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BIOSORPTION OF REMAZOL NAVY BLUE DYE FROM AN AQUEOUS SOLUTION USING *PSEUDOMONAS PUTIDA*

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Abstract: Biosoprtion of **Remazol navy blue dye**, from an aqueous solution was studied by adsorption on powdered *Pseudomonas putida*. The biosoprtion of the dye on putida was investigated during a series of batch adsorption experiments to determine the effect of initial dye concentration, contact time, initial pH and adsorbent dosage. The Langmuir and Freundlich isotherm models were tested for their applicability. The equilibrium data satisfied both Langmuir and Freundlich models. The biosoprtion capacity of *pseudomonas putida* was found to be 20 mg dye per gram of adsorbent. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy and entropy of adsorption. Adsorption of Remazol navy blue dye is an exothermic reaction with ΔHo of -11.14 kJ/mol. The experimental data were analyzed using the pseudo-first-order and pseudo-second-order adsorption kinetic models. The experimental data fit the second-order kinetic model.
Keywords: Remazol Navy Blue; *Pseudomonas putida*; Biosorption; Isotherm; kinetics.

1. Introduction

Treatment of dyed effluents presents several problems mainly due to toxicity and recalcitrance of dyestuffs. The wastewater generated by textile industry is rated as one of the most polluting among all industrial effluents. The toxic wastes from industries affect visibility, photosynthesis and also aquatic life. There are more than 10,000 dyes available commercially and are used for coloring [1]. Thus, decolorization of textile wastewaters has been a major environmental concern for a long time. Colour removal has been the target of significant attention in the last few years, not only because of its toxicity but also to its visibility. The presence of these dyes in water even at very low concentration is highly visible and undesirable [2]. Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. These are presently used for coloring cotton fibers. They differ from all other classes of dyes in that they bind to the textile fibers such as cotton to form covalent bonds [3]. At

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present colored wastewater is treated by physical, chemical and biological methods. Biological methods which include Biosorption process employing biopolymers (such as sawdust, wood chips, chitin/chitosan, starch, cyclodextrin and cross linked chitosan / cyclodextrin) and non-viable microbial (fungi, algae and bacteria) biomass has emerged as one of the powerful and attractive option since it is inexpensive, effective and simple to operate. Biosorption involves a combination of active and passive transport mechanisms starting with the diffusion of the adsorbed component to the surface of the microbial cell. A number of biomaterials have been used as biosorbents in the lieterature [4]. Since little is known on the biosorption of dyes to microbial biomass, adsorptive properties of the microorganism for dyes should be investigated. The present study included effect of initial dye concentration, biosorbent dosage, temperature and pH on biosorption of dye using dead biomass. Studies were carried out to fit the equilibrium data obtained from batch studies to suitable Isotherm (Langmuir isotherm, and Freundlich isotherm). The sorption capacity of the dye was studied using the adsorption isotherms.

2. Materials and methods

2.1. Psedomonas Putida and Dye

Pseudomonas putida is a gram-negative rod-shaped saprotrophic soil bacterium. It demonstrates a very diverse metabolism, including the ability to degrade organic solvents such as toluene. This ability has been put to use in bioremediation, or the use of microorganisms to biodegrade oil. *Pseudomonas putida* NCIM sp 2650 was chosen for the present study to analyze their effectiveness for biosorption of the dye. Microorganisms were obtained from National Chemical Laboratory, Pune. The strain was periodically sub cultured once in a fifteen days on agar slants. The pseudomonas culture was then dried in oven at around 100^{o}C overnight. Commercial textile dye such as RB21, Remazol navy blue dye was procured from a local company Campbell KNITWEAR LTD, Belgaum, India.

2.2 Batch adsorption experiments

The aqueous dye solutions of desired concentrations were prepared from 1000 mg/l stock solutions. Batch adsorption experiments were carried out in 100 ml conical flask containing the aqueous dye solution of the desired concentration and the known amount of bio-sorbent. Initial pH was adjusted to the desired level with 1 N NaOH or 1 N HCl solutions. The solution was agitated at constant speed of 120 rpm and at 30^{o}C temperature till the equilibrium condition was reached. The dye solution was then separated from the adsorbent by centrifugation and the dye concentration of supernatant was determined by using UV spectrophotometer. Batch experiments were performed at different biosorbent dosage in the range of 0.2 g/l to 1.2 g/l, initial dye concentration in the range of 10 to 40 mg/l and pH varying from 2 to10.

