MAPLE TREE PUBLISHING HOUSE

INTERNATIONAL RESEARCH JOURNAL OF MULTIDISCIPLINARY TECHNOVATION (IRJMT)

http://www.mapletreejournals.com/index.php/IRJMT
Received 21 August 2019 ISSN 2582-1040
Accepted 26 October 2019 2019; 1(6); 560-568
Published online 02 November 2019

Biosorptive Decolorization of Basic Blue Using the Waste Biomass

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Doi: https://doi.org/10.34256/irjmtcon81

ABSTRACT

The study addresses the bio sorption of Basic blue from aqueous solution using red seaweed Gracilaria corticata as adsorbent for equilibrium isotherm analysis in batch mode of operation. Many species of seaweed have been identified in the past as potent bio sorbents for waste-water treatment processes. For the first time Gracilaria corticata, a natural dead algal biomass served as a sorbent material potentially suitable for removal of Basic blue from aqueous solution. The effect of experimental parameters namely pH, initial dye concentrations and bio sorbent dosage in the percentage of decolourization of synthetic Basic blue dye solution were investigated and were found to be at the optimum. Both the initial sorbate solution and sorbent dose were found to favourably catalyse the sorption process. Langmuir, Freundlich, Redlich-Peterson and Toth model were investigated to monitor the adsorption behaviour of Gracilaria corticata. According to the Langmuir and Toth model, the Maximum Basic blue uptake of 95.41 mg/g and 90.99 mg/g was observed at pH 8 and at a temperature of 30°C.

Keywords: Seaweed, Basic blue, Isotherm, Kinetics, Wastewater, Biosorption.

INTRODUCTION

Population explosion and industrial advancements have resulted in a sharp deterioration on several ecosystems, posing serious threats to human health and environment. Several civic bodies have promulgated regulations monitoring the emission of contaminants from industrial waste streams. Correspondingly research is focusing towards the wide range of technologies for waste water treatments. Effluents from the dyeing and finishing processes in the textile industry are known to contain color, high amounts of surfactants, dissolved solids and possibly heavy metals such as Cr, Ni and Cu (Grau, 1991; Nagarethinam and Sundaram, 2001).

Various physical, chemical, biological methods have been used for the treatment of dye-containing wastewater. Biological processes such as biosorption (Ramakrishna and Viraraghavan, 1997), bioaccumulation (Gupta et al, 1992; Aksu, 2003) and biodegradation (Chao and Lee, 1994; Banat et al., 1996) have been proposed as having potential application in removal of dyes from textile effluents. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic and, consequently, their treatment cannot depend on biodegradation alone (Reife, 1993; Pagga and Braun, 1986). Hence, decolorization of dye house effluent via the removal of dyes has become an important aspect of textile wastewater treatment.

Seaweed biomass is a renewable natural resource (Kang et al, 2011; Ortiz et al., 2006) and it is considered to be a cost effective and efficient biosorbent due to its physico-chemical

characteristics (Padilha et al., 2005). Currently, seaweed biomass is cultivated and harvested to manufacture hydrocolloids (agar, alginate and carrageenan) for use in the food and chemical industries. Apart from these uses, seaweed biomass is utilized for the purpose of industrial effluent treatment (Hashim and Chu, 2004).

To best of our knowledge, this is the first attempt to propagate the potential of algae *Gracilaria corticata* asbiosorbent to remove methylene blue from aqueous solution on the different experimental parameters like pH, initial dye concentration, biosorbent dosage on the percentage decolonization were studied in batch mode of operation. Adsorption isotherms (Langmuir, Freundlich, Redlich-Peterson, and Toth model) were analysed.

