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Kinetic and Thermodynamic Studies on Biosorption of Direct Red 81 from Aqueous Solutions by Chamomilla Plant

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Abstract: In this study, Chamomilla plant biomass used as a sorbent for biosorption of a textile dye, direct red 81, from an aqueous solution. The batch sorption was studied with respect to dye concentration, adsorbent dose and temperature. Also, kinetic and isotherm parameters were determined for biosorption of Direct red 81 by Chamomilla plant. The maximum biosorption capacity (q_m) of Direct red 81 10 mg g^{-1} was obtained at 25^{o}C. The kinetic and isotherm studies indicated that the biosorption process obeys a pseudo-second order and Langmuir isotherm models. In addition, various thermodynamic parameters, such as changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have been calculated. The biosorption process of Direct Red 81 dye onto activated carbon prepared from Chamomilla plant was found to be spontaneous and exothermic. The findings of this investigation suggest that this procces is a physical biosorption. The experimental studies indicated that Chamomilla plant had the potential to act as an alternative biosorbent to remove the Direct Red 81 dye from an aqueous solution.

Keywords: Biosorption, Direct red 81, Kinetic study, Langmuir isotherm

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INTRODUCTION

Reactive azo dyes are versatile colorants used by industries worldwide. The textile industry is an important and major sector in many countries economy. However, it has a high potential to produce pollutants. Effluents, consisting of a complex mixture of colored and toxic compounds are generated from thier processes. During processing, significant amounts of water, energy and chemicals are consumed, and around 10–20% of dyes are lost into the effluent during dyeing processes [1]. Not only aesthetic problems occur due to dyes, but also biotoxicity and the possible mutagenic and carcinogenic effects of azo dyes have been reported [2].

The color of dye affects photosynthetic activity in the water body. Moreover, the released dyes on degradation form toxic amines in sediments [3]. Although some of the dyes are adsorbed on-to aerobic sludge in wastewater treatment plants, the applied aerobic microbial process cannot readily remove it from wastewater [4]. Additionally the dye reduces the treatment efficiency in these plants [5,6], which may lead to a collapse in the biological treatment facility.

However, treatment can be difficult due to the synthetic origin and the complicated aromatic molecular structures of the most common dyes, which are designed chemically stable and therefore not easily biodegradable [7].

The treatments of dyes in wastewaters can be classified as: (*i*) destructive, which leads to the partial or total degradation of the dye molecules; and (*ii*) non-destructive, which eliminates the color by transferring the molecules of the dye to some appropriate (solid) supports [8-11]. Several adsorbents are currently used which are by-products from agriculture and industries, which include seaweeds, molds, yeast, bacteria, crabshells, agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee [12], waste tea [13], walnut skin, coconut fiber [14], cork biomass [15], seeds of *Ocimum Basilicum* [16], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls [17,18], wheat bran, hardwood (Dalbergia sissoo) sawdust, pea pod, cotton and mustard seed cakes, [19,20]. Adsorption/biosorption using low cost adsorbents could be technically feasible and economically viable sustainable technology for the treatment of wastewater streams. Low cost adsorbents are nothing but materials that require little processing, are abundant in nature or are byproducts or waste materials from another industry.Hence in this paper, the removal of Direct red 81 by Chamomilla plant was presented. The present investigation aimed at studying the kinetics and isotherms of the biosorption of Direct red 81 with an object to explore optimum conditions for separation of the dye by biosorption method.

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MATERIALS AND METHODS

Commercial grade Direct red 81 was obtained as water-soluble powder from the Merck Company and used for the study without any further purification. The chemical structure of the dye is shown in Figure 1.

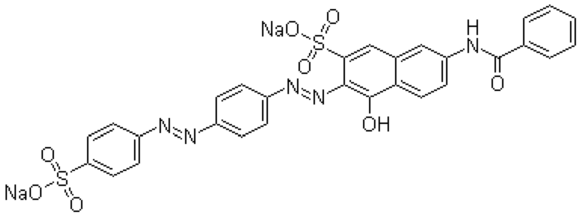

Figure 1. Structure of Direct red 81

Preparation of fungal biomass

The biosorption of Direct Red 81 dye from aqueous solutions on Chamomilla plant as local low-cost, available and renewable biological adsorbent was studied. Activated carbon was prepared from Chamomilla by chemical activation with 28% H_3PO_4 followed by pyrolysis at 150ºC and 500 ºC**.**

Preparation of dye solution

Direct red 81 (λ_{max} = 510 nm), is a direct dye and its chemical structure is given in Figure 1. Dye was dissolved in distilled water at a desired concentration.

