Evaluation of non-viable biomass of *Laurencia papillosa* for decolorization of dye waste water

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The uptake of fast orange dye by the red seaweed *Laurencia papillosa* has been demonstrated in order to explore its potential use as low-cost adsorbent. The adsorption kinetics of fast orange dye on the alga with respect to initial dye concentration, contact time, particle size and pH were investigated. The dye removal percentage increased from 25.92 to 67.08% and the equilibrium states were attained at almost 60 min within the experimental concentration range. The adsorption kinetic was analyzed using pseudo-first-order and pseudo-second-order models. The pseudo-second-order model was more appropriate to describe the sorption kinetics based on the relatively high values of the linear squared regression correlation coefficient. The nature of the possible adsorbent and fast orange interactions was examined by the Fourier transform infrared technique. This technique confirmed that hydroxyl, carboxyl, amine, sulfonyl, carbonyl and alkyl groups are responsible for the dye binding process. Significant increase in dye adsorption was observed with the decrease in sorbent particle size coupled with its large surface area. Maximum removal efficiency was determined to be 65.7% at a solution pH of 5. However, *Laurencia papillosa* proved to be a promising material for removing fast orange dye from aqueous solutions.

**Key words:** Dye adsorption, Macroalga, *Laurencia papillosa*, kinetics.

INTRODUCTION

Textile processing operations are considered as important part of the industrial sector in both developing and undeveloped countries (Mahmoud et al., 2007). Several types of textile dyes are available for usage with various types of textile materials (Marungruenga and Pavasant, 2006). Over 7x10^5 tons and about 10,000 different types of dyes are produced in the world. Unfortunately, about 10 to 15% of the total produced dyes is released into the aquatic ecosystems without being removed from the effluents and large volumes of highly polluted wastewater are produced (Sheng and Chi, 2003; Hoda et al., 2006; Senthilkumara et al., 2006; Bukallah et al., 2007). The presence of these pollutants in water reduces light penetration and photosynthesis (Chen et al., 2003). In addition, dyes in the water bodies undergo chemical and biological changes that consume dissolved oxygen resulting in fish kills and the destruction of other aquatic organisms (Muthuraman and Palanivelu, 2006). Some dyes have been also reported to cause allergy irritation, cancer and even mutation in humans (Bhattacharyya and Sharma, 2004). Therefore, removal of dyes from the effluents of textile industries is of vital importance for the proper maintenance of the ecosystem health (Cengiz and Cavas, 2008).

Dye molecules comprise of two components: the chromophores, responsible for producing the color, and the auxochromes, which cannot only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity toward the fibers (Gupta et al., 2003). Some of the techniques used in treatment of
wastewater containing dyes are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques and ozonation (Dabrowski, 2001). Nevertheless these processes are not always effective and economic. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives by utilizing many types of biosorbents as fungi (Kaushik and Malik, 2009; Mishra et al., 2011), bacteria (Banat et al., 1996; Yang et al., 2011) and yeasts (Ertugrul et al., 2009; Phugare et al., 2010). As well, one of the growing interest and promising biosorbents is “algae” (Veglio and Beolchini, 1997; Penghhamkeerati et al., 2008; Kousha et al., 2012) due to its high sorption capacity and its availability in almost unlimited amounts (Klimmek et al., 2001). Both viable and non-viable algae have been used in color removal from dyes and wastewater. This is may be achieved via bioconversion and biosorption. Through bioconversion, some algae can break down the dyes to more simple compounds (Lim et al., 2010). On the other hand, Biosorption is known as a promising technique concerned with the uptake of undesired ions from aqueous solutions using biological materials. Biosorption in algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role (Davis et al., 2003). In many cases, algal cell walls frequently consisting of proteins and carbohydrates provide functional groups for binding various metals and dyes (Volesky, 1990; Srinivasan and Viraraghavan, 2010). Research in the field of biosorption has mostly concerned itself with brown algae (Matheickal and Yu, 1999; Matheickal et al., 1999; Yu et al., 1999), green algae (Dönmez et al., 1999; Aksu et al., 1997, 1999) and red algae (Holan and Volesky, 1994). The cell walls of most red algae include a rigid inner part composed of micro fibrils and a mucilaginous matrix. The matrix is composed of sulfated polymers of galactose such as agar and carrageenan, which are responsible for flexible, slippery texture of the red algae (Prescott et al., 2002).

