

BIOSORPTION OF BASIC BLUE NINE FROM WATER SOLUTION BY MARINE ALGAE *ULVA LACTUCA*

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ABSTRACT

Biosorption of colors is an important technology for treatment of different types of industrial wastewaters containing dyes. The objective of this study was to convert green algae *Ulva lactuca* to dye adsorbents for wastewater treatment. The important of commonly available green algae *U. lactuca* was investigated as viable biomaterials for biological treatment of synthetic basic blue 9 (5-Chloro-*N,N,N',N'*-tetramethyl-5 λ^4 -phenothiazine-3,7-diamine) effluents. The results obtained from the batch experiments revealed the ability of the green algae in removing the blue colour and was dependent on the dye concentration, pH and algal biomass. Maximum dye colour removal was observed on the third day for all the system conditions. We investigated the equilibrium and kinetics of adsorption as well as the Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption isotherm of basic blue followed both of Langmuir and Freundlich model with a correlation coefficient of ~ 0.96 to 0.99 and the adsorption kinetic follow the pseudo-second-order model ($R^2 > 1.0$). The maximum adsorption capacity was about 40.2 mg of dye per one gram of dry green algae. However the adsorption capacity of *U. lactuca* for methylene blue was equivalent to rice husk carbon (37.7 mg g^{-1}) and Straw carbon (42.6 mg g^{-1}) but higher than the bamboo dust carbon (7.2 mg g^{-1}), coconut shell carbon (8.16 mg g^{-1}) and groundnut shell carbon (7.5 mg g^{-1}) (Kannan and Meenakshi. 2001). This study demonstrated that the green algae could be used as an effective biosorbent for the treatment of dye containing wastewater streams.

INTRODUCTION

Effluents from the dyeing and finishing process 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). The effluents from the dyestuff manufacturing and some similar industries are also generally highly colored with a large amount of suspended organic solids and hence are the important sources of water pollution (Kannan and Meenakshi 2001). 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 (Reife 1993), and it is difficult or impossible to remove by conventional biological treatment processes (Pagga and Braun 1986).

Biological treatment processes are reported to be efficient in the removal of suspended solids and reduction of chemical oxygen demand but are largely ineffective in removing color from waste water (Brower and Reed 1985). Hence, investigations have been conducted on physico-chemical methods of removing colour from textile

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effluent (Kannan and Meenakshi 2001). These studies include the use of coagulants (Majewska 1989), oxidizing agents (Ding *et al.* 1987), Ultra-filtration, electro-chemical and adsorption techniques (Brower and Reed 1985). Adsorption has been found to be an efficient and economic process to remove dyes, pigments and other colourants and also to control the biochemical oxygen demand (Namasivayam *et al.* 1996 and 1998).

The studies on the use of aquatic plants as a biosorbent for dyes are relatively few. Low *et al.* (1993) reported the potential of *Hydrilla verticillata* as absorbent for removal of basic dye methylene blue under various conditions. The *Ulva lactuca* is another species of algae that is widespread along the shores. It grows well in intertidal waters and accumulates high nutrient levels in urban areas contaminated by domestic sewage (Ho 1990).

In the present study, aqueous solution of methylene blue dye was used as a model compound in an attempted to use *Ulva lactuca* as an adsorbent. Although not strongly hazardous, methylene blue can have various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces sensation and may cause nausea, vomiting, diarrhea, and gastritis (Crauford and Clina 1990). The purpose of this work was to investigate the adsorption capacity of *U. lactuca* to remove methylene blue from aqueous solution and the kinetics and mechanisms of adsorption of methylene blue on various weights of algae.

MATERIAL AND METHODS

Ulva lactuca collected was washed with seawater, tap water and then with distilled water for several times. The clean algae were subjected to sun for several days followed by oven drying at 100 °C for 24 hours and the dried algae was milled and sieved. Methylene blue (MB) supplied by BDH was used as adsorbate and was not purified prior to use.

All the other chemicals used in this study were reagent grade. Double distilled water was employed for preparing all of the solutions and reagents.

