The Application of Low-Cost Adsorbent for Reactive Blue 19 Dye Removal from Aqueous Solution: Lemna Minor

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Background & Aims of the Study: Due to widespread use and adverse effect of dyes, the removal of dyes from effluents is necessary. This study was aimed to remove the reactive blue 19 dye removal from aqueous solution by dried Lemna minor.

Materials and Methods: The effect of various parameters including contact time, solution pH, adsorbent dosage and dye concentration was investigated in this experimental-lab study. Also, the isotherm and kinetic studies was performed for RB19 dye adsorption process.

Results: The results indicated that RB19 dye removal efficiency increases by increasing of contact time and adsorbent dosage. The equilibrium time was 75 min ad the maximum dye removal efficiency was obtained in pH=3. Also, the dye removal efficiency decreases by increasing of pH and initial concentration. It was found that the equilibrium data was best follow by Langmuier isotherm. Also, the pseudo-second-kinetic model was best applicable for RB 19 dye adsorption.

Conclusion: It can be concluded that the dried Lemna minor can be considered as an effective adsorbent to remove the RB19 dye.

Keywords:
Lemna minor, Adsorption, Kinetic, Isotherm, Reactive blue 19 dye


Background

Nowadays, the synthetic dyes have an indispensable function in a variety of industries including textile, leather, printing, laundry, tannery, rubber, plastic, painting, etc., (1-2). Despite the widespread use of dyes, they are supposed to be a significant agent to generate the numerous objectionable effects onto water and marine life such as aesthetic problems, diminution of sunlight penetration into water and photosynthetic activity (3-4). Furthermore, human health is another target point of dyes which can be affected by their carcinogenic and mutagenic features. This point suggests that dyes can contribute to development of some illnesses and disorders in kidney, reproductive system, liver, brain and central nervous system(5-6). Reactive dyes are a large group of dyes which are used for various types of fabricates. The reactive blue 19 (RB19) dye is one of most important dyes among this group having an aromatic anthraquinone structure, which makes this dye more resistant (7-8).
Thus, dyes should be considered a significant environmental problem and serious attempts should be carried out to remove them. The adsorption, membrane separation, electrochemical, flocculation-coagulation, reverse osmosis, ozone oxidation, biological treatments, etc are among the variously used approaches to remove the dyes (9-11). The economic and environmental problems such as high capital and operating cost, sludge production and complexity of the treatment processes are associated with these methods (12). Nevertheless, it has been found that adsorption is an outstanding and successful method to remove the dyes (13-17). Its simple operation and cost-effectiveness are the important characteristics of adsorption process (17). The commercial adsorbents such as activated carbon has revealed excellent potential in dye removal but their high cost is nominated as an enormous problem which restricts their application. This issue has led to strong motivation in scientists to use various low-cost materials such as adsorbent (18). The literature review has clarified that numerous material such as Canola (19), Chitosan (20), Rice husk (21), Sorel’s cement (22), Cotton plant wastes (23), Wood shavings (24), Cupressus sempervirens cones (25), pine tree leaves (23) and etc, have been studied for dye removal. Lemna minor is a common category of duckweeds which grows rapidly. The high water purification capacity of this aquatic plant is identified as a unique property which has become extraordinarily valuable in water treatment (27-28). Furthermore, it can successfully tolerate cold weather (29). Several studies have been conducted to remove the pollutants by this plant, which have indicated the significant ability of Lemna minor in removing these pollutants (29-31). Recently, the dried Lemna minor was also applied for acid red 88 dye removal by Balarak et al. and the dye removal efficiency was obtained to be up to 98% (14).

In this experiment, the potential of dried Lemna minor for RB19 dye removal has been assessed. The effect of contact time, pH, dye concentration and dosage of adsorbent were determined and the isotherm and kinetic of RB19 dye adsorption were studied.

### Materials & Methods

#### Adsorbent preparation:

Lemna minor was supplied from Agricultural University, Tabriz, Iran. It was sun dried, crushed and then sieved into particle sizes at the range of 1–2 mm. The prepared particles were treated with 0.1 M HCl for 5 h and then washed by distilled water and dried in the shed (32). The resultant adsorbents were stored for further experiments.

The characteristics of the adsorbent were demonstrated as follows: the BET method was utilized to determine the specific surface area of adsorbent by a Gemini2357 surface area analyzer of Micromeritics Instrument Corporation, USA. Scanning electron microscopy (SEM) of the prepared adsorbent was achieved using a Philips XL30 scanning electron microscope to describe the morphological and surface characteristics.

### Materials:

The Reactive Blue19 (RB19) dye was purchased from Alvan Sabet Corporation, Hamadan, Iran.

### Table 1) Chemical structure and properties of RB19 dye

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Maximum wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3} | 626.54 | 592 |
The stock solution (1000 mg/L) of RB19 dye was prepared and diluted to prepare the desired experimental solutions. Table 1 shows the chemical structure and general characteristics of RB19 dye.

**Batch adsorption experiments:**
The evaluation of the dried Lemna minor ability was performed in batch adsorption system in lab scale experiments. All experiments were carried out in 250 ml Erlenmeyer flasks. The effect of contact time (10-180 min), pH (3-11), dosage of adsorbent (0.1-1 g/100 mL) and initial dye concentration (10-500 mg/L) on adsorption efficiency were investigated. The pH of RB19 dye solution was adjusted by 1 M of HCl or NaOH. 100 mL of RB19 dye solution was mixed with certain amount of adsorbtion in flasks using a magnetic stirrer at 180 rpm for 75 min and then was centrifuged at 3600 rpm for 10 min. The DR-4800 spectrophotometer was utilized to measure the residues RB19 dye in the obtained samples (32). The adsorption capacity ($q_e$) was calculated by Eq 1 (33):

$$q_e = \frac{(C_0 - C_e) V}{m}$$  (1)

Where $q_e$ is the adsorption capacity (mg/g), $C_0$ and $C_e$ is the initial and equilibrium concentrations of dye (mg/L), respectively. V is the volume of the RB19 dye solution (L), and m is the mass of the adsorbent (g).

**Adsorption isotherms:** It has been stated that adsorption isotherm is utilized to obtain the information which can facilitate the design of adsorption system. A number of isotherm models are used for this purpose; however four common models were applied in this study and their equations are presented in table 2.

### Table 2) The equation of isotherm models (31)

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$C_i / q_e = 1 / q_0 k_1 + C_i / q_m$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\log q_e = 1/n \log C_e + \log K_F$</td>
</tr>
<tr>
<td>Tempkin</td>
<td>$q_e = B_1 \ln(k_i) + B_1 \ln (C_e)$</td>
</tr>
<tr>
<td>BET</td>
<td>$C/q_e = 1/A q_m + A-1/A$</td>
</tr>
</tbody>
</table>

**Adsorption kinetic:** the kinetic models are applied to determine the rate of adsorption. The obtained data were analyzed by 3 kinetic models which are shown in Table 3.

### Table 3) the equation of kinetic models (14)

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pseