EGYPTIAN JOURNAL OF AQUATIC RESEARCH 1687-4285
VOL. 31, SPECIAL ISSUE, 2005: 86-98.

REMOVAL OF CHRYSOPHENINE DYE (DY-12) FROM AQUEOUS SOLUTION USING DRIED *ULVA LACTUCA*

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Keywords: Biosorption, Dyes; Direct Yellow 12; Chrysophenine; Green algae; Ulva lactuca; Wastewater

ABSTRACT

Removal of dyes from industrial wastewaters using biosorption is an effective technology for decolorize of different type of dyes. The potential of commonly available green algae *Ulva lactuca* was approved as viable biomaterials for biological treatment of synthetic azo dye Chrysophenine (Direct Yellow 12) effluents. Experimental results revealed the ability of the *U. lactuca* in removing the dye colour and were dependent on the dye concentration, pH and algal biomass and not much dependent on the particle size of the *U. lactuca*. Maximum dye colour removal was observed on the third day for all the system conditions. The equilibrium and kinetics of adsorption was investigated and the Langmuir and Freundlich equations were used to fit the equilibrium isotherm. It was determined that adsorption isotherm followed only Freundlich model with a correlation coefficient of 0.99. Adsorption kinetic was consistent with the pseudo-second-order model (R^2 = 1). The maximum adsorption capacity was about 80 g of Chrysophenine per one kilogram of dry *U. lactoca* at pH 7.0. This study demonstrated that the green algae *U. lactuca* could be used as an effective method for the treatment of Chrysophenine containing wastewater effluents.

INTRODUCTION

Synthetic dyes are widely used in industries such as rubber, textiles, plastics, paper, cosmetics etc. to colour their products. Dyes are synthetic aromatic water-soluble, having potential application increase day by day due to tremendous increase of industrialization. There are more than 9000 dyes belonging to various chemical classes (azo, anthraquinone, phthalocyanine, xanthene, nitro, thiazine, etc.) and application classes (direct acid, basic, disperse, reactive, vat etc.) which have been incorporated in the colour Index (Shenai 1995). Among the dyes, azo group of dyes is the largest and most versatile class of dyes, and more than half of the annually produced amount of dyes are azo dyes (Stolz 2001). The major consumer of the dye is the textile industries in usage of the dye (about 60% of the total dye production) for colouration of various fabrics. About 10-15% of the dyes used in the textile as processing during the dyeing do not bind to the fibers and it is therefore released into the aquatic environment (Brown and Anliker 1988; Reisch 1996). Azo dyes are considered toxic to the aquatic biota and carcinogenic to humans and the azo group present in the dye molecule form carcinogenic degradation products (Chung and Cerniglia 1992; Shenai 1995). Therefore, removal of dye from process or waste effluents becomes environmentally important.

Marine algae are biological resources, which are available in large quantities in many parts of the world. Biosorptive processes are generally rapid and are in theory suitable for the extraction of colour and metal ions from large volumes of water (Brady *et al.* 1999). Macroalgae can sequester colour by the same adsorption and

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absorption mechanisms as other biological biomass. The use of biomass of marine algae, *Ascophyllum nodosum* (Chong and Volesky 1995), *Ecklonia radiate* (Matheickal and Yu 1996), *Spirogyra* species (Gupta *et al.* 2001) and *Padina* species (Kaewsarn 2002) for heavy metal removal has been reported. Algae *Spirogyra* species have been used in the removal of Reactive Yellow 22 dye by adsorption (Mohan *et al.* 2002).

The present study aims to investigate the adsorption capacity of commonly available green algae *Ulva lactuca* on adsorption of Direct Yellow 12 (DY-12) from aqueous solution and the effects of initial dye concentration, contact time, particle size, concentration of algal biomass and pH. The DY-12 was selected for the adsorption experiment due to its presence in media of different wastewater for several industries (Rathi, *et al.* 2003; Isik and Sponza 2005).

MATERIALS AND METHODS

a- Materials

Fresh marine green algae *U. lactuca* was collected from Mediterranean Sea coast, Alexandria, Egypt. The biomass collected was washed with seawater, tap water and then with distilled water for several times. The clean algae was dried subjected to sun for several days followed by oven drying at 100 °C for 24 hours. The dried algae was milled and sieved for different particle sizes.

