BIOSORPTION OF REACTIVE DYE BY GRACILARIA VERRUCOSA A MARINE ALGA: BATCH STUDIES

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ABSTRACT

The biosorption of Reactive Orange 16 by *Gracilaria verrucosa* was evaluated under several parameter conditions. The biosorption method consisted of adding 0.2 g *G.verrucosa* biomass in 50 ml of dye solution concentrations (10-1000 mg/L) together in an orbital rotary shaker. The biosorption profile was highly dependent upon the initial pH concentration, temperature, the adsorbent dosage and size. *G.verrucosa* biomass exhibited higher uptakes at pH 4 of all concentrations examined. The high uptake values of 0.2 g/50 mL was observed and then decreased for the further increase in dosage. As the temperature increased the uptake of dye increases up to room temperature and the uptake decreases with further increase in temperature. As the size increased the uptake of dye increased up to 0.5mm and the uptake decreases with further increase in size. Therefore size was taken as 0.5mm/50mL, for biosorption experiments.Biosorption isotherms have been correctly represented by Langmuir and Freundlich non linear isotherm model. Biosorption isotherm data fitted better into Langmuir model.

KEY WORDS: Reactive dye, De-colorization, Reactive Orange 16, isotherm, Red seaweed, Macroalga

I. INTRODUCTION

Combating environmental pollution is a thrust area at this present juncture. In this context, dye effluent of the textile industries has been identified as one of the major pollutant of waterways. Biosorption is a technique that can be used for the removal of pollutants from waters. This technology employs various types of biomass such as dead bacteria, yeast and fungi as source for the decontamination of dye containing effluents. The process basically involves the passive uptake of pollutants from aqueous solutions by the use of non-growing and non –living biomass, that allowing the recovery and/or environmental accepTable- disposal of the pollutants. Recent investigations by various groups have shown that selected species of sea weeds possess impressive adsorption capacities for a range of heavy metal ions but there are few studies on the color removal.

Reactive dyes, the removal of which is examined here, are widely used in many industrial uses due to their bright color, excellent color fastness and ease of application .Reactive dyes are typically azo based chromophores combined with different reactive groups.[1]

In this study, the biosorption of Reactive Orange 16 by *Gracilaria Verrucosa* was evaluated under several parameter conditions. The initial pH concentration, the adsorbent dosage, the adsorbent size and the temperature of the dye solution have been investigated. Two equilibrium non linear isotherm models were used to fit the experimental data namely Langmuir and Freundlich models.

II. MATERIALS AND METHODS

A. Marine Alga & Dye

Gracilaria Verrucosa, was collected from Mandapam and Pulicat, India. It was then sun dried and crushed to particle sizes in the range of 0.1 to 1.0 mm. The crushed particles were then treated with 0.1 M HCl for 5 h followed by washing with distilled water and then kept for shaded dry over night. The resultant biomass was subsequently used in sorption experiments. Reactive orange 16 is obtained from Sigma–Aldrich Corporation, Bangalore, India.

III. RESULTS AND DISCUSSIONS

A. Batch Experiments

Batch biosorption experiments were performed in an orbital rotary shaker at 150 rpm using 250 ml Erlenmeyer flasks containing 0.2 g *Gracilaria Verrucosa* biomass in 50 ml of solution containing different reactive dye concentrations. After 12 h, the reaction mixture was centrifuged at 3000 rpm for 10 min. The dye content in the supernatant was determined using UV-Spectrophotometer (Hitachi, Japan) at 494 nm. The amount of dye biosorbed was calculated from the difference between the dye quantity added to the biomass and the dye content of the supernatant using the following equation:

$$Q = (C_0 - C_f) * V / M \quad (1)$$

where Q is the dye uptake (mg/g); C_0 and C_f are the initial and equilibrium dye concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g).