Batch adsorption experiments were carried out using appropriately diluted 1000 mg l⁻¹ stock solutions to the required initial concentrations. Adsorption experiments were carried out at room temperature (Low *et al.* 1993). The initial concentrations (5, 10, 15, 20, 25 mg l⁻¹) of MB were obtained by measuring the adsorption at 663 nm (λ_{\max}) using UV-VIS spectrophotometer (Milton Roy, Spectronic 21D). Exactly 100 ml of MB solution of known initial concentration (concentration range from 5-25 mg l⁻¹) was shaken at a constant agitation speed (200 rpm) with a required dose of algae (0.125, 0.25, 0.5, 0.75 and 1.0 g of a fixed particle size (0.315-0.8 mm) for a specific period of contact time (range 5-120 min). The pH of the solutions were adjusted to the required value (range: 2-10) by adding either 1M HCl or 1M NaOH solution. After equilibration, the final concentrations (C_f) were measured at λ_{\max} 663 nm. The percentage removal of dye and amount adsorbed (mg g⁻¹) were calculated using the following relationships:

$$\text{Percentage removal} = 100 \times (C_i - C_f)/C_i \quad (1)$$

$$\text{Amount adsorbed (} q_e \text{)} = (C_i - C_f)/m \quad (2)$$

Where, C_i and C_f are the initial and final concentration (mg l⁻¹) of dye, respectively, and m is the mass of algae (mg).

RESULTS AND DISCUSSION

The results obtained from the present investigation revealed the ability of *Ulva lactuca* in treating MB.

1- Effect of contact time

Removal of different concentration of dye color by *U. lactuca* biomass was monitored at various contact time and represented in Figures 1 and 2. The dye uptake profiles distinctly showed three phases: The rate of

removal/uptake was less initially (phase 1), progressively increased and attained a rapid phase with progression of contact time (phase 2) and finally leveled and attained saturation after a contact time of 45 min and remained more or less constant thereafter up to 120 min. The pattern of graphs was almost same for all the dye concentrations and biomass concentrations. From the results, it can be noted that 30 min of contact time is required for the initial acclimatization of the algal biomass. After acclimatization phase, the dye uptake was maximum and reached saturation at contact time of around 45 min. The rate of dye uptake level reached saturation more or less at the same time (45 min) for all concentrations of biomass and removal remained constant.

2- Effect of algal biomass

The variations of dye removal (saturation) values were depicted in Figure 3 for all the studied algal biomass and dye concentration. The increase in dye adsorption was due to increase in availability of dye binding sites resulting from an increase in adsorbent dosage. This study is in agreement with the results obtained by Namasivayam *et al.* (1996), Low *et al.* (1995) and Lee *et al.* (1996).

3- Effect of pH

The pH value of the solution was an important controlling parameter in the adsorption process, and the initial pH value of solution has more influence than the final pH. Basic dye upon dissolution released colored dye cation in solution and the adsorption of these charged dye groups onto the adsorbent surface was primarily influenced by the surface charge on the adsorbent which in turn was influenced by the pH solution (Figs. 4 and 5). The maximum affinity for this dye cation could be expected at alkaline pH values. At acidic pH value a fewer anionic adsorption sites on the dried *U. lactuca* are generated and sorption was unfavorable, probably because of excess H^+ competing with dye molecule for sorption

sites on the dried *U. lactuca*. The observed values also agree well with the results reported in literature (Low and Lee 1990; Low *et al.* 1993, 1995; Mittal and Gupta 1996; Ramakrishna and Viraraghavan 1997). Another possible interference to biosorption mechanisms was high ionic strength-high ionic strength which significantly reduced the binding of cation to biomass (Schiewer and Wong 2000).