A. Materials and Methods

Preparation of bio sorbent and chemicals

The red seaweed, Gracilaria corticated, was collected from the beaches of Mandapam region, Tamil Nadu, India. After collection, the seaweed samples were extensively washed with deionised water. After washing, the biomass was subsequently sun-dried and then grounded in a blender to prepare particles with average size of0.75 mm for sorption experiments. All chemicals used in this study were of analytical grade and purchased from Ranbaxy Fine Chemicals Ltd., India; whereas ethylene blue was obtained from Sigma-Aldrich Corporation, Bangalore, India.

Bio sorption experimental procedure

The pH of the ethylene blue solution was initially adjusted using 0.1 M HCl or 0.1 M NaOH. In all experiments, 0.5 g of Gracilaria corticatabiomass was contacted with 100 mL of dye solution in 250 mL Erlenmeyer flasks. The contents were then agitated in an incubated rotary shaker at 150 rpm for 2 h at 30°C. Once equilibrium was reached, samples were centrifuged at 3500 rpm for 5 min and the supernatant liquid was analyzed in a spectrophotometer (UV-1800, Shimadzu, Japan) at 665 nm. The amount of dye bios orbed was calculated from the difference between the dye quantity initially added to the seaweed biomass and the dye content of the supernatant using the following equation:

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

Where Q is the dye uptake (mg/g); C0 and Cf are the initial and final dye concentrations in the solution (mg/L), respectively; V is the volume of dye solution (L); and M is the mass of bio sorbent (g). For pH edge experiments, initial ethylene blue concentration was fixed at 150 mg/L and pH was varied from 4 – 9. In the case of isotherm experiments, initial ethylene blue concentrations were varied from 50 – 300 mg/L. The kinetic experiments were also conducted with ethylene blue concentrations in the range of 50 – 300 mg/L and samples were withdrawn at specific time intervals.

EQUILIBRIUM STUDY

Four equilibrium isotherm models were used to describe the ethylene blue bio sorption data as follows:

Freundlich model:

$$Q = K_F C_f^{\,1/n_F} \qquad (2)$$

Langmuir model:

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \qquad (3)$$

Redlich-Peterson model:

$$Q = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta_{RP}}} \quad (4)$$

Toth model:

$$Q = \frac{Q_{\max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \quad (5)$$

where Qmax is the maximum methylene blue uptake (mg/g), b is the Langmuir equilibrium constant (L/mg), KF is the Freundlich constant (mg/g) (L/mg)1/n, nF is the Freundlich exponent, KRP is the Redlich-Peterson isotherm constant (L/g), aRP is the Redlich-Peterson isotherm constant (L/mg)1/βRP, βRP is the Redlich-Peterson model exponent, bT is the Toth model constant (L/mg), and nT is the Toth model exponent.

Table 1. *Isotherm constant of models for Methylene Blue onto Gracilaria corticata*

Isother	**Parameters**	**Methylene blue**
Langmuir	q_{max} (mg/g)	95.41
	b_L (L/mg)	0.0474
	R^2	0.9627
	% Error	9.52
Freundlich	K_F (L/g)	6.91
	n	1.59
	R^2	0.9589
	% Error	10.76
Redlich-Peterson	K_{RP} (L/g)	4.48
	a_{RP}(L/mg)	0.044
	β_{RP}	0.98
	R^2	0.9628
	% Error	9.47
Toth	q_{max}(mg/g)	90.99
	b_T(L/mg)	0.0486
	n_T	0.95
	R^2	0.9629
	% Error	9.43

C. RESULTS AND DISCUSSIONS

BATCH STUDIES

The interaction between dye molecule and adsorbent is basically a combined result of charges on dye molecules and the surface of the adsorbent (MeenaSoni et al., 2012; Maurya et al., 2006). The solution pH is an important monitoring parameter influencing the sorption behavior of

solute onto the surface of biosorbent. The impact of pH on both the active biosorbent surface binding-sites and the dye solution chemistry is of great significance (Vijayaraghavan and Yun, 2008; Chowdhury and Saha, 2012).

