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# Biosorption Of Reactive Black 5 Onto *Grateloupia lithophila.,* A Marine Alga.

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## ABSTRACT

The biosorption of Reactive Black 5 by deactivated marine macro alga *Grateloupia lithophila* was investigated in batch mode. Langmuir and Freundlich adsorption models were used for the mathematical description of the batch biosorption equilibrium data and model constants were evaluated. The adsorption capacity was pH dependent with a maximum value of 132.19 mg/g at pH 3.

**Keywords:** Bio sorption; Reactive Black 5; Biomass; *Grateloupia lithophila*; Adsorption Isotherms.

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## INTRODUCTION

Large amounts of dyes are annually produced and applied in textile, cosmetics, paper, leather, pharmaceutical, food and other industries. The textile industry accounts for two-thirds of the total dyestuff market, consuming a large proportion of reactive dyes due to the high demand for cotton fabrics with brilliant colors.Environmental regulations exist to ensure the quality of the environment and these regulations include the characteristics of the water discharged by manufacturing locations. Industry is constantly searching for more effective and economical methods for meeting these regulations. However, there is no effective and universal method for the removal of colour resulting from the presence of all dye types. Chemical and physical decolorization processes which include flocculation combined with flotation, membrane filtration, electro kinetic coagulation, ozonation, oxidation, precipitation, ion-exchange and adsorption are often expensive and inefficient and little adaptable to a wide range of dye wastewaters . Most of these, furthermore, are based on physical displacement or chemical replacement, generating yet another problem in the form of toxic sludge, the disposal of which adds further burden on the techno-economic feasibility of the treatment process. Biological materials such as algae, fungi, bacteria and yeast for the dyes removal and recovery technologies have gained importance during recent years. Biosorption using dead cells has many advantages over the live cell systems [1, 2]. The aim of this study is to determine the adsorption capacity of algal dead *Grateloupia lithophila* biomass

## MATERIALS AND METHODS

### *Grateloupia lithophila*

Dead *Grateloupia lithophila* biomass was obtained from Muthukadu, Chennai. It was sun dried then crushed and finally sieved to particle sizes in the range of 0.1–1.0 mm. The biomass was then treated with 0.1MHCl for 5 h followed by washing with distilled water and then dried in shade. The resultant biomass was subsequently used in sorption experiments.

### *Dyes*

Reactive Black 5 were obtained from Sigma–Aldrich Corporation, Bangalore, India. The properties of the dyes used are given in Table 1.

**Table 1: Properties of the dyes**

| C.I. name | Molecular weight | $\lambda_{max}$ (nm) | Molecular formula |
|---|---|---|---|
| Reactive Black 5 | 991.82 | 597 nm | $C_{26}H_{21}N_5Na_4O_{19}S_6$ |

## RESULTS AND DISCUSSIONS

### BATCH EXPERIMENTS

Batch biosorption experiments were performed in a rotary shaker at 150 rpm using 250mL Erlenmeyer flasks containing 0.2 g of *Grateloupia lithophila* biomass in 50mL of solution containing different reactive dye concentrations at desired pH conditions (using 0.1M HCl and 0.1M NaOH). After 12 h, the reaction mixture was centrifuged at 3000 rpm for 10 min. The dye content in the supernatant was determined using UV (2004) Spectrophotometer (Hitachi, Japan) at $\lambda_{max}$ value of 597 nm.

The amount of dye biosorbed was calculated from the differences between the dye quantity added to the biomass and the dye content of the supernatant using the following equation:

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

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 3 and the results are presented in Fig. 1.

The uptake was declined sharply with further increase in pH upto 8. 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 [4]. 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 [3]. A similar trend for binding of reactive and acid dyes by fungus *Rhizopus arrhizus* and alga *Enteromorpha prolifera* has shown maximum values in the range pH 2–3 with a sharp drop off at higher values [1, 4].

### 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 [5,6]. The present results showed essentially no thermal deactivation of biosorption activity under operational temperatures.

### 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 [7, 8] .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 [9]. 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.

## 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 Black 5 onto Marine alga *Grateloupia lithophila* 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.

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

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[10] .

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

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

$K_F$ 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.

