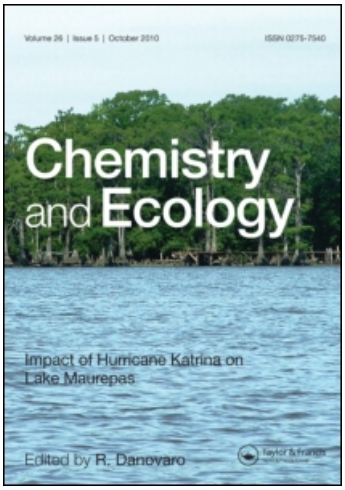

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Biosorption of Direct Yellow 12 from aqueous solution using green alga Ulva lactuca

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Biosorption of Direct Yellow 12 from aqueous solution using green alga *Ulva lactuca*

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The potential of commonly available green alga *Ulva lactuca* was investigated as viable biomaterials for removal of synthetic azo dye (Direct Yellow 12, DY-12) from aqueous solution. The results obtained from the batch experiments revealed that the ability of the *U. lactuca* to remove DY-12 from its aqueous solution was dependent on the dye concentration, pH, and algal biomass but less dependent on the particle size of the *U. lactuca*. The equilibrium conditions and kinetics of adsorption were investigated, and the adsorption kinetic was consistent with the pseudo-second-order model ($R^2 = 1$). The adsorption isotherm followed only the Freundlich model with a correlation coefficient $R^2 = 0.99$. This study demonstrated that the *U. lactuca* could be used as an effective biosorbent for the removal of DY-12 from its aqueous solution.

Keywords: Biosorption; Removal; Dyes; Direct Yellow 12; Green alga; *Ulva lactuca*

1. Introduction

Synthetic dyes are widely used in industries such as rubber, textiles, plastics, paper, cosmetics, etc. to colour their products. Dyes are synthetic, aromatic, and water-soluble, with potential applications increasing due to the tremendous increases in 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, etc.) which have been incorporated into the Colour Index [1]. Among the dyes, the azo group of dyes is the largest and most versatile class of dyes, and more than half of the annually produced amounts of dyes are azo dyes [2]. The major consumer of the dye is the textile industry (about 60% of the total dye production) for coloration of various fabrics. About 10–15% of the dyes used in the textile processing during the dyeing does not bind to the fibres and is released into the aquatic environment [3, 4]. Azo dyes are considered toxic to the aquatic biota and carcinogenic to humans, and the biodegradation of azo dyes produces carcinogenic products [1, 5]. Unless properly treated, dyestuffs present in wastewaters can significantly

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affect photosynthesis activity due to reduced light penetration and may be toxic to certain forms of aquatic life due to the presence of different active substituents [6]. Therefore, the removal of dye from process or waste effluents has become important both to health and to the environment.

Research indicates that algae have the ability to accumulate pollutants by biosorption and bioaccumulation. Biosorption is a term designated for all of the passive interactions with pollutants. In certain sites of the algae cell wall, adsorption reactions occur between the cell wall and the active sites of the wastes. Depending on the binding site (functional group on the binding site) and the type of metal, any of several various adsorption reactions can occur. Biosorption of metals consists in adsorptive binding of metals to inactive dead biomass, using purely physicochemical uptake pathways [7]. The implied mechanisms in biosorption differ qualitatively and quantitatively according to the type of biomass, its origin, and its processing [8]. Currently used methods for the treatment of textile wastewater are adsorption, precipitation, chemical oxidation, photodegradation, and membrane filtration [9–11]. The adsorption processes is preferable over the other methods due to the clean and complete removal of dyes in most adsorption cases. Several dyes can be removed from aquatic solutions by adsorption on activated carbon or aluminium and silicon oxides as well as agriculture wastes. Activated carbon is the most widely used adsorbent for this purpose, but unfortunately commercially available activated carbons are very expensive, and this has led to the search for cheaper substituents [12–14]. The coagulation method can be used in treating dye-bearing effluents, but the problems associated with handling chemical sludge coupled with the cost limited its usage [13, 15]. The textile industry is seeking to develop environmentally friendly and cost-effective wastewater remediation technologies, especially those that allow colour removal that is largely unaffected by conventional treatment methods [16].

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 [17]. Macroalgae can sequester colour by the same adsorption and absorption mechanisms as other biological biomass. The use of marine algae, such as *Ascophyllum nodosum* [18], *Ecklonia radiate* [19], *Durvillaea potatorum* [20], *Spirogyra* species [21, 22], and *Padina* species [23] for heavy-metal removal has been reported. Alga *Spirogyra* species have been used in the removal of Reactive Yellow 22 dye by adsorption [24], and *Ulva lactuca* has been used to remove Methylene Blue [25].

The present study aims to investigate the adsorption capacity of the commonly available green alga, *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. DY-12 dye was selected for the adsorption experiment due to its presence in several industrial effluents such as textile, tannery, paper, soap, cosmetics, polish, wax, etc.

2. Materials and methods

2.1 *Materials*

The fresh marine green alga, *U. lactuca*, was collected from the Mediterranean Sea coast, Alexandria, Egypt. The biomass collected was washed with sea water, tap water, and then distilled water several times. The clean alga was dried and left in the sun for several days followed by oven drying at 100°C for 24 h [26]. The dried alga was milled and sieved with the topmost sieve shaken on a mechanical shaker 'Betriebsanleitung vibration testing sieve mechanical machine Thyr 2' for 20 min to give different particle sizes.

