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# The Comparative Study on Sorption of Basic Violet 10 By Cost-Effective Sorbents

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**Abstract:** This present study was conducted to compare the potential of various sorbents (*Spirulina platensis, Lyngbya wollei, Sargassum muticum, Gracilaria edulis*) in sorption of basic violet 10. The effect of different parameters, namely solution pH, sorbent dose, temperature, agitation speed, contact time and dye concentration were investigated and optimal conditions were established. The dye uptake was very fast and reached equilibrium within 60 min at 50 °C. The studies showed that the chitosan was a better adsorbent than chitin. Both chitin and chitosan gave best adsorption results at pH 3. The pseudo second order, intraparticle diffusion and Elovich models were used to describe the kinetic data. The data were best fitted with pseudo second order kinetic model. The maximum monolayer capacity of *Sargassum muticum* obtained from Langmuir is 76.92 mg $g^{-1}$.The SEM and FTIR images are the evident for the sorption activity.

**Keywords:** Sorption kinetic studies, Isotherm, Seaweed, Fresh water algae, Rhodamine B.

## Introduction

Adsorption is a major industrial separation technique for the purification of effluent media[1]. Adsorption has been found to be superior compared to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants[2].

Basic violet 10 (Rhodamine B) could be an extremely water soluble, basic red dye of the xanthene category. It is harmful if swallowed by human beings and animals, and causes irritation to the skin, eyes and respiratory tract[3]. Hence it should be removed from effluent. In this study, the efficiency of four sorbents (*Spirulina platensis*, *Lyngbya wollei*, *Sargassum muticum*, *Gracilaria edulis*) was explored and compared for treating BV 10 from aqueous solution. Also The effect of parameters such as initial concentration, solution pH, adsorbent dose, temperature and agitation speed on the process performance was investigated. Kinetics and isotherm studies were also carried out to estimate the adsorption capacity of the adsorbents.

## Materials and Methods

### Sorbent preparation

The *Spirulina platensis* was collected from the pond in Annamalai nagar, Chidambaram. The *Lyngbya wollei* was collected from Veeranam Lake, Cuddalore District, Tamilnadu. The seaweeds *Sargassum muticum* and *Gracilaria edulis* were collected from Mandapam, Rameshwaram. Then it was extensively washed several times with tap water and then deionised water to remove dirt and small aquatic organisms. Afterwards, it was dried at room temperature for 24 hours. The algal sample was ground and sieved to different particle sizes and subsequently used for sorption experiments.

### Dyestuff

The Basic Violet 10 ($C_{28}H_{31}ClN_2O_3$) was widely used in textile industry and the structure of BV 10 is revealed in Fig.1. The Basic violet 10 (C.I. 45170) was purchased from HiMedia Private Ltd, India, with analytical grade and was further used without any purification. The molecular weight of the dye is 479.01 g/mol. The stock dye solution was prepared by using deionised water to achieve concentration of 1000 mg/L. The requisite concentrations were obtained by diluting the stock solution of BV 10. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted using 0.1N sodium hydroxide or hydrochloric acid solutions.

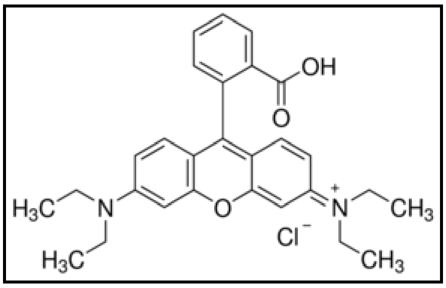


**Fig. 1: Chemical structure of Basic violet 10**

### Sorption experiment

Batch experiments were carry out to examine the adsorption of basic dye on sorbents. Exactly 100 ml of dye solution of known initial concentration was shaken at the certain agitation speed with a required dose of adsorbents for a specific period of contact time in an orbital shaker, with optimum pH at room temperature (30 ± 2°C). The final concentration ($C_o$) was measured. The concentration in the test solution was determined using a UV Double beam spectrophotometer, (HITACHI U-2001) at a wavelength (549 nm) corresponding to the maximum absorbance, $\lambda_{max}$. The percentage removal of dye and adsorption capacity $q_t$ (mg/g) at any time was calculated using the following equations:

$$\text{Removal efficiency (\%)} = \left(\frac{C_i - C_o}{C_i}\right) * 100 \qquad (1)$$

$$q_t = (C_i - C_o) * \left(\frac{V}{m}\right) \qquad (2)$$

## Results and Discussion

### Sorbent characterization

Scanning electron microscopy (SEM, Jeol JSM 60) images exemplify the surface morphology and fundamental physical properties of the adsorbent. SEM images of sorbents were taken before and after sorption of dye. The SEM images are evidence for the possibility of dye molecules to be adsorbed into sites of sorbent.