In the present study, the effect of pH on biosorption of methylene blue by *Gracilaria corticata* was studied over a pH range of 4-9. The effect of pH on decolorization of methylene Blue is shown in Figure 1, which indicated that the solution pH has significantly affected the biosorption of methylene blue by *Gracilaria corticata*. The amount of dye removed at equilibrium increased with increasing pH, appreciably up to a pH of 8.0.

The pH of the aqueous solution affects both the surface charge of the biosorbent material as well as the degree of ionization of the dye molecule. Protonation of these functional groups at low pH values renders a net negative charge to the biosorbent surface while deprotonation of the functional groups at high pH values render it positively charged (Weng et al. 2009); hence, it is completely ionized at low pH and exists as cationic species. Same observation was noticed in this present study also. At low pH value, the uptake of methylene blue dye molecule by *Gracilaria corticata*was less. On the contrary, as the pH of the dye solution increases, a considerable increase in adsorptive removal of dye is observed due to strong electrostatic attraction between negatively charged sites on the biosorbent and the dye cations.

Thereafter a decreasing trend was noticed *Gracilaria corticata*biosorbent achieved its optimum biosorption capacity of methylene blue at pH of 8. The reason for decreasing dye uptake with an increase in pH (after a pH of 8) was unclear but it might be the alteration of activity of binding sites in the *Gracilaria corticata*biosorbent (Vijayaraghavan and Yun, (2008)).

The biosorption of methylene blue onto *Gracilaria corticata* biomass was carried out at different initial concentrations of 50 - 300 ppm and presented in figure 2. The methylene blue biosorption capacity increased with increasing initial dye concentration up to 150 ppm of the initial dye concentration. Thereafter a decreasing trend was noticed. This trend leads to the inference that a higher initial dye concentration provides an important driving force to overcome mass transfer resistances between the biosorbent and the biosorption medium. The same observation was reported by Kang et al., (2011) and Yalcin et al., (2010).

A rapid removal was observed at the initial stages and it then proceeds slowly until it reached equilibrium. This may be due to the availability of number of vacant biosorption sites at the initial stage. The equilibrium biosorption capacity of methylene blue is increased from 90.40% to 96.30% mg/g with increasing concentration from 50 to 150 ppm of initial concentration. This is due to the fact that the available biosorption sites were relatively high and consequently the dye species could easily find the accessible biosorption sites. Contradictorily at higher dye concentrations i.e., above 150 ppm of initial dye concentration a decreasing trend was noticed. This may due to the fact that at higher concentrations the available site for biosorption become fewer and consequently the dye ions take more time in order to reach the last available sites (Soni et al., (2012) and Ben Hamissa et al., (2007)).

Biosorbent dosage plays a vital role in decolorizing the dye solutuion due to its strong biosorption capacity at given initial concentration (Chowdhury and Saha, 2012). The effect of biosorbent dosage on removal of methylene blue was examined by varying adsorbent dosage from 0.2 gm to 0.8 gm and presented in Figure 3. As concluded by Vijayaraghavan and Yun, (2008), the dosage of a biosorbent strongly influences the extent of biosorption.

Methylene blue removal efficiency increases with the increase in biosorbent dosage with least value of 50.75% obtained with 0.2g and highest value of 94.94% with 0.5g of the biosorbent. This is due to the increase in surface area and availability of biosorption sites. Also, the reason might be a strong ability of the biosorbent to biosorb the dye molecules at a given initial concentration of dye solution. The same was concluded upon by Owoyokun, (2009); Donmez et al., (1999); Vasanth Kumar et al, (2006); Sun Xue-Fei et al., (2008). In addition to this, the lower biosorbent dosages yield higher uptakes and lower percentage removal efficiencies (Vijayaraghavan et al., (2006); Aksu Z and Cagatay, (2006))

