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Adsorption of Reactive Orange 16 onto *Gracilaria* Species a Marine Alga

D. RAJHA AMARNATH* and T.V.N. PADMESH
Department of Chemical Engineering, Sathyabama University
Jeppiaar Nagar, Chennai-600 119, India
Fax: (91)(44)(24503202; E-mail: rajhaamy@gmail.com

Decolourization of reactive orange by *Gracilaria verrucosa* was evaluated under several parameter conditions. The decolourization method consisted of adding 0.2 g marine alga biomass in 50 mL of solution containing dye of different concentrations together in a rotary shaker. The decolourization profile was highly dependent upon the initial pH concentration, the adsorbent dosage and the temperature of the dye solution. Marine alga biomass exhibited higher uptakes at pH 4 of all concentrations examined. The high uptakes values at 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. Adsorption isotherms have been correctly represented by Langmuir, Freundlich isotherm model.

Key Words: Reactive dye, Decolourization, Reactive orange 16, Red seaweed, Macroalgae.

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, especially that are not easily biodegradable such as metals and dyes. This technology employs various types of biomass 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 comparatively there is few studies on the colour removal.

In this study, the de-colourization of reactive orange 16 by *Gracilaria verrucosa* was evaluated under several parameter conditions. The initial pH concentration, the adsorbent dosage and the temperature of the dye solution have been investigated. Two equilibrium isotherm models were used to fit the experimental data namely Langmuir and Freundlich.

EXPERIMENTAL

Marine alga and dye: *Gracilaria verrucosa* was collected from Mandapam and Pulicat, India. It was then sun dried and crushed to particle sizes in the range of 1 to 2 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. The resultant biomass was subsequently used in sorption experiments. Reactive orange 16 is obtained from Sigma-Aldrich Corporation, Bangalore, India.

Batch experiments: Batch biosorption experiments were performed in a rotary shaker at 150 rpm using 250 mL Erlenmeyer flasks containing 0.2 g Marine algae 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). 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:

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

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).

RESULTS AND DISCUSSION

Effect of pH: Dye sorption is highly pH dependent. The pH of the solution 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^{-1} initial dye concentration. The biosorbent dosage and agitation speed (150 rpm) were kept constant. Marine algae biomass exhibited higher uptakes at pH 4 and the results are presented in Fig. 1. The uptake was declined sharply with further

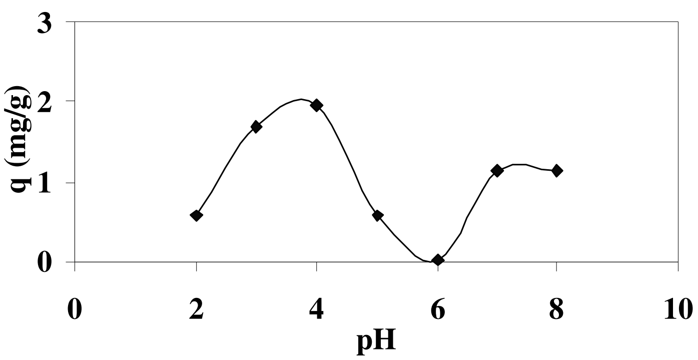

Fig. 1. Effect of initial pH on the equilibrium uptake capacity of *Gracilaria verrucosa* of reactive orange 16 (temperature 30 ºC, agitation rate 150 rpm, Co = 10 mg/L)

increase in pH upto 6. A similar observation has been reported, where reactive dye adsorption decreases as the pH increases. 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[1]. 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[2]. It is worth noting that earlier studies on reactive dye biosorption reported the necessity of strong acidic condition for optimum biosorption.

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 to 50 ºC at an initial dye concentration of 10 mg L^{-1}. 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 with further increase in temperature. Therefore room temperature was taken as an optimum temperature for biosorption experiments. Further increase in temperature from 30 ºC 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.

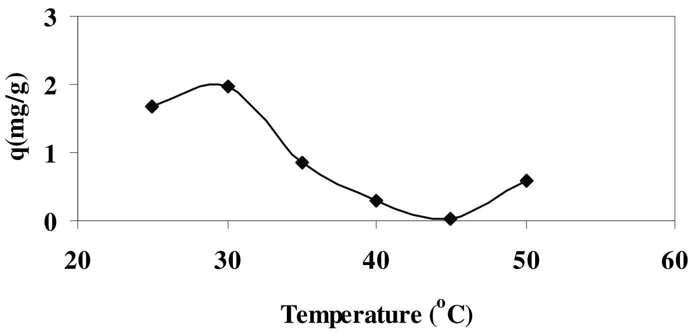

Fig. 2. Effect of temperature on the equilibrium uptake capacity of *Gracilaria verrucosa* of reactive orange 16 (initial pH 4.0, temperature 30 ºC, Co = 10 mg/L, agitation rate 150 rpm)