4- Adsorption dynamics

Adsorption rate constant is determined from the first-order rate expression given by Lagergren rate equation (Lee *et al.* 1996) as follows:

$$\log (q_e - q_t) = \log q_e - k_{ad} \times t/2.303 \quad (3)$$

where, q_e and q_t are the amounts of phenol adsorbed ($mg\ g^{-1}$) at equilibrium and at time t (min), respectively, and k_{ad} the rate constant of adsorption (min^{-1}). Values of k_{ad} were calculated from the plots of $(q_e - q_t)$ versus t for different concentration of methylene blue (Table 1). The experimental q_e values do not agree with the calculated ones obtained from the linear plots. This shows that the adsorption of MB on *U. lactuca* is not a first-order reaction.

The second order kinetic model (McKay and Ho 1999) is expressed as follows:

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (4)$$

where, k_2 is the rate constant of second-order adsorption ($g\ mg^{-1}\ min^{-1}$). If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship (Figs 6 and 7). There is no need to know any parameter beforehand and the adsorption capacity at equilibrium q_e can be calculated from equation (4). Also, it is more likely to predict the behavior over the whole range of adsorption (McKay and Ho 1999). Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t versus t . This show a good agreement between experimental and calculated q_e values (Table 1). The correlation coefficients for the second-order kinetic model are 1.0. These indicate that the adsorption system belongs to the second-order kinetic model. Similar

phenomena have been observed in the biosorption of dye removal black B on biomass (Aksu and Tezer 2000, Aksu 2001) and adsorption of Congo red on Coir pith carbon (Namasivayam and Kavitha 2002).

5. Adsorption isotherms

The adsorption data were analyzed with the help of the following linear forms of Freundlich and Langmuir isotherm (Ghosh and Bhattacharyya 2002) as follows:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (5)$$

where, $\log k_f$ is roughly a measure of the adsorption capacity and $1/n$ is an indicator of adsorption effectiveness.

Langmuir isotherm:

$$C_e/q_e = (1/ab) + (C_e/b) \quad (6)$$

where, q_e is the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}), a and b are the Langmuir constants, which are the measure of monolayer (maximum) adsorption capacity in (mg g^{-1}) and energy of adsorption (g l^{-1}), respectively. The values of Freundlich and Langmuir parameters were obtained from linear correlations between the values of (i) $\log q_e$ and $\log C_e$ and (ii) C_e/q_e and C_e , respectively (Table 2). The adsorption isotherms along with the correlation coefficient are presented in Figures 8 and 9. The observed linear relationships as evidenced by the r -values (close to unity) indicate the applicability of these two adsorption isotherms and the monolayer coverage on adsorbent surface. The monolayer adsorption capacities of the adsorbents are possess high adsorption capacity and hence it could be employed as

low-cost adsorbent for the removal of MB. Further, the essential characteristics of Langmuir isotherm can be described by a adsorption factor R_L ; which is defined by the following equation

$$R_L = 1/(1 + bC) \quad (7)$$

where, C is any adsorbate concentration of dye at which the adsorption is carried out (mg l^{-1}) and b is the Langmuir constant (g l^{-1}). The value of adsorption factor R_L indicates the nature of the adsorption process as given below (Table 3). In the present study, the values of R_L computed are in the range of 0 to 1 indicating that the adsorption process is favorable for all weights which may indicate low-cost adsorption.

CONCLUSIONS

The results from the present study showed a broader pH sorption and the kinetics data showed that sorption was quite rapid. Since this aquatic plant (*U. lactuca*) is readily available in the environment, it is more economical and can yield sorbent of higher sorption capacity than others. Furthermore, regeneration is not necessary because it is available biological material. Since this study was performed using synthetic waste water and at laboratory scale, results obtained may has some variation if apply to real waste water. Parameters such as equilibrating time, pH, dosage and concentrations may not stand as indicated. Further study focused on the real waste water from different sources is needed.

Table (1). Comparison of the first- and second-order adsorption rate constants for calculated and experimental q_e values at 25 mg l⁻¹ initial methylene blue concentration and different *U. lactuca* concentrations.