On increasing the initial dye concentrations, the total dye uptake increased and the total percent removal decreased. For instance, on changing initial Reactive Black 5 concentrations from 10 to 1000 mg/L, the amount sorbed increased from 2.48 to 132.19 mg/L at pH 3.But the removal efficiency decreased from 78.67 to 52.87% as the Reactive Black 5 concentration increase from 10 to 1000 mg/L. Langmuir model fitted with the experimental data well, showing correlation coefficient greater than 0.95 for Reactive Black 5 onto *Grateloupia lithophila.*$Q_{\max}$ increases with increasing initial pH and reached maximum at pH 3 .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 2.

Fig.5. represents Comparison of the experimental and predicted isotherms for Reactive Black 5 on *Grateloupia lithophila* **(**initial pH 3.0, temperature 30 °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 3.

The maximum capacity $Q_{\max}$ determined from the Langmuir isotherm defines the total capacity of the biosorbent for Reactive Black 5 as 132.362 mg/g at 30°C. The maximum adsorption capacity of biomass deceased with further increasing temperature. From the Figure 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 and sizes with the correlation coefficients are also presented in Table 4 and 5.

Table 2: Langmuir and Freundlich model parameters at different pH

| pH | Langmuir Parameters | | | Freundlich Parameters | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ (mg/g) | b (L/mg) | $R^2$† | $K_F$ (L/g) | n | $R^2$† |
| 2 | 86.39071 | 0.006933 | 0.9848 | 1.104528 | 1.459114 | 0.8907 |
| 3 | 132.362 | 1.293831 | 0.955 | 37.40133 | 3.73479 | 0.8451 |
| 4 | 109.8951 | 0.004574 | 0.9726 | 0.902944 | 1.26019 | 0.8157 |
| 5 | 78.66149 | 0.011131 | 0.9912 | 2.084193 | 1.70819 | 0.8876 |
| 6 | 70.00522 | 0.012547 | 0.9559 | 2.87566 | 2.017108 | 0.923 |
| 7 | 65.01838 | 0.008385 | 0.9897 | 1.122012 | 1.532484 | 0.8956 |
| 8 | 60.11909 | 0.012673 | 0.9781 | 1.223166 | 1.690167 | 0.9292 |

† Correlation coefficient

Table 3: Langmuir and Freundlich model parameters at different Temperature

| Temp | Langmuir Parameters | | | Freundlich Parameters | | |
|---|---|---|---|---|---|---|
| °C | $q_{max}$ (mg/g) | b (L/mg), | $R^2$† | $K_F$ (L/g) | n | $R^2$† |
| 25 | 128.5849 | 0.027948 | 0.9385 | 0.859201 | 0.995929 | 0.64 |
| 30 | 132.362 | 1.293831 | 0.955 | 37.40133 | 3.73479 | 0.8451 |
| 35 | 94.0323 | 0.006846 | 0.9315 | 1.285513 | 1.345459 | 0.7282 |
| 40 | 86.37148 | 0.009148 | 0.9734 | 0.512887 | 1.13811 | 0.7715 |
| 45 | 84.91684 | 0.006389 | 0.9825 | 2.577398 | 1.877475 | 0.906 |
| 50 | 70.00759 | 0.00859 | 0.9902 | 1.700031 | 1.726769 | 0.9023 |

† Correlation coefficient

Table 4: Langmuir and Freundlich model parameters at different Dosage

| 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 | 131.0051 | 0.01951 | 0.9877 | 3.308427 | 1.56102 | 0.7655 |
| 0.2 | 132.362 | 1.293831 | 0.955 | 37.40133 | 3.73479 | 0.8451 |
| 0.3 | 81.51872 | 0.030838 | 0.9636 | 3.71424 | 1.664871 | 0.7267 |
| 0.4 | 70.53624 | 0.022867 | 0.9737 | 1 | 1 | 0.6227 |
| 0.5 | 31.90768 | 0.006728 | 0.991 | 0.415266 | 1.35398 | 0.8182 |