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 g. For each biosorbent dosage the dye uptake varied. From Fig. 3, Marine algae biomass exhibited high uptakes values in low dosage and then decreased for the further increase in

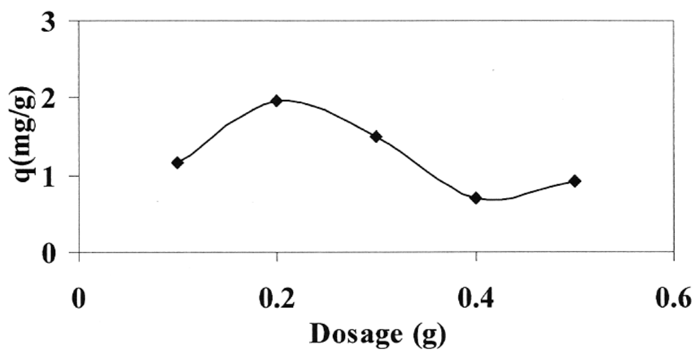

Fig. 3. Effect of dosage on the equilibrium uptake capacity of *Gracilaria verrucosa* of reactive orange 16 (initial pH 4.0, temperature 30 ºC, Co = 10 mg/L, agitation rate 150 rpm)

in dosage. Therefore optimum dosage was taken as 0.2 g/50 mL 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]. 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[2,7]. 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[8].

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 16 onto Marine algae *Gracillaria verucossa* were estimated using two equilibrium models *i.e.*, Langmuir and Freundlich isotherm models.

The Langmuir and Freundlich models are the most frequently used two parameter models in the literature describing the non-linear equilibrium between adsorbed pollutant on the cells (qe) and pollutant in solution (Ce) 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 eqn.

$$\text{Langmuir: } q = \frac{q_{max} bC_f}{1 + bC_f} \tag{2}$$

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[7].

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

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

K_F the Freundlich constant $(L/g)^{1/n}$ which corresponds to the binding capacity and n which characterizes the affinity between the sorbent and sorbate, is the Freundlich affinity constant. The main reason for the extended use of these isotherms is that they incorporate constants are easily interpretable.

Langmuir model fitted with the experimental data well, showing correlation coefficient greater than 0.96 for reactive orange 16 onto *G. verucossa*. Q_{max} and b increases with increasing initial pH and reached maximum at pH 4. Thus for good biosorbents in general, high Q_{max} are desirable. It is worth noting that Freundlich constant (K_F) also reached their maximum values at pH 4. 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 ºC, Co = 10 mg/L, 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 ºC) most favoured biosorption. The constants evaluated from the isotherms at different temperature with the correlation coefficients are also presented in Table-2.

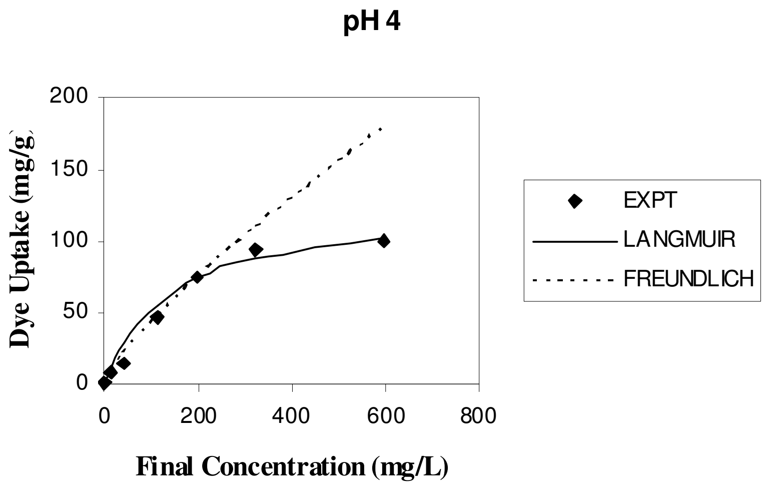

Fig. 4. Comparison of the experimental and predicted isotherms for reactive orange 16 on *Gracilaria verrucossa* (initial pH 4.0, temperature 30 ºC, Co = 10 mg/L, agitation rate 150 rpm)

TABLE-1
LANGMUIR AND FREUNDLICH MODEL PARAMETERS AT DIFFERENT pH

pH	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R^2†	K_F $(L/g)^{1/n}$	n	R^2†
2	70.00009	0.004565	0.9645	0.133495	0.991295	0.8282
3	73.04237	0.007295	0.9645	0.687645	1.309835	0.8713
4	127.2479	0.007186	0.9767	11.119320	1.259880	0.8717
5	99.31201	0.004047	0.9873	0.923985	1.426397	0.9277
6	86.02577	0.006504	0.9783	1.454342	1.482704	0.8141
7	71.55094	0.006730	0.9979	2.980241	1.995056	0.9394
8	52.83387	0.001010	0.9892	1.053023	1.579113	0.8675

†Correlation coefficient.

