Studies on adsorption potential of oil-extracted marine macro algae *Padina gymnospora* for the removal of methylene blue

Mohammed Khan Faisal

Department of Chemical Engineering,
A.C. Tech Campus, Anna University,
Chennai - 600 025, India
Email: basso925@gmail.com

Parthasarathy Saranya

Centre for Biotechnology,
A.C. Tech Campus, Anna University,
Chennai - 600 025, India
Email: saranharry@gmail.com

Lingesan Prameela

Department of Chemical Engineering,
A.C. Tech Campus, Anna University,
Chennai - 600 025, India
Email: pramee92@yahoo.com

Sahadevan Renganthan*

Centre for Biotechnology,
A.C. Tech Campus, Anna University,
Chennai - 600 025, India
Email: rengsaha@gmail.com
*Corresponding author

Abstract: The biosorption potential of *Padina gymnospora* for the methylene blue dye from the aqueous dye solution was studied. The effect of sorbent dosage, agitation, temperature, contact time and initial dye concentration on the uptake capacity of the biomass was studied in batch. The uptake capacity at equilibrium varied from 73.64 mg g^{-1} to 460.26 mg g^{-1} with increasing initial dye concentration of 20–100 mg L^{-1} for a biomass of 0.2 g. It was found that the biomass showed maximum adsorption capacity at 100 mg L^{-1} dye solution for a sorbent dosage of 0.2 g at 20°C with an agitation speed of 100 rpm. The equilibrium data was found to fit well with Freundlich isotherm and the reaction was found to follow the pseudo second order kinetics. The surface morphology of the biomass and the presence of various functional groups responsible for the adsorption were examined using SEM and FTIR.

Keywords: biosorption; FTIR; isotherm; kinetics; methylene blue; *Padina gymnospora*; SEM; textile dye.

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Biographical notes: Faisal Mohamed Khan, an undergraduate student at the Department of Chemical Engineering, A.C. Tech Campus, Anna University, has done various mini non-academic projects in the field of Environmental Technology.

Saranya Parthasarathy (BSc Biotechnology, MSc Biochemistry) is currently doing her PhD at Centre for Biotechnology in the field of Bioremediation of Textile Dyes. She has 6 research articles in international and national journals to her credit.

Prameela Lingesan, Masters' student in the Department of Chemical Engineering, A.C. Tech Campus, Anna University, has done her Masters Academic Project in the field of Environmental Biotechnology.

S. Renganathan, Professor at the Centre for Biotechnology, A.C. Tech Campus, Anna University, is an Active Researcher in a wide range of interdisciplinary fields such as Bioremediation, Biofuel Production, and Nanobiotechnology. He has 110 research articles in reputed international and national journals to his credit. He has been awarded 'The Best Researcher' by Department of Chemical Engineering for the academic year 2012–13.

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1 Introduction

Coloured wastewater has been a major concern for the processing industries both during the dye manufacturing and dye consuming processes (Pearce, Lloyd and Guthrie, 2003). Dyes are commonly used in industries such as textile, paper, leather, cosmetic, pharmaceutical, food and plastic in order to impart colour to their product (Saranya et al., 2004). The textile industries account for nearly 60% of the total dye use (Zollinger, 2004) and cotton fibres account for nearly half of the cellulose fibres on which textile dyes are used. Unfortunately for the environment, textiles dyes when disposed of untreated in water bodies can cause pollution. In recent times dye removal has become a major topic of research and the consequences of untreated dye include the increase of the COD of water bodies and prevention of light penetration into the water systems (Bulut and Aydin, 2006). Many different techniques such as electrochemical methods, coagulation - flocculation methods, oxidation and filtration have been used to treat dyes (Rajamohan et al., 2009). The preferred method of any given dye is based on the effectiveness of the given physical and chemical method with respect to the economic feasibility of the particular process. Some of the common limitations for the different methods are requirement of excessive amounts of reagents, accumulation of concentrated sludge with

serious disposal problems, expensive plant requirements or large operational costs, as well as lack of effective colour reduction (Aksu, Tatli and Tunc, 2008).