Parameter	First-order kinetic model				Second-order kinetic model		
	Algae wt (g l ⁻¹)	q _e (exp.)	K _{ad}	q _e (Calc.)	R ²	K ₂	q _e (calc.)
1.25	16.603	0.032	2.203	0.846	0.040	16.75	1.000
2.50	7.835	-0.302	0.815	0.657	0.116	7.15	1.000
5.00	3.660	-0.025	0.102	0.565	0.883	3.66	1.000
7.50	2.394	-0.058	0.060	0.841	2.503	2.40	1.000
10.00	1.782	-0.063	0.014	0.637	7.173	1.78	1.000

Conc. = concentration; exp. = experimental; Calc. = calculated.

Table (2). Experimental conditions for the various of adsorption experimental for the removal of methylene blue dye on algae.

Parameter	Weight of algae <i>U. lactuca</i> (in g l)				
	1.25	2.5	5.0	7.5	10.0
Freundlich					
log K _f	1.432	1.603	1.101	1.134	1.453
1/n	3.978	3.283	1.908	1.095	1.955
r	0.954	0.959	0.948	0.957	0.996
Langmuir					
a	0.625	1.038	0.742	0.824	0.936
b	3.012	6.268	7.001	9.013	10.994
r	0.958	0.999	0.962	0.954	0.999
R _L	0.66	0.66	0.54	0.46	0.52

Data used: pH 7.5, speed 200 rpm, contact time 5-12 min, particle size 0.315-0.8 nm, room Temperature, concentration of dye 5-25 mg l⁻¹.

Table (3). The value of adsorption factor and corresponding nature of adsorption process.

Adsorption value RL	Nature of adsorption process
R _L > 1	unfavorable
R _L = 1	Linear
0 < R _L < 1	Favorable
R _L = 0	Irreversible

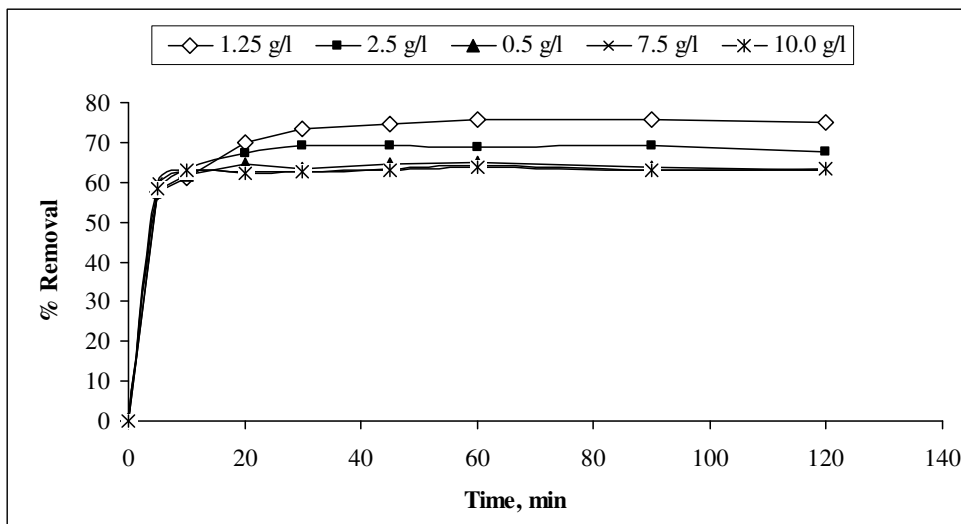


Fig.1. Effect of different weights of algae on the adsorption of dye , initial concentration of MB = 15 mg/l.