Laurencia papillosa is a red alga (Rhodophyta) notable for its importance as an agarophyte. Its cylindrical thallus may reach 15 cm tall and having pale-brown, sometimes yellowish color. The main focus of this study was to discuss the adsorption behavior of fast orange dye using L. papillosa as low cost and renewable biosorbent material. Additionally, the equilibrium and kinetics of dye adsorption from aqueous solutions were investigated. The effects of initial dye concentration, contact time, particle size and pH on the adsorption capacity were also considered.

MATERIALS AND METHODS

Adsorbent material

The raw biomass of L. papillosa (Forskal) Greville was harvested from Abou-kir, Alexandria coastline of the Mediterranean Sea during the spring season. The wet algal material was carried to the laboratory in an aquarium. Samples were preliminary visual cleaned of impurities followed by several washes with copious quantities of deionized water to remove extraneous materials and common ions (e.g. Na⁺ and Ca⁺) present in seawater. The washed biomass was sun-dried then oven dried at 60°C for 8 h, crushed to a fine powder, sieved and preserved for further use.

Dye solutions preparation

Fast orange 37 was supplied by a local manufacturer (Dyestuffs and Chemicals Company at Kafr El-Dawar, Egypt) and used in commercial purity as received. The molecular structure of the dye is represented in Figure 1. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the concentration of 1000 mg/l. The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to different initial concentrations (10, 20, 30, 40 and 50 mg/l). Dye concentration determination was performed calorimetrically using a Perkin Elmer Lambda ultraviolet and visible (UV-Vis) spectrophotometer. The absorbance of the colors was read at 428 nm (λ_max).

Adsorption procedure

Adsorption experiments were carried out in batch conditions. A series of 250 ml Erlenmeyer flasks containing 120 ml dye solution of known initial concentrations in the range of 10 to 50 mg/l were prepared at room temperature (25 ± 2°C). Weighed amounts (2 g) of dry algal biomass were added to each flask and stirred. The pH of the mixtures was kept without measurement. Equilibrium process is directly correlated with time. Samples were drawn at suitable time intervals 10, 20, 30, 40, 50, 60, 90, 120 and 150 min and then centrifuged for 15 min at 5000 rpm. The left out concentration of dye in the supernatants were analyzed using the spectrophotometer by monitoring the absorbance changes at a wavelength of 428 nm. The removal percentage of the dye was calculated by using the following equation:

\[
\text{Removal} \% = \frac{C_i - C_e}{C_i} \times 100
\]  

(1)

Where, \(C_i\) and \(C_e\) are the initial and equilibrium dye concentrations, respectively. The adsorbed dye quantity per gram of biomass at any time \(t\) can also be calculated from the difference between the initial and the equilibrium concentrations as shown in the following equation:

\[
q = \frac{(C_i - C_e)V}{M}
\]  

(2)

Where, \(q\) is the dye uptake capacity \((\text{mg g}^{-1})\), \(M\) the adsorbent dosage \((\text{g})\), and \(V\) the solution volume.
Figure 2. Dye removal percentage as a function of contact time and initial dye concentration (adsorbent dose = 2 g, temperature = 25 ± 2°C).

Kinetic models

Several kinetic models were available to understand the behavior of the adsorbent, to examine the controlling mechanism of the adsorption process and to test the experimental data. In this investigation, the kinetic data obtained were analyzed by using pseudo-first order and pseudo-second order models. The first-order rate expression of Lagergren (1898) is given as:

$$\log(q_e - q) = \log(q_e) - \frac{K_1}{2.303} t$$

Where, $q_e$ and $q$ are the amounts of dye adsorbed on adsorbent at equilibrium and at time $t$, respectively (mg/g) and $K_1$ is the rate constant (min⁻¹).

In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (Lagergren, 1898; McKay and Ho, 1999). The linear form of pseudo-second order equation expressing the chemisorption behavior of the reaction (Ho and McKay, 1999; Marunrueng and Pavasant, 2006; Ncibi et al., 2007) was calculated as follows:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where, $K_2$ is the pseudo-second order rate constant (g/mg.min).

The best-fit model was selected based on the linear regression correlation coefficient, $R^2$, values.

Fourier transform infrared spectroscopy analysis

After incorporating of an algal sample into a KBr pellet, detection of functional groups located on algal surface after and before adsorption process was specified. FTIR analyses within the range of 500 to 4000 cm⁻¹ were recorded with Perkin Elmer Fourier transform infrared spectrophotometer (RXIFT-IR system).