Chrysophenine (C.I. 24895, DY-12) was obtained from ASMA Dye Company of Egypt, with ~75% Dye content and its structure represented in Fig. 1. A stock solution of 1000 mg/L of DY-12 was prepared using distilled water and any of the working solutions used in the experiments were obtained from the stock solution by dilution in distilled water to the required concentration.

Throughout this work, dye concentrations in aqueous solution were determined by comparison with standard solutions in the visible range of the spectrum. UV-VIS spectrophotometer (Milton Roy, Spectronic 21D) was employed for absorbance measurements using silica cells of path length 1 cm. The maximum wavelength λ_{max} for the DY-12 was determined at 389 nm. Change in pH (1 to 7) of DY-12 solution has no effect on its color concentration.

b- Methods

Adsorption experiments were carried out by shaking algae biomass with 100 ml dye solution of required concentration and pH at room temperature in shaker operated at 150 rpm. The samples were withdrawn from the shaker and the dye solution was separated from the adsorbent by centrifugation. Dye concentration in the supernatant solution was estimated by measuring absorbance at maximum wavelength (λ_{max} 389 nm) and computing from a calibration curve. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye colour from aqueous solution at different time intervals. The isothermal studies were performed by varying the initial dye concentrations from 25 to 100 mg/l and addition of various concentrations of algae (1.25, 2.5, 5.0, 7.5 and 10.0 g/l) followed by shaking the reaction mixture at 150 rpm for the equilibrium time. Influence of the pH was studied by adjusting the reaction mixture to different initial pH (1.0 to 7.0) value using 0.1M HCl or NaOH before addition of biomass. The pH measurements were carried out using pH electrode (Check: mate 90, Corning Incorporated, NY).

The amount of dye adsorbed onto algae, the adsorption capacity at steady-state q_e (mg/g), was calculated by mass balance relationship equation.

$$q_e = (C_0 - C_e)\, V/W \qquad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye, respectively (mg/l), V is the volume of the solution (l) and W is the mass of the algae used (g).

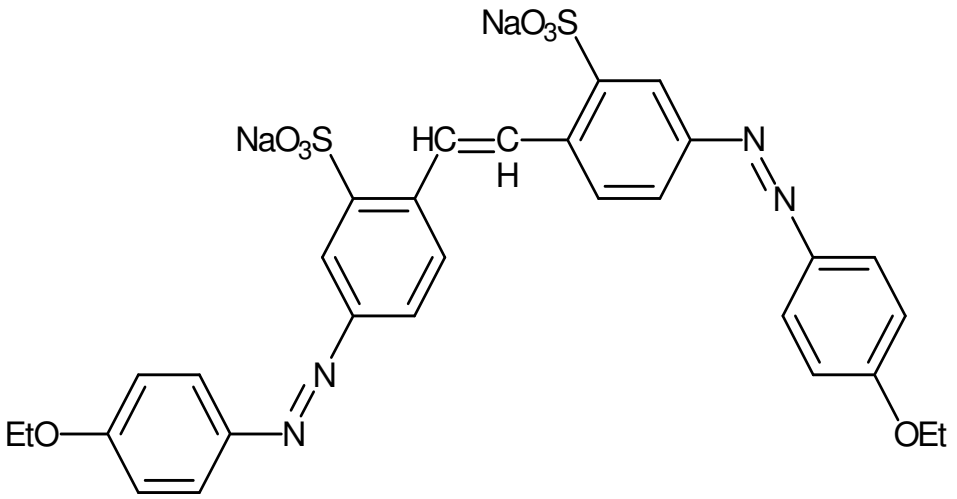


Figure 1. Chrysophenine (DY-12) chemical structure

RESULTS AND DISCUSSION

In this study, adsorption capacities of dried algae are investigated considering several factors, which are important in the biosorption of dyes. These factors include time, pH, initial dye concentration, amount of adsorbent all in distilled water where no other competitive chemicals.