The FTIR spectra of the samples were recorded on Perkin Elmer FTIR spectrophotometer (Spectrum BX-II) using a pellet (pressed-disk) technique. For this, the adsorbent was intimately mixed with approximately 100mg of dry, powdered KBr. The infrared spectra of sorbents and dye-loaded sorbents samples were recorded in the range 4,000–400 cm−1.

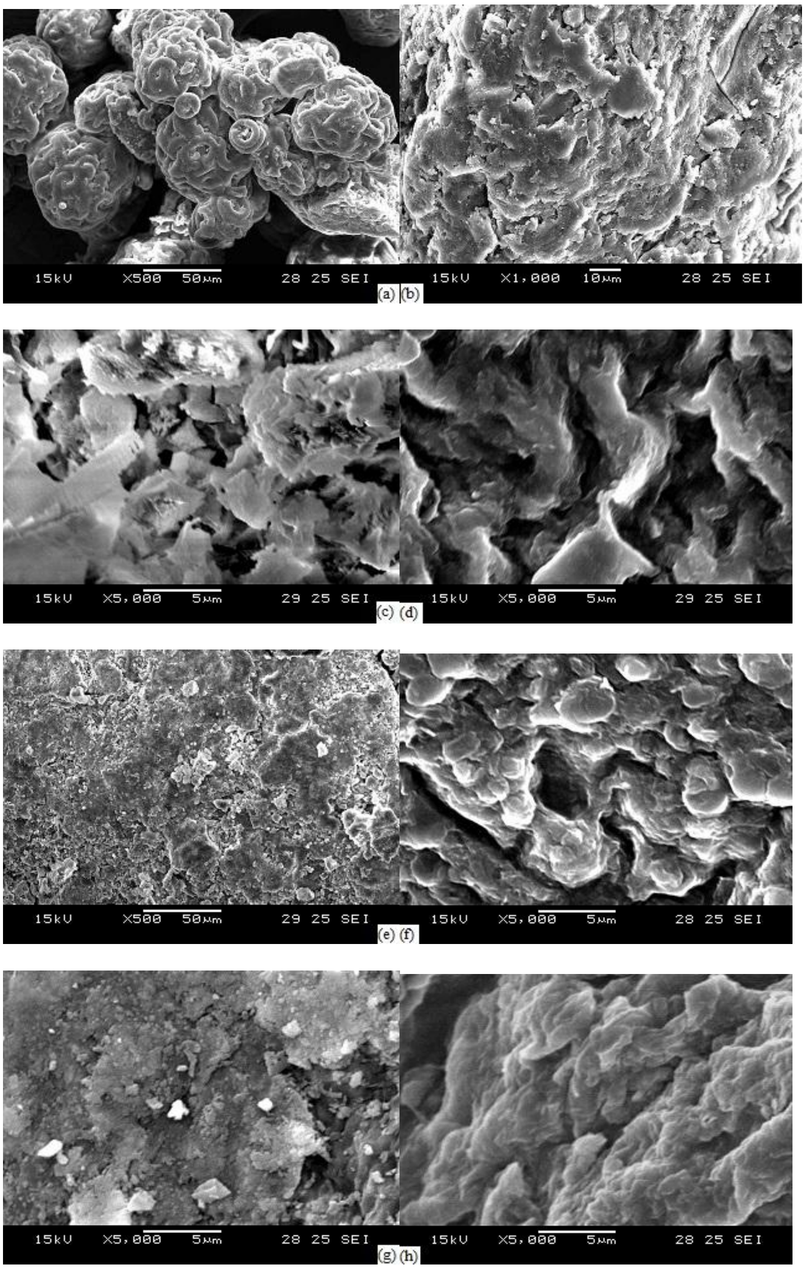
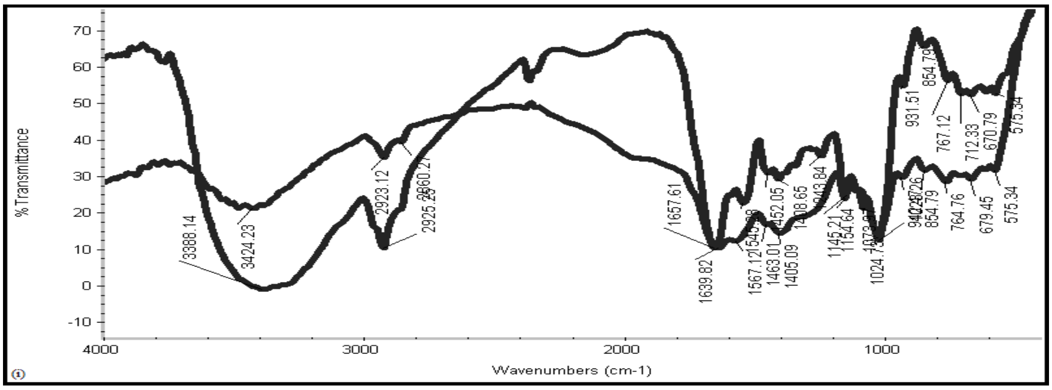


**Fig. 2: Scanning electron micrographs of (a) *S. platensis*, (b) dye-loaded *S. platensis* (c) *L.wollei*, (d) dye-loaded *L.wollei*, (e) *S.muticum*, (f) dye-loaded *S.muticum*, (g) *G.edulis*, (h) dye-loaded *G.edulis***



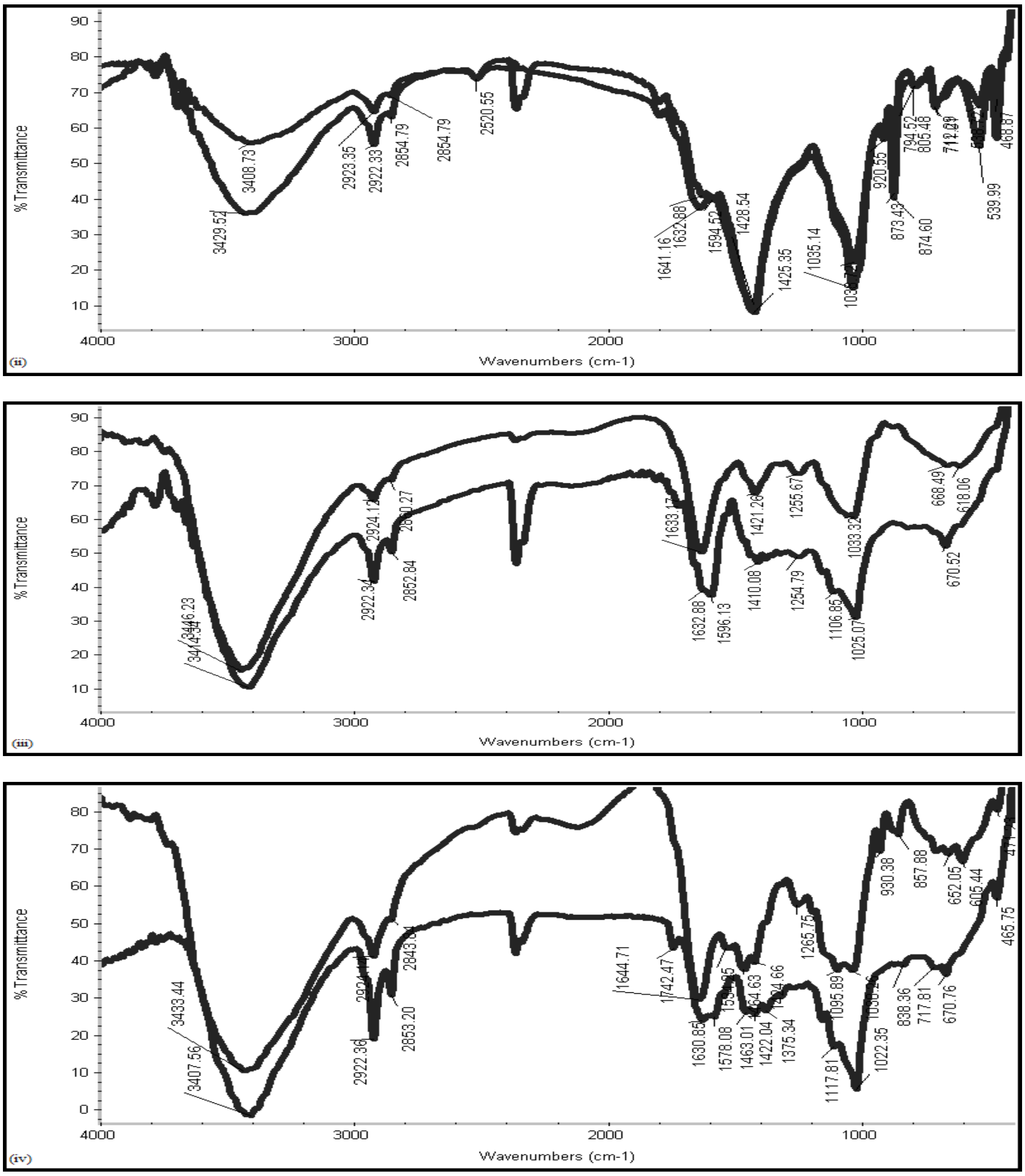


**Fig. 3: FTIR spectra of (i) *S. platensis* and dye-loaded *S. platensis* (ii) *L.wollei* and dye-loaded *L.wollei*, (iii) *S.muticum* and dye-loaded *S.muticum*, (iv) *G.edulis* and dye-loaded *G.edulis***

## Effect of pH

The effect of initial pH was examined for pH range 3 to 12, when the initial dye concentration of 50 mg/L, amount of sorbent of 0.20 g, contact time as 60 min and temperature was fixed at 30 °C. The maximum adsoption capability was achieved at pH 3 in all sorbents. At lower pH values, the RB molecules remain in their monomeric form and can easily enter into the pores of the adsorbent[4]. At a pH value higher than 4.5, the zwitterions of RB in water may increase the aggregation of RB to form a bigger molecular form (dimer) and become unable to enter into the pore structure of