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Short communication

Biosorption of malachite green, a cationic dye onto *Pithophora* sp., a fresh water algae

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Abstract

Batch sorption experiments were carried out for the removal of malachite green from its aqueous solution using *Pithophora* sp., a fresh water algae as biosorbent. Dye uptake was found to increase with contact time and initial malachite green concentration. Equilibrium uptake was found to be pH dependent and maximum uptake was observed at a pH of 6. The effect of algae concentration on equilibrium uptake was also estimated. The equilibrium data tend to fit Freundlich isotherm equation. Kinetic studies showed that the biosorption process follows first order rate kinetics with an average rate constant of 0.9213 min^{-1}. The study confirms that the fresh water algae can be used as biosorbent for the removal of malachite green from its aqueous solution. The biosorption process was found to be surface diffusion controlled with an effective diffusion coefficient of 0.011361 cm^2/s.

Keywords: Biosorption; Malachite green; Cationic dye; *Pithophora* sp.; Kinetics; Equilibrium

1. Introduction

Most industries use dyes and pigments to color their products [1], which include textile, tannery, food, paper and pulp, printing, carpet and mineral processing industries. Perhaps these are the serious polluters of our environment as far as color pollution is concerned. Discharge of dye effluents into the natural streams may be toxic to the aquatic lives. Color affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity [2]. Some of the dyes are carcinogenic and mutagenic [2].

Color is a visible pollutant and the presence of even very minute amount of coloring substance makes it undesirable due to its appearance. Removal of color from dye bearing wastewaters is a complex problem because of difficulty in treating such wastewaters by conventional treatment methods. The most commonly used method for color removal is biological oxidation and chemical precipitation. However, these processes are effective and economic only in the case where the solute concentration is relatively high. Currently sorption process is proved to be an effective alternate for the treatment of dye wastewaters [1–3]. Activated carbon is the most commonly used adsorbent for the treatment of dye bearing wastewaters. However, this process is proved to be uneconomic due to the high cost of activated carbon and also the additional cost involved in regeneration. This process becomes economic, if the sorbent is inexpensive and does not require any expensive pretreatment. Thus there is a continuous search for alternate low-cost adsorbent material to replace high cost activated carbon for water and wastewater treatment. The use of biomaterials as sorbents for the treatment of wastewaters will provide as a potential alternate to the conventional treatment.

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The process of uptake of solute using biomaterials (microbial cells), whether dead or alive, is known as biosorption. In the present investigation, the biomass of *Pithophora* sp. a fresh water algae was used as biosorbent and its capacity to remove malachite green a basic (cationic) dye was evaluated. Previously different algal species have been proved to be very effective biosorbent for the treatment of wastewaters. But almost all the studies have been focused only on the removal of metal cations from wastewaters [4–6]. A survey of literature sowed that no work has been done so far on dye removal process using algae as biosorbent.

In the present study the efficiency of *Pithophora* sp., a fresh water algae was used as biosorbent for the removal of malachite green, a cationic (basic) from its aqueous solutions. Malachite green is selected as model compound in order to evaluate the efficiency of *Pithophora* sp. as biosorbent for the removal of dye from aqueous solutions.

2. Experimental

2.1. Materials

The dark green colored *Pithophora* sp. used in the present study was collected from the CEG fountain, Anna University, India. The collected species were washed with deionised water several times to remove dirt particles. The washing process was continued till the wash water contained no color. The washed materials were then completely dried in sunlight for 10 days. The resulting half white color product was directly used as biosorbent. The dried algae were then cut into small pieces and powdered using domestic Sumeet mixie. The powdered materials were then directly used as adsorbents without any pretreatment. The particle size in the range of 1–3 mm was used in the present study.

The dye used in all the experiments was malachite green, a basic (cationic) dye was obtained from CDH Chemicals, New Delhi. Synthetic dye solutions were prepared by dissolving weighed amount of malachite green in 1 L of double distilled water. The NaOH pellets and HCl solution used for pH study were obtained from Qualigens Fine Chemicals, Mumbai, India.

2.2. Biosorption experiments

Batch biosorption experiments were conducted in 50 mL beaker on a magnetic stirrer at 250 RPM running at different time intervals. All the experiments were carried out at room temperature (30 °C). The concentration of dye ions before and after sorption was determined using UV spectrophotometer (Deep Vision 301 E) by monitoring the absorbance changes at a wavelength of maximum absorbance for malachite green.

The influence of initial solution pH was determined by agitating 0.03 g of *Pithophora* sp. and 30 mL of dye solution of initial malachite green concentration 50 mg/L using magnetic stirrer at different solution pH ranging from 2 to 7. Agitation was provided for 10 h which is more than sufficient to reach equilibrium with a constant agitation speed of 250 RPM.