DY-12 (C.I. 24895) was obtained from ISMADYE (Egypt), with ∼75% dye content; its structure is shown in figure 1. A stock solution of 1000 mg l^{-1} 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 the aqueous solution were determined by comparison with standard solutions in the visible range of the spectrum. A 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. A change in initial pH (1–7) of DY-12 solution has no effect on its colour concentration.

2.2 *Methods*

Adsorption experiments were carried out by shaking different weights of green alga biomass with 100 ml of dye solution of the required concentration and pH at room temperature (25 ± 2°C) in a shaker operated at 150 rpm. The samples were withdrawn from the shaker, and the dye solution was separated from the adsorbent by centrifugation. The dye concentration in the supernatant solution was estimated by measuring the absorbance at maximum wavelength (λ_{max} 389 nm) and computing from the calibration curve.

As the biosorption studies were carried out using the adsorption technique, the adsorption behaviour of samples was studied using Gupta's mathematical relation [21], in which he used the following relation between contact time and percent of dye to calculate the adsorption kinetic constants of alga:

$$E = \alpha(t)^{\beta}, \tag{1}$$

where E is the efficiency of adsorption of DY-12 (mg g^{-1}), α and β are the constants, and t is the contact time in minutes. The linearized relationship of equation (1) can be written as follows:

$$\log E = \log \alpha + \beta \log t$$

or (2)

$$\log E = K + \beta \log t.$$

The kinetics of adsorption was determined by analysing the adsorptive uptake of the dye colour from aqueous solution at different contact time intervals.

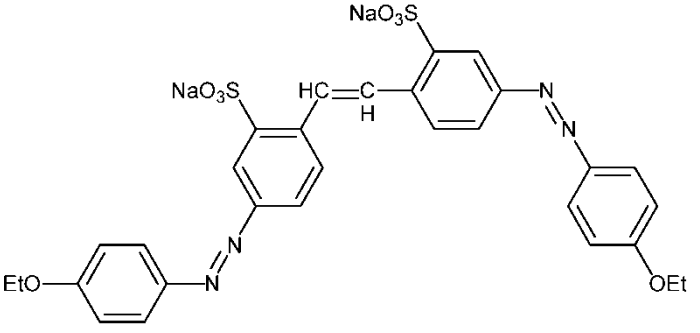

Figure 1. Chemical structure of DY-12.

The isotherm studies were performed by varying the initial dye concentrations from 25 to 100 mg l^{-1} and addition of various concentrations of algae (1.25, 2.5, 5.0, 7.5 and 10.0 g l^{-1}) followed by shaking the reaction mixture at 150 rpm for the equilibrium time.

The influence of pH was studied by adjusting the reaction mixture to a different initial pH (1.0–7.0) value using 0.1 M HCl or NaOH before addition of biomass. The initial pH measurements were carried out using a pH electrode (Check: mate 90, Corning, New York).

The amount of dye adsorbed onto green alga, the adsorption capacity at steady-state, q_e (mg g^{-1}), was calculated by the mass-balance relationship equation:

$$q_e = (C_0 - C_e)V/W, \tag{3}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye, respectively (mg l^{-1}), V is the volume of the solution (l), and W is the mass of the alga used (g).

3. Results and discussion

In this study, the adsorption capacities of dried algae are investigated considering several factors, which are important in the biosorption of dyes. These factors include contact time, initial pH, initial dye concentration, and amount of adsorbent. The results obtained from the present investigation revealed the ability of *U. lactuca* to remove DY-12 from aqueous solution.

3.1 *Conformational structure of DY-12*

The structure of DY-12 was studied using parameterization method 3 (PM3) in MOPAC 6 (table 1), and the charge distributions (figure 2) as well as solvent accessibility (figure 3) were studied using Extended Huckel charge and Extended Huckel surface methods, respectively, using the Chem3D program (2004). The charge distribution for DY-12 molecule was mainly found around the two SO_3Na groups in the central of the molecule as represented in figure 2. The solvent-accessible surface area (SASA) method is built around the assumption that the greatest amount of interaction with the solvent is the area very close to the solute molecule. This is accounted for by determining a surface area for each atom or group of atoms that is in contact with the solvent, which is represented in figure 3. If contact of dyes with solvent is

Table 1. PM3 computation of DY-12 using MOPAC 6.

Parameters	Data
Heat of formation	34.79 kcal mol^{-1}
Electronic energy	−67 738.55 eV
Core–core repulsion	60 421.85 eV
Dipole moment	15.60 Debye
Symmetry	C1
Charge on molecule	2
Ionization potential	12.80 eV
E_{HOMO}	−12.79 eV
E_{LUMO}	−7.95 eV
Sterric energy	71.43
Ovality	1.8576
Molecular weight	680.657

Note: E_{HOMO}: energy of the highest occupied molecular orbital; E_{LUMO}: energy of the lowest unoccupied molecular orbital.