Apparatuse

Concentration of the dye in water before and after biosorption was analyzed by a UV-Visible spectrophotometer (Perkin Elmer Lambda 25).

Batch biosorption studies

The biosorption of Direct red 81 was investigated in a batch system at different temperatures, biomass concentrations and contact times to calculation the rate constant and extent of dye uptake by the biosorbent.

The effect of initial concentrations of the dye on the biosorption rate and capacity was determined in the range 0.1 to 25 mg l^{-1} dye concentration. The effect of temperature on biosorption capacity was studied at five different temperatures, in the range 25 ºC to 55ºC. The effect of biosorbent mass on biosorption process was obtained by using different biomass concentrations (*i.e.*, 0.1, 0.5, 1 and 1.5 gr).

RESULTS AND DISSUASION

Effect of temperature on dye biosorption

The effect of temperature on the equilibrium biosorption capacity was studied in the temperature range of 25-55ºC at different initial dye concentration (20-80 mg l^{-1}). The optimum adsorption temperature was determined as 25ºC. As shown in Figure 2, the biosorption of the dye decreased with increasing temperature up to 55ºC. The increase in biosorption could be due to increased surface activity and increased kinetic energy of the dye molecule [21]. The decrease in biosorption capacity above 25ºC may be attributed to the deactivation of the biosorbent surface or the destruction of some active sites on the biosorbent surface.

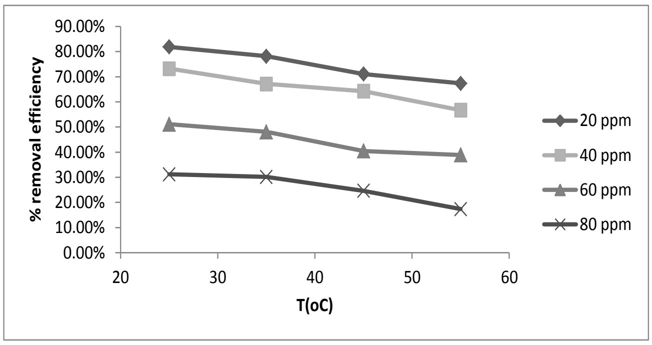

Figure 2. Temperature impact on removal efficiency at different concentrations

Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of Direct red 81 by Chamomilla plant at C_o = 20 mgL^{-1} is shown in the Fig. 3. It can be seen that the Direct red 81 removal increases up to a certain limit and then it remains constant. The increase in the biosorption with the biosorbent dosage can be attributed to greater surface area and the availability of more biosorption sites [22] . At biosorbent dosage greater than 1.5 g the surface Direct red 81 concentrations and the solution Direct red 81 concentration come to equilibrium with each other.

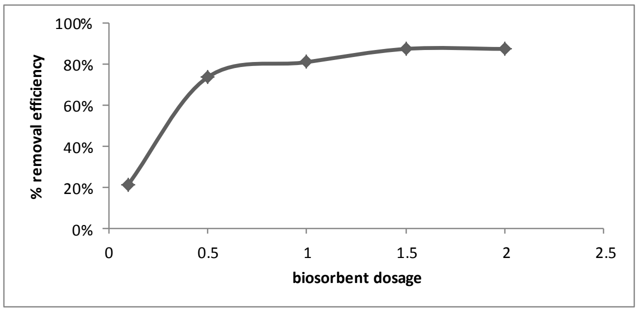

Figure 3. Effect of biosorbent dosage on removal efficiency

Effect of Direct red 81 concentrations

The influence of initial dye concentration on its biosorption was investigated and shown in Fig. 4. The removal efficiency decreased from 81.39 to 20.67 with increasing initial dye concentration from 20 to 80 mg L^{-1}. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites [23].

