Adsorption Acid Red18 Dye using Sargassum Glaucescens Biomass from Aqueous Solutions

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Abstract
Background and purpose: Dyes are one of the main pollutants in the various industrial wastewaters. Therefore, the aim of this study was to assess the biosorption of acid red 18 dyes from aqueous solutions by brown macroalgae biomass “Sargassum glaucescens.”

Materials and Methods: This research was a lab study. S. glaucescens was used as an adsorbent to remove acid red 18. The effect of various parameters such as pH, initial dyes concentration, adsorbent dose and equilibrium contact time were evaluated in batch adsorption. The dye concentration was measured in the wavelength of 506 nm by spectrophotometer.

Results: The results showed that the equilibrium time of biosorption was 120 min. Increasing of contact time and adsorbent dose and initial dye concentration can lead to increasing of the removal efficiency. The maximum adsorption capacity of the dye was at pH: 6 respectively. It was found that the data fitted to Freundlich better than Langmuir isotherms of adsorption model.

Conclusion: The S. glaucescens biomass had a satisfactory quality in dye adsorption. It can be used as an effective, inexpensive adsorbents for the dye adsorption from textile wastewater or similar industries.

Key words: Sargassum Glaucescens, Acid Red 18, Biosorption, Equilibrium Isotherm, Wastewater Treatment
1. Introduction

Today, the elimination of pollutants and their effects is one of the most significant concerns of societies. The discharge of untreated or partially treated wastewaters and industrial effluents into natural ecosystems play an important role to create the serious issues on the environment. Among the industrial wastewaters, the dye removal from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. The synthetic dyes are considered as chemicals with high stability and difficulty biodegradable due to the presence of complex aromatic molecular in their structure (1).

Dye removal from the textile industry is one of the major challenges in treating industrial waste. Even small amount of dye creates serious problems (2). The color is the first pollution, which it can be observed in wastewater and the general acceptance of water, and aquatic solutions quality is affected by the color. The effect on photosynthetic activity in aquatic life due to reducing the light penetration is one of the adverse effects of dyes in waters. Moreover, synthetic dyes are harmful to human health as they have been shown to cause mutagenic effects as well as allergic dermatitis and skin irritation (3). Therefore, dye removal is considered as most important issues to preserve the environmental and public health.

The common methods have been used for dye removal from wastewater include biological methods (anaerobic treatment) and physicochemical methods such as coagulation, electrocoagulation, floating, filtration, ion exchange, membrane filtration and advanced oxidation (4). Among the various techniques, the adsorption onto activated carbon is considered as high ability and promising technique to remove the dyes from effluents. However, there are economic problems with the application of the activated carbon. Therefore, many researchers have been attempted to find new low-cost adsorbent. Algae have been found to be potential, suitable biosorbent because of their fast and easy growth and their wide availability. Algal cell wall offers a host of functional groups including amino, carboxyl, sulfate, phosphate and imidazoles associated with polysaccharides alginic acid and proteins for binding various pollutants (1). Therefore, in this study the ability of algae Sargassum biomass as an adsorbent is investigated for the removal of dyes from aqueous. The aim of this study included for determining the isotherm, and adsorbed synthetic reaction, the effect of initial dye concentration, adsorbent dose, contact time and pH on the adsorption process.

2. Materials and Methods

The dye acid red 18 is a mono azo dye. The used dye was the analytical grade which was purchased from company “Alvan Sabet/Iran. The chemical structure of the used dye is shown in figure 1. also some properties of used dye are given table 1. The dye concentration was measured by the ultraviolet (UV) - visible spectrophotometer (the model UV - 1700) at a wavelength of 506 min. Hydrochloric acid and sodium hydroxide were used for pH adjustment.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>C_{20}H_{11}N_{2}Na_{3}O_{10}S_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Single azo</td>
</tr>
<tr>
<td>Molecular weight, g/mol</td>
<td>604.48</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>506</td>
</tr>
</tbody>
</table>

Table 1. The properties of the acid red 18 dye (5)

Figure 1. Chemical structure acid red 18 (5)
The algae that have been collected from the shores of the Persian Gulf in the Kish Island have been washed with ordinary tap water. They were rinsed with distilled water and after that they were exposed to the sunlight in order to dry. Then, the dried biomass was activated by using 0.1 M hydrochloric acid for 5 h. after that it was washed 3 times with the distilled water that has gone through distillation twice, and it was exposed to sunlight in order to dry again. Moreover, then by using a 10-18 mesh sieve, the biomass was turned to the sizes 1-2 mm and was prepared to be used.