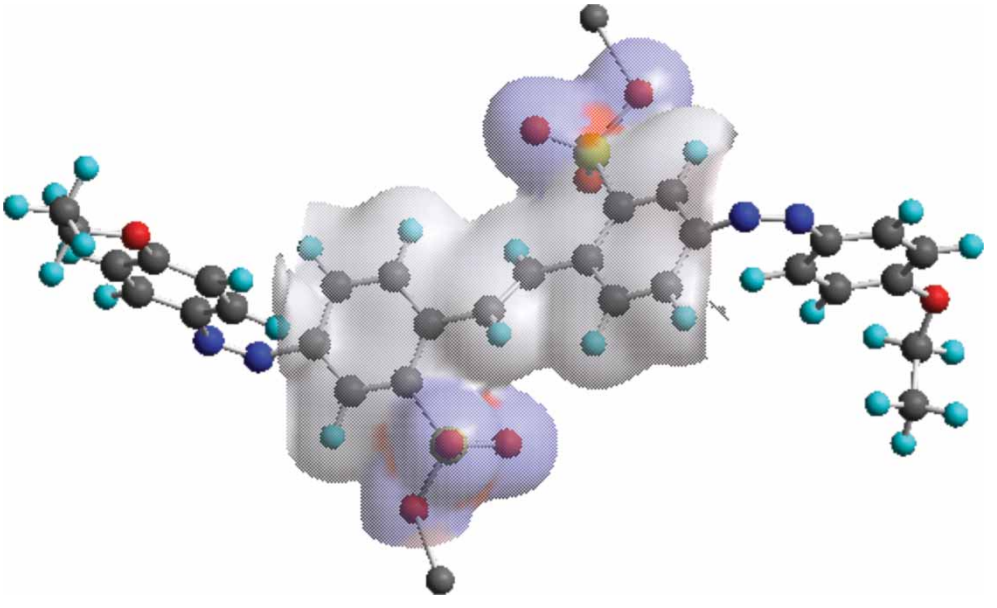

Figure 2. Charge distribution of DY-12 using Extended Huckel Charge in the Chem3D Ultra program 2004.

stronger than its contact with sorbent the biosorption of dyes from the solvent will be poor, while weak contact between dyes and solvent should lead to good biosorption of dyes. The symmetry of the molecule is C1, and the charge on the molecule is 2. A strong dipole moment (15.60 Debye) was found, which indicated strong polarizability for DY-12. The green alga used contains cellulose and hemicelluloses, which can adsorb the dye via contact with its

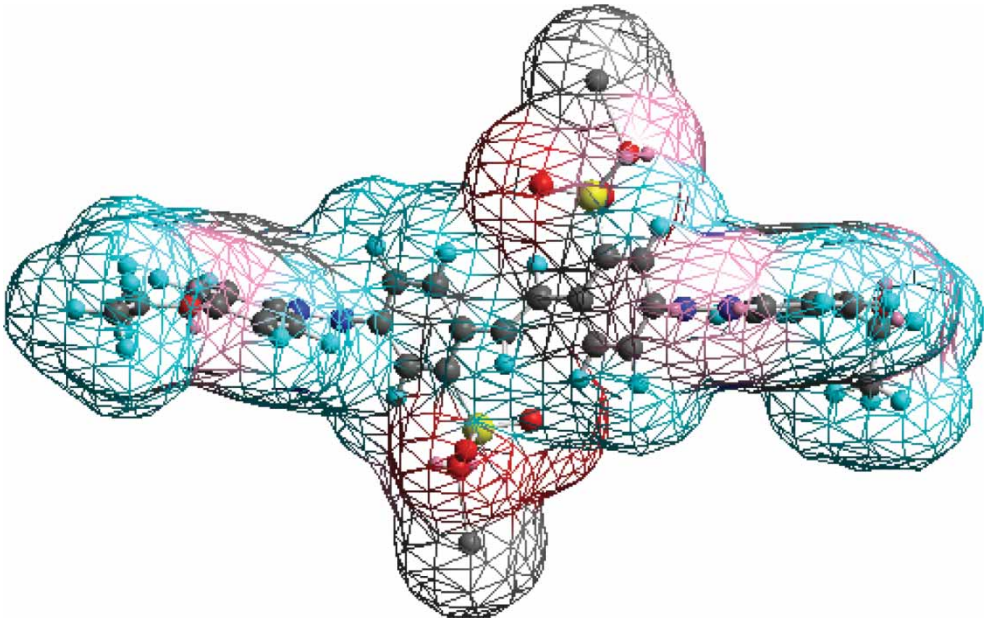

Figure 3. Water accessibility of DY-12 using Extended Huckel Surfaces in the Chem3D Ultra program 2004.

negative and positive centres with the positive and negative centres in the dye, respectively. If the charge centre of the dye lies outside of the dye surface, a good contact between the green alga and the dye will be obtained. Figures 2 and 3 show that the positive centres in the dye lie outside the molecule surface followed by the negative centre (SO_3 and N=N groups), which is slightly closed to the dye centre. However, this may be a general feature for the Direct Dyes, which may explain why the cotton (>80 cellulose) can adsorb it.

3.2 *Effect of contact time*

Figure 4 represents the variation of percentage biosorption of DY-12 with contact times and initial concentration of DY-12 using 1.25 g l^{-1} of alga and an initial pH of 7.0. As contact time increases, percentage adsorption also increases initially but then gradually approaches a constant value. The rate of dye adsorption is high in the first 10 min, and the rate then significantly decreases and eventually approaches an almost constant rate, indicating that the adsorption rate is equal to the desorption rate (i.e. an equilibrium point has been attained). These changes in the rate of adsorption may be due to the fact that initially, all adsorbent sites are vacant, and the solute concentration gradient is high. The decrease in rate with time indicates the slow approach to equilibrium possibly by internal diffusion.

