

Biosorption of Reactive Red 198 from an Aqueous Solution Using *Morinda Tinctoria*

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Research Article

Abstract: *Morinda tinctoria* seed used for the removal of reactive red 198 from an Aqueous solution was studied by batch biosorption system process. The equilibrium dye uptake capacity of *Morinda tinctoria* was determined with the influence of various environmental parameters such as sorbent dosage (0.02–0.1 g 100mL⁻¹), initial pH (1–6), and initial dye concentration (10–50 mg L⁻¹). Batch experiments were carried out for biosorption kinetics and isotherm studies. The results showed that dye uptake capacity was found to increase with decreases in biosorbent dosage. Equilibrium uptake capacity was found to be more at pH2, when compared with all other pH values studied. The equilibrium data was analyzed with the use of Freundlich and Langmuir adsorption isotherm models. The equilibrium data was found to be fitted very well with the Freundlich isotherm model when compared with the Langmuir isotherm model. Adsorption kinetics data modeled with the application of pseudo-first order and pseudo-second order models revealed that the pseudo-second order model was the best fitting model. The biosorbent characteristics were observed by SEM and FTIR analysis.

Keywords: Biosorption; reactive dye, isotherm, kinetics, *Morindatinctoria*

1. Introduction

Dyes from dyeing processing wastewaters coming from the textile, papers, plastics, food and cosmetic industries cause severe environmental pollution if they are emitted to the environment without any proper treatment¹. The traditional physical or chemical decolorization methods including flocculation using chemicals, coagulation using chemicals, irradiation, ion exchange, precipitation using chemicals, ozonation and adsorption using activated carbon or a combination of these methods have been used for dye removal from dye effluent². Considerable work has been done to remove toxic dyes from waste water using low cost adsorbents from various non-conventional waste materials from industries and agriculture. Adsorbents derived from agricultural wastes have demonstrated outstanding capabilities for the removal of dyes from dye effluent[3]. Many research groups have investigated the possibility of using different types of sorbent obtained from carbonaceous materials (such as wood, peat, rice husk and coconut shell) [4] raw agricultural solid wastes

[5](such as sawdust, wheat straw, orange peels and bagasse), industrial solid wastes (such as fly ash, red mud and metal hydroxide sludge), natural materials (such as clays, zeolites, siliceous materials) and biological materials. The materials to be used as sorbents for the removal of dyes should meet the following criteria: (1) economically viable and abundantly available, (2) high uptake capacity with minimum duration, (3) applicable for wide variety of dyes, and (4) ability to remove textile dyes in the presence of co-pollutants such as salts, heavy metals and other conditions of wastewater [6]. *Morinda tinctoria* belongs to family Rubiaceae. The plant is extensively cultivated in India and its leaves and roots are used in traditional medicine and to relieve pain in the gout [7]. In the present investigation, *Morinda tinctoria* bio mass was used for removal of reactive red 198 dyes from aqueous solution with the effect of initial sorbent dosage, solution pH and initial dye concentration in a batch mode. The equilibrium data was analyzed using Langmuir and Freundlich adsorption isotherm model. The kinetics data was analyzed using Pseudo first order and Pseudo second order kinetics model.

2. Experimental Methods

2.1 Preparation of adsorbent

The *Morinda tinctoria* seeds were broken up into small pieces and washed with water, dried in an oven and transferred to the muffle furnace and the seeds pieces were burnt distinctively in the furnace for 2 hours fixing the temperature at 400°C. Adsorbent thus produced were withdrawn from the furnace, cooled, washed with water and dried in an oven at 110°C and ground in a mortar by means of a pestle applying moderate pressure. It was cooled in the desiccator for an hour then removed and ready for use as an adsorbent.

2.2 Preparation of dye solutions

Reactive red 198 were obtained from Balaji chemicals Ltd., Chennai, India. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 10,000 mg L⁻¹. The

experimental solutions were obtained by diluting the dye stock solutions in accurate proportions for different initial dye concentrations. The chemical structure is illustrated in figure 1.