Bio sorption Isotherm and Modeling

The quality of a biosorbent is usually judged by how much pollutant it can bind and retain in an immobilized form. To evaluate the full potential of *Gracilaria corticata*in methylene blue removal, which is useful in the biosorption isotherm curve which is a plot of equilibrium methylene blue concentration versus methylene blue uptake by *Gracilaria corticata*. Isotherms were evaluated by varying initial methylene blue concentrations in the range of 50 - 300 mg/L at pH 8. An isotherm of L-shaped without strict plateau was observed Figure 4. This means that the ratio between the concentration of dye molecules remaining in solution and biosorbed on the seaweed surface decreases when the solute concentration increases, providing a concave curve (Limousin et al., (2007). From this study, the maximum experimental uptake was observed as 54.4 mg/g whereas the maximum theoretical uptake was recorded as 95.41 mg/g based on the Langmuir isotherm which slope was found to be steep. In general, the steep slope represents higher affinity of the sorbate toward the sorbent (Vijayaraghavan, K.; Yun, Y.S. (2008)).

Isotherm pertaining to the biosorption of methylene blue onto *Gracilaria corticata*was tested using the two-parameter (Freundlich and Langmuir) and three-parameter (Redlich-Peterson and Toth) models. The Freundlich model is an empirical equation based on an exponential distribution of sorption sites and energies. It also assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Relatively low R^2 (0.959) and high % error (10.8%) were obtained. The binding capacity constant (K_F) and constant associated with affinity of sorbent and sorbate (n_F) were determined as 6.91(mg/g) $(L/mg)^{1/n}$ and 1.59, respectively. The classical Langmuir model incorporates two easily interpretable constants: Q_{max}, which corresponds to the maximum achievable uptake by a system; and b, which is related to the affinity between the sorbate and sorbent. The Langmuir model was originally developed to describe the gas-solid phase adsorption of activated carbon. Later, the model was successfully used to quantify and contrast the performance of different adsorbents and biosorbents (Vijayaraghavan, K.; Yun, Y.S. (2008)).In its formulation, the Langmuir model assumes binding to the surface was primarily by physical forces and all sites possess equal affinity for the sorbate. The model constants, Q_{max} and b were recorded as 95.41 mg/g and 0.0474 L/mg, respectively with R^2 and % error values of 0.9627 and 9.52 %, respectively

The application of three-parameter model drastically improved the fitness of methylene blue biosorption isotherm. The Redlich-Peterson model is a combination of the Langmuir and Henry's model. The model incorporates three parameters (K_{RP}, a_{RP} and β_{RP}) into an empirical isotherm, and thus can be applied to either homogenous or heterogeneous systems. When β_{RP} = 0, the model reduces to the Langmuir model, while when β_{RP}=1, the model transforms to Henry's law form. For the present system, β_{RP} was estimated as 0.98 which indicates that methylene blue isotherm data were more of the Langmuir form. The other constants, K_{RP} and a_{RP} were estimated as 4.48 L/g and $0.044(L/mg)^{1/\beta_{RP}}$, respectively. The Redlich-Peterson model resulted in better R^2 (0.9628) and % error (9.47%) values. Further, the Toth model was examined for its compatibility with the methylene blue isotherm data. The Toth model constants, Q_{max}, b_T and n_T were recorded as 90.99 mg/g, 0.0486 L/mg and 0.95, respectively.The Toth model resulted in R^2 (0.9629) and % error (9.43%).The Toth model derived from potential theory, has proven useful in describing sorption in heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have sorption energy less than the mean value (Ho et al., (2002).