Increase in the removal rate according to the initial dye concentration and contact time can be represented by the variation of adsorption rates with initial dye concentrations, as shown in figure 5.

3.3 *Effect of pH on DY-12 uptake*

The equilibrium of DY-12 uptakes at various pH values as presented in figures 6 and 7. 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, but decreased with increasing suspension at pH 1.0–4.0. Figures 6 and 7 show that the lowest biosorption occurred at an initial pH of 4.0. The highest biosorption obtained at pH 7.0 may be attributed to the uncharged alga surface and the presence of DY-12

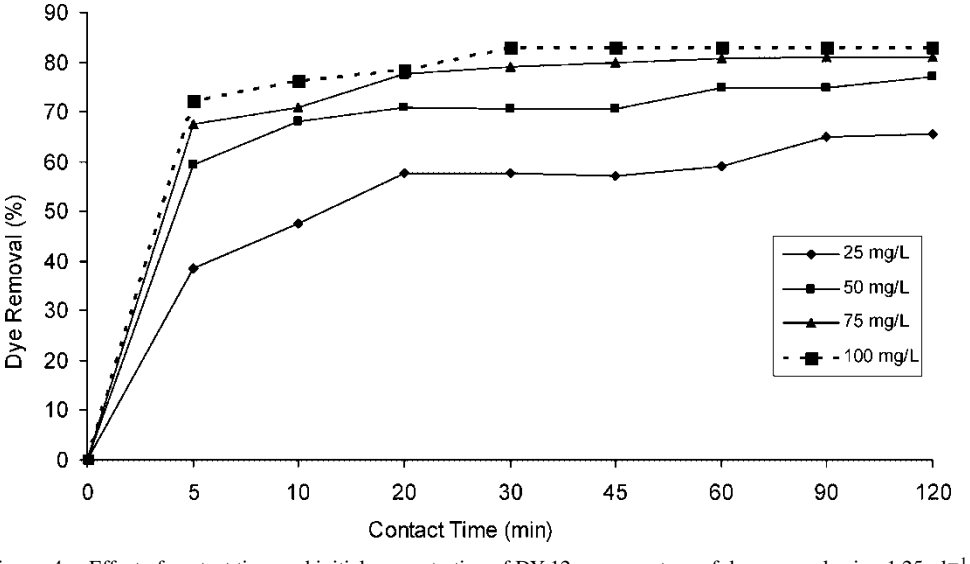

Figure 4. Effect of contact time and initial concentration of DY-12 on percentage of dye removal using 1.25 g l^{-1} of green alga at pH 7.0.

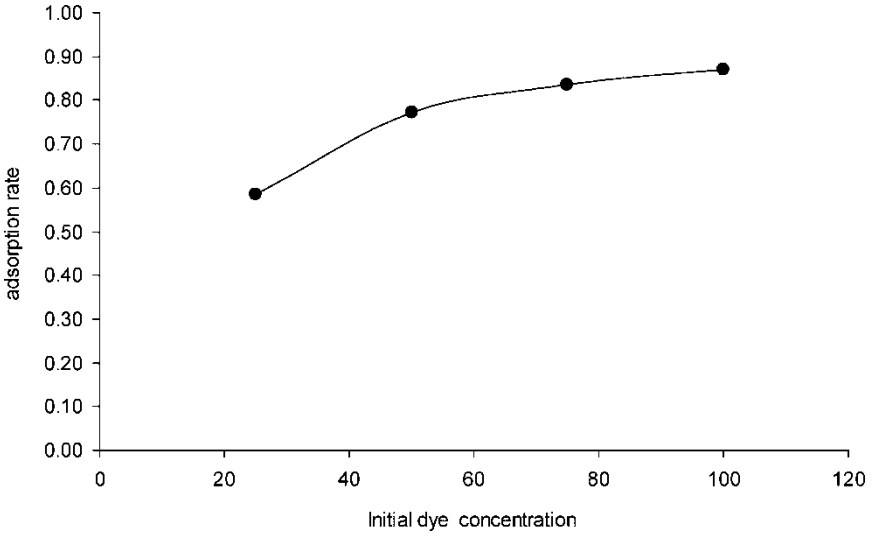

Figure 5. Effect of contact time and initial concentration of DY-12 on the adsorption rate of dye using 1.25 g l^{-1} of green alga at pH 7.0.

as sodium salt. The high percentage removal observed at initial pH 1.0 can be attributed to the positive surface charge gained depending on the adsorption of H^+ ions on the algal surface, and also the hydrolysis of alga may occur, resulting in different dye removal mechanisms. On the other hand, the results observed at initial pH 4–6 may be attributed to the change in charge on the dye and alga surface. 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 the type and ionic state of these functional groups and also on the DY-12 chemistry in solution (table 1; figures 2 and 3). The uptake was high at neutral pH (∼natural pH), thus making the experiment more environmentally friendly by not adding any other chemicals to the wastewater.