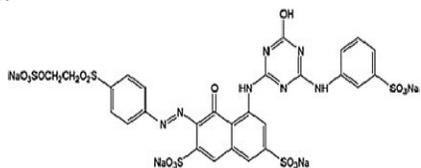


Figure 1: Chemical structure of reactive red 198 dye

2.3 Batch experimental process

Biosorption experiments were carried out in a Rotary shaker (Scigenics Biotech Pvt. Ltd., Chennai, India) at 180 rpm and at 30°C. Reactive Red 198 solution was prepared to get required concentration. *Morinda tinctoria* biomass was added in the dye solution. Samples were withdrawn at predetermined time interval (0, 30, 60, 90, 120, 150 and 180 min), centrifuged at 12,000 rpm for 10 min and the absorbance of the supernatant were determined at maximum wavelength ($\lambda_{\text{max}} = 520 \text{ nm}$), using UV-spectrophotometer. Results were reported on the basis of the dye uptake capacity.

2.3.1 Studies of biosorbent dosage

The dye solution with the concentration of 50 mg/L was equally dispersed in to five conical flasks (100 ml in each flask) and added with different dosages (0.02–1.0 g/L) of biosorbent. These flasks were kept in a rotary shaker and absorbance values were determined using UV-spectrophotometer.

2.3.2 Studies of pH

The dye solution with the concentration of 50 mg/L was prepared. The initial pH values ranging from 1 to 7 were adjusted with HCl and NaOH. The optimum dosage of biosorbent were added in to the each flask and kept in a rotary shaker. The absorbance values were determined using UV-spectrophotometer

2.3.3 Studies of initial dye concentration

The dye solution with five different concentrations ranging from 30 to 90 mg/L was prepared in different conical flask. The optimum dosage of biosorbent was added in to each flask and adjusted to optimum pH and kept in a rotary shaker at 30°C. The absorbance values were determined using UV-spectrophotometer.

3. Results and Discussion

3.1. SEM imaging

Scanning electron microscopy (SEM) (JEOL JSM-6360) is an important technology, which has been increasingly used to examine morphology of the biological specimens. The surface morphology of the *Morinda tinctoria* sorbent was exemplified by the scanning electron microscope. As shown in Fig. 2

(biomass without dye adsorption), the rough and porous surface was found to be more in biomass. This surface property should be considered as a factor for providing an increase in the porous surface of the biosorbent [8]. Thereby this porous surface is increasing the uptake capacity of Reactive Red 198 dye.

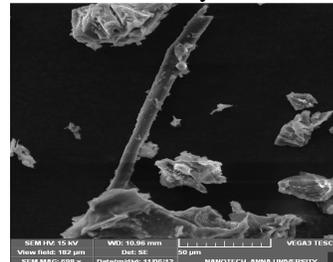


Figure 2: Scanning electron microscopy imaging of *M. tinctoria* biomass (without adsorption of reactive red 198)

3.2 Fourier Transform Infrared spectroscopy analysis

The FTIR was carried to confirm the existence of amine, carboxyl groups as shown in figure 3. The spectrum showed the peaks at 1575 cm^{-1} representing the carboxylic groups [9]. The FTIR spectrum showed some characteristics of an amine groups such as N-H bonding bands at 2358 cm^{-1} , N-H out of plane bending band near 880 cm^{-1} and N-H rocking bands at $700\text{--}900 \text{ cm}^{-1}$ [10].

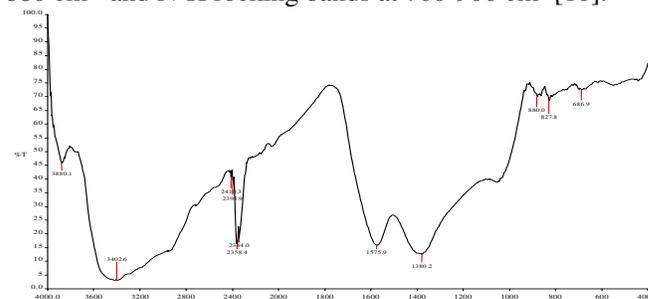


Figure 3: FTIR spectrum of *M. tinctoria* biomass without adsorption of reactive red 198

3.3. Effect of biosorbent dosage

The effect of biosorbent dosage on the equilibrium dye uptake capacity was shown in Fig. 4. It was observed that 0.02 g/L biosorbent dosage was found to be optimum for the dye removal. The equilibrium dye uptake capacity was found to be decreased with increases in biosorbent dosage. This can be attributed to the difference in solute transfer rate onto the biosorbent surface. Further there is a distribution of the dye compounds to unit weight of biosorbent with increase in biosorbent dosage. The decrease in equilibrium uptake capacity may have been due to the solute transfer rate on the adsorbent surface. In addition, the amount of dye compounds adsorbed on to the unit weight of the adsorbent was split with increasing adsorbent dosage [11].