1- Effect of contact time

Figure 2 represents the variation of percent removal of DY-12 with contact times and initial concentration of DY-12 using 1.25 g/L of algae and pH 7.0. As contact time increases, percent removal also increases initially, but then gradually approaches a constant value. The rate of removal of dye is high in the first 10 min, then the rate significantly decrease and eventually approaches almost zero, finally the equilibrium point has been attained. These changes in the rate of removal may be due to the fact that, initially all adsorbent sites are vacant and the solute concentration gradient is high. The decrease in the rate with time indicates of the slow approach to equilibrium possibly by internal diffusion.

2- Effect of pH on DY-12 uptake

The equilibrium DY-12 uptakes at various pH values are presented in Fig. 3. The effect of pH was studied by varying the suspension pH from 1.0 to 7.0. The uptake of dye was high at pH 7.0 and 1.0 while it decreases with the increasing suspension of pH from 1.0 to 4.0. Fig. 3 shows that the lowest biosorption occurred at pH 4.0. The high percentage removal observed at pH 1.0 can be attributed to the positive surface charge grained depending on the adsorption of H^+ ions on the algal surface, and also the hydrolysis of algae may occurs resulting in different dye removal mechanisms. The cell wall of *U. lactuca* contains a large number of surface functional groups. The pH dependence of DY-12 adsorption can largely be related to type and ionic state of these functional groups and also on the DY-12 chemistry in solution. The uptake was high at the neutral pH (~ natural pH) make the experimental more friendly to the environmental conditions, which means no other addition of chemical to the wastewater.

3- Effect of sorbent concentration

Adsorption is highly dependent on the initial amount or concentration of the sorbent. The effect of the algae *U. lactuca* concentration on the removal of DY-12 from aqueous solutions was studied by conducting adsorption experiments using 100 mg/L initial DY-12 concentration at room temperature and initial pH 7.0 with varying the sorbent concentrations from 1.25 to 10.0 g/l and the results are represented in Fig. 4. It is apparent that the removal percent of dye increases rapidly in the first five minutes with increasing concentration of sorbent, due to the increase of the exchangeable sites at higher concentration of the alga. However, the change in percent removal of the dye was slightly increased with the increasing of the alga concentration.

4- Effect of particle size

The Effect of particle size was studied for its possible importance in the treatment of solution containing dye. The influence of contact time on the removal of DY-12 by five different particle sizes (0.2, 0.3, 0.5, 0.9 and 1.5 mm) of *U. lactuca* is shown in Fig. 5. The removal dye by different particle size was almost similar, which indicates that the removal of DY-12 did not depend on the particle size of the *U. lactuca*.

5- Adsorption Isotherms

The original adsorption isotherm drawn between the amounts of DY-12 adsorbed per unit adsorbent and DY-12 remaining in solution at equilibrium time is shown in Fig. 6. The figure indicates that complete saturation of DY-12 on the algae's surface is not attained.

Adsorption isotherms were obtained to the previous data using four different concentrations of algae and under constant solution pH values. Freundlich adsorption isotherm was adopted to correlate the data. For determining the equilibrium parameters the following equation was used

$$X/M = K_F C_e^{1/n} \quad (2)$$

Where X/M is the amount of DY-12 adsorbed per unit weight of adsorbent (mg/g), C_e is the dye concentration remaining in solution at equilibrium (mg/l), K_F (mg/g) and n (g/L) are Freundlich constants, which are the empirical constants and indicative of sorption capacity and sorption intensity, respectively (Weber, 1972). To calculate K_F and 1/n, experimental data were fitted by logarithmic transfer of equation (2) to:

$$\text{Log } (X/M) = \log K_F + (1/n) \log C_e \quad (3)$$

The values of K_F and n were calculated from the intercepts and slopes of the plots and are listed in Table 1.

Linear plots of Log (X/M) vs. Log C_e (Fig. 7) (correlation coefficient ~0.99) show that the adsorption of DY-12 onto *U. lactuca* follows the Freundlich isotherm. The Freundlich constant K_F also represents the predicted amount of dye sorbed in mg/g of a sorbent at an equilibrium concentration. The results showed that *U. lactuca* exhibits good capacity to remove the bulky dye molecules without any pretreatments.