lignin surface. The greater aggregation of the zwitterions is due to the attractive electrostatic interaction between the carboxyl and Xanthane groups of the monomer[5]. It's clear that the sorption process not littered with the sorbent morphology. The similar result was obtained for removal of Rhodamine B from aqueous solutions and wastewater by walnut shells [4] and adsorption of Congo Red, Rhodamine B and Disperse Blue dyes from aqueous solution onto raw flint clay [6].

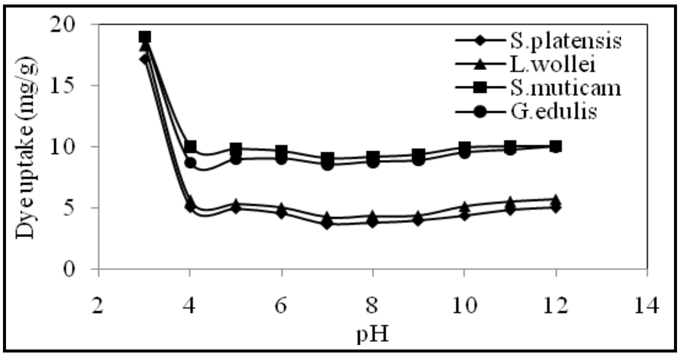


**Fig. 4: Effect of pH on sorption of BV 10**

### Effect of sorbent dosage

The influence of the sorbent dosage was observed by agitating 100 ml of 50 mg/L of dye solution with an amount of sorbents of 0.1, 0.2, 0.3, 0.4 and 0.5 g at room temperature while pH -3, initial dye concentration-50 mg/L and agitation speed-150 rpm. The amount of dye adsorbed decreases with an increase in adsorbent dosage (Fig. 5). This is due to the split in the flux or the concentration gradient between solute concentrations in the solution and on the sorbent surface [7].