Adsorption of dyes has been commonly used to treat dye contaminated solutions due to the simplicity of the process, ability to remove varied compounds and by virtue of its easy operation (Ardejani et al., 2007). A commonly used adsorption agents in the treatment of dyes is activated carbon apart from which many other alternative adsorption agents have been used such as saw dust (Garg et al., 2004), sly ash (Pavel, Buchtova and Ryznarova, 2003), apple pomace and wheat straw (Robinson, Chandra and Nigam, 2002), soy meal hull (Arani et al., 2006), and spent tea leaves (Hameed, 2008a). In this report we shall reuse crushed and dried *Padina gymnospora* plant previously used for the production of biodiesel.

Methylene blue was initially discovered in 1876 by German chemist Heinrich Caro. Methylene blue has been used in various industries such as the pharmaceutical industry as a treatment for Malaria (Guttmann and Ehrlich, 1891) as well being widely used in labs. Methylene blue when combined with light has also found use in the treatment of plague resistant psoriasis (Salah, Samy and Fadel, 2009), IDS-related Kaposi's sarcoma (Tardivo et al., 2006), West Nile virus (Papin, Floyd and Dittmer, 2005), and to inactivate Staphylococcus aureus (Zolfaghari et al., 2009), HIV-1 (Floyd, Schneider and Dittmer, 2004), Duck hepatitis B (Wagner et al., 2001), Adenovirus vectors (Schagen et al., 1999), hepatitis C(Mohr and Muller-breitkreutz., 1998) as well as the photodynamic treatment of cancer when combined with plant auxin. In the present investigation we use adsorption of varied concentrations of methylene blue samples on marine micro-algae samples. The algal species used in this investigation is *P. gymnospora*.

2 Materials and methods

2.1 Dye solution

Methylene blue is an aromatic chemical compound used in the textile industry. At room temperature it is in the form of an odourless solid of dark green colour that yields a blue solution when dissolved in water. The dye was purchased from Balaji chemicals, Chennai, India. The stock solution of the dye was prepared by dissolving 1 g of methylene blue powder in 100 mL of distilled water. The test solutions were prepared by diluting the stock solution.

2.2 Preparation of biomass

The biomass *P. Gymnospora* is a species of algae belonging to the family Dictyotaceae. It was collected from the Mandapam, a coastal region in the Ramanathapuram, Tamil Nadu, India. The algal biomass generated after the oil extraction process for the biodiesel production was used for this study. This biomass was dried at 53°C for 2 days, crushed and sieved using 70–80 mesh to particulate the size. The biomass particles that was passed through the 70 mesh size but stayed on mesh size 80 were segregated from the rest biomass. This powdered algal biomass was used for the batch experiment of dye removal.

2.3 Dye analysis

The change in dye concentration due to adsorption was determined by UV-vis spectrometer. Absorbance was measured at wavelength 670 nm. The percentage of dye removal due to biosorption was calculated as % dye as removal = $[C_o - C_i/C_o] \times 100\%$, where C_i and C_o are the initial and final concentration of dye solution (mg L^{-1}), respectively.

2.4 Study of sorbent dosage

20 mg L^{-1} of the dye solution was prepared and the effect of initial sorbent dosage on the removal of dye solution was studied by varying the sorbent dosage from 0.2 to 1 g per 100 mL of dye solution. The set up was maintained in a thermostatic shaker at a temperature of 28°C and an agitation of 100 rpm. The change in concentration of the dye was observed for the given solution at 24 hours' time interval for 6 days using colorimeter at the wavelength 670 nm.

$$q_e = \frac{C_o - C_e}{W} \times V$$

Where C_o is initial dye concentration (mg L^{-1}), C_e is the final dye concentration (mg L^{-1}), V the volume of the sample (L), and W is the weight of the biomass (g).

2.5 Study of initial dye concentration

Methylene blue solutions of different concentrations varying from 20 mg L^{-1} to 100 mg L^{-1} were prepared by dissolving the methylene blue powder in distilled water in order to study the initial dye concentration. To these varying quantities of dyes solution an equilibrium concentration of sorbent dosage learned from the previous study (20 mg L^{-1}) were added. The conical flasks were then placed in a Thermostatic shaker and agitated at 28°C at 100 rpm. The samples were periodically tested at 24 hours' time interval for four days using UV-Vis Spectrophotometer at 670 nm.

$$\text{Percentage colour removal} = \frac{C_o - C_e}{C_o} \times V$$

where C_o and C_e are equilibrium concentrations of dye in the solution (mg L^{-1}), V the volume of the sample (L).