The effect of biomass concentration on the amount of dye adsorbed was predicted by agitating 0.02 g, 0.03 g, 0.05 g and 0.06 g of algae with 30 mL of malachite green solution of initial dye concentration 100 mg/L for 10 h of contact time at a predetermined optimum solution pH of 6.

Biosorption equilibrium studies were carried out by agitating 0.03 g of algae in a series of beaker containing 30 mL of malachite green solution of different dye concentrations at room temperature (30 °C). Agitation was provided for 10 h, which is more than sufficient time to reach equilibrium. After equilibrium the concentrations in the samples were analyzed as before.

Kinetic experiments were carried out by agitating 0.03 g of algae in a series of beaker containing 30 mL malachite green solution of known concentration using magnetic stirrers running at different contact time intervals at room temperature (30 °C). All the kinetic experiments were carried out at an optimum pH of 6.0.

2.3. Dye uptake

The amount of dye adsorbed onto unit weight of adsorbent, q_e (mg/g) was calculated using the mass balance equation given by:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where C_0 and C_e represent the concentrations of malachite green (mg/L) in the solution at time, $t = 0$ and at any time t (h).

3. Results and discussions

3.1. Effect of initial pH

Fig. 1 shows the effect of initial solution pH on the amount of dye adsorbed (mg/g) at equilibrium conditions. From Fig. 1, it was observed that maximum of 64.4 mg/g of dye was adsorbed at a pH of 6 and it decreased below and above this pH. This behavior can be explained on the basis of zero point charge for *Pithophora* sp. which may lie at around a pH near 3 [6]. At lower pH below this point, the H^+ ions compete effectively with dye cations causing a decrease in % color removal. At a slightly higher pH above this zero point charge, the surface of biomass gets negatively

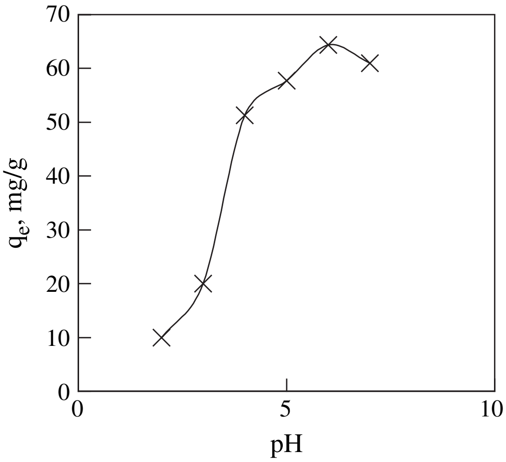

Fig. 1. Effect of pH (V: 30 mL; C_0: 50 mg/L; M: 0.03 g; Temp: 30 °C).

charged, which enhances the positively charged dye cations through electrostatic force of attraction. This can be observed from the very high increase in sorption capacity from 20 mg/g to 51.1 mg/g for an increase in pH from 3 to 4.

3.2. Effect of biomass loading

Fig. 2 shows the plot of equilibrium uptake capacity, q_e (mg/g) and % color removal against biomass concentration (g). From the figure it was observed that the amount of dye adsorbed decreases with increasing biomass concentration. The dye uptake decreased from 42.2 mg/g to 9.2 mg/g for an increase in biomass concentration from 0.02 g to 0.06 g. Whereas the % color removal increases from 57.8% to 90.8%. The decrease in q_e value may be due to the splitting effect of flux (concentration gradient) between sorbate and sorbent with increasing biomass concentration causing a decrease in amount of dye adsorbed onto unit weight of biomass. The increase in % color removal is because, at higher biomass concentration, there is a very fast superficial adsorption onto the cell that produces a lower solute concentration in the solution than when cell concentration is lower [6].

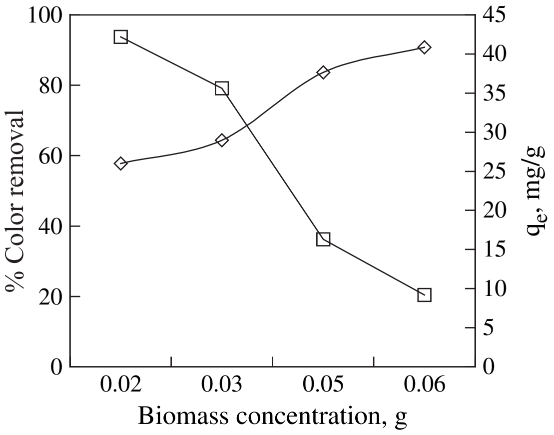

Fig. 2. Effect of biomass loading (V: 30 mL; C_0: 100 mg/L; Temp: 30 °C; pH: 6).