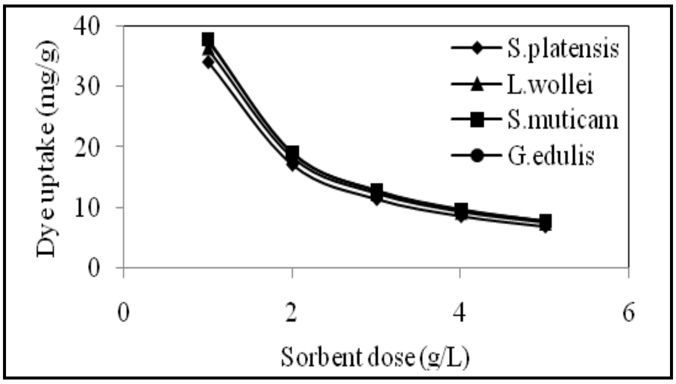


**Fig. 5: Effect of sorbent dosage on sorption of BV 10**

### Effect of temperature

The effect of temperature was determined with a temperature range of 30, 35, 40, 45 and 50 °C, while the initial dye concentration, shaking time and amount of sorbent were fixed at 50 mg/L, 60 min, and 0.10 g respectively. The dye uptake increases slightly with the increasing temperature (Fig. 6). It may be of reaction of dye molecules and surface functional group is enhanced by increased temperature of reaction[8]. The similar result was obtained for sorption of basic dye using zeolite MCM-22[9].

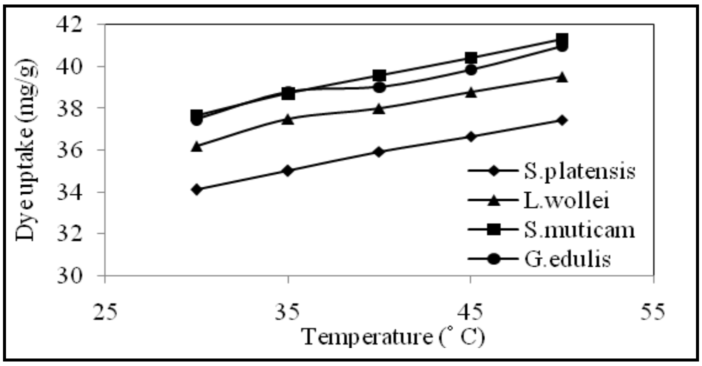


**Fig. 6: Effect of temperature on sorption of BV 10**

### Effect of agitation speed

The consequence of agitation speed on the sorption competence of sorbents was studied by varying the shaking speeds 25, 50, 100, 150 and 250 rpm for 60 min, while pH-3, initial dye concentration-50 mg/L, sorbent dose-0.1g and temperature- 50 °C. The sorption capability will increase with a rise in speed and reached most at 150 rpm then, starts to decrease with increase in speed. The similar result was obtained for Sorption of Reactive blue 19 onto freshwater algae and seaweed [10].

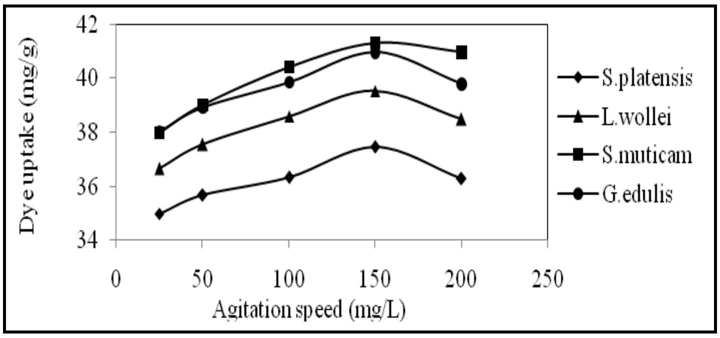
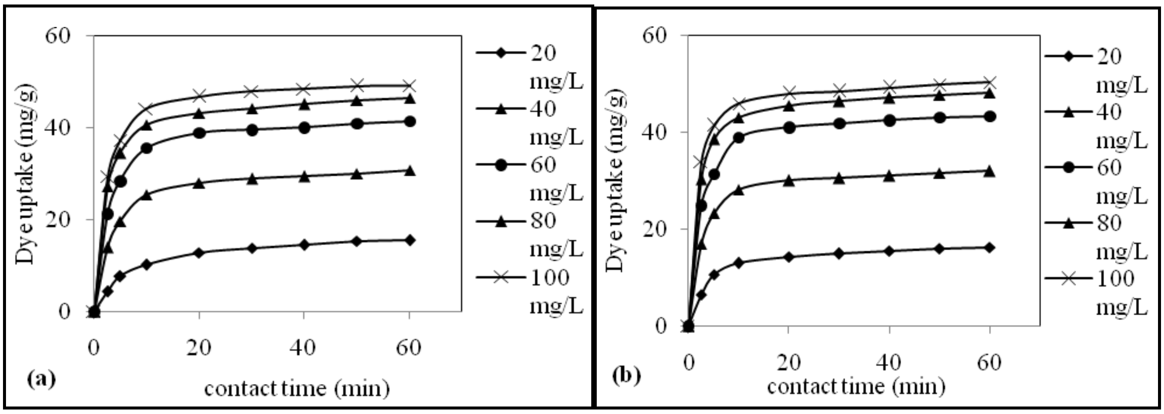