On the other hand, the isothermal equilibrium data were also studied using Langmuir's isotherm equation. The Langmuir equation, which has been successfully applied to many adsorption (El-Geundi 1991 and 1994; Annadurai *et al.* 1999; Malik, 2003) is given by

$$q_e = (K_L S_m C_e)/(1 + K_L C_e) \quad (4)$$

Where S_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg/g), C_e the adsorbate equilibrium concentration (mg/g) and K_L the Langmuir constant (mg/l). S_m represent a practicl limiting adsorption capacity when the surface is fully covered with adsorbate molecules and assists in the comparison of adsorption performance. Equation (4) can be rearranged to a linear form

$$C_e/q_e = 1/(K_L S_m) + C_e/S_m \quad (5)$$

A linearized plot of C_e/q_e versus C_e was not obtained, which indicated that our experimental results did not follow the Langmuir model.

6- Adsorption rate constant

The rate constant of adsorption is determined from the first-order rate expression given by Lagergen (Gündoğan *et al.* 2004) as:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - (K_1/2.303) \times t \quad (6)$$

Where q_e and q_t are the amounts of DY-12 adsorbed (mg/g) at equilibrium and at time t (min), respectively and K_1 the rate constant of adsorption (min^{-1}). Values of K_1 were calculated from the plots of Log ($q_e - q_t$) versus t for different concentrations of DY-12. The experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 2). This shows that the adsorption of DY-12 onto *U. lactuca* is not a pseudo first-order reaction.

The pseudo second-order kinetic model is expressed as:

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \quad (7)$$

where K_2 is the rate constant of second-order adsorption (g/(mg min)). If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption capacity q_e can be calculated from Equation 7. Also, it is more likely to predict the behavior over the whole range of adsorption. Values of K_2 and q_e were calculated from the intercept and slope of the plots of t/q_t versus t. The linear polts of t/q_t versus t (Fig. 8) show a good agreement between experimental and calculated q_e values (Table 2). The correlation coefficients for the pseudo second-order kinetic model are greater than 0.99. These indicate that the adsorption system belongs to the pseudo second-order kinetic model (McKay and Ho 1999).

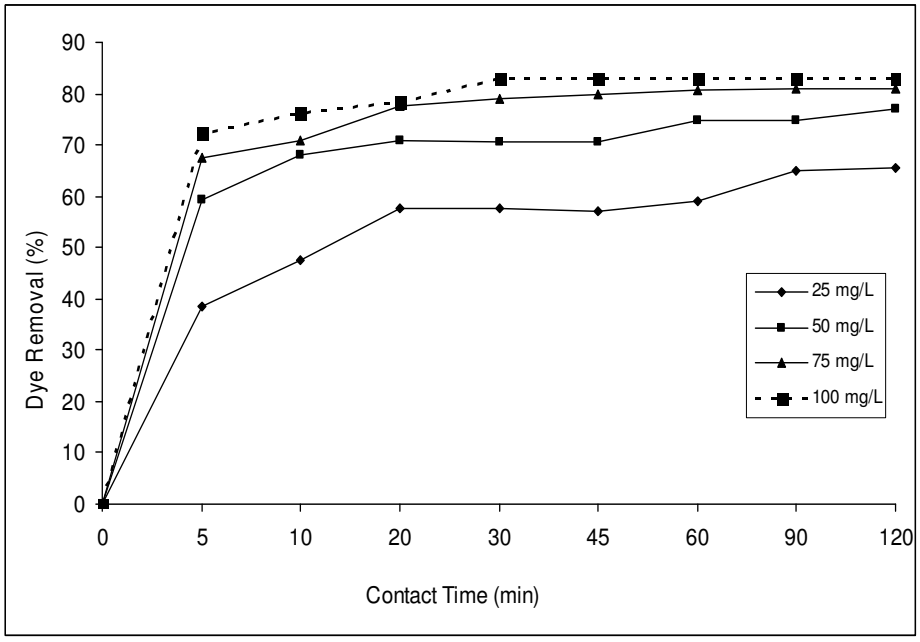
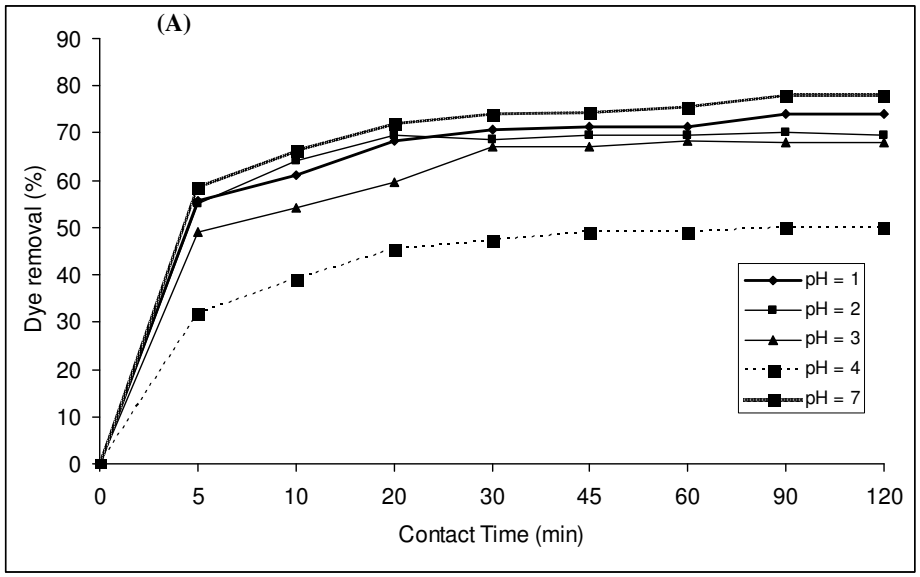


Figure 2. Effect of contact time and initial concentration of DY-12 on percentage of dye removal using 1.25 g/l algae at pH 7.0.



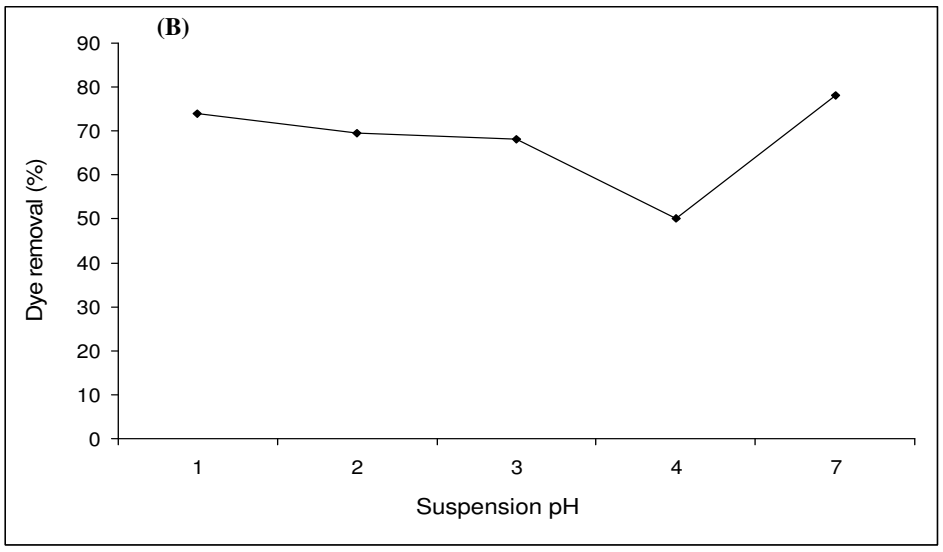


Figure 3. Effect of initial pH value on the percentage of dye removal using 1.25 g/l of *U. lactuca.*