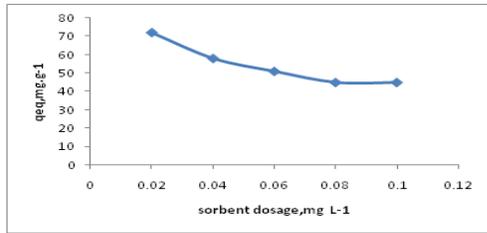


Figure 4: Effect of sorbent dosage on the equilibrium dye uptake capacity of *M. tintoria* biomass for reactive red 198 dye (initial dye concentration = 50mgL⁻¹; temperature=30°C, agitation rate=180revmin⁻¹)

3.4 Effect of pH

The effect of pH on biosorption was examined at a dye concentration of 50 mg/L and pH using 0.1 HCl and 0.1N NaOH solution, to determine optimum pH for the biosorption as shown in figure 5. It was found that the uptake capacity of dye increased with increase in pH value up to 2 and then decreased sharply with increase in pH value above 2. At lower pH values, the biomass will have a net positive charge [12].The reduction in the uptake capacity of dye on *Morinda tintoria* with increasing pH can be attributed to a change in surface characteristics and charge. As the pH of the system increased, the number of negatively charged sites increased, and the number of positively charged site decreased in the biomass[13]. A negatively charged surface site on the sorbent did not favour the adsorption mechanisms with respect to the pH[14].So, the pH 2 was taken as the optimum value for the corresponding experiments [15].

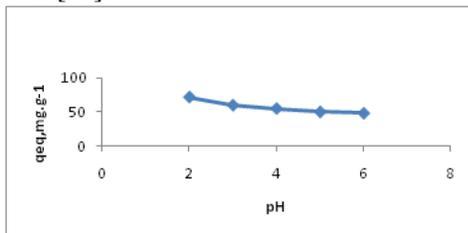


Figure 5: Effect of pH on the equilibrium dye uptake capacity of *Morinda tintoria* seeds biomass for reactive red 198 dye (initial dye concentration = 50mg L⁻¹; sorbent dosage = 0.02 g 100 mL⁻¹; temperature = 30°C, agitation rate = 180 rev min⁻¹)

3.5 Effect of initial dye concentration

The uptake capacity of dye with the influence of initial Dye concentration 30, 45, 60, 75, and 90 mg/L were studied. The optimum biosorbent dosage 0.02 g of adsorbent was added to 100 ml of dye solution with pH value of 2. These flasks were then kept in the rotary shaker at 180 rpm and 30°C. The samples were withdrawn at pre determined time interval. The samples were centrifuged at 12,000 rpm for 10 min. The absorbance values were measured and dye uptake capacity was found to increase linearly with contact time in the beginning, then nonlinearly at slower rate and

finally attained saturation called equilibrium time as illustrated in figure 6. The biosorption capacity of biomass for Reactive Red 198 was determined. Increase in dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake [16]. In addition, higher initial dye concentration increases the number of collisions between dye molecules and sorbents, which enhances the sorption process [17].The same type of result was reported by Agarawal and Sahu for adsorption of Cadmium on Manganese nodule residue [18].

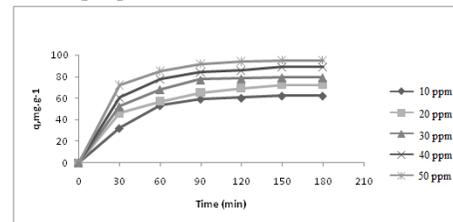


Figure 6: Effect of initial dye concentration on the uptake capacity of *Morinda tintoria* seeds biomass for reactive red 198 dye (sorbent dosage=0.02g 100mL⁻¹; pH=2; temperature= 30°C; agitation rate=180rev min⁻¹)

3.6. Equilibrium modeling

The most widely used isotherm models for solid-liquid adsorption are the Langmuir and Freundlich.

3.6.1. Langmuir isotherm

Langmuir adsorption isotherm model assumes a monolayer adsorption onto a surface containing finite number of identical sites [19].This isotherm can be defined according to the Folling equation;

$$q_{eq} = \frac{Q^o b C_{eq}}{1+b C_{eq}} \quad \text{--- (1)}$$

where q_{eq} is the quantity of dye adsorbed per unit weight of biosorbent at equilibrium (mg/g); Q_o is the maximum possible amount of dye that can be adsorbed per unit dry weight of biosorbent to form a complete monolayer on the surface (mg/g); C_{eq} is the equilibrium concentration of unadsorbed dye in the solution (mg/L); b is the empirical constant, indicating the affinity of sorbent towards the sorbate [20]. Figure 7 shows the equilibrium data fitted to the Langmuir isotherm expressions.