**Fig. 7: Effect of agitation speed on sorption of BV 10**

### Effect of Contact time and initial dye concentration

The effect of contact time was determined a sorbent dose of 0.10 g, a solution volume of 100 ml, an agitation speed of 150 rpm and a temperature of 50 °C for various dye concentrations of 20, 40, 60, 80 and 100 mg/L. The process was terribly fast and attains within 60 min. The similar result obtained for removal of rhodamine B dye from aqueous solution using the acid activated Cynodon dactylon carbon[11] and sorption of rhodamine B from aqueous solution on the surface of *Moringa oliefera* bark carbon [12].

The effect of initial dye concentration was studied for various dye concentrations of 20, 40, 60, 80 and 100mg/L, while the pH, shaking time, amount of sorbent and temperature were fixed at 3, 60 min, 0.1 g and 50 °C, respectively. The sorption capacity was increased with the increase in initial dye concentration (Fig. 6). It is observed that initial rate of adsorption was greater for higher initial dye concentration because as the resistance to the dye uptake decreased the mass transfer driving force increased[12].



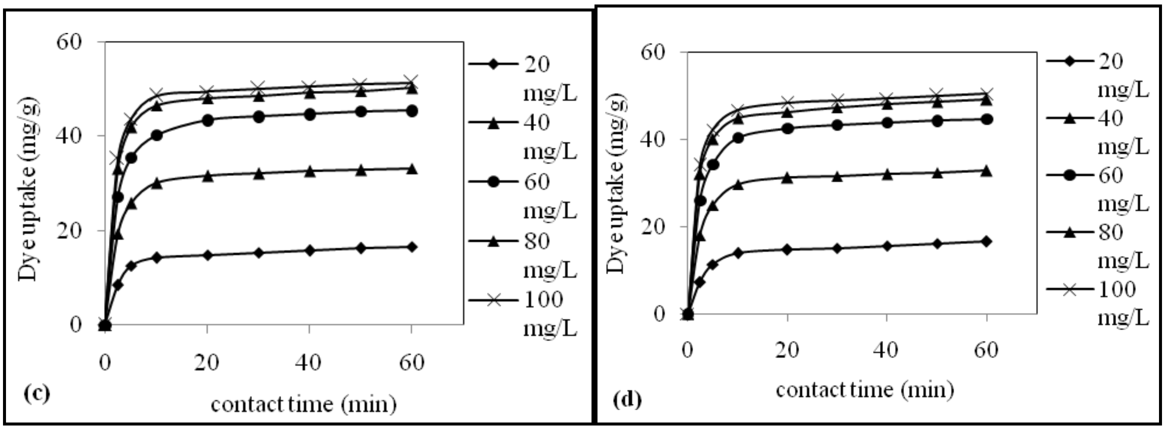


**Fig. 8: Effect of contact time and initial dye concentration on sorption of BV 10 by (a) *S. platensis,* (b) *Lyngbya wollei,* (c) *Sargassum muticum,* (d) *Gracilaria edulis.***