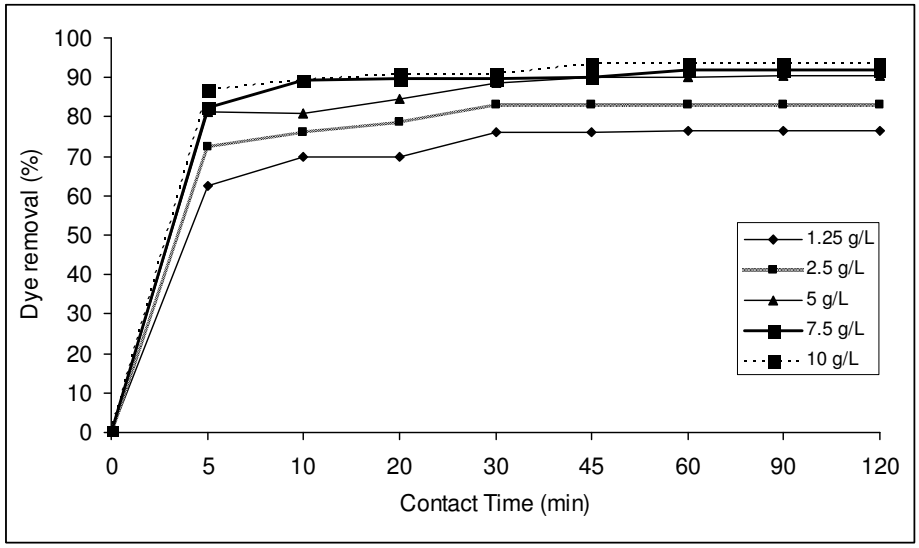


Figure 4. Effect of concentration of *U. lactuca* on the dye uptake at initial pH = 7 and initial dye concentration = 100 mg/l.

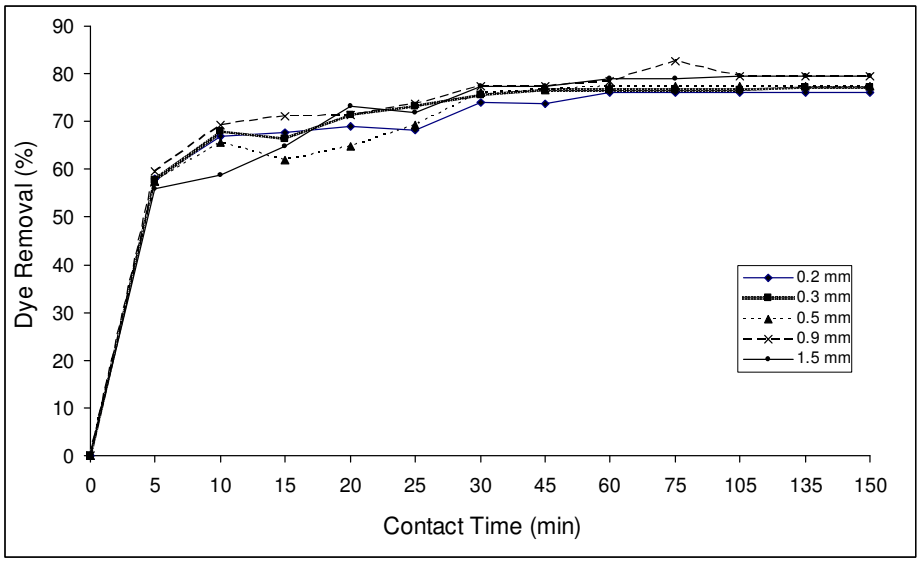


Figure 5. Effect of particle size of *U. lactuca* (1.25 g/l) on the dye uptake at initial pH = 7 and initial dye concentration = 100 mg/l.