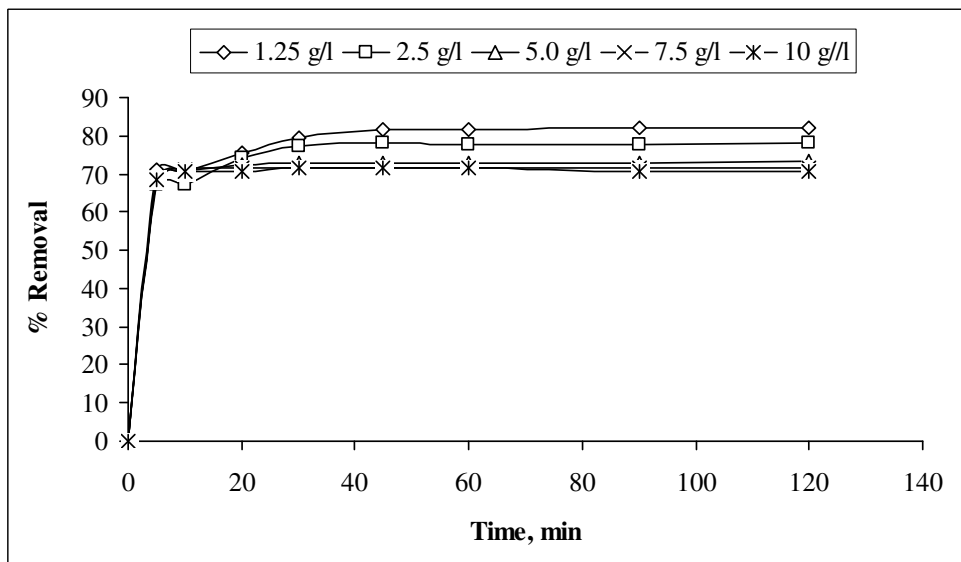


Fig (2). Effect of different weights of algae on the adsorption of dye, initial concentration of MB = 25 mg/l.

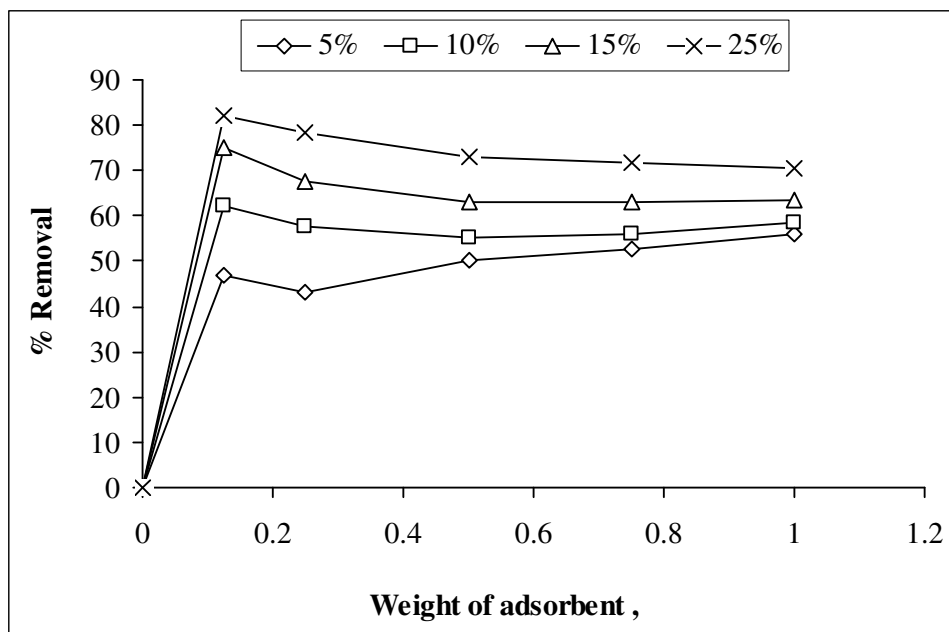


Fig (3). Effect of weight of algae on the removal efficiency at different dye concentrations.