2.6 Study of temperature change

The effect of temperature on the uptake capacity of methylene blue on the biomass was studied with 0.2 g of sorbent and at initial dye concentration of 100 mg L^{-1}. The conical flasks were then placed in a thermostatic shaker maintained at 100 rpm and various temperature ranges (20, 24, 28, and 36°C). The solution in varying temperature was analysed for every 24 hours for four days using UV-Vis spectrophotometer at 670 nm.

2.7 Study of adsorption isotherms and kinetics

The adsorption kinetics of the given experiment is understood by plotting two isotherms namely Langmuir and Freundlich. Adsorption isotherm and kinetic experiments were carried using the batch method. In five 0.25 L conical flasks 100 ml of solution containing 20 mg L^{-1}, 40 mg L^{-1}, 60 mg L^{-1}, 80 mg L^{-1} and 100 mg L^{-1} of methylene blue solutions were prepared with a sorbent dosage of 0.2 g in each flask. The conical flasks were then placed in a thermostatic shaker which agitated the solution at 100 rpm at 28°C. The amount of dye adsorbed at equilibrium was calculated from the equation

$$q_e = \frac{C_o - C_e}{W} \times V$$

where C_o and C_e are the concentration of the dye in the solution in the beginning and at equilibrium respectively (mg L^{-1}), V is the volume of the solution (L), W is the mass of dry algae powder (g). In order to understand the effect of temperature, initial dye concentration and sorbent dosage on the absorbance of dye preliminary experiments were carried out using varied agitation speeds and the best agitation speed was found to occur at 100 rpm.

2.8 Langmuir isotherm

The Langmuir isotherm is derived from the assumption that the adsorbed layer formed is monolayer and is given by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e$$

where C_e the equilibrium concentration of dye (mg L^{-1}), q_e is the amount of dye sorbent per unit mass of sorbent at equilibrium (mg g^{-1}), Q_o (mg g^{-1}) and b (l mg^{-1}) are the Langmuir constants related to the sorption capacity and energy of separation respectively.

2.9 Freundlich isotherm

The Freundlich isotherm describing heterogeneous reversible multilayer adsorption on catalytic surface is given empirically by the formula

$$q_e = \mathrm{K} C_e^{\frac{1}{n}}$$

where C_e is the sorbent concentration at equilibrium (mg L^{-1}), q_e is the amount of dye adsorbed per unit mass of sorbent (mg g^{-1}), K and n represents the Freundlich adsorption isotherm constants which varies according to the heterogeneity of the material.

The values of the adsorption constants can be estimated by plotting a graph between log q_e vs log C_e. The slope of the linear graph gives $1/n$ and intercept gives log K.

2.10 Fourier transform infrared spectroscopy

The FTIR analysis of the dye for the change in functional groups before and after adsorption on the biomass was undertaken. 2 ml of methylene blue control and treated sample were taken and a drop from each sample was placed on a glass slide located

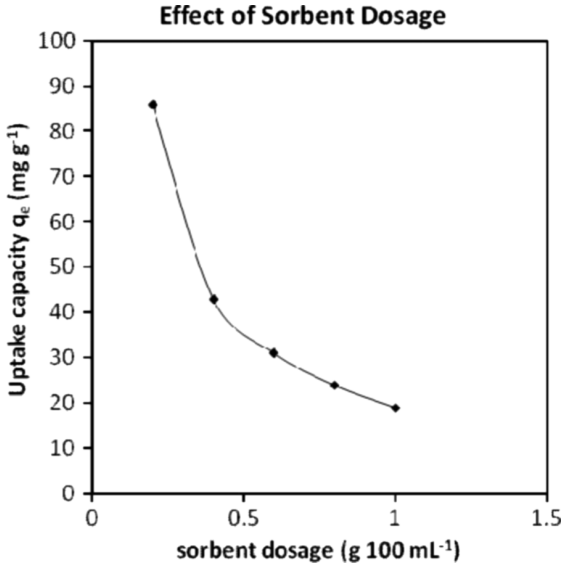
between two KBr crystals and analysed. The peaks were labelled at their wavelengths and the transmittance was analysed.