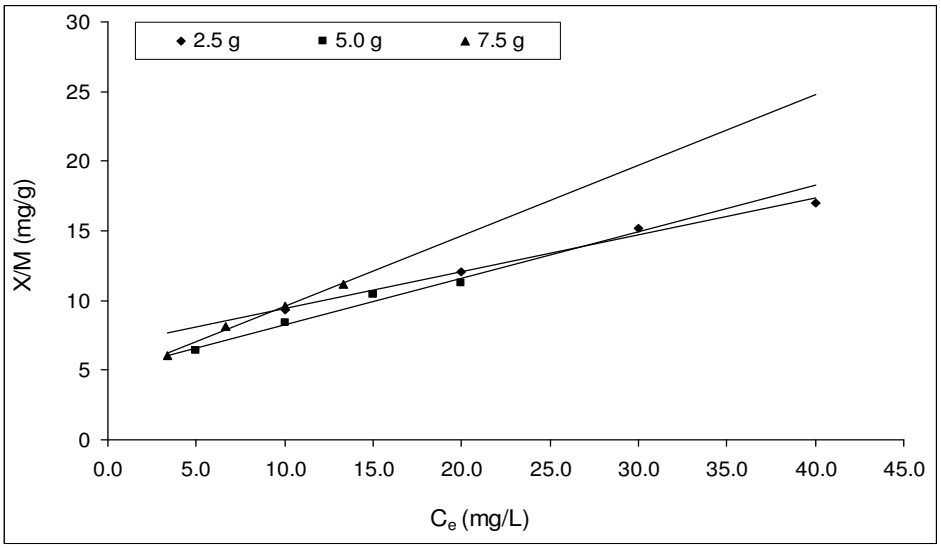


Figure 6. Adsorption isotherm of DY-12 onto *U. lactuca* at room temperature and pH 7.

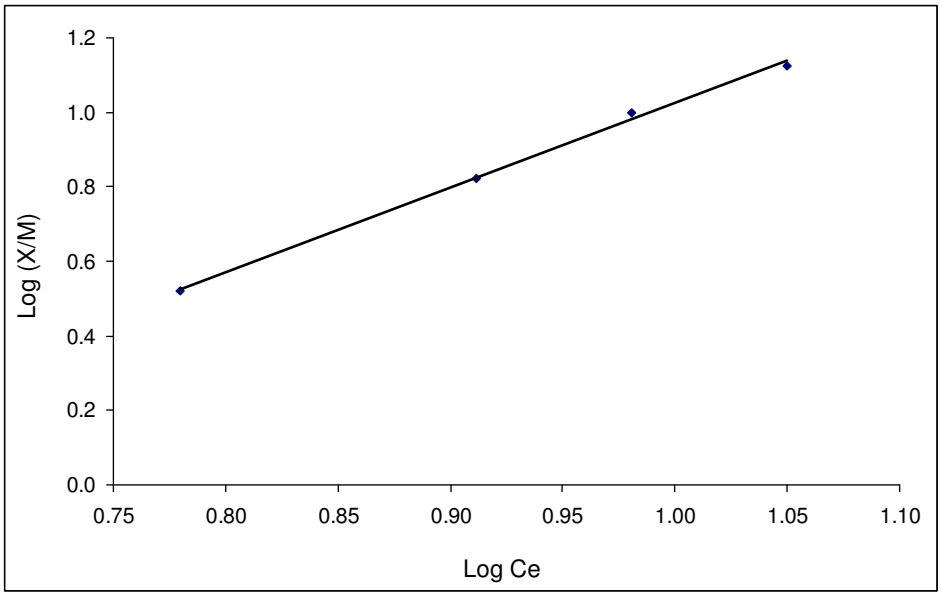


Figure 7. Freundlich plot for the DY-12 adsorption onto *U. lactuca* (7.5 g/l) at room temperature, pH 7 and 25-100 mg/l dye concentration.