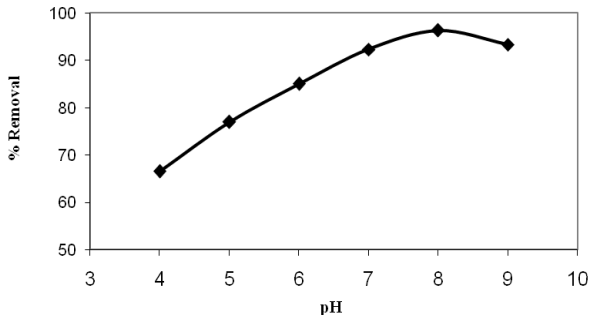

Fig 1. *Removal efficiency (%) vs. pH*

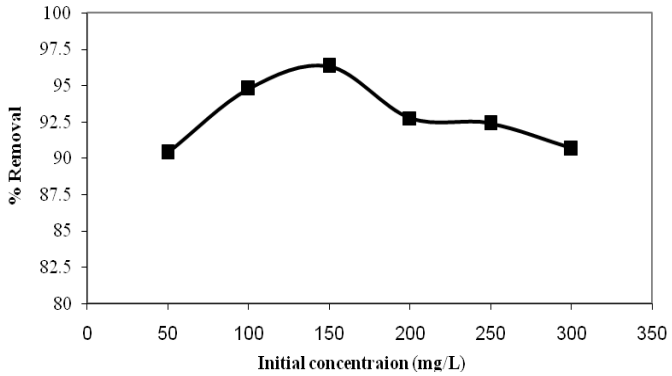

Fig 2. *Removal efficiency (%) vs Initial Concentration*

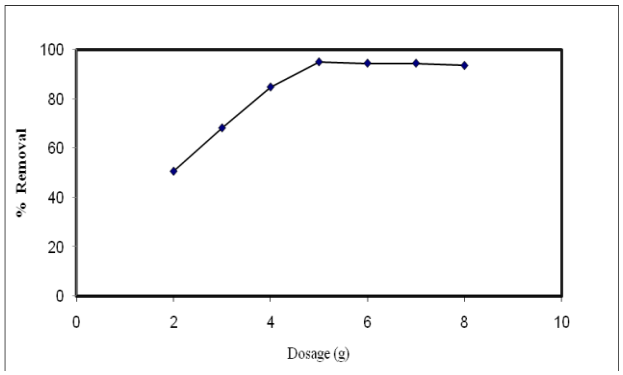

Fig 3. *Removal efficiency (%) vs Dosage*

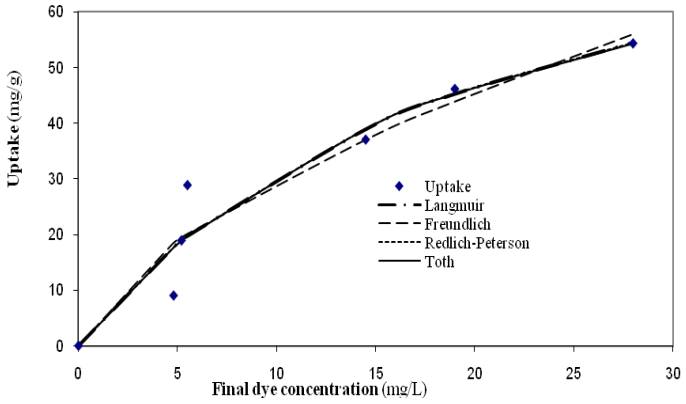

Fig 4. *Biosorption isotherm of Methylene Blue at pH 8 (temperature = 30°C)*

D. CONCLUSIONS

This paper examined the bio sorption of ethylene blue by red marine alga Gracilaria corticated. The main results obtained can be summarized as below:

- The biosorption capacities were solution pH dependent and optimum pH was found to be 8 for methylene blue removal by *Gracilaria corticata*.
- Biosorption isotherm was modeled using the Langmuir,Freundlich, Redlich-Peterson and Toth models. The seaweed biomass exhibited methylene blue uptake of 95.41 mg/g, based on the Langmuir model.
- Of the different biosorbent dosage examined, 5 g/L seaweed dosage was selected as optimum as it exhibited highest methylene blue removal efficiency (94.94%).
- Considering the results obtained from the present study, it can be concluded that *Gracilaria corticata* possess good adsorption potential and can be effectively to remove methylene blue from aqueous solution

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Conflict of Interest

None of the authors have any conflicts of interest to declare.