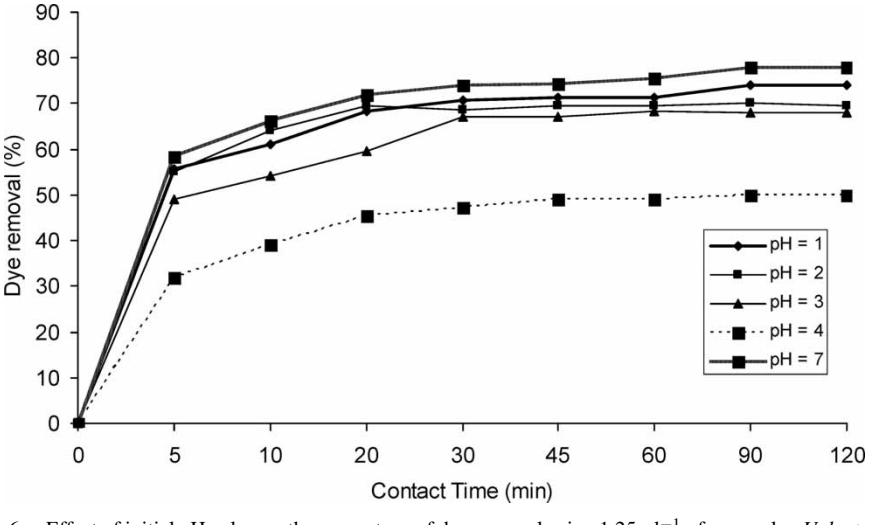

Figure 6. Effect of initial pH value on the percentage of dye removal using 1.25 g l^{-1} of green alga *U. lactuca* and 50 mg l^{-1} initial dye concentration.

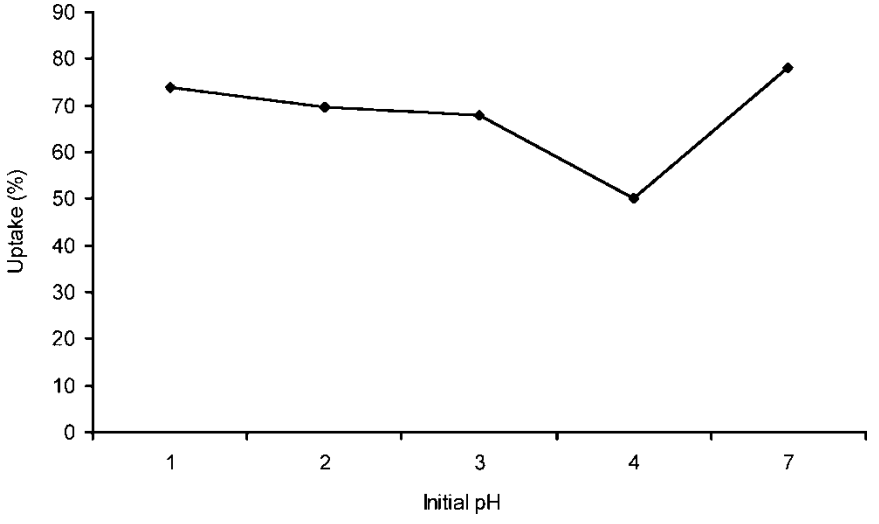

Figure 7. Dye uptake (%) by alga at different pH using initial dye concentration = 25 mg l^{-1}, adsorbent concentration = 1.25 g l^{-1}, temperature = 25°C, agitating rate = 150 rpm and contact time = 120 min.

3.4 *Effect of sorbent concentration*

Adsorption is highly dependent on the amount or concentration of the sorbent. The effect of the green alga *U. lactuca* concentration on the removal of DY-12 from aqueous solutions was studied by conducting adsorption experiments using 100 mg l^{-1} (initial DY-12 concentration) at room temperature and at an initial pH of 7.0 with varying sorbent concentrations from 1.25 to 10.0 g l^{-1}; the results are shown in figure 8.

It is apparent that the percentage removal of dye increases rapidly in the first 5 min with increasing concentration of sorbent, due to the increase in the exchangeable sites or surface

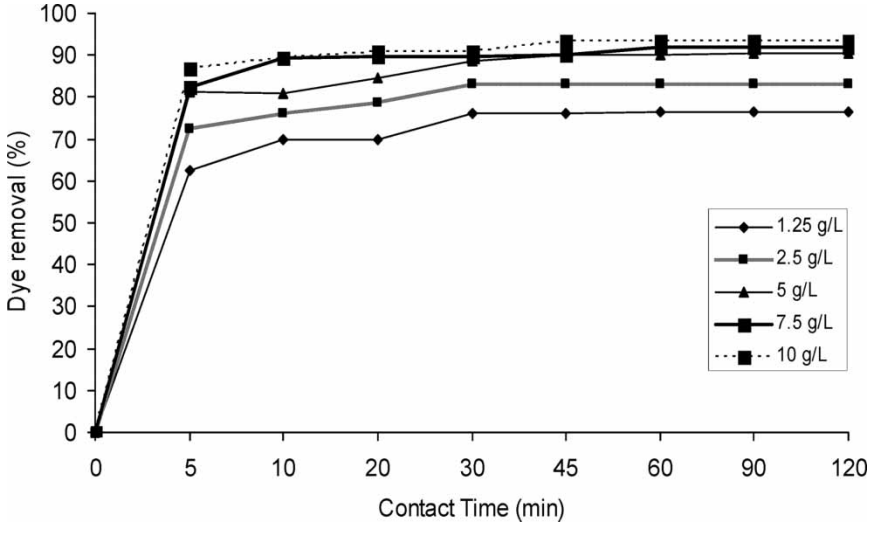

Figure 8. Effect of concentration of green alga *U. lactuca* on the dye uptake at initial pH = 7 and initial dye concentration = 100 mg L^{-1}.

area at higher concentrations of alga. However, the change in percentage removal of the dye was slightly increased with increasing alga concentration.