RESULTS AND DISCUSSION

Effect of contact time and different dye concentrations

To design effective and user friendly adsorption model, it was considered necessary to carry out adsorption with a kinetic view-point as a function of contact time and initial dye concentration. The dye removal percentage (%) was represented in Figure 2. The results show that the equilibrium states were attained at almost 60 min within the experimental concentration range. Furthermore, raising the dye concentration from 10 to 50 mg/l allows the dry alga to increase their adsorption capacities from 25.92 to 67.08%, respectively. The curve of contact time is smooth and continuous leading to saturation due to intra particle diffusion process. These data indicate the possible monolayer coverage of dye on the surface of dry algal biomass (Dogan and Alkan, 2003).
Equilibrium adsorption

It is obvious from Figure 3 that most of the dye was adsorbed to achieve adsorption equilibrium in about 60 min although the data were measured in 150 min. In the view of this result, the dye uptake capacity (q) increased with time and at certain time period; it reached a constant value indicated that no dye was further removed from the solution. It is interesting to note that the surface of adsorbent may contain a large number of active sites and the uptake of dye can be linked to the active sites on equilibrium time. The higher sorption rate at the initial period may be due to an augmented number of vacant sites available. Also, it indicates the strong electrostatic force of attraction between dye molecules and the sorbent binding-sites (Kaewsarn and Yu, 2001). As time proceeds this sorption rate is reduced due to the accumulation of dye particles in the vacant sites (Uddin et al., 2009). This result suggests that there is a high affinity between fast orange dye and functional groups on the wall surface of L. papillosa. A similar finding was reported by Marungrueng and Pavasant (2007) and Cengiz and Cavas (2008).

Sorption kinetics

Adsorption involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface for evaluating the applicability of sorption process as a unit operation. In order to characterize the kinetic behavior of a reaction, it is desirable to determine how the rate of reaction varies as the reaction progresses. In the present investigation, the validity of the pseudo-first order model can be checked by linearized plot of log (q_e - q) versus t (Figure 4). It was evident that the linear dependency was not obtained between log (q_e-q) and t. Therefore, first-order Lagergren rate kinetics is not convenient for the adsorption of the dye onto the alga. On the other hand, the linear plots of t/q versus t for the pseudo-second order were illustrated in Figure 5. Regressing the observed values of t/q on t afforded coefficients of correlation allowing estimation of the amount of dye adsorbed at equilibrium and the rate constant. It is clearly found from the model parameters q_e and K_2 given in Table 1 that pseudo-second order model data fall on straight lines. This indicates that this model is in good agreement with the experimental data. Besides it is more appropriate to describe the sorption kinetics of fast orange dye onto the alga based on the relatively high values of the linear squared regression correlation coefficient R^2. This finding supports the assumption that the sorption process was due to chemisorption which required exchange or sharing of electrons between dye cations and functional groups of adsorbent (Ho, 2003; Marungrueng and Pavasant, 2007).

Fourier transform infrared spectroscopy analysis

The FTIR spectroscopy has been frequently used to detect vibrational frequency changes in seaweeds (Park et al., 2004; Sheng et al., 2004; Figueira et al., 1999). It offers excellent information on the nature of the bonds
Figure 4. Pseudo-first-order sorption kinetics of fast orange dye by *Laurencia papillosa* at different initial dye concentrations (adsorbent dose = 2 g, temperature=25 ± 2°C).

Figure 5. Pseudo-second-order sorption kinetics of fast orange dye by *Laurencia papillosa* at different initial dye concentrations (adsorbent dose = 2 g, temperature=25 ± 2°C).
Figure 6. Changes in the spectra of the dried Laurencia papillosa before (a) and after (b) fast orange adsorption.

present and allows identification of different functionalities on the cell surface. The assignment of FTIR bands and detailed spectroscopy for the dried pure and treated alga are summarized in Figure 6. The functional groups on algal surface exhibits adsorption bands that ranged between 3250 to 3700, 2400 to 3300, 3300 to 3500, 1050 to 1300, 1040 to 1200, 1670 to 1780, 550 to 650 and 2500 to 3100 which indicate the presence of O-H, COOH, NH₂, C-O, S=O, C=O, S-O and C-H groups respectively. In comparison between pure and treated algal biomass, it was observed that there was a shift in wave number of dominant peaks associated with the loaded dye. This shift in the wavelength showed that there was a dye binding process taking place on the surface of the alga.
The extent of band shifting gives an indication of the degree of interaction of functional groups with dye and once equilibrium had been achieved, no further band shifting was observed in the FTIR spectra. Definitely, all the dominant functional groups seemed to play an important role for dye sorption as a shift in the wavelengths was always found.