TABLE-2
LANGMUIR AND FREUNDLICH MODEL PARAMETERS AT
DIFFERENT AT DIFFERENT TEMPERATURE

Temp. (ºC)	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R^2†	K_F $(L/g)^{1/n}$	n	R^2†
25	87.99869	0.010442	0.9750	4.521422	2.23113	0.9681
30	146.24500	0.042000	0.8839	14.950000	2.23000	0.9681
35	135.02200	0.018300	0.9606	4.860000	2.33000	0.8773
40	100.00000	0.010000	0.8680	2.165000	1.71500	0.8884
45	104.71000	0.006018	0.9910	4.100000	1.52500	0.7535
50	86.53000	0.006018	0.9771	1.000000	2.18920	0.9864

†Correlation coefficient.

As represented in 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 16 as 146.0 mg/g at 30 ºC. The maximum adsorption capacity of biomass decreased with further increasing temperature. A large value of b also implied strong binding of reactive orange 16 to the dried *G. verucossa*.

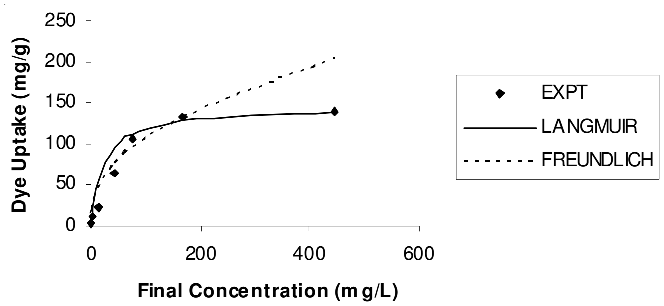

Fig. 5. Comparison of the experimental and predicted isotherms for reactive orange 16 on *Gracilaria verrucossa* (initial pH 4.0, temperature 30 ºC, Co = 10 mg/L, agitation rate 150 rpm).

From the Fig. 3, the biosorption uptake capacity increase up to 0.2 g 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.

TABLE-3
LANGMUIR AND FREUNDLICH MODEL PARAMETERS AT DIFFERENT DOSAGE

Dosage	Langmuir parameters			Freundlich parameters		
	q_{max} (mg/g)	b (L/mg)	R^2†	K_F $(L/g)^{1/n}$	n	R^2†
0.1	90.10967	0.017116	0.9549	1.150138	1.392526	0.8058
0.2	110.0041	0.016835	0.9023	0.761429	0.79849	0.4948
0.3	68.45187	0.061838	0.9493	5.821751	2.404902	0.8231
0.4	26.85852	0.044336	0.8553	1.034588	1.900918	0.8746
0.5	100.5387	0.012489	0.8336	18.25071	7.493727	0.8299

†Correlation coefficient.

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 16 as 110.0 mg/g at 0.2 g.

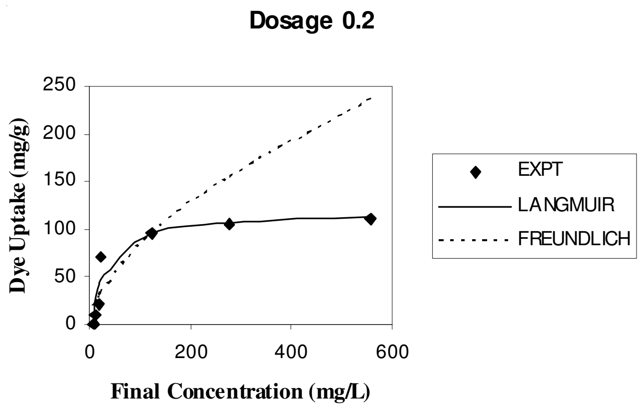

Fig. 6. Comparison of the experimental and predicted isotherms for reactive orange 16 on *Gracilaria verrucossa* (initial pH 4.0, temperature 30 ºC, Co = 10 mg/L, agitation rate 150 rpm)

Conclusion

Present results showed 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 aquatic plant (*Gracillaria verucossa*) is readily available in the environment and more economical and can yield sorbet of higher sorption capacity. In addition regeneration is not necessary because it is available biological matter. Since this work was performed using synthetic waste water and at laboratory scale, results obtained may have some variation if apply to real waste water. Parameters such as pH, dosage and temperature may not hold good as indicated. 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.

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