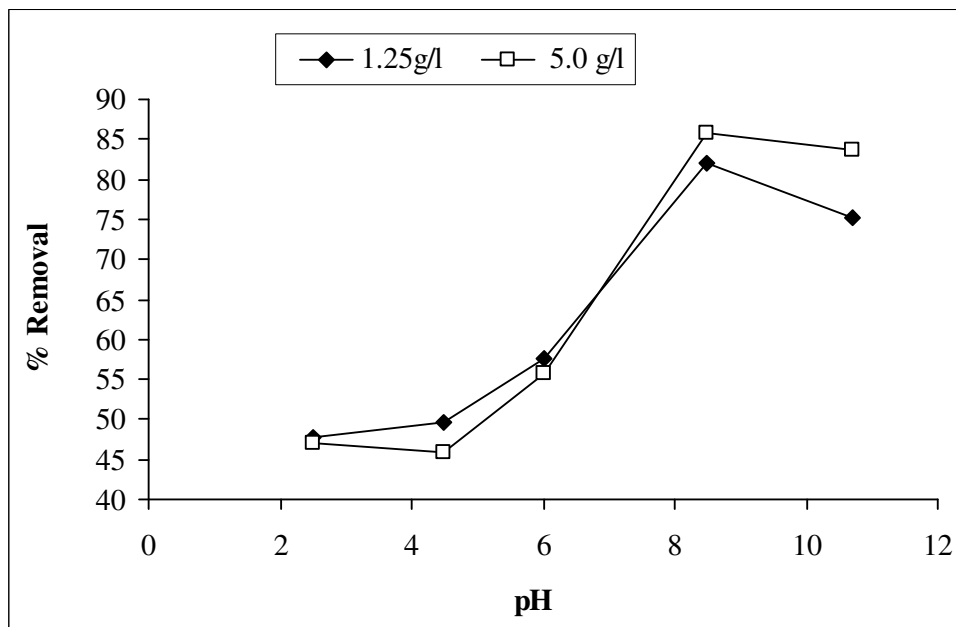


Fig (4). Amount of MB removed for two weights of algae at different pH of dye concentration 5 mg/l.

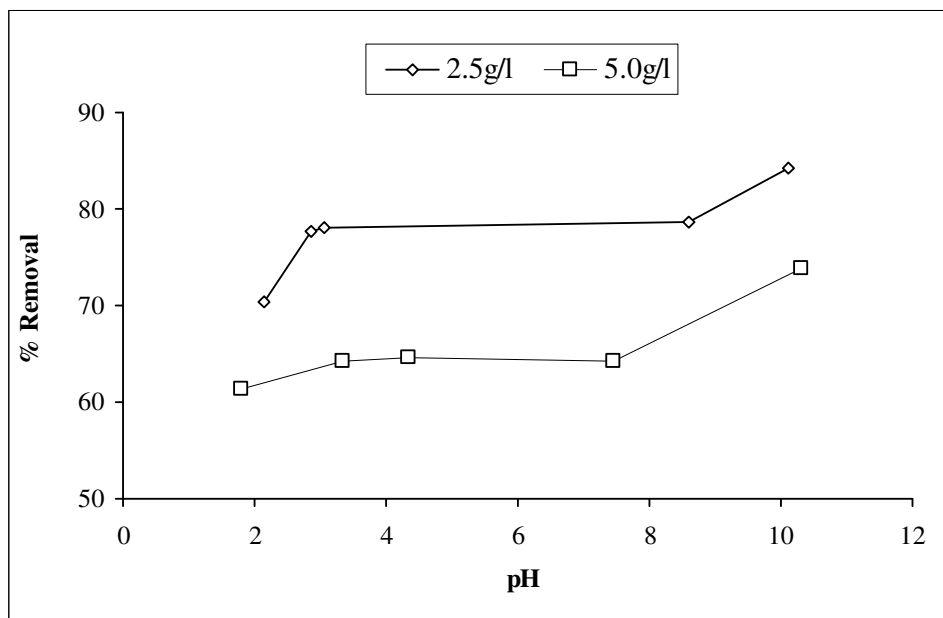


Fig. (5). Amount of MB removed for two weights of algae at different pH of the dye concentration 15 mg/l.

