}$) is shown in Figure 3. There was a rapid increase in dye adsorption from 16.19mg/g to 52.29mg/g with increase in $P^H$ of the dye solution from 2 to 8. On further increase in $P^H$ caused no significant increase in $q_{eq}$ values, found to be almost constant. This may be due to that, at lower $P^H$, $H^+$ ions compete with the dye cations for active sites of adsorption on the adsorbent. Hence, amount of dye adsorbed was very low at $P^H$ 2-4. At higher $P^H$, the surface of adsorbent becomes more negative and it prospers the adsorption of cationic (positively charged) dye molecules by electrostatic forces of attraction [28]. Hence, there was a rapid increase in dye adsorption with increase in $P^H$ from $>4$-8. The same trend was reported with *Posidonia oceanica* (L.) fibers when used for the adsorption of MB [29]. It was inferred from the studies that, $P^H$ has profound influence on dye uptake by the adsorbent through affecting the surface binding active sites of the adsorbent and ionization of dye molecules. In the present study, $P^H$ 8 was found to be the optimum value for the adsorption of MB onto *T.populnea* biosorbent.

Figure 3. Influence of $P^H$ on adsorption

3.2.3 Effect of initial dye concentration and contact time. Influence of initial dye concentration and contact time on adsorption of MB onto biosorbent is presented in Figure 4. From the figure it is evident that, with the increase in initial dye concentration, dye adsorption has increased till equilibrium state, after which there is no significant increase in the adsorption. It was noticed that with increase in initial dye
concentration from 50mg/L to 130mg/L, q (mg/g) increased from 42.02mg/g to 69.49mg/g. This linear relationship between initial dye concentration and amount of dye adsorbed could be due to that, increase in concentration of the dye overcomes all the mass transfer barriers between aqueous and solid phases, thus thrive the adsorption [29]. Hence, in the present case, the amount of dye adsorbed onto the biosorbent increased with increase in dye initial concentration from 50mg/L to 130mg/L.

Figure 4. Effect of initial dye concentration and contact time on adsorption

From the figure 4, it can also be inferred that, the time taken for each initial dye concentration to reach its equilibrium state varies with the concentration. Among the initial dye concentrations experimented, 50mg/L and 70mg/L have reached their equilibrium adsorption states in almost 150mis whereas, for higher concentrations (90mg/L, 110mg/L and 130mg/L), the equilibrium states shifted to right on time scale. It was observed that the time taken for 90mg/L and 110mg/L to reach their equilibrium was 180min whereas, in the case of 130mg/L, the equilibrium was almost achieved by 210min. Albeit all the concentrations have reached equilibrium state in 210min, the experimental data was recorded till 270min for more accuracy in the adsorption. This trend of increased time for equilibrium with increase in dye concentration, coincides with the results reported on the adsorption of MB with tea waste as low cost adsorbent [30]. Initially, the adsorption was rapid with contact time, on further prolongation of contact time, adsorption rate has slow down. It may be due to the Vander Waal’s and electrostatic forces of attraction between dye molecules and the adsorbent surface. These attractive forces cause the diffusion of dye molecules onto adsorbent surface, followed by intra particle matrix and facilitate interaction between chemical functionalities. In addition, during the initial stages of adsorption, the availability of dye ions as well as active sites for adsorption is very high, thus creates a concentration gradient between adsorbate and surface of adsorbent. This concentration gradient acts as a driving force for the accumulation of dye molecules on to active adsorbent sites. However, on time prolongation, the reduction in concentration gradient leads to the reduced rate of adsorption [30, 31].

3.3 Isotherm model analysis:

In order to optimize the removal of MB by T.populnea derived biosorbent from aqueous solutions, correlation between the equilibrium curves was established through standard isotherm models of Langmuir and Freundlich at 30°C. Sorption isotherm analysis provides the basic physicochemical idea for evaluating sorption process as a unit operation. In the present study, isotherm constants for Langmuir and Freundlich isotherm models were calculated from the linear plots resulted on applying equations 2 & 3 respectively. The plot drawn between C eq/concentration of dye at equilibrium) and C eq/qeq for Langmuir isotherm model is shown in figure 5 a) and that for Freundlich model was drawn between ln(C eq) and
ln(qeq) is shown in Figure 5 b). Based on the value of regression correlation coefficient $R^2$, the best fit isotherm model was determined. It was inferred that the adsorption fit well with the Freundlich model with high regression factor ($R^2$) of 0.9824 than Langmuir model with 0.9754 $R^2$ value. The Freundlich model represents the heterogeneity of biosorbent surface and multilayer mode of adsorption [15].

4. Conclusion:

From the outcomes of the present study, it can be inferred that the used biomass derived from *T. populnea* can be used as a potential cost effective adsorbent material for the removal basic dyes. Optimization of adsorption parameters was found vital and the amount of dye adsorbed has shown inverse relation with the adsorbent dosage. With increase in adsorbent dosage, the uptake efficiency has decreased. On increasing initial dye concentration, increments in amount of dye adsorbed were noticed. In case of pH, at low pH, the adsorption has increased and reaches saturation after certain point. At optimized conditions, the adsorption followed Freundlich isotherm model, suggesting a multilayer adsorption.

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