Effect of pH

Dye sorption is highly pH dependent. Solution pH is one of the most important environmental factors, which

influences both the cell surface dye binding sites and the dye chemistry in water. In batch experiments, the effect of initial solution pH on dye uptake was studied by varying the pH from 2 to 8 at 10 mg/L initial dye concentration. The biosorbent dosage and agitation speed (150 rpm) were kept constant. Marine alga biomass exhibited higher uptakes at pH 4 and the results are presented in Fig. 1. The uptake was declined sharply with further increase in pH upto 6. The enhancement of uptake of reactive dyes at acidic pH may be explained in terms of electrostatic attraction between the positively charged surface of the biomass and the dye particles. Reactive dyes are also called anionic dyes because of the negative electrical structure of the chromophore group [2]. As the initial pH increases, the number of negatively charged sites on the biosorbent surface increases and the number of positively charged sites decreases. A negative surface charge does not favour the adsorption of dye anions due to the electrostatic repulsion [1]. A similar trend for binding of reactive and acid dyes by fungus R. arrhizus and alga Enteromorpha prolifera has shown maximum values in the range pH 2–3 with a sharp drop off at higher values [2,3].

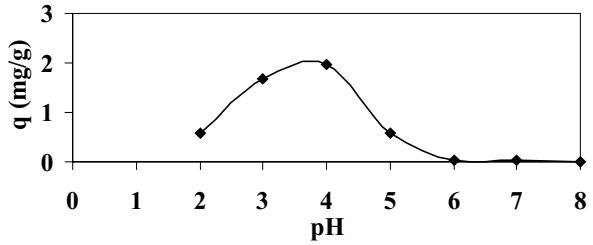

Fig. 1. The effect of initial pH on the equilibrium uptake capacity of *Gracilaria Verrucosa* of Reactive Orange 16 (temperature 30 ø% C, adsorbent dosage 0.2 g/50mL, adsorbent size 0.5mm/50mL,agitation rate 150 rpm,*C*o = 10 mg/L).

Effect of Temperature on dye biosorption

The effect of temperature also influenced the equilibrium dye uptake. From Fig 2, the temperature range was taken from 25°C to 50°C at an initial dye concentration of 10 mg/L. It was exhibited that the surface activity decreased with increasing temperatures. As the temperature increased the uptake of dye increases up to room temperature and the uptake decreases further increase in temperature. Therefore room temperature was taken as optimum temperature for biosorption experiments. Further increase in temperature from 30°C may alter the surface activity of biomass result in a decrease in removal value, indicating that this process is exothermic in nature. The exothermic nature of dye biosorption has also been reported for the biosorption of Remazol Black B and Acid Red 274 dyes by R. arrhizus and E. prolifera, respectively [3, 4]. The present results showed essentially no thermal deactivation of biosorption activity under operational temperatures.

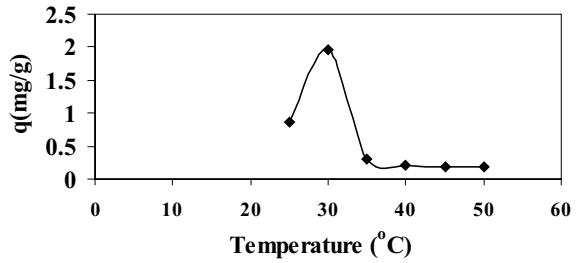

Fig. 2. The effect of temperature on the equilibrium uptake capacity of *Gracilaria verrucosa* of Reactive Orange 16 (pH 4.0, adsorbent dosage 0.2 g/50mL, adsorbent size 0.5mm/50mL,agitation rate 150 rpm,*C*o = 10 mg/L).

Effect of Biosorbent Dosage

In batch experiments, the effect of biosorbent dosage on dye uptake was studied by varying the dosage from 0.1 to 0.5 gm. For each biosorbent dosage, the dye uptake varied. From Fig 3, marine alga biomass exhibited high uptakes values in low dosage and then decreased for the further increase in dosage. Therefore optimum dosage was taken as 0.2 g/50mL for biosorption experiments. The dosage of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes and lower percentage removal efficiencies [5,6].