Effect of particle size on adsorption

The effect of sorbent particle size on the rate of fast orange adsorption was studied in the range of 50 to 100, 100 to 150, 150 to 200, 200 to 250 and 250 to 300 μm keeping the other parameters as constant [dye concentration (20 mg/l); adsorbent dose (2 g); contact time (60 min) and temperature (25±2°C)]. Significant increase in dye adsorption was observed with the decrease in sorbent particle size (Table 2). For larger sorbent particle size (200 to 300 μm), the internal surface area of the particles may not be utilized for adsorption. However, for smaller sorbent particle size (50 to 200 μm), the increase in the dye adsorption is associated with large surface area of the particles. This showed that the grind dried biomass more rapidly adsorbed the dye ions, and the equilibrium was reached faster than those achieved with the whole algal thallus. This was because particles with smaller size allowed a faster contact between the dye molecules and the binding sites (Doğan et al., 2009).

Effect of pH on adsorption

The effect of pH on adsorption of dye was investigated over a range of pH values from 1 to 10 under constant parameters [dye concentration (20 mg/l); adsorbent dose (2 g); contact time (60 min) and temperature (25±2°C)]. The pH was adjusted using 0.1 N HCl and 0.1 N NaOH. Magnetic stirrer was used to agitate the solution continuously. The removal percentages of fast orange dye at different chosen pH are shown in Figure 7. The results show that the adsorption of dye on the biomass surface is controlled by ionic attraction. When pH value was raised from 1 to 5, the adsorption capacity was enhanced significantly from 28.7 to 65.7% and then the dye removal percentages were not significantly altered beyond pH 5. As pH decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. Also, lower adsorption of fast orange at acidic pH is due to the presence of excess H+ ions competing with dye cations for the adsorption sites. Similar findings were reported by many researchers (Doğan et al., 2004; Wang et al., 2005; Vadivelan and Vasanth Kumar, 2005; Bhattacharyya and Sharma, 2005; Hamdaoui, 2006). At higher pH, the surface of biomass gets negatively charged, which enhances the positively charged dye cations through electrostatic force of attraction. Higher uptakes obtained at lower pH values may be due to the electrostatic attractions between these negatively charged dye anions and positively charged cell surface. Hydrogen ion also acts as a bridging ligand between the algal cell wall and the dye molecule (Srinivasan and Viraraghavan, 2010)

Conclusion

Dead algal biomass L. papillosa was considered to serve potentially as sorbent material. The maximum removal percentage was 67.08% and the adsorption equilibrium took place within 60 min. A relatively high correlation coefficient (R=1.002) implied that the pseudo-second-order kinetic model was encouraging for the fast orange dye adsorption on L. papillosa. FTIR results in the current work offered the possibility of the coupling between the dye species and the functional groups on the algal surface. Small particle size was recommended for optimum adsorption process. At a pH of 5, the maximum

<table>
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<th>Dye concentration(mg/L)</th>
<th>Qe (mg/g)</th>
<th>k2 (g/mg min)</th>
<th>R2</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>0.259</td>
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</tr>
<tr>
<td>20</td>
<td>0.786</td>
<td>0.0212</td>
<td>1.122</td>
</tr>
<tr>
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<td>0.01</td>
<td>0.904</td>
</tr>
<tr>
<td>40</td>
<td>2.111</td>
<td>0.0078</td>
<td>1.002</td>
</tr>
<tr>
<td>50</td>
<td>2.684</td>
<td>0.0062</td>
<td>1.018</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Dye removal percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 - 100</td>
<td>65.3</td>
</tr>
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<td>100 - 150</td>
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<td>200 - 250</td>
<td>43.3</td>
</tr>
<tr>
<td>250 - 300</td>
<td>39.2</td>
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</table>
removal capacity of the biomass was 65.7%. Owing to lower equilibrium time and considerable adsorption capacity, the dried red marine alga *L. papillosa* could be used as an alternative low-cost material for dye adsorption.

**REFERENCES**


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![Figure 7](image-url)
and future potential. Environ. Int. 35:127-141.