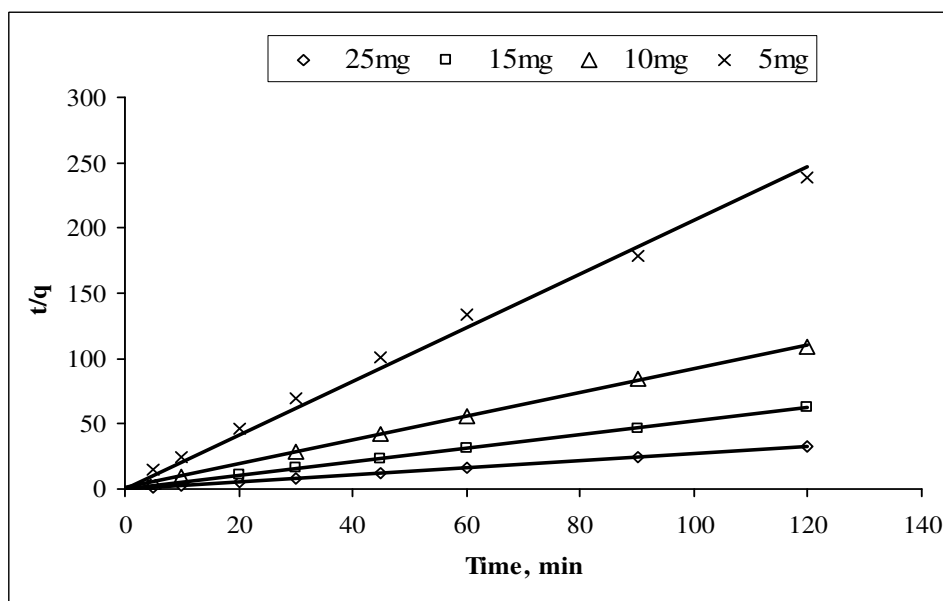


Fig 6. Pseudo second order model at different initial dye concentrations and 5 g/l concentration of algae.

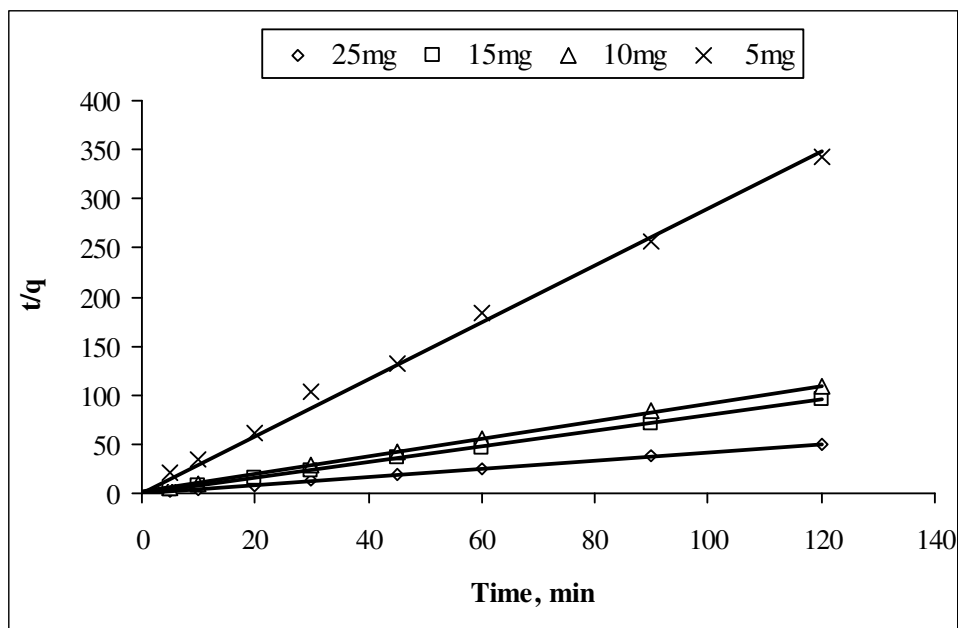


Fig 7. Pseudo second order model at different initial dye concentrations , 7.5 g/l concentration of algae.