3 Results and discussions

3.1 Effect of sorbent dosage

The influence of sorbent dosage of *P. gymnospora* with regards to the dye uptake capacity is inspected and the maximum equilibrium uptake capacity (q_e) is found to occur for a sorbent dosage of 0.2 g of dry weight. The equilibrium uptake capacity was found to decrease with an increasing sorbent dosage (Figure 1). This could be explained by the fact that the amount of dye to be adsorbed is split among the increased dye adsorption sites with increasing sorbent dosage leading to lower specific dye uptake capacity. Similar results were obtained with methylene blue adsorption with rosewood saw dust (Garg et al., 2004). The following experiments were thus conducted with an adsorbent dosage of 0.2 g.

Figure 1 Effect of sorbent dosage on equilibrium dye uptake capacity of *Padina gymnospora* for Methylene blue dye (initial dye concentration = 20 mg L^{-1}, temperature = 28°C)

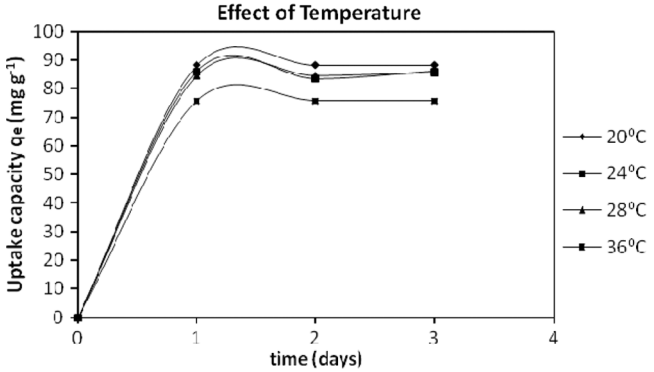


3.2 Effects of temperature

The effect of temperature on the equilibrium uptake capacity of Methylene Blue sorption on *P, gymnospora* was studied with initial dye concentration of 20 mg L^{-1} .The temperatures of study taken were 20°C, 24°C, 28°C and 36°C. The most effective equilibrium uptake capacity was found to occur for 20°C. There was a noticeable trend of decrease in adsorption capacity of *P. gymnospora* with increase in temperature (Figure 2). These results show that the adsorption of *P. gymnospora* is an exothermic process and the strength of the physical bonds between the dye molecules and the active sites of the

P. gymnospora decreases with an increasing temperature. Similar results were observed by (Hu et al., 2010) who investigated the effect of temperature on the removal of the dye Congo red from aqueous solution by cattail root and indicated adsorption decreasing with increasing temperature.

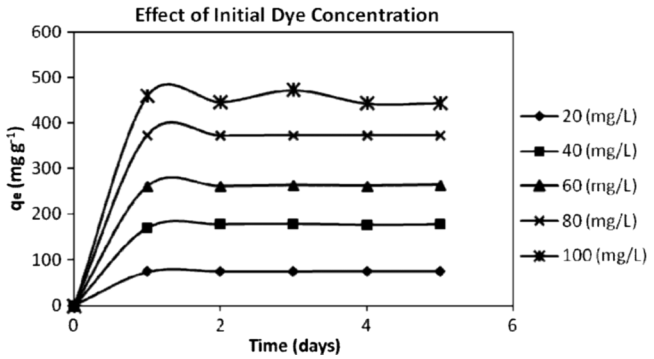
Figure 2 Effect of temperature on equilibrium dye uptake capacity of *Padina gymnospora* for methylene blue dye (initial dye concentration = 20 mg L^{-1}, temperature = 28°C)



3.3 Effect of initial dye concentration

Dye concentrations ranging from 20 mg L^{-1} to 100 mg L^{-1} were studied and the equilibrium uptake capacity for100 mg L^{-1} dye concentration was found to be the largest. The calculated value of equilibrium uptake capacity for 100 mg L^{-1} was 472.586 (mg g^{-1} dry biomass) (Figure 3).The equilibrium uptake can be explained by the presence of an increasing concentration gradient which provides an increasing driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phase leading to an increasing equilibrium adsorption until saturation is reached. A similar trend was reported with methyl violet onto sunflower seed hulls (Hameed, 2008b) fact a large amount of dye particles are available for adsorption on the sorbent surface are hence increasing the uptake capacity of the material along with the formation of multilayer adsorption system.