3. Results and discussion

3.2 Effect of pH

Since pH is one of the main variables affecting the biosorption process [5]. The initial pH values of dye solutions affect the chemistry of both the dye and biosorbent. It is known that ionic dyes upon dissolution release colored dye anions/cations into solution. The biosorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent which is in turn influenced by the solution pH [6]. Hence the batch adsorption experiments were conducted at different initial pH conditions ranging from 2 to 9. Fig. 1 shows the effect of pH on percentage biosorption at equilibrium, with initial dye concentration of 50mg/l and biosorbent dosage of 1.0g/l. The percentage removal of dye by biosorption has decreased with the increase in pH from 2 to 8. Marginal decrease in percentage adsorption has been observed with the increase in pH from 2 to 6**.** At a pH above 6, a considerable decrease in biosorption takes place. The decrease in biosorption with increase in pH may be explained on the basis of acid-base dissociation at solid/liquid interface [7]. Previous researchers have reported similar observations for the sorption of dye [8, 9, 10]

3.3. Effect of contact time

The contact time variation for percentage removal of remazol navy blue during batch biosorption with various initial dye concentrations is shown in Fig. 2. It can be observed that the biosorption is rapid within around 25 minutes of initial time, but the adsorption progressed at a lower rate for the remaining time. As at the initial times the bulk solution concentrations are higher, the driving forces are the maximum, leading to maximum rates. But as the biosorption proceeds, the bulk concentration reduce approaching the equilibrium values and the rate decreases.

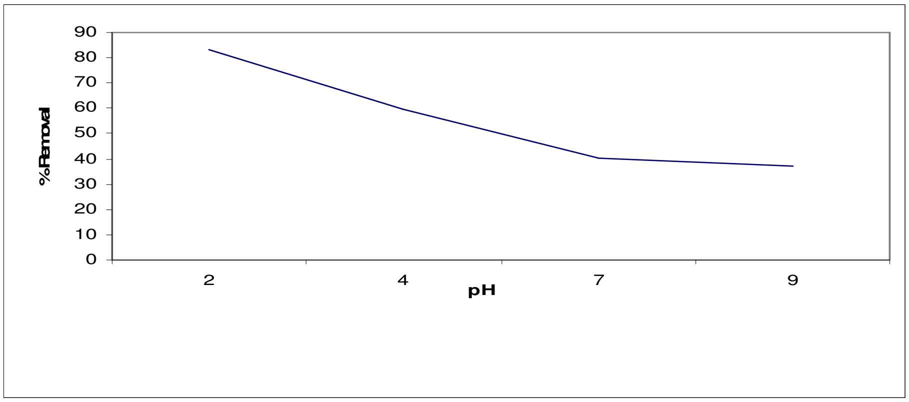

Figure 1. Effect of initial pH on percentage adsorption of dye. Initial concentration 50mg/l and biosorbent dosage 1.0 g/l

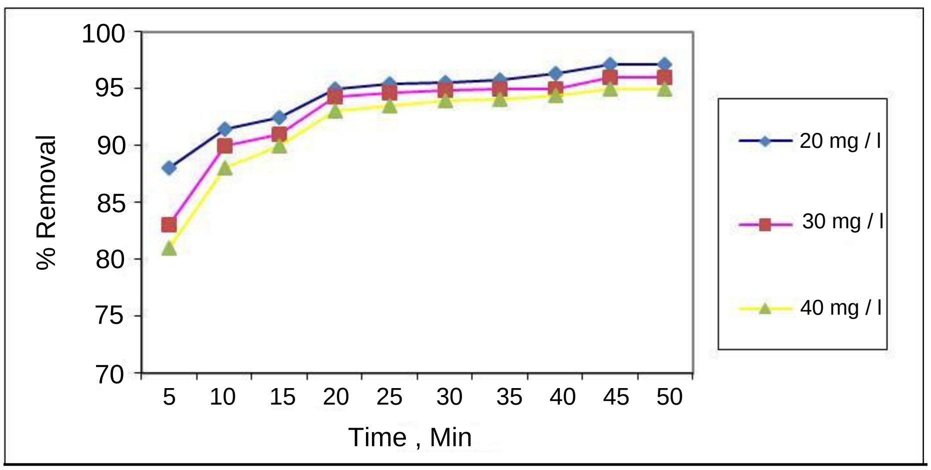

Figure 2. Effect of contact time on percentage biosorption at different initial dye concentration. pH2 and biosorbent dosage 1.0 g/l

It can be observed from Fig.2 that, with a fixed amount of biosorbent, the percentage remazol navy blue dye adsorption has increased with time and then attained a constant value at 45 min. The time to reach equilibrium conditions appears to be independent of initial dye concentrations. This can be shown as an evidence of time for attainment of equilibrium being governed by the rate of mass transfer. Similar trend was obtained for the adsorption of dyes such as MG onto treated sawdust [11], reactive dyes onto activated sludge [2], rhodamine B on activated carbon [12].