3.5 *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 for five different particle sizes (0.2, 0.3, 0.5, 0.9, and 1.5 mm) of *U. lactuca* is shown in figure 9. The removal dye by different particle size was similar, which indicates that the removal of DY-12 did not depend on the particle size of the *U. lactuca*.

3.6 *Adsorption isotherms*

The original adsorption isotherm between the amounts of DY-12 adsorbed per unit adsorbent and DY-12 remaining in solution at equilibrium time is shown in figure 10. The figure indicates that complete saturation of DY-12 on the algae's surface is not attained. Adsorption isotherms were obtained for the previous data using four different concentrations of alga and at constant solution pH values. Freundlich's adsorption isotherm was adopted to correlate the data. To determine the equilibrium parameters, the following equation was used:

$$X/M = K_F C_e^{1/n}, \tag{4}$$

where X/M is the amount of DY-12 adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the dye concentration remaining in solution at equilibrium (mg l^{-1}), and K_F (mg g^{-1}) and n (g l^{-1}) are Freundlich's constants, which are the empirical constants and indicative of biosorption capacity and biosorption intensity, respectively [27]. To calculate K_F and $1/n$, experimental data were fitted by logarithmic transfer of equation (4) to:

$$\log(X/M) = \log K_F + (1/n) \log C_e. \tag{5}$$

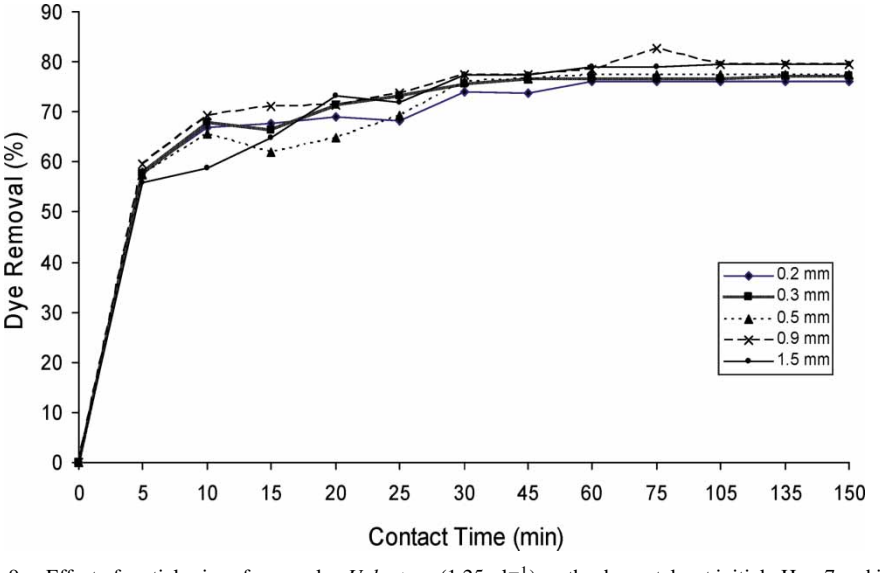

Figure 9. Effect of particle size of green alga *U. lactuca* (1.25 g l^{-1}) on the dye uptake at initial pH = 7 and initial dye concentration = 100 mg l^{-1}.

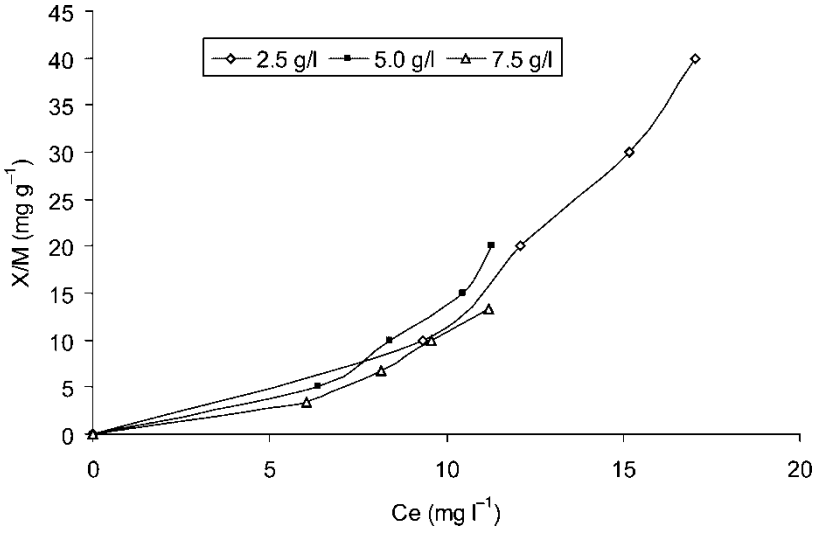

Figure 10. Adsorption isotherm of DY-12 onto green alga *U. lactuca* at room temperature (25 ± 2°C) and pH 7.