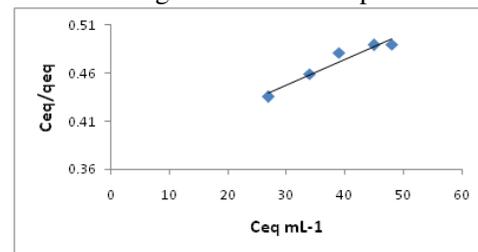


Figure 7: Plots for the Langmuir isotherm for the sorption of reactive red 198 at different initial dye concentrations (sorbent dosage = 0.02 g 100 mL⁻¹; pH= 2; temperature= 30°C; agitation rate = 180 rev min⁻¹)

3.6.2. Freundlich isotherm

The Freundlich's adsorption isotherm equation [21] is given by

$$q_{eq} = K_F C_{eq}^{1/n} \text{-----(2)}$$

where K_F and n indicators of adsorption capacity and adsorption intensity, respectively. The value of K_F and n are obtained by plotting $\ln q_{eq}$ versus $\ln C_{eq}$ is shown in Fig. 7. The calculated isotherm constants at different temperature are given in Table 1. In view of the values of linear regression coefficients in Table 1, the Freundlich model exhibited a slightly better fit to the equilibrium data when compared to the Langmuir model studied. The best fit of equilibrium model was determined based on the coefficient of determination R_2 . The similar trend of the result was previously reported by Naveen Prasad et al.,[22] for removal of Coomassie Brilliant Blue dye using coir pith. The maximum equilibrium uptake capacity of reactive red 198 dyes was previously reported as 60 mg g^{-1} at 50 mg L^{-1} of dye concentration by using *A. indica*. In the present investigation, the maximum equilibrium uptake capacity of *Morinda tinctoria* was observed as 72 mg g^{-1} at 50 mg L^{-1} of dye concentration. So, the adsorption capacity of *Morinda tinctoria* was found to be comparable with other adsorbents.

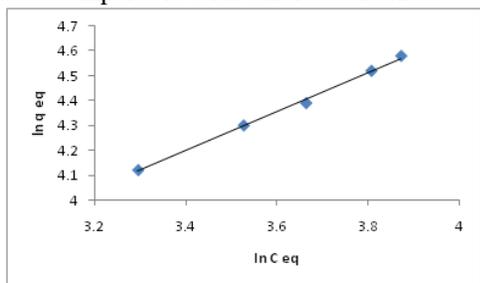


Figure 8: Plots for the Freundlich isotherm for the sorption of reactive red 198 at different initial dye concentrations (sorbent dosage=0.02 g 100mL⁻¹; pH= 2; temperature= 30°C; agitation rate=180 revmin⁻¹)

Table 1: Langmuir and Freundlich isotherm constants and coefficient of determination for the sorption of Reactive red 198 using *Morinda tinctoria* seeds biomass

Parameters	Isotherm constants for the biosorption of reactive red 198 using <i>M.tintoria</i>	
	Langmuir adsorption isotherm	
Q0(mg g ⁻¹)	370.3	
b (L mg ⁻¹)	0.001	
R ²	0.9306	
Freundlich adsorption isotherm		
KF(mg g ⁻¹)	32.3817	
n	1.2648	
R ²	0.9972	

3.7. Kinetic modelling

In order to investigate the biosorption processes of Reactive Red 198 on the *Morinda tinctoria*. Pseudo-first order and Pseudo-second order kinetic models were used.

3.7.1 Pseudo-first order kinetic model

Lagergren's pseudo-first order rate expression is represented in Eqⁿ (3) [23]

$$\frac{dq}{dt} = k_{1,ad}(q_{eq}-q) \text{-----(3)}$$

Where q_{eq} and q are equilibrium uptake capacity and uptake capacity at any time, respectively. The $k_{1,ad}$ is the first order biosorption rate constant (min⁻¹). The integrated form of Eqⁿ (3) is given by Eqⁿ (4).

$$\log(q_{eq}-q) = \log q_{eq} - \frac{k_{1,ad}}{2.303} t \text{-----(4)}$$

The pseudo-first order rate constant, $k_{1,ad}$ and q_{eq} were determined from the slope and intercept of the plot(Fig. 9). The pseudo-first order rate constant values were presented in Table 2 for different initial dye concentration.