3.4 Effect of initial dye concentration

The effect of initial dye concentration on percentage biosorption of the dye is presented in Fig.2. The uptake of dye at equilibrium decreased from 97% to 95 % with increase in dye concentration from 20 mg/l to 40 mg/l for a fixed biosorbent dosage of 1.0 g/l. In sufficient number of active sites available for the biosorption of all the dye molecules, lead to higher residual concentration in solution, with increasing initial dye concentrations.

3.5 Effect of biosorbent dosage

The variation of biosorption of the dye with varying amount of biosorbent was studied for different initial dye concentrations and the results of this study are shown in Fig.3. The uptake increases with increasing dosage. The uptake increased by 10 % when the quantity of biosorbent used was doubled. As the amount of biosorbent was increased further to 1.0 g/l, the uptake increased by only 2%. As such, 1.0 g/l of adsorbent was considered to be quite appropriate. Further increase in dosage did not show much increase in uptake of dye. The increase in the amount of dye removal with adsorbent dosage is due to greater availability of adsorbent surface area [13] and hence more active sites.

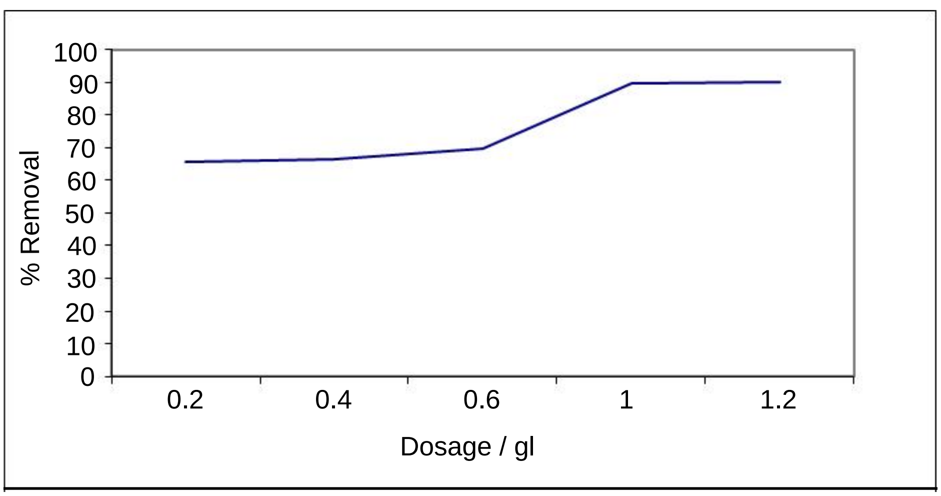

Figure 3. Effect of biosorbent dosage on percentage adsorption. pH 2 and temperature 30^{o}C

3.6 The isotherm analysis

The relationship between the amount of remazol navy blue dye adsorbed and the equilibrium dye concentration remaining in solution is described by an adsorption isotherm. The equilibrium isotherm is of fundamental importance for the design and optimization of adsorption system for removal of the dye from aqueous solution. The two most common isotherm types for describing adsorption system are the Langmuir and the Freundlich isotherm.

The most important model of monolayer adsorption is the Langmuir isotherm given in Eq (1).

$$qe = \frac{Q_0 b C_e}{1 + b C_e} \qquad \text{........ (1)}$$

The Langmuir model [13], [14] is based on the assumption that the maximum biosorption occurs when a saturated monolayer of solute molecules is present on the biosorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. Langmuir equation can be linear zed as shown in Eq (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{C_e Q_0} \qquad \text{........ (2)}$$

Where C_e is the bulk solution concentration of remazol navy blue dye (mg/l) at equilibrium q_e is the amount of adsorbed dye per unit mass of biosorbent (mg/g), Q_0 the monolayer capacity of the adsorbent (mg/g) and *b* is the Langmuir adsorption constant indicating the biosorption energy (l/mg).