The values of K_F and n were calculated from the intercepts and slopes of the plots, and are listed in table 2.

Linear plots of $\log(X/M)$ vs. $\log C_e$ (figure 11; 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 (mg g^{-1}) of sorbent at an equilibrium concentration. The results showed that *U. lactuca* shows a good capacity to remove the bulky dye molecules without any pretreatment.

On the other hand, the isothermal equilibrium data were also studied using the Langmuir isotherm equation. The Langmuir equation, which has been successfully applied to many adsorption [14, 28–30], is given by:

$$q_e = (K_L S_m C_e)/(1 + K_L C_e), \tag{6}$$

where S_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg g^{-1}), C_e the adsorbate equilibrium concentration (mg g^{-1}), and K_L the Langmuir constant (l mg^{-1}). S_m represents a practical limiting adsorption capacity when the surface is fully covered with adsorbate molecules and assists in the comparison of adsorption performance. Equation (6) can be rearranged to a linear form:

$$C_e/q_e = 1/(K_L S_m) + C_e/S_m. \tag{7}$$

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

Table 2. Freundlich isotherm constants.

Concentration of alga (g l^{-1})	K_F (mg g^{-1})	n^{-1} (l g^{-1})	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

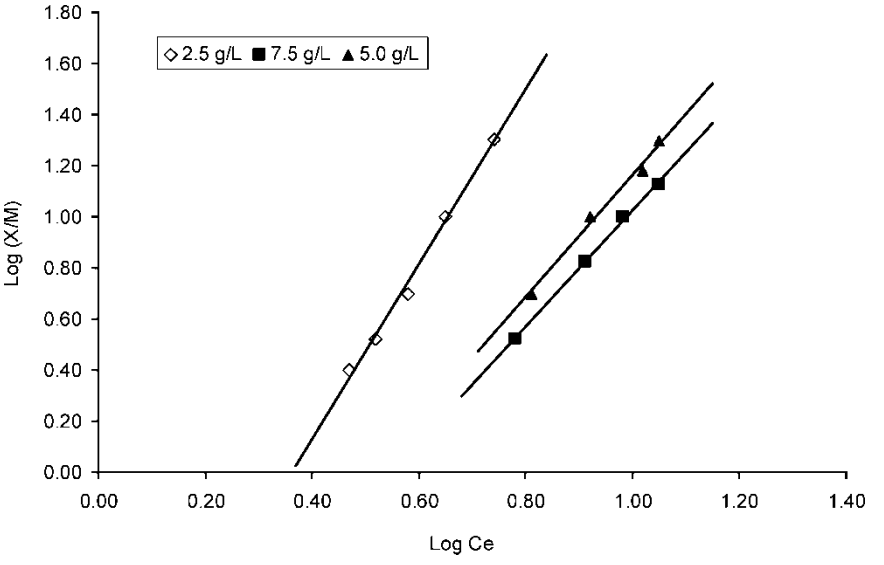

Figure 11. Freundlich plot for the DY-12 adsorption onto green alga *U. lactuca* at room temperature (25 ± 2°C), pH 7 and 25–100 mg l^{-1} dye concentration.

3.7 *Adsorption kinetic studies using the Gupta model*

As the biosorption studies have been carried out using the adsorption technique, the Gupta mathematical relation between contact time and percentage removal has been used to determine the adsorption kinetics constant for alga (equations (1) and (2)). The influences of contact time on the adsorption of DY-12 on alga, using different concentration of sorbent, were studied for various initial concentrations of dye. It was observed that most of the dye was removed at the first 30 min of mixing. No further significant adsorption was observed beyond this period until the end of the experiment (120 min). The percentage removal of dye ranged from 65% to 94% with various algal concentrations. Equation (1) was fitted to the experimental data; constants K and β were calculated, and the values are shown in table 3. It was noticed that there is an increase in the values of K, suggesting a faster DY-12 removal rate. This may be attributed to a large surface area or large pore volume for the alga.

3.8 *Adsorption rate constant*

The rate constant of adsorption is determined from the first-order rate expression given by Lagergen [31, 32] as:

$$\log(q_e - q_t) = \log q_e - (K_1/2.303) \times t, \tag{8}$$

where q_e and q_t are the amounts of DY-12 adsorbed (mg g^{-1}) 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 $\log(q_e - q_t)$ vs. t for different concentrations of DY-12. The experimental q_e values do not agree with the calculated values obtained from the linear plots (table 4). 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:

$$t/q_t = 1/(K_2/q_e^2) + t/q_e, \tag{9}$$

Table 3. Value of adsorption kinetic constant at different experimental conditions.

Dye concentration ($mg\,l^{-1}$)	Weight of alga (g)	K	β	R^2
100	0.125	3.995	0.094	0.96
	0.250	4.177	0.066	0.97
	0.500	4.301	0.051	0.91
	0.750	4.337	0.046	0.99
	1.000	4.420	0.029	0.95
75	0.125	3.821	0.118	0.95
	0.250	4.084	0.082	0.95
	0.500	4.290	0.042	0.85
	1.000	4.300	0.037	0.91
50	0.125	3.820	0.086	0.98
	0.250	4.020	0.066	0.87
	0.500	4.037	0.082	0.98
	1.000	4.210	0.062	0.89
25	0.250	3.350	0.208	0.97
	0.500	3.535	0.185	0.84
	0.750	3.694	0.14	0.84
	1.000	3.807	0.129	0.82

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 vs. 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 (9). In addition, it is more likely to predict the behaviour over the

Table 4. Comparison of the first- and second-order adsorption rate constants for calculated and experimental q_e values at different initial DY-12 concentration and green alga *U. lactuca* concentrations.