† Correlation coefficient

Table 5: 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 | 108.9132 | 0.015956 | 0.96 | 32.96208 | 5.679017 | 0.8532 |
| 0.2 | 117.9949 | 0.023899 | 0.91 | 5.672325 | 1.778498 | 0.6706 |
| 0.3 | 118.9989 | 0.024916 | 0.93 | 1.060691 | 1.080818 | 0.556 |
| 0.4 | 128.5862 | 0.014128 | 0.943 | 0.244959 | 0.810495 | 0.498 |
| 0.5 | 132.362 | 1.293831 | 0.955 | 37.40133 | 3.73479 | 0.8451 |
| 0.6 | 104.195 | 0.016731 | 0.9403 | 25.70253 | 4.712749 | 0.8802 |
| 0.7 | 100.9994 | 0.016002 | 0.8885 | 0.85346 | 1.104858 | 0.5716 |
| 0.8 | 100.0173 | 0.006064 | 0.9812 | 0.346609 | 1.031947 | 0.7755 |
| 0.9 | 93.86965 | 0.011247 | 0.9399 | 2.59465 | 1.560913 | 0.6984 |
| 1 | 75.18367 | 0.03023 | 0.95 | 1.185612 | 0.793641 | 0.662 |

† Correlation coefficient

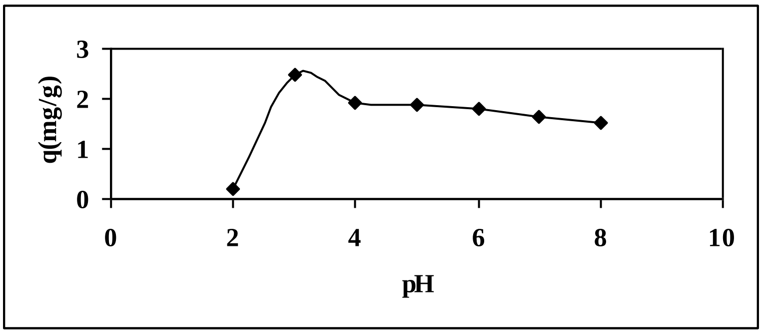

**Fig.1.The effect of initial pH on the equilibrium uptake capacity of *Grateloupia lithophila* of Reactive Black 5 (temperature 30 °C, adsorbent dosage 0.2 g/50mL, adsorbent size 0.5mm/50mL,agitation rate 150 rpm, *Co* = 10 mg/L).**

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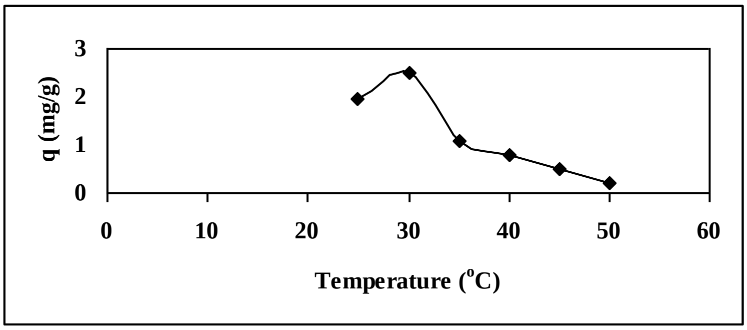

**Fig.2.The effect of temperature on the equilibrium uptake capacity of *Grateloupia lithophila* of Reactive Black 5 (pH 3.0, adsorbent dosage 0.2 g/50mL, adsorbent size 0.5mm/50mL,agitation rate 150 rpm,*Co* = 10 mg/L).**

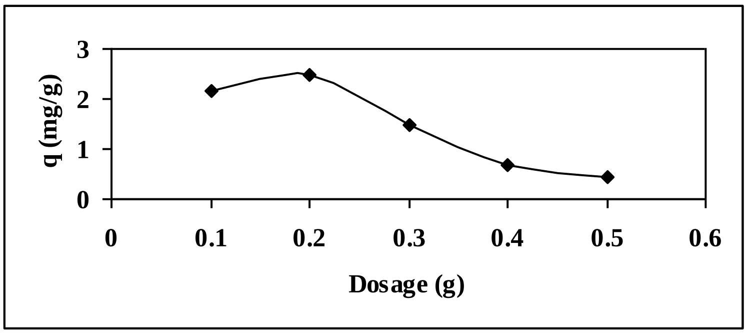

**Fig.3. The effect of dosage on the equilibrium uptake capacity of *Grateloupia lithophila* of Reactive Black 5 (pH 3.0, temperature 30 °C, adsorbent size 0.5mm/50mL,agitation rate 150 rpm,*Co* = 10 mg/L).**