Figure 3 Represents the equilibrium uptake capacity of different of *Padina gymnospora* for different initial dye concentration (sorbent dosage = 0.2 g, temperature = 20°C)



3.4 Equilibrium modelling

Equilibrium modelling was done for the adsorption of methylene blue onto the surface of the sorbent by the preparation of 20 mg L^{-1} dye solution and then dissolving the sorbent into the solution. The solution containing the sorbent is maintained at a constant temperature of 20°C and shaking was maintained at 100 rpm. The dye concentration is tested at an interval of 24 hours. It was determined from the observed values that the maximum adsorption of up to 95% occurred within the first 24 hours after which equilibrium is reached due to the lack of availability of adsorption sites.

3.5 Equilibrium isotherms

Figures 4 and 5 show the fitting of Langmuir and Freundlich isotherms respectively for methylene blue sorption on *P. gymnospora*. The adsorption isotherm constants are summarised in Table 1. Analysis of R^2 values show that the Freundlich isotherms are a more appropriate fit for the given data. The Freundlich isotherm had a R^2 value of 0.936 for the plot of ln q_e vs ln c_e. This is also an indication of surface heterogeneity of *P. gymnospora* responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. The value of K_f was found to be 6.347 (mg g^{-1}) and the value of n was found to be 0.524 indicating that methylene blue adsorption was not favourable.

Figure 4 Fitting of Langmuir isotherm to the equilibrium results for methylene blue dye adsorption on *Padina gymnospora* (temperature = 20°C)

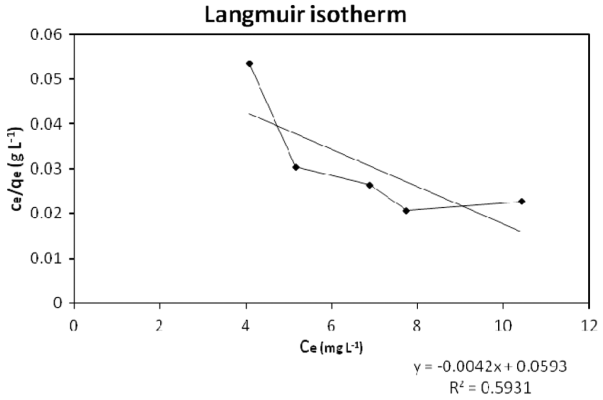


Figure 5 Fitting of Freundlich isotherm to the equilibrium results for methylene blue dye adsorption on *Padina gymnospora* (temperature = 20°C)

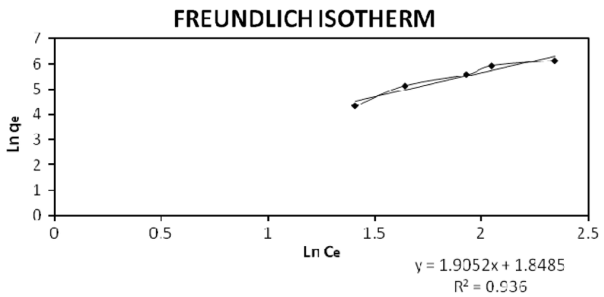


Table 1 The constants of Langmuir and Freundlich isotherms and there regression coefficients

	Langmuir isotherm			*Freundlich isotherm*		
Parameter	Q_o *(mg* g^{-1}*)*	*b (L* mg^{-1}*)*	R^2	K_f	*n*	R^2
Constant value	–250	–0.0677	0.593	6.347	0.524	0.936

3.6 Kinetic studies

The kinetic studies provide useful information for modelling and designing adsorption processes. The kinetics of methylene blue sorption on *P. gymnospora* was studied under pseudo first order and second order kinetics models as shown in Figures 6 and 7, respectively.