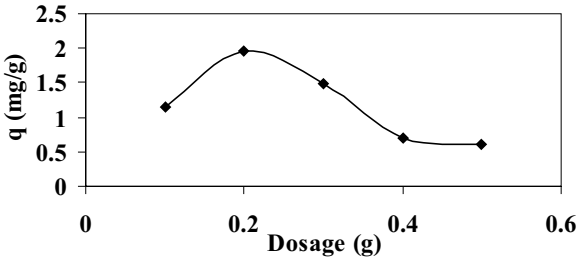

Fig. 3. The effect of dosage on the equilibrium uptake capacity of *Gracilaria Verrucosa* of Reactive Orange 16 (pH 4.0, temperature 30 ø% C, adsorbent size 0.5mm/50mL,agitation rate 150 rpm,*C*o = 10 mg/L).

An increase in the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites. Conversely, the quantity of biosorbed solute per unit weight of biosorbent decrease with increasing biosorbent dosage, which may be due to the complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake .

Effect of Biosorbent Size

The size of the biosorbent also plays a vital role in biosorption. Smaller sized particles have a higher surface area, which in turn favors biosorption and results in a shorter equilibration time. Simultaneously, a particle for biosorption should be sufficiently resilient to withstand the applicable pressures and extreme conditions applied during regeneration cycles [7]. Therefore, preliminary experiments are mandatory to decide the suiTable- size of a biosorbent. The size range was taken from 0.1 to 1.0 mm/50mL. From Fig 4, as the size increased the uptake of dye increased up to 0.5grams and the uptake decreases with further increase in size. Therefore size was taken as 0.5g/50mL, for biosorption experiments.

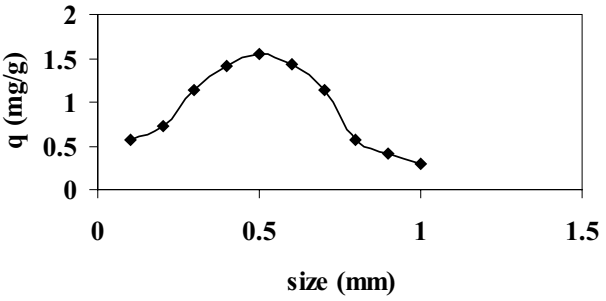

Fig. 4. The effect of size on the equilibrium uptake capacity of *Gracilaria Verrucosa*of Reactive Orange 16 (initial pH 4.0, temperature 30 ø% C , adsorbent dosage 0.2 g/50mL, agitation rate 150 rpm,*C*o = 10 mg/L).

IV. BIOSORPTION ISOTHERM MODELS

Effect of Adsorption Isotherms

Isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and the liquid phase dye concentration. In the present study, the biosorption capacity and equilibrium isotherm for Reactive Orange onto Marine alga *Gracillaria Verucossa* were estimated using two equilibrium models: Langmuir and Freundlich isotherm models.

The Langmuir and Freundlich model are the most frequently used two parameter models in the literature describing the non-linear equilibrium between adsorbed pollutant on the cells (q_e) and pollutant in solution (C_e) at a constant temperature. The Langmuir equation, which is valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites is given by Eq.

$$\text{Langmuir:} \quad q = \frac{q_{\max} b C_f}{1 + b C_f} \qquad (2)$$

where q_{max} is the maximum dye uptake (mg/g), *b* the Langmuir equilibrium constant (L/mg), relates to bonding energy of adsorption which are functions of the characteristics of the system as well as time[8] .

The Freundlich model is the earliest known relationship describing the sorption equilibrium and is expressed by the following equation

$$\text{Freundlich:} \quad q = K_F C_f^{1/n} \qquad (3)$$

K_F the Freundlich constant (L/g) which corresponds to the binding capacity and *n* which characterizes the affinity between the sorbent and sorbate, the Freundlich affinity constant. The main reason for the extended use of these isotherms is that they incorporate constants that are easily interpreTable-.