## Isotherm studies

Langmuir, Freundlich, Dubinin- Radushkevich and Temkin adsorption isotherms models were employed to describe the relationship between adsorbate to adsorbent at constant temperature. The Langmuir isotherm model (Langmuir, 1918) assumes that the adsorption occur at homogeneous sites at adsorbent surface, and saturation happen when the dye molecule fill the site where no more adsorption can occur at that site[13]. The Freundlich isotherm is describing the sorption deals with surface heterogeneity[14]. The Temkin isotherm model assumes that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage, in adsorbent–adsorbate interactions[15]. Dubinin – Radushkevich (D-R) isotherm model is used to evaluate the sorption free energy and nature of bonding[16].

The linear form of isotherm models are represented as

**Langmuir isotherm model:**

$$\frac{1}{q_e} = \frac{\frac{1}{q_{\max}+1}}{k_L q_{\max} \square C_e} \qquad (3)$$

Freundlich isotherm model:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

Dubinin- Radushkevich isotherm model:

$$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2 \qquad (5)$$

Polanyi potential ($\varepsilon$) is given as

$$\varepsilon^2 = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (6)$$

Temkin isotherm model:

$$q_e = \frac{RT}{B_t} \ln A_t + \left(\frac{RT}{B_t}\right) \ln C_e \qquad (7)$$

The correlation coefficients $R^2$ suggest that the Dubinin- Radushkevich, Langmuir, Temkin isotherm provides a good fit to the isotherm data. The $R^2$ values are less than 0.871, indicating less fitting of the adsorption data to the Freundlich model. The monolayer adsorption capacity of the sorbents was presented in Table 1. Dubinin – Radushkevich isotherm model implies that sorption of BV 10 follows chemisorptions.

**Table 1. Isotherm constants and their coefficients of BV 10 sorption on to various sorbents**

| **Model parameter** | **Sorbents** | | | |
|---|---|---|---|---|
| | ***S.platensis*** | ***L.wollei*** | ***S.muticum*** | ***G.edulis*** |
| **Langmuir** | | | | |
| $K_L$ (L/mg) | 0.059 | 0.076 | 0.087 | 0.086 |
| $q_{max}$ (mg/g) | 76.91 | 71.42 | 76.92 | 71.43 |
| $R^2$ | 0.973 | 0.975 | 0.962 | 0.965 |
| **Freundlich** | | | | |
| $K_F$ (mg/g) | 9.39 | 11.22 | 12.79 | 12.56 |
| n | 2.19 | 2.38 | 2.51 | 2.52 |
| $R^2$ | 0.844 | 0.871 | 0.834 | 0.839 |
| **Dubinin- Radushkevich** | | | | |
| $K_{ad}$ | $3.8X10^{-6}$ | $2.7X10^{-6}$ | $2.28X10^{-6}$ | $2.3X10^{-6}$ |
| $q_s$ (mg/g) | 46.06 | 46.99 | 49.40 | 47.94 |
| $R^2$ | 0.976 | 0.975 | 0.985 | 0.984 |
| **Temkin** | | | | |
| $A_t$ (L/mg) | 0.86 | 1.19 | 1.54 | 1.52 |
| $B_t$ | 194.96 | 204.77 | 208.59 | 213.39 |
| $R^2$ | 0.956 | 0.943 | 0.910 | 0.914 |

## Sorption kinetics

The kinetic models were used to find the potential rate-controlling steps involved in the process of adsorption of BV 10 onto Sorbents.

The pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent.[17]. The intraparticle diffusion model determines the rate-controlling step of the kinetics[18]. The Elovich equation is used for chemisorptions kinetics with a rapid equilibrium rate in the early period and slows down at later periods of the sorption process, which often the adsorbing surface is heterogeneous [19, 20]. The linear form of kinetic models are represented as

The pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{kq_e{}^2} + \frac{1}{q_e t} \qquad (8)$$

Intra-particle diffusion model:

$$q_t = K_{id}\, t^{0.5} + I \qquad (9)$$

Elovich equation:

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln t \qquad (10)$$

The higher correlation coefficient values (0.999) implies that sorption of BV 14 onto both sorbents track the pseudo-second order kinetic model ie, chemisorption. Also, the calculated $q_e$ *(cal)* values agreed well with the experimental data.