Figure 6 Pseudo first order kinetics for methylene blue dye adsorption on 0.2 g of *Padina gymnospora* (temperature = 20°C)

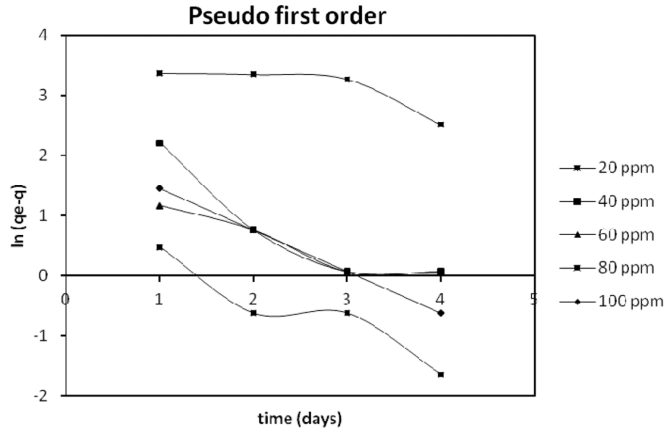
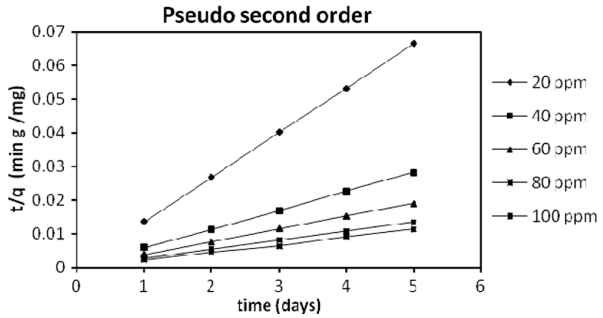


Figure 7 Pseudo second order kinetics for methylene blue dye adsorption on 0.2 g of *Padina gymnospora* (temperature = 20°C)



From the slope and intercept of the graph plotted between in $((q_t - q_e)$ vs ln t, for the initial dye concentrations of 20 mg L^{-1}, 40 mg L^{-1}, 60 mg L^{-1}, and 100 mg L^{-1} for a sorbent dosage of 0.2 at temperature of 20°C, the first order rate constant k_1 and equilibrium adsorption capacity $q_{1eq,cal}$ were determined. Comparing calculated value of

q_e with observed value of q_e it becomes clear that the system does not follow pseudo first order kinetics. This information is supported with a low R^2 co-efficient of only 0.691.

The slope and intercept of the graph plotted between t/q vs. t gave the pseudo second order coefficients k_2 and $q_{1eq,cal}$ Comparing calculated values of q_e with observed values of q_e shows the adsorption of methylene blue on *Padina gymnospora* is relatively well explained by pseudo second order kinetics. This assessment of the kinetics of the system is supported by a R^2 coefficient in the range of 0.999 to 1. This results suggests that adsorption of methylene blue was likely controlled by chemisorption and took place through surface exchange reactions until the surface active sites were fully occupied; then the dye molecules diffuse into the adsorbent network for further interactions (Crini, 2008). The summary of the constants obtained in both pseudo first order and pseudo second reactions are summarised in Table 2.

Table 2 Kinetics of biosorption of methylene blue by *Sargassum longifolium*

	Pseudo first order			*Pseudo second order*		
Concentration	k_1*(1/day)*	q_1*(mg g^{-1})*	R^2	$k_{1\times10}{}^{-2}$ *(g/mg day)*	q_2*(mg g^{-1})*	R^2
20 mg L^{-1}	–0.263	44.03	0.691	0.292	76.923	1
40 mg L^{-1}	–0.711	12.922	0.828	0.427	200	0.99
60 mg L^{-1}	–0.398	4.558	0.899	1.088	333.33	0.99
80 mg L^{-1}	–0.636	2.685	0.899	0.595	500	1
100 mg L^{-1}	–0.693	8.602	1	2.312	500	0.99