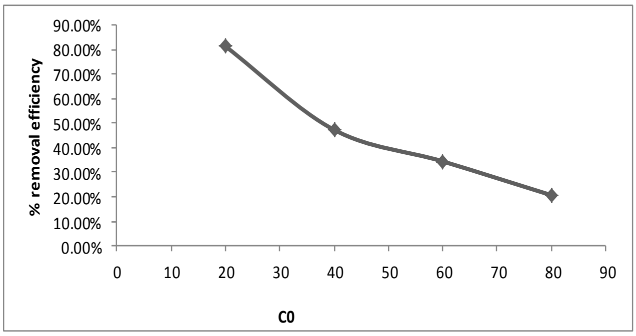

Figure 4. Effect of initial concentration on removal efficiency

Biosorption equilibrium time and isotherm models

Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. In the present investigation the equilibrium data are analyzed using the Langmuir (Equation 1) and Freundlich isotherm expressions (Equation 2).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

Where C_e and q_e are equilibrium concentration and equilibrium adsorption capacity, q_m is the maximum adsorption capacity reflecting a complete monolayer (mg g^{-1}); K_L is adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption.

A plot C_e/q_e versus C_e should indicate a straight line possessing a slope of $1/q_m$ and an intercept of $1/(K_L q_m)$. The value of q_m and K_L constants and the correlation coefficients obtained from Langmuir model are presented in Figure 4 and Table 1. The isotherm of activated carbon was found to be linear over the whole concentration range studies and the correlation coefficients were extremely high as shown in Table 1. The values of q_m decrease with increase in temperature, thereby confirming that the process is exothermic [24].

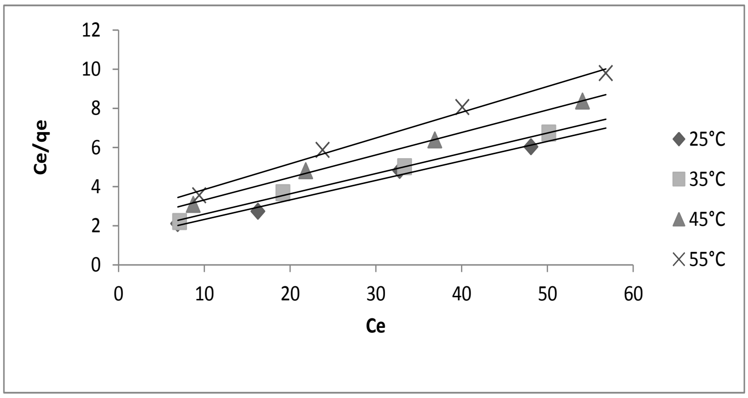

Figure 5. langmuir plot for Direct red 81 biosorption at different temperature

Freundlich isotherm

The Freundlich isotherm model is the earliest known relationship describing the sorption process. The model is applied to evaluate the adsorption on heterogeneous surfaces considering interactions between adsorbed molecules. The application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation, which can be employed to describe heterogeneous systems and is expressed as follow:

$$q_e = K_F\, C_e^{\frac{1}{n_F}} \qquad (2)$$

Where, K_F is the Freundlich constant (L g^{-1}) related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n_F$ is the heterogeneity factor and nF is a measure of the deviation from linearity of adsorption. Equation 2 can be linearized in the logarithmic form as Equation 3 and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \qquad (3)$$

the plot of log (q_e) versus log (C_e) was employed to generate the intercept value of K_F and the slope of $1/n_F$ (Table 1).

Table1. Comparison of the Langmuir and Freundlich isotherm parameter for biosorption of Direct red 81 at different temperature

T(K)	Freundlich isotherm			Langmuir isotherm		
	K_F	1/n	R^2	K_L	q_m	R^2
298	1.5066	0.439	0.937	0.0742	10.1	0.988
308	1.3867	0.438	0.991	0.0650	9.708	0.997
318	1.0592	0.462	0.991	0.0531	8.695	0.998
328	1.0069	0.433	0.999	0.0516	7.633	0.991

Thermodynamic study

The thermodynamics parameters are calculated using the following equations [25]

$$\Delta G^\circ = -RT \ln K \qquad (4)$$

Where, ΔGº is the free Gibbs energy change (kJ mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), K the thermodynamic equilibrium constant and T is the absolute temperature (K).