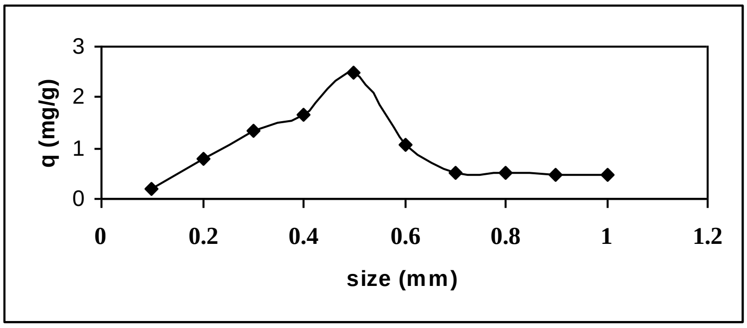

**Fig.4. The effect of size on the equilibrium uptake capacity of *Grateloupia lithophila* Of Reactive Black 5 (initial pH 3.0, temperature 30 °C , adsorbent dosage 0.2 g/50mL, agitation rate 150 rpm,*Co* = 10 mg/L).**

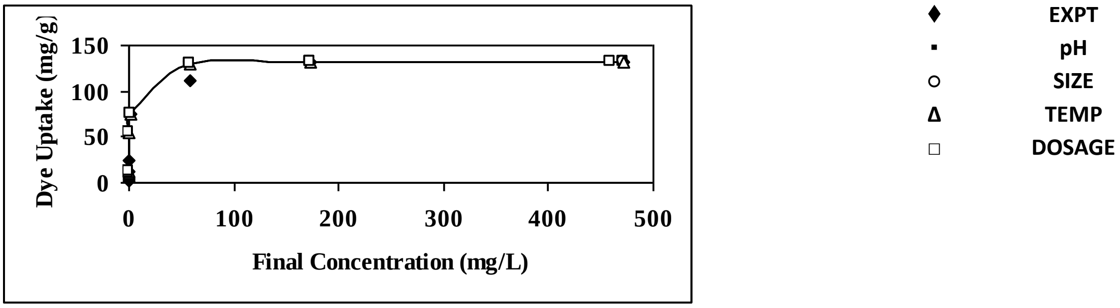

**Fig.5.Comparison of Langmuir non linear model to experimental isotherm data obtained during Reactive Black 5 biosorption by G. *lithophila* (pH 3.0, temperature = 30 °C, biosorbent dosage = 0.2 g/L, biosorbent size=0.5mm, agitation rate = 150 rpm).**

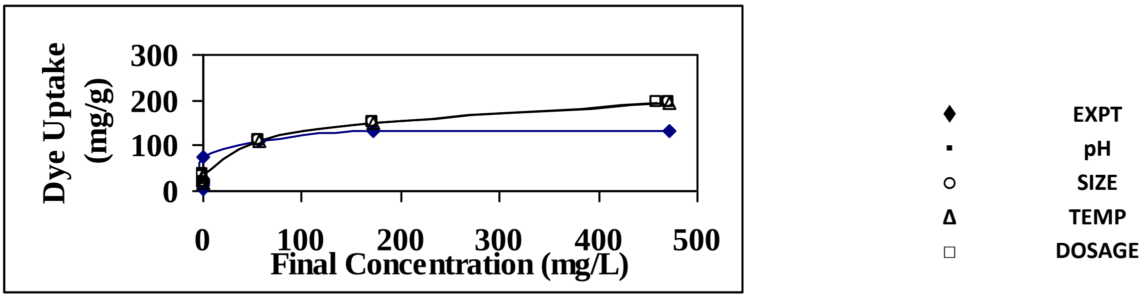

**Fig.6.Comparison of Freundlich non linear model to experimental isotherm data obtained during Reactive Black 5 biosorption by Grateloupia lithophila (pH 3.0, temperature = 30 °C, biosorbent dosage = 0.2 g/L, biosorbent size=0.5mm, agitation rate = 150 rpm).**

## 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 *Grateloupia lithophila* 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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