3.3. Effect of initial dye concentration and contact time

Fig. 3 shows the plot between amount of dye adsorbed q versus time t at different dye concentrations, where q represents the amount of dye adsorbed at any time t. From Fig. 1 it was observed that the amount of dye adsorbed varies with varying initial dye concentration and increases with increase in initial dye concentration. Also from the figure it was observed that dye uptake was rapid for the entire sorption period from time $t = 0$ to equilibrium time and no slow phase was observed for all dye concentrations. The dye uptake rates were found to be 13.00 mg/g h, 26 mg/g h, 38.522 mg/g h, 51.414 mg/g h and 59.038 mg/g h for initial dye concentrations of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L, respectively.

3.4. Kinetic modeling

The prediction of batch sorption kinetics gives the most important information for designing batch sorption systems. Adsorption kinetics explain how fast the sorption process occurs and also the factors affecting the reaction rate. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full scale batch process. Also it is important to establish the time dependence of adsorption systems under various process conditions. The nature of sorption process will depend on the physical or chemical characteristics of the adsorbent system and also on the system conditions. The principle behind the

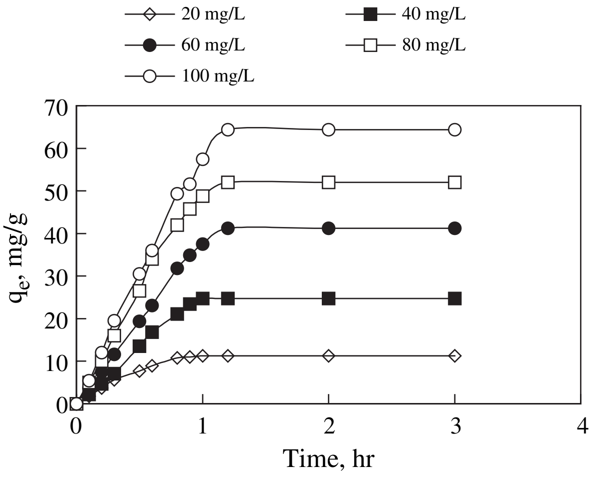

Fig. 3. Biosorption kinetics for malachite green onto *Pithophora* sp. (V: 30 mL; M: 0.03 g/30 mL; Temp: 30 °C; pH: 6).

adsorption kinetics involves the search for a best model that well represent the experimental data. Numerous kinetic models have been used to describe the reaction order of the system. In the present investigation the sorption data were analyzed using two simplest kinetic models, first and second order models which are explained as follows.

3.4.1. First order model

This model is based upon the assumption that the change in dye concentration with respect to time is proportional to the power one. It is also based on the assumption as the following reaction proceeds: thus the rate of reaction *r*, can be expressed as:

$$-r = -\frac{dC}{dt} = K_1 C \tag{2}$$

Separating and integrating Eq. (2) with respect to limits $C = C_0$ at $t = 0$ and $C = C$ at any time t:

$$-\int_{C_0}^{C} \frac{dC}{C} = K_1 \int_0^t dt \tag{3}$$

or

$$\ln\frac{C}{C_0} = -K_1 t \tag{4}$$

Thus the rate constant K can be calculated from the slope of plot between $\ln(C/C_0)$ versus time t. Fig. 4 shows the plot between $\ln(C/C_0)$ versus time t at five different dye concentrations. The calculated K_1 values and their corresponding linear regression correlation coefficient r_1^2 values are shown in Table 1. From Table 1 it was observed that the sorption data were very well represented by first order kinetic model at all initial dye concentrations with an average higher correlation coefficient of 0.98332. The very higher correlation coefficient shows that this model is an appropriate one in predicting the sorption kinetics of malachite green onto *Pithophora* sp.

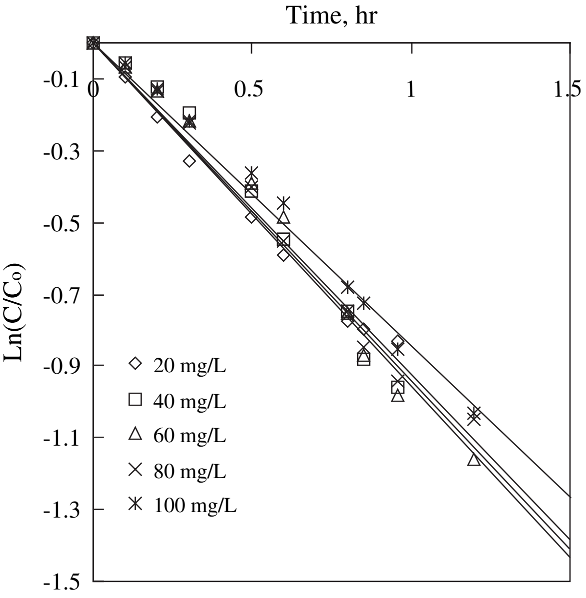

Fig. 4. First order kinetics for malachite green onto *Pithophora* sp. (*V*: 30 mL; *M*: 0.03 g/30 mL; Temp: 30 °C; pH: 6).