Table 1. Langmuir and Freundlich model parameters at different pH

Temp	Langmuir Parameters			Freundlich Parameters		
°C	q_{max} (mg/g)	b (L/mg),	R^2†	K_F (L/g)	n	R^2†
25	134.0889	0.004062	0.976	0.579992	1.162984	0.8375
30	129.9682	0.005744	0.981	1.074831	1.254078	0.8706
35	109.9377	0.003427	0.9827	0.766039	1.290474	0.8904
40	89	0.01016	0.9772	0.717669	1.279245	0.8699
45	86.53052	0.006466	0.9788	0.641982	1.216824	0.7878
50	78	0.006018	0.9627	0.777426	1.317821	0.7636

On increasing the initial dye concentrations, the total dye uptake increased and the total percent removal decreased. For instance, on changing initial Reactive Orange 16 concentrations from 10 to 1000 mg/L , the amount sorbed increased from 1.96 to 100.02 mg/L at pH 4.But the removal efficiency decreased from 79 to 66.8% as the Reactive Orange 16 concentration increase from 10 to 1000 mg/L. Langmuir model fitted with the experimental data well, showing correlation coefficient greater than 0.94 for Reactive Orange 16 onto *G.Verucossa*.Q_{max} increases with increasing initial pH and reached maximum at pH 4 .Thus for good biosorbents in general, high Q_{max} are desirable .The constants evaluated from the isotherms at different pH with the correlation coefficients are also presented in Table- 1. Fig.4 represents comparison of the experimental and predicted isotherms for Reactive Orange 16 on *Gracilaria Verrucossa* (initial pH 4.0, temperature 30 ø% C, biosorbent dosage 0.2 g /50ml, biosorbent size 0.5mm/50 mL, agitation rate 150 rpm).The biosorption uptake capacity increase up to room temperature and then decreases by further increasing the temperature. Therefore among the room temperature (30° C) favoured biosorption .The constants evaluated from the isotherms at

different temperature with the correlation coefficients are also presented in Table- 2

Table 2. Langmuir and Freundlich model parameters at different Temperature

pH	Langmuir Parameters			Freundlich Parameters		
	q_{max} (mg/g)	b (L/mg)	R^2†	K_F $(L/g)^{1/n}$	N	R^2†
2	118.9821	0.003611	0.9637	2.422683	1.782747	0.9004
3	119.9973	0.003324	0.9686	0.687584	1.309809	0.8665
4	129.9682	0.005744	0.981	1.074831	1.254078	0.8706
5	115.0085	0.002115	0.9575	0.639579	1.330026	0.8889
6	113.9821	0.004649	0.9446	1.460166	1.485467	0.8011
7	109.9762	0.003595	0.974	0.924905	1.426792	0.8887
8	53.32655	0.010027	0.9894	1.04958	1.577273	0.8673

Correlation coefficient

Table 3. Langmuir and Freundlich model parameters at Different dosages

Dosage	Langmuir Parameters			Freundlich Parameters		
g/ 50mL	q_{max} (mg/g)	b (L/mg),	R^2†	K_F (L/g)	n	R^2†
0.1	90.10967	0.017116	0.9549	1.150138	1.392526	0.8058
0.2	129.9682	0.005744	0.981	1.074831	1.254078	0.8706
0.3	68.45187	0.061838	0.9493	5.821751	2.404902	0.8231
0.4	26.85852	0.044336	0.8553	18.25071	7.493727	0.8299
0.5	100.5387	0.012489	0.8336	1.034588	1.900918	0.8746