3.7 Fourier transform infrared spectroscopy (FTIR)

FTIR was carried out analyse the functional groups present in the dye solution before and after adsorption and the spectrum is shown in Figures 8 and 9. The FTIR analysis for the initial dye solution showed strong bands at 3463.0 cm^{-1}, indicative of asymmetric N-H stretch bonds in the amine group. Absorption peaks were also detected at points 2926.6 and 2854.0 cm^{-1} indicating the presence of C-H stretch bonds. The spectroscopy also showed bands at 2361.6 and 2347.5 cm^{-1} indicating presence of CO_2 impurities in sample dye solution. Other bands present are at 2076.0 cm^{-1} indicating R-N=C=S bonds, 1638.1 cm^{-1} aromatic C=C bending and at 706.5 cm^{-1} indicating =C-H bending bonds other weak bands were found at 435.8 and 424.7 cm^{-1} indicating the presence of aryl disulfide (S-S stretch bonds). Similar adsorption bands in the 3416.0 cm^{-1} but no adsorption peaks in the 2926.6 and 2854.0 cm^{-1} range and adsorption peaks at 2360 cm^{-1} and 23461 cm^{-1} indicating the presence of CO_2 impurities in sample dye solution another peak is found at 2092.3 cm^{-1} indicating R-N=C=S bonds also adsorption peaks were found in 1226.7 cm^{-1} indicating presence of aromatic C-H in-plane bend bonds and adsorption bands in 680.8 cm^{-1} indicating aromatic C-H out of plane bending. The percentage transmission between the two figures shows the degree to which the dye has been adsorbed on the *P. gymnospora* surface. The absence of peaks in 435.8 and 424.7 cm^{-1} indicate the degradation of the aryl disulfide (S-S stretch bonds). The additional peaks in 2926.6, 2854.0 cm^{-1} indicating the presence of additional C-H stretch bonds formation from the initial dye solution. From the structure of methylene blue we

can disregard peaks 2092.3, 2076.0, 435.8 and 424.7 cm^{-1} as impurities as no R-N=C=S bonds and aryl disulphide (S-S stretch bonds) are present in the structure. From this investigation we can see that *P. gymnospora* can be used as a potential solution for the treatment of methylene blue waste water as new C-H bonds are being formed in the dye solution indicating formation of bonds between dye sample and sorbent.

Figure 8 FTIR for methylene blue solution before adsorption on *Padina gymnospora* (see online version for colours)

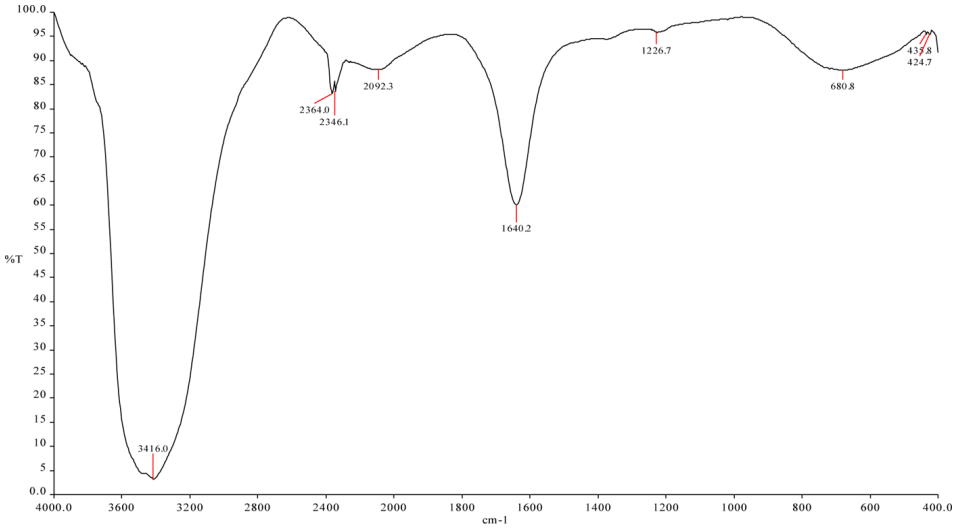
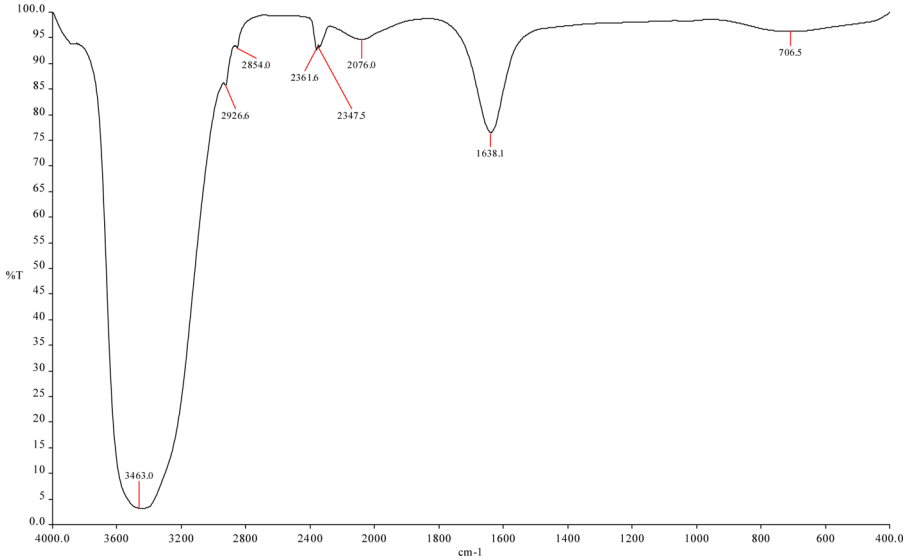