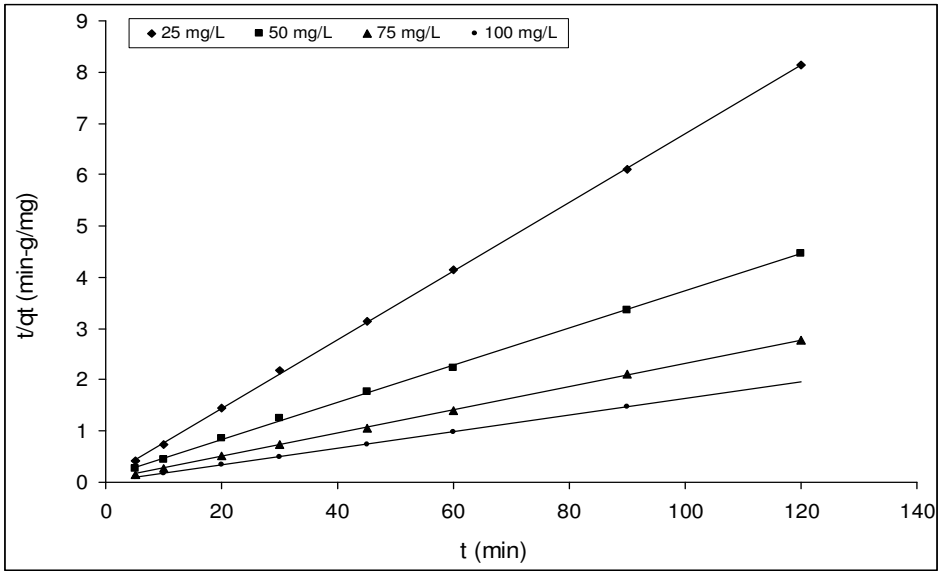


Figure 8. Plot of the pseudo-second-order model at different initial DY-12 concentrations. Adsorbent dose, 1.25 g/l; pH 7.0; DY-12 concentration 25, 50, 75 and 100 mg/l at room temperature.

Table 1. Freundlich isotherm constants for Lab. Experiments on removal of DY-12.

Concentration of algae (g/l)	**K_F (mg/g)**	**n^{-1} (g/l)**	**R^2**
2.5	14.95	2.26	0.99
5.0	16.8	2.39	0.99
7.5	17.76	2.27	0.99
10.0	17.62	3.43	0.99

Table 2. comparison of the first- and second-order adsorption rate constants for calculated and experimental q_e values at different initial DY-12 concentration and *U. lactuca* concentrations.

Parameter		First-order kinetic model				Second-order kinetic model		
Algae weight (g/L)	Initial DY-12 Conc. (mg/L)	q_e (exp.) (mg/g)	K_1 (min^{-1})	q_e (Calc.) (mg/g)	R^2	K_2 (g/mg-min)	q_e (calc.) (mg/g)	R^2
1.25	25	14.76	0.007	2.43	0.937	0.04	14.95	1
	50	27.63	0.008	10.02	0.959	0.01	27.62	1
	75	43.42	0.009	11.59	0.958	0.01	44.05	1
	100	61.22	0.015	11.01	0.832	0.02	61.73	1
2.5	25	6.55	0.008	3.07	0.829	0.06	6.76	0.997
	50	15.04	0.01	4.77	0.969	0.03	15.36	1
	75	23.94	0.012	2.65	0.41	0.05	24.09	1
	100	33.18	0.011	3.11	0.185	0.03	33	0.996
5	25	3.4	0.007	1.32	0.875	0.078	3.59	0.999
	50	7.96	0.01	4.77	0.969	0.034	8.24	0.999
	75	12.85	0.017	1.95	0.889	0.129	12.91	1
	100	18.09	0.016	3.78	0.928	0.05	18.35	1
7.5	25	2.26	0.008	1.79	0.929	0.218	2.29	1
	50	6.04	0.011	3.15	0.894	0.514	6.06	1
	75	8.72	0.035	2.82	0.919	0.298	8.76	1
	100	12.24	0.006	1.29	0.735	0.129	12.29	1
10	25	1.81	0.01	2.83	0.735	0.264	1.82	0.995
	50	3.91	0.011	2.57	0.942	0.436	3.92	1
	75	6.27	0.014	1.46	0.965	0.328	6.3	1
	100	9.33	0.011	1.27	0.954	0.197	9.38	1

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

CONCLUSIONS

In conclusion, *U. lactuca*, which is inexpensive and widely available, show high efficiency in the removal of DY-12 from dilute aqueous solutions and these materials can be used as a promising alternative for the treatment of wastewaters containing dyes. The results obtained from the present investigation revealed the ability of *U. lactuca* in removing DY-12 from aqueous solution. The kinetics of adsorption by this biomass was rapid with ~80% removal of total adsorption occurring within 20 min. The adsorption capacities were solution pH dependent and a maximum adsorption capacity was obtained to be 0.15 mmol/g at a solution pH ~7.0. Although, further studies are needed in understanding the interaction behavior between the activated biomass and other dyes, the results indicate that *U. lactuca* could be employed as low-cost alternative to commercial materials in wastewater treatment for the removal of dyes.

ACKNOWLEDGEMENTS

Authors are thankful to Dr. Abir Abdelwahab from Mobark Academy of Science and Technology for her variable help.

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