The experiment was done in the batch system. The effective factors of this process that is being studied have been the time of contact (15, 30, 60, 90, 120, 180 and 240 min), pH (2, 4, 6, 8, 10 and 12), the dose of adsorption (2, 4, 6, 8 and 10 g/L), the concentration of the dye (20, 25, 50, 100, 150, and 200 mg/L). In order to study the isotherms of adsorption, the two models Langmuir and Freundlich have been used.

In order to determine the optimum pH by keeping constant other variables, the experiments will be done in 200 ml beaker with a constant concentration of dye. Then this combination was shaken with a shaker device of enforce model with 175 rpm and room temperature. In the first stage, the pH optimum was obtained by keeping constant the other variables. After that, the optimum dose of absorbent was obtained.

Finally, the effect of contact time on efficiency was reviews. The equilibrium experiments of adsorption process will occur after the determination of equilibrium time in order to evaluate the effect of adsorbent mass on dye removal to obtain the adsorption isotherms.

3. Results

Effect of pH

The adsorption experiments in various pH of the dyed solution were done by keeping constant other laboratorial conditions including the dye concentration, adsorbent dose, and the contact time. The experiments in different pH showed that the removal percent of dye changes with the change of pH (Figure 2). Optimum pH was 7.

Effect of contact time

The effect of contact time between the absorbent and the absorbate substance on adsorption efficiency was shown in figure 3. As shown in figure 3, the dye adsorption increases with the increase of the contact time. It reaches equilibrium after 240 min. The most removal was obtained in 60 min.

Effect of the initial dye concentration

The effect of the initial dye concentration on
the adsorption efficiency was shown in figure 4 showed that by increasing the initial dye concentration, the adsorption efficiency has a perceptible increase. The most adsorption was obtained in 15 mg/L of the dye concentration (Figure 4).

To determine the isotherm models, Langmuir and Freundlich isotherms data obtained from the experiments with linear models adjusted the general case of linear equations in equations 1 and 2 are respectively the model results are shown in figures 6 and 7 parameters calculated of the isotherm equations is give in equation 1 and 2 Langmuir isotherm model form onto layer adsorption, while the Freundlich adsorption equation in a heterogeneous level of energy states.

\[
\frac{1}{q} = \frac{1}{q_m} \left( \frac{1}{c} \right) + \frac{1}{q_m} \\
\log q_e = \log k + \frac{1}{n} \log c_e
\]  

**Langmuir isotherm**

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\]  

**Langmuir isotherm**

Effect of adsorbent dose

The biosorption of the dye on the absorbent was reviewed by 10-20 mg of adsorbent dose. The most adsorption rate was achieved in the 20 mg/L of adsorbent dose. The effect of adsorbent dose on the adsorption efficiency was shown in figure 5.

**Effect of solute concentration**

Figure 4. Effect of solute concentration (T = 60 min, adsorbent dosage 20 g/L, pH = 6)

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**Effect of adsorbent dose**

Figure 5. Effect of adsorbent dose (T = 60 min, pH = 6, con: 25 mg/L)
4. Discussion

Effect of the pH
The studies showed that the adsorption has greatly dependent to pH and is effective on the efficiency of the adsorption and the features of the absorbent surface and the degree of ionization. According to the results, the dye’s biosorption was increased to some extent by increasing pH. In a way that the most rate of adsorption for the acid red was obtained in pH: 6 (6).

Tahir et al. were stated that the best pH for dye removal was 7 (7).

Researches on azo dyes adsorption by various species of the algae showed that the optimum pH was ranged 4.5 and 7 (1,8,9) which is in compliance with the findings of this research.

Effect of the time
The adsorption rate increases by increasing the contact time. It reaches equilibrium in 120 min. These showed that the quick adsorption of the dye was happened by Sargassum biomass. Thus alage has the proper ability for dye adsorption. The gradual decreasing in adsorption capacity after 60 min can be the due to the reduction of the adsorption sites on the absorbent surface. Other researchers showed that equilibrium time for the dye acid red 18 by Sargassum glaucescens reached 120 min (1,3,6,9,10). These results were in compliance with the findings of the present research.

Effect of the adsorbent dose
The results showed that by increasing the adsorbent dose, the dye adsorption rate increases by decreasing the adsorbent dose, the adsorption efficiency will decrease due to the rapid saturation of adsorption sites with ions of the dye.