Parameter		First-order kinetic model				Second-order kinetic model		
Alga weight ($g\,l^{-1}$)	Initial DY-12 conc. ($mg\,l^{-1}$)	q_e (exp.) ($mg\,g^{-1}$)	K_1 (min^{-1})	q_e (calc.) ($mg\,g^{-1}$)	R^2	K_2 ($g\,mg^{-1}\,min^{-1}$)	q_e (calc.) ($mg\,g^{-1}$)	R^2
1.25	25	14.76	0.007	2.43	0.937	0.040	14.95	1.000
	50	27.63	0.008	10.02	0.959	0.010	27.62	1.000
	75	43.42	0.009	11.59	0.958	0.010	44.05	1.000
	100	61.22	0.015	11.01	0.832	0.020	61.73	1.000
2.5	25	6.55	0.008	3.07	0.829	0.060	6.76	0.997
	50	15.04	0.010	4.77	0.969	0.030	15.36	1.000
	75	23.94	0.012	2.65	0.410	0.050	24.09	1.000
	100	33.18	0.011	3.11	0.185	0.030	33.00	0.996
5.0	25	3.40	0.007	1.32	0.875	0.078	3.59	0.999
	50	7.96	0.010	4.77	0.969	0.034	8.24	0.999
	75	12.85	0.017	1.95	0.889	0.129	12.91	1.000
	100	18.09	0.016	3.78	0.928	0.050	18.35	1.000
7.5	25	2.26	0.008	1.79	0.929	0.218	2.29	1.000
	50	6.04	0.011	3.15	0.894	0.514	6.06	1.000
	75	8.72	0.035	2.82	0.919	0.298	8.76	1.000
	100	12.24	0.006	1.29	0.735	0.129	12.29	1.000
10.0	25	1.81	0.010	2.83	0.735	0.264	1.82	0.995
	50	3.91	0.011	2.57	0.942	0.436	3.92	1.000
	75	6.27	0.014	1.46	0.965	0.328	6.30	1.000
	100	9.33	0.011	1.27	0.954	0.197	9.38	1.000

Note: conc.: concentration; exp.: experimental; calc.: calculated.

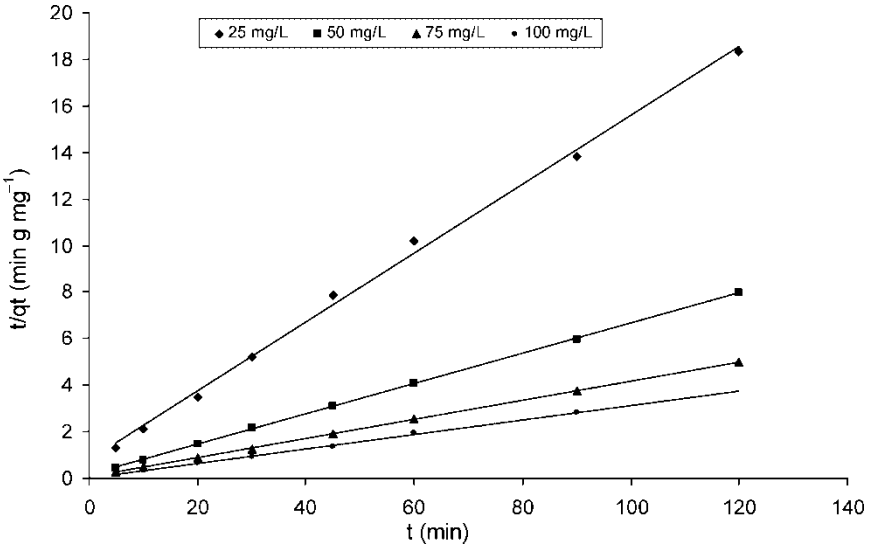

Figure 12. Plot of the pseudo-second-order model at different initial DY-12 concentrations. Adsorbent dose, 1.25 g l^{-1}; pH 7.0; DY-12 concentration 25, 50, 75, and 100 mg l^{-1} at room temperature (25 ± 2°C).

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 vs. t. The linear plots of t/q_t vs. t (figure 12) show a good agreement between experimental and calculated q_e values (table 4). 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 [33].

4. Conclusions

In conclusion, green alga *U. lactuca*, which is inexpensive and widely available, was highly efficient in removing DY-12 from dilute aqueous solutions, and these materials can be used as a promising low-cost alternative to commercial materials for the treatment of wastewaters containing DY-12. The kinetics of adsorption by this biomass was rapid, with ~80% removal of total adsorption occurring within 20 min. The adsorption capacities were dependent on solution pH, and the maximum adsorption capacity was found to be 0.15 mmol g^{-1} at a solution pH of ~7.0. However, further studies are needed to help understand the interaction behaviour between the activated biomass and other dyes.

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