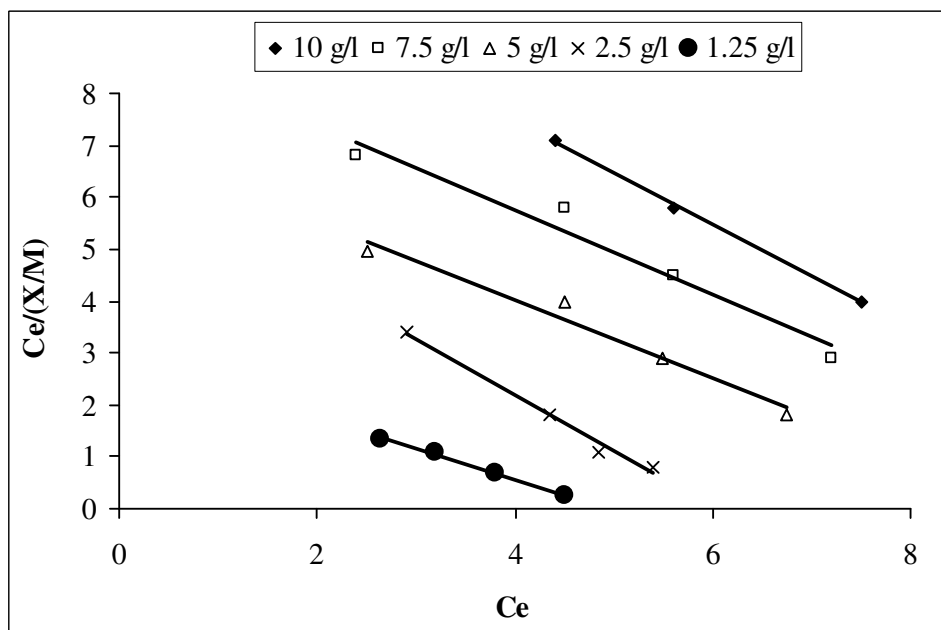


Fig. (8). Fitting of adsorption data with Langmuir.

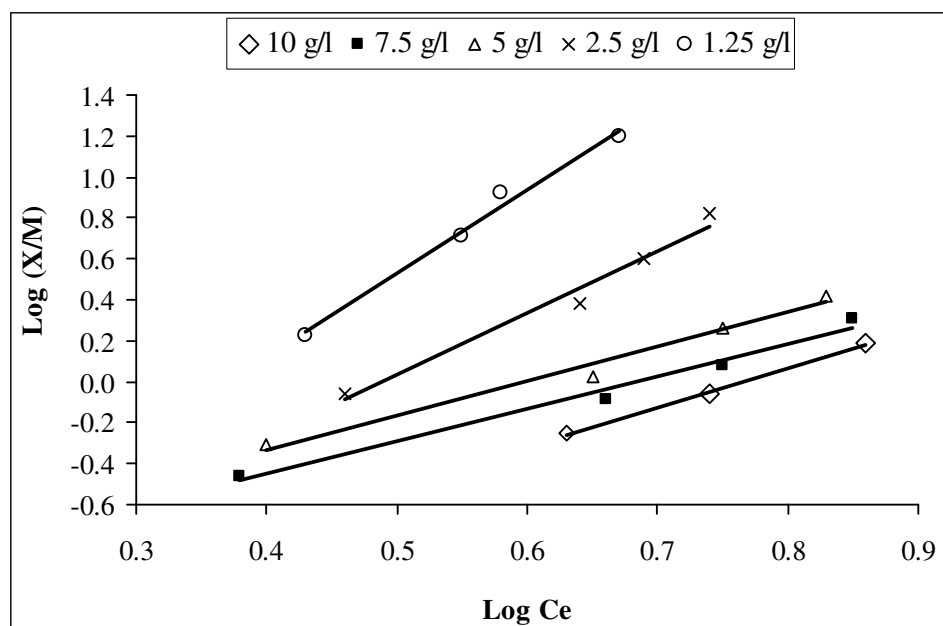


Fig. (9). Fitting of adsorption data with Freundlich.

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