These finding is in compliance with the studies of other researchers (3,7,9,11) they claimed that polysaccharides were produced due to the interaction between alginic acid and alkaline earth elements from the seawater metal ion uptake by biomass is believed to occur through interaction with the cell walls. This is due to the presence of various functional groups such as carboxyl, amino sulfate and hydroxyl groups, which can act as binding agents include ionic interaction and complex formation between metal cations and ligands on the surface of the seaweeds (1,12-16).

Effect of the dye concentration
The results showed that with increase initial concentration of the dye acid red 18 removal efficiency was associated with a relative increase. While other researchers reported that the concentration increases, the rate of removed was reduced. The maximum absorption was observed at a concentration of 100 ppm.

Isotherms model
Isotherms of adsorption equilibrium data that describes how the compounds by sorbent pay. Efficiency in absorbing vital to communicate in a way suitable for the adsorption equilibrium and optimize the design of a system for the removal of critical dye. Studying of isotherms could explain the reactions between absorbent and absorbptive. Isotherm shows the relation between soluble dye acid red 18 concentration and the rate of absorbed dye acid red 18 by the solid phase when the two-phase are in balance. Figures 6 and 7 show the balanced isotherms for dye acid red 18 adsorption by S. glaucescens biomass a and data of balanced adsorption analyzed with Freundlich and Langmuir isotherms. Results showed that the Freundlich isotherm model is more consistent which represents a homogenous distribution of activities on the adsorbent is multilayered. The optimum time of 60 min, optimum pH 6, optimal adsorbent dose of 15 mg/g and also fit the Freundlich adsorption isotherm model.

Table 2 shows the comparison of surveys conducted in connection with the removal of
Table 2. Comparison of the various adsorbents in contaminants removal a basis on literature reviews

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Year</th>
<th>Adsorbent</th>
<th>Contaminant</th>
<th>Optimum time min</th>
<th>Optimal pH</th>
<th>Adsorption isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubin et al. (15)</td>
<td>2005</td>
<td>Sargassum</td>
<td>Methylene blue</td>
<td>120</td>
<td>5.5</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Aravindhan et al. (1)</td>
<td>2007</td>
<td>Green alga</td>
<td>Yellow dye</td>
<td>125</td>
<td>4.5</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Tahir et al. (7)</td>
<td>2008</td>
<td>Brown algae</td>
<td>Methylene blue</td>
<td>25</td>
<td>7</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Sivarajasekar et al. (2)</td>
<td>2009</td>
<td>Spirogyra algae</td>
<td>Brown</td>
<td>120</td>
<td>3</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Esmaeili et al. (17)</td>
<td>2012</td>
<td>Sargassum</td>
<td>Cr (VI)</td>
<td>120</td>
<td>2</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Ruangsomboon et al. (6)</td>
<td>2013</td>
<td>Padina algae</td>
<td>Malachite green</td>
<td>120</td>
<td>6</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Zazouli et al. (18)</td>
<td>2013</td>
<td>Red mud</td>
<td>Reactive</td>
<td>45</td>
<td>3</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Bazrafshan et al. (19)</td>
<td>2014</td>
<td>Moringa peregrina</td>
<td>Phenol</td>
<td>45</td>
<td>6</td>
<td>Langmuir</td>
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<tr>
<td>Zazouli et al. (20)</td>
<td>2013</td>
<td>Azolla</td>
<td>Choropheno</td>
<td>60</td>
<td>5</td>
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<tr>
<td>Zarei et al. (21)</td>
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<td>Peregrina tree shell ash</td>
<td>phenol</td>
<td>45</td>
<td>6</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Shokoohi et al. (10)</td>
<td>2015</td>
<td>Activated carbon from poplar wood</td>
<td>OR16</td>
<td>180</td>
<td>2</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Diyanati et al. (22)</td>
<td>2014</td>
<td>Rice stem waste</td>
<td>Acid orange 7</td>
<td>75</td>
<td>3</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Zazouli et al. (23)</td>
<td>2014</td>
<td>Azolla</td>
<td>Acid black 1</td>
<td>120</td>
<td>2</td>
<td>Langmuir</td>
</tr>
<tr>
<td>Sreeramanan et al. (24)</td>
<td>2010</td>
<td>Yam leaf fibers</td>
<td>Methylene orange 7</td>
<td>45</td>
<td>3</td>
<td>Freundlich</td>
</tr>
</tbody>
</table>

contaminants, especially dyes with process adsorption variables such as, pH, the adsorption, isotherms model of rate of removal of the separately was demonstrated.

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