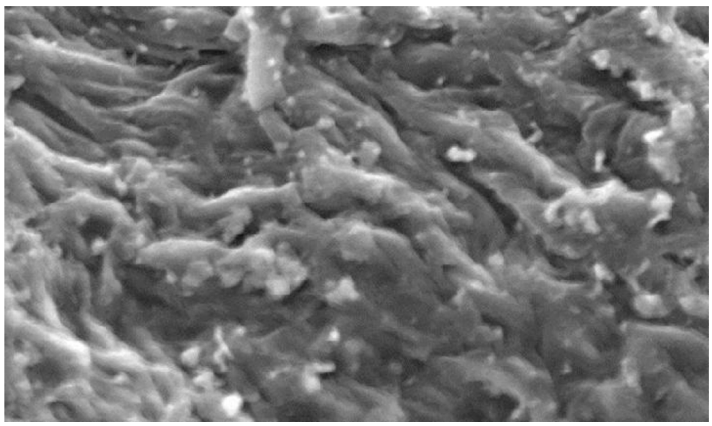
Figure 9 FTIR for methylene blue solution after adsorption on *Padina gymnospora* (see online version for colours)



3.8 Scanning electron microscopy (SEM)

SEM has been used to study the physical structural of the plant species *P. gymnospora.* The biomass was analysed before the accumulation of Methylene Blue dye using SEM. SEM is a very common method used to study the surface morphology and physical properties of the adsorbent. From Figure 10, it can be seen that surface of *P. gymnospora* is highly irregular and uneven hence leading to higher adsorption area. This increased surface area provides larger area for adsorption and hence increases the uptake capacity of the dye.

Figure 10 Scanned electron microscopic image of the surface of *Padina gymnospora* after biosorption



4 Conclusion

In this investigation of the equilibrium uptake capacity of the dye methylene blue by *P. gymnospora* were studied. The crushed *P. gymnopsora* particles were subjected to five initial dye concentrations (20, 40, 60, 80 and 100 mg L^{-1}). The equilibrium uptake capacity of methylene blue was found to be highest at a concentration of 100 mg L^{-1} and showed increasing uptake capacity trend with initial dye concentration. The uptake capacity was also tested against the influence of different temperature (20, 24, 28 and 36°C)and sorbent dosages (0.2, 0.4, 0.6, 0.8 and 1.0 g) and the uptake capacity of the methylene blue by *P. gymnospora* was found to increase with decreasing temperatures and sorbent dosage. The highest uptake capacity was found to occur for sorbent dosages of 0.2 g and at a temperature. The equilibrium data fitted well with Freundlich adsorption isotherm, confirming multilayer adsorption of methylene blue on *P. gymmnospora*. The reaction kinetics was found to follow pseudo second order kinetics with good correlations. The FTIR analysis of the sample of methylene blue was done before and after adsorption and transmittance of the initial dye sample was found to decrease along with the loss of certain absorbance peaks indicating the reformation and degradation of the substance. SEM analysis of the biomass was conducted showing irregular surface having high surface area per volume. Taking these information into consideration, it can be summarised that *P. gymnopsora* can be used as an effective and cost-effective method for the removal of methylene blue dye wastewater.

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