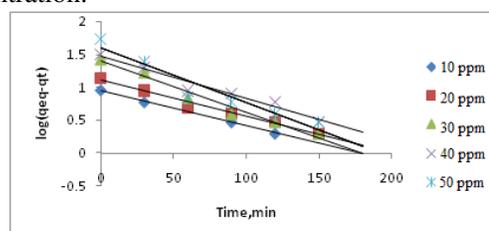


Figure 9: Plots for the pseudo-first order for the sorption of reactive red 198 at different initial dye concentrations (sorbent dosage = 0.02 g 100mL⁻¹; pH=2; temperature = 30°C; agitation rate = 180 revmin⁻¹)

Table 2: Pseudo-first and pseudo-second order rate constants, calculated and experimental q_{eq} values for the biosorption of reactive red 198 using *Morinda tinctoria* seeds biomass

Initial concentration (mg L ⁻¹)	Q _{eq,exp} (mg g ⁻¹)	Pseudo-first order			Pseudo-second order		
		k _{1,ad} (min ⁻¹)	Q _{eq,c} (mg g ⁻¹)	R ²	k _{1,ad} (min ⁻¹)	Q _{eq,c} (mg g ⁻¹)	R ²
10	62	.01220	9.0361	0.9849	0.00509	62.893	0.9986
20	74	0.0124	12.653	0.9788	0.00455	74.072	0.9988
30	81	0.01796	24.887	0.9720	0.00440	83.333	0.9983
40	92	0.0147	29.444	0.9599	0.00232	90.909	0.9982
50	98	0.01911	39.039	0.9116	0.00153	100.000	0.9964

3.7.2 Pseudo-second order kinetic model

The pseudo-second order kinetic model is generally expressed as in Eqⁿ (5)

$$\frac{dq}{dt} = k_{2,ad}(q_{eq}-q)^2 \text{-----(5)}$$

Where $k_{2,ad}$ is the second order biosorption rate constant (mg⁻¹ min⁻¹).

Integrating Eqn (5) gives Eqn (6):

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t \quad (6)$$

The pseudo-second order rate constant, $k_{2,ad}$ and q_{eq} were determined from the slope and intercept of the plot (Fig. 10). The pseudo-second order rate constant values were presented in Table 2 for different initial dye concentrations. The calculated coefficients of determination for Pseudo-second order kinetic model was found to be closer to unity when compared to Pseudo-first order kinetic model. The equilibrium adsorption capacity was found to be increased with increase in initial dye concentration. The $q_{eq,cal}$ calculated values were found to be very closer to q_{eq} experimental values in Pseudo-second order kinetic model when compared to the Pseudo-first order kinetic model (Table 2). Therefore, the kinetic data was found to be fitted very well with the Pseudo-second order kinetic model when compared to Pseudo-first order kinetic model for the biosorption of Reactive Red 198 using *Morinda tinctoria*

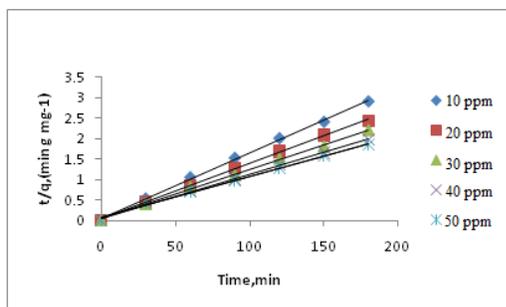


Figure 10: Plots for the pseudo-second order for the sorption of reactive red 198 at different initial dye concentrations (sorbent dosage=0.02 g 100mL⁻¹; pH=2; temperature=30°C; agitation rate=180rev min⁻¹)

4. Conclusions

From the present investigation, it was observed that *A. indica* waste biomass could be used as a potential low cost biosorbent to treat the textile effluent. The initial biosorbent dosage, synthetic dye solution pH, and dye concentration values were found to affect the biosorption capacity of the seeds of *Morinda tinctoria*. The equilibrium data were found to be fitted very well with the Freundlich adsorption isotherm model with higher coefficient of determination when compared to the Langmuir adsorption isotherm model. The kinetic data fit very well with the pseudo second-order rate equation when compared to pseudo first-order rate equation. The surface morphology of the sorbent was analyzed using SEM micrograph. The functional groups were analyzed using FTIR. The adsorbent prepared from *Morinda*

tinctoria was found to be one among the effective adsorbents for the removal of reactive dyes from waste water.

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