Table 4. Langmuir and Freundlich model parameters at different size

Size	Langmuir Parameters			Freundlich Parameters		
mm/ 50mL	q_{max} (mg/g)	b (L/mg)	R^2†	K_F (L/g)	n	R^2†
0.1	104.3087	0.00854	0.9785	2.760421	1.695341	0.8505
0.2	107.8187	0.025548	0.9128	1.611102	1.268273	0.62
0.3	120.7088	0.009302	0.9341	2.713566	1.534594	0.7614
0.4	122.0011	0.006962	0.9855	1.701309	1.362708	0.8628
0.5	129.9682	0.005744	0.981	1.074831	1.254078	0.8706
0.6	99.02681	0.010931	0.9855	1.191294	1.306333	0.7808
0.7	92.63062	0.004183	0.9875	0.766156	1.290541	0.8946
0.8	89.47569	0.010076	0.9834	0.827325	1.219592	0.7642
0.9	74.34926	0.012184	0.9405	0.799148	1.327397	0.8034
1	68.87625	0.049094	0.6827	0.144364	0.96407	0.8155

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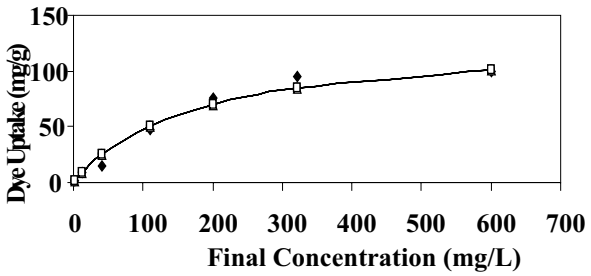

Fig. 5. Comparison of Langmuir non linear model to experimental isotherm data obtained during Reactive Orange 16 biosorption by G*. verucossa* (pH 4.0, temperature = 30 ø% C, biosorbent dosage = 0.2 g/L, biosorbent size=0.5mm, agitation rate = 150 rpm).

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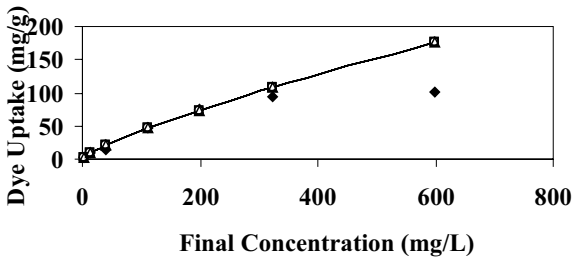

Fig. 6. Comparison of Langmuir non linear model to experimental isotherm data obtained during Reactive Orange biosorption by G*. verucossa* (pH 4.0, temperature = 30 ø% C, biosorbent dosage = 0.2 g/L, biosorbent size=0.5mm, agitation rate = 150 rpm).

As represented in fig. Fig.5 the Langmuir model exhibited slightly better fit to the biosorption data for the dye than Freundlich models in the studied concentration and temperature ranges. The maximum capacity Q_{max} determined from the Langmuir isotherm defines the total capacity of the biosorbent for Reactive Orange as 129.96 mg/g at 30°C. The maximum adsorption capacity of biomass deceased with further increasing temperature. From the Fig 3, the biosorption uptake capacity increase up to 0.2 gms and then decreases by further increasing the dosage. Therefore among the dosages 0.2 g favoured biosorption. The constants evaluated from the isotherms at different dosages with the correlation coefficients are also presented in Table- 3

From Fig.6.the Langmuir model exhibited slightly better fit to the biosorption data for the dye than Freundlich model in the studied concentration and dosage ranges. The maximum capacity Q_{max} determine from the Langmuir

isotherm defines the total capacity of the biosorbent for Reactive Orange as 129.96mg/g at 0.2 g.

IV. SUMMARY AND CONCLUSIONS

The results from this research show that the biosorption is a viable process for the removal of textile reactive dyes from aqueous solutions. In this study, the biosorption examined superior biosorption uptake in batch operations. Since this seaweed (*Gracillaria Verucossa)* is readily available in the environment; it is more economical and can yield sorbet of higher sorption capacity Further study focused on the industrial waste water is needed. The experimental data was fitted with nonlinear isotherm models such as Langmuir and Freundlich, in batch mode of experiments. Langmuir sorption model served to estimate the maximum uptake values, where they could not be reached in the experiments and have high correlation coefficients..

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