Values of K may be calculated from the relation of ln q_e/C_e versus q_e at different temperatures followed by extrapolation to zero [26]. The thermodynamic parameters are listed in Table 2. The negative ΔGº values confirm the spontaneous nature and feasibility of the adsorption process. The values of other parameters such as enthalpy change (ΔHº) and entropy change (ΔSº), may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (5)$$

Table 2. The thermodynamic parameters for biosorption of Direct red 81 in different temperature

T (K)	ΔG^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})
298	-6.44	-1.73×10^{-3}	-10.74
308	-6.99	-1.46×10^{-3}	
318	-7.74	-1.13×10^{-3}	
328	-8.07	-9.79×10^{-4}	

Kinetics approach

In order to study the adsorption rates of reactive dye by biosorbent, the pseudo first-order and pseudo second-order rates models were investigated. The Lagregren equation describes pseudo first-order model [27], as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (6)$$

Where q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t respectively, k_1 is the rate constant of pseudo first-order adsorption process (min^{-1}). Integration of Equation 6 for the boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$) gives:

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad (7)$$

By plotting of log (q_e - q_t) versus t, first-order rate constant k_1 and equilibrium adsorption density q_e were calculated from slope and intercept of plot (Figure 6). The pseudo second-order model, gives:

$$\frac{dq_t}{dt} = k_2(q_e - q_t) \qquad (8)$$

Where k_2 is the equilibrium rate constant for pseudo second order adsorption (g $mg^{-1}.min^{-1}$). Also integration of Equation 8 by applying boundary conditions t = 0 to t and
$q_t = 0$ to q, gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

$$h_i = k_2 q_e^2 \qquad (10)$$

Where h_i is the initial dye adsorption (mg $g^{-1}.min^{-1}$). The slope and intercept of plot of (t/q_t versus t) were used to calculate the pseudo second-order rate constant k_2 and q_e. The results are shown in Figure 7 and Table 3.

The correlation coefficients of all examined data were found very high for pseudo second-order equation. It showed a good compliance with the pseudo second-order equation. These results determined that the experimental data for the adsorption kinetics of reactive dye on biosorbent were fitted by the pseudo second-order kinetic model. Similar phenomenon was observed for the adsorption of basic dyes onto pomegranate peel, cotton and apricot stone [28].

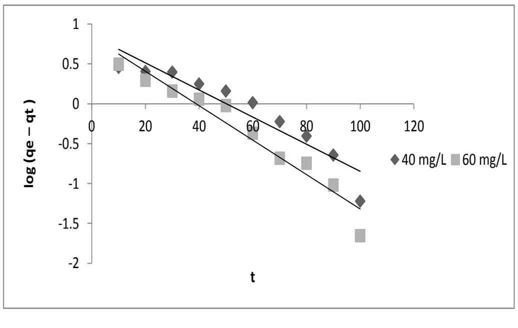

Figure 6. Plot of log (q_e - q_t) versus t for biosorption of Direct red 81 by using the pseudo first-order kinetic model

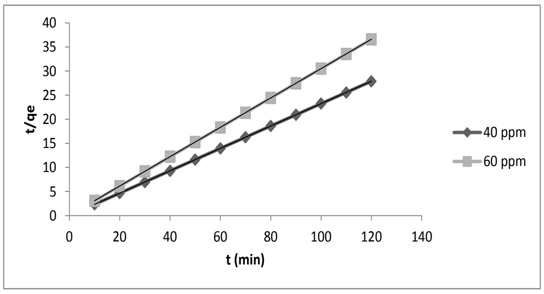

Figure7. Plot of 1/qe versus t for biosorption of Direct red 81 by using the pseudo second-order kinetic model

Table 3. Kinetic parameters calculated by using pseudo first-order and pseudo second-order rates models for biosorption of Direct red 81

Concentration of Direct red 81(mg L^{-1})	pseudo first-order kinetic model		pseudo second-order kinetic model	
	k_1(g mg^{-1}.min^{-1})	R^2	k_2(g mg^{-1}.min^{-1})	R^2
40	0.0391	0.8905	4.1666×10^{-4}	1
60	0.497	0.9439	1.8617×10^{-4}	1

CONCLUSION

The results obtained from this investigation demonstrate that active carbon prepared from Chamomilla plant is very efficient in biosorption of Direct red 81 from textile wastewater. The biosorption capacity is strongly dependent on the temperature and decreases significantly with increase in temperature from 25 to 55^{o}C. The kinetics was found to follow pseudo- second order kinetic model with high degree of correlation coefficient (R^2=1). The biosorption equilibrium data were analyzed by using Langmuir and freundlich isotherm models and the results have shown that biosorption behavior of this dye could be follow to Langmuir isotherm model.

Furthermore, it was also found that the Chamomilla plant can be used as a low cost material for azo dye biosorbtion.

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