It is seen that there are two adsorption stages for all the cases. If the regression of *q*t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step[21]. In this case the line passes through the origin implies that diffusion may be the rate limiting step for first 5 minutes. Intercept values implies the thickness of the boundary layer, i.e. the larger the intercept, the greater is the boundary layer effect. The obtained correlation coefficient values for the Elovich model imply that the Elovich rate equation could not be suitable to depict the kinetics of BV 10.

**Table 2. Kinetic parameters of BV 10 sorption on to various sorbents**

| **Sorbents** | **$q_e$ (exp) mg/g** | **Pseudo-second order** | | | **Intra-particle diffusion model** | | | | | | **Elovich model** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **$K$** | **$q_e$ (cal) (mg/g)** | **$R^2$** | **$K_{id1}$ (mg/g min$^{0.5}$)** | **$I_1$** | **$R^2$** | **$K_{id2}$ (mg/g min$^{0.5}$)** | **$I_2$** | **$R^2$** | **$\alpha$ (mg/g/ min)** | **$\beta$ (g/mg)** | $R^2$ |
| *S.platensis* | 49.18 | 0.016 | 50.00 | 0.999 | 17.01 | 0.56 | 0.992 | 1.86 | 36.39 | 0.784 | 583.19 | 0.17 | 0.908 |
| *L.wollei* | 50.28 | 0.020 | 55.55 | 0.999 | 19.03 | 0.85 | 0.986 | 1.39 | 40.25 | 0.850 | 5301.7 | 0.22 | 0.899 |
| *S.muticum* | 51.31 | 0.025 | 71.43 | 0.999 | 20.03 | 0.79 | 0.989 | 1.12 | 43.34 | 0767 | 13095.1 | 0.23 | 0.833 |
| *G.edulis* | 50.42 | 0.022 | 62.5 | 0.999 | 19.35 | 0.77 | 0.988 | 1.25 | 41.50 | 0.806 | 7044.4 | 0.22 | 0.864 |

## Conclusion

The efficiency of various sorbents in sorption of basic violet 10 from aqueous solution was explored and compared. The rate of uptake was rapid and attains equilibrium within 60 min at a temperature of 50° C. The Dubinin- Radushkevich model fitted well than other models. Among the tested sorbents, *Sargassum muticum* eliminate the BV 10 very well from aqueous solution and having higher monolayer capacity than others. The adsorption kinetics of BV 10 can be well described by the pseudo-second-order model equation. The intraparticle diffusion is the sole rate-limiting step in initial stage. The SEM and FTIR images confirmed the sorption of BV 10 on all sorbents.

## Nomenclature

$A_T$ -Temkin isotherm related to equilibrium binding constant (*L/g*)
$\alpha$ - Elovich rate equation constants representing initial rate of sorption (mg /g /min)
$B_T$ -Temkin isotherm constant
$\beta$- Extent of surface coverage and the activation energy of chemisorptions (g/mg)
$C_e$ - Equilibrium (residual) concentration of adsorbate in solution (mg/L)
$C_i$ - Initial dye concentration (mg/L)
$C_o$ - Dye concentration at any time (mg/L)
$I$ -Intercept
$k$ - Equilibrium rate constant of pseudo-second order sorption (g /mg /min)
$K_{ad}$ - Dubinin–Radushkevich isotherm constant (mol$^2$/kJ$^2$)
$K_F$ - Freundlich isotherm constant (mg/g)
$k_{id\,1}$, $k_{id\,2}$ and $k_{id\,3}$ - Diffusion rates of the first, second and third stages of adsorption (mg/g-min$^{0.5}$)
$K_L$ - Langmuir isotherm constant (L/mg)
m - Mass of the dry adsorbent used (g)
$n$ - Adsorption intensity
$q_e$ - Amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)
$q_{max}$ - Maximum monolayer coverage capacity (mg/g)
$q_s$ - Theoretical isotherm saturation capacity (mg/g)
$q_t$ - Amount of dye sorbed at time‘*t*’ (mg/g)
$R$- Universal gas constant (8.314 J/mol/K)
t - Sorption contact time (min)
$T$ -Temperature (K)
$V$ - Volume of the solution (L)

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