The Freundlich isotherm is derived to model the multi layer biosorption and for the biosorption on heterogeneous surfaces. The Freundlich model is formulated as shown in Eq. (3).

$$qe = k C_e^{\frac{1}{n}} \qquad \text{........ (3)}$$

The Freundlich isotherm model assumes that different sites with several adsorption energies are involved [13] [15]. The equation may be linearized by taking the logarithm on both sides of Equation and linear form of Freundlich isotherm can be given by Eq (4).

$$ln q_e = ln k + \frac{ln C_e}{n} \qquad \text{........ (4)}$$

Where, *k* is the sorption capacity (mg/g) and *n* is an empirical parameter which is an indicator of adsorption intensity [16]. The equilibrium data obtained from the experiments were fitted into these two types of isotherms to test the validity of these for navy blue dye adsorption system. The values of the constants for isotherms were obtained from the slope and intercept of the plots of linear form of each of the isotherm equations. The values of parameters of the isotherms at three different temperatures of 20, 30 and 40°C, along with the corresponding R^2 values representing the goodness of fit are presented in Table 1.The R^2 values indicate that the equilibrium for remazol navy blue dye-adsorbent system can be represented by both Langmuir and Freundlich isotherms under the conditions of the study, but Freundlich model has been found

Table 1: Biosorption Isotherm parameters at different temperature

Temperature °C	Langmuir model	Freundlich Model
20	Q_0=49 mg/g b =0.75 l/mg R^2=0.872	n =3.38 k =20.04 mg/g, R^2=0.91
30	Q_0=36 mg/gram b =1.28 l/mg R^2=0.83	n =3.5, k =19 mg/g R^2=0.90
40	Q_0=35.5 mg/g b =1 l/mg R^2=0.84	n =3.38, k =17 mg/gram R^2=0.90

to fit better. With Freundlich isotherm, the values of n obtained are greater than one. This indicate that the adsorption is much more favorable [17]. However the smaller the value of n ($1 < n < 10$) the higher the adsorption intensity [17, 18]. The greater the k values the higher the biosorption capacity of the adsorbent for the adsorbate. Decrease in k and n with increasing temperature, suggest that biosorption capacity is higher at lower temperatures and adsorption is more favorable as the temperature is decreased. From the results of Langmuir isotherm parameters, it is clear that the values of monolayer capacity Q_0 and adsorption energy b of the biosorbent decreases with the increase in temperature.

3.7. Thermodynamic Analysis

In addition, changing the temperature will change the equilibrium capacity of the biosorbent for a particular adsorbate. The variation of the removal of the dye with varying temperature (20°C to 40°C) was studied. The uptake increases with decrease in temperature for all the initial concentrations. The isotherm parameters of adsorption at different temperatures are presented in

Table 2. From the table it can be seen that the biosorption capacity decreases with temperature. Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG^0, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process.

Reactions occur spontaneously at a given temperature if ΔG^0, is a negative quantity. Thermodynamic parameters, i.e., free energy change ΔG^0, enthalpy ΔH^0 and entropy ΔS^0 were evaluated using Van't Hoff's Eq. (5)

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{........ (5)}$$

Where K_c is the Langmuir equilibrium constant ΔH^0 and ΔS^0 are the standard enthalpy and entropy changes of adsorption respectively and the values ΔH^0 and ΔS^0 are calculated from the slopes and intercepts of the linear plot of lnK_c vs 1/T. The free energy ΔG^0 of specific adsorption calculated using the following Eq. (6).

$$\Delta G^0 = -RTlnK_c \quad \text{........ (6)}$$

The thermodynamically parameters calculated Table 3. The negative values of ΔG^0 indicate the feasibility and spontaneous nature of Remazol navy blue dye biosoprtion on *pseudomonas putida.* The change in enthalpy ΔH^0 for absorbent was found to be negative. The positive values confirm the exothermic nature of adsorption.

Table 2. Thermodynamic Parameters for the adsorption of RBB on red mud

ΔG^0, **kJ/mol**	ΔH^0, **kJ/mol**	ΔS^0, **kJ/mol**
20°C		
-9.27	11.14	0.36

Conclusion

Biosorption on pseudomonas putida has been investigated for removal of Remazol Navy Blue dye from aqueous solution. Dye biosorption on pseudomonas putida is an exothermic reaction and biosorption isotherm can be fitted by Langmuir and Freundlich isotherm in which the Freundlich model is the best fitted. The suitability of first- and second-order kinetic models for the sorption of dye onto biosorbent was also discussed.

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