3.4.2. Second order model

The sorption kinetics were further analyzed using second order model. This model is based on the assumption as the following reaction proceeds:

$$2A \rightarrow \text{products} \tag{5}$$

where A is the dye component, which is being accumulated onto solid adsorbent. Then the rate of reaction *r* can be written as:

$$-r = -\frac{dC}{dt} = K_2 C^2 \tag{6}$$

Integrating Eq. (6) with respect to limit $C = C_0$ at time $t = 0$ and $C = C$ at any time t, equation simplifies to:

$$\frac{1}{C} = \frac{1}{C_0} + K_2 t \tag{7}$$

The second order rate constant K_2 can be calculated from the slope of plot between $1/C$ versus time t (Fig. 5). The determined second order rate constants K_2 and their corresponding linear regression correlation coefficient r_2^2 values are shown in Table 1. From the table it was observed that the kinetic data fit second order 0.95052. Though the higher r_2^2 values show the applicability of this model, these values were found to be lower than that of r_1^2 values at all dye concentrations confirming that the dye sorption process tends to follow first order rate kinetics.

3.5. Biosorption mechanism

From a mechanistic viewpoint to interpret the experimental data, it is necessary to identify the steps involved during adsorption [7] described by external mass transfer (boundary layer diffusion) and intraparticle

Table 1
Kinetic constants for the biosorption of malachite green onto *Pithophora* sp.

C_0 (mg/L)	K_1 (min^{-1})	r_1^2	K_2 (L/mg s)	r_2^2
20	0.9381	0.989	0.0091	0.9753
40	0.95361	0.975	0.0054	0.944
60	0.9533	0.9788	0.004	0.931
80	0.9198	0.9847	0.0027	0.9632
100	0.8418	0.9886	0.002	0.9391

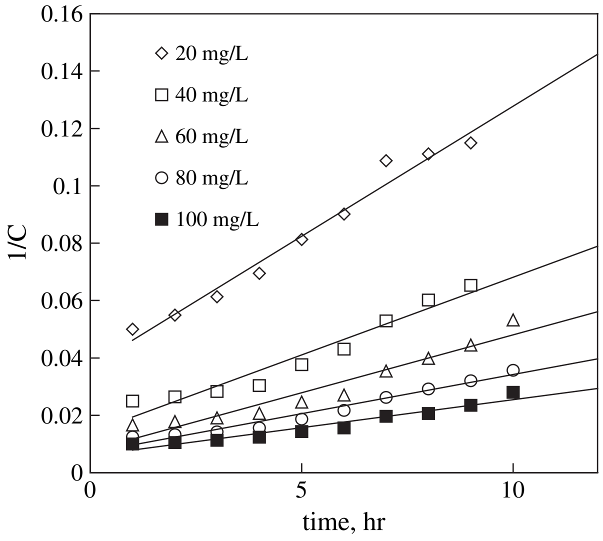

Fig. 5. Second order kinetics for malachite green onto *Pithophora* sp. (*V*: 30 mL; *M*: 0.03 g/30 mL; Temp: 30 °C; pH: 6).

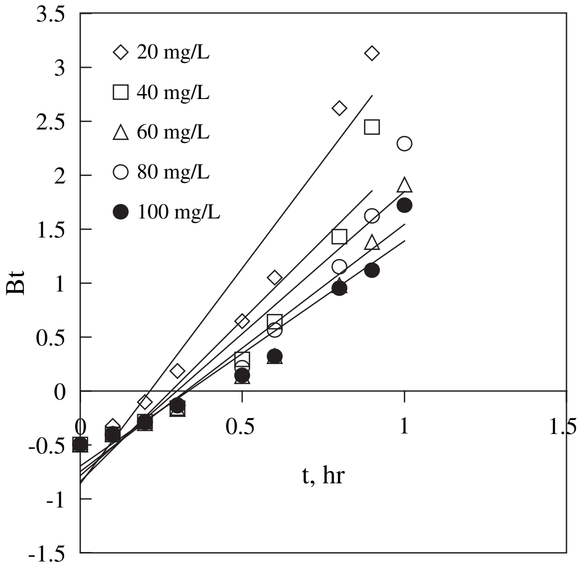

Fig. 6. Boyd plot for malachite green onto *Pithophora* sp.

diffusion. From design aspect, it is important to estimate which is the rate-limiting step (pore or surface diffusion) involved in the sorption process. Thus kinetic data have been analyzed using the model given by Boyd et al. [8]:

$$F = 1 - \left(6/\pi^2\right)\exp(-Bt) \tag{8}$$

and

$$F = q/q_0 \tag{9}$$

where q_0 is the amount of malachite green adsorbed at infinite time (mg/g) and q represents the amount of dye adsorbed at any time t (min), F represents the fraction of solute adsorbed at any time t and Bt is a mathematical function of F.

Substituting Eq. (9) in Eq. (8), Eq. (8) simplifies to

$$1 - F = \left(6/\pi^2\right)\exp(-Bt) \tag{10}$$

or

$$Bt = -0.4977 - \ln(1 - F) \tag{11}$$

Eq. (11) is used to calculate Bt values at different time, t. The calculated Bt values were plotted against time as shown in Fig. 6. The linearity in the plot is used to distinguish whether external and intraparticle transport controls the adsorption rate. From the figure it was observed that the relation between Bt and t was linear at all dye concentrations but does not pass through origin, confirming that surface diffusion is the rate-limiting step [7,9]. The calculated B values were used to calculate the effective diffusion coefficient, D_i (cm^2/s) using the relation [9]:

$$B = \Pi^2 D_i / r^2 \tag{12}$$

where r represents the radius of the particle calculated by sieve analysis and by assuming as spherical particles. The calculated D_i values at different initial dye concentrations were given in Table 2. The average D_i values were estimated to be 0.011361 cm^2/s.

3.6. Biosorption equilibrium

The analysis and design of adsorption process requires equilibrium to better understand the adsorption process. Sorption equilibria provide fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation [10]. In the present investigation the equilibrium data were analyzed using the Freundlich and Langmuir isotherm expression. As the Langmuir isotherm poorly fits the equilibrium data, the data fitting Freundlich isotherm alone are presented here. The Freundlich expression is given by [10]:

$$q_e = K_f C_e^{1/n} \tag{13}$$

where K is related to the sorption capacity (mg/g) (L/mg)^n and n is related to the adsorption intensity. The

Table 2
Effective diffusivity at different dye concentrations

C_0 (mg/L)	D_i (cm^2/s)
20	0.016221
40	0.012141
60	0.009298
80	0.010692
100	0.008456

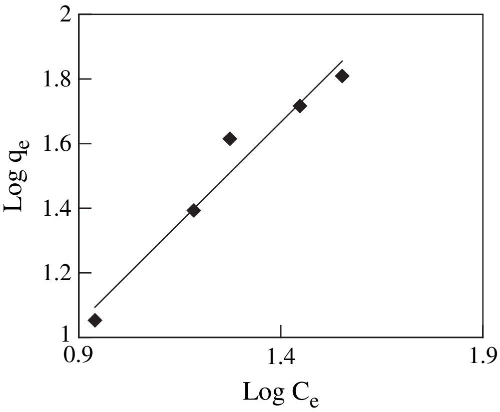

Fig. 7. Freundlich isotherm plot at 30 °C (*V*: 30 mL; *M*: 0.03 g; pH: 6; Temp: 30 °C).

linearised form of Freundlich equation can be written as follows:

$$\log q_e = \log K_f + 1/n(\log C_e) \quad (14)$$

Fig. 7 shows the fitted equilibrium data in Freundlich isotherm expressions at 30 °C. From the figure, it was observed that the equilibrium data fitted well in Freundlich expression with a correlation coefficient value of 0.9592. The higher correlation coefficient predicts the coverage of malachite green onto *Pithophora* sp. particles may be multilayer (heterogeneous sorption).

The equilibrium data fitted in Freundlich isotherm equation is given by:

$$q_e = 0.8450K^{1/0.8046} \quad (15)$$

4. Conclusion

The present study shows that the biosorbent *Pithophora* sp. a fresh water algae can be effectively used as an adsorbent for the removal of malachite green from its aqueous solutions. The kinetic data were very well represented by first order kinetics with an average rate constant of 0.9213 min^{-1}. The equilibrium dye uptake (mg/g) was found to decrease with increase in biomass loading. The biosorption process was found to be surface diffusion controlled. Best fit of equilibrium data in Freundlich isotherm relation confirms the multilayer sorption of malachite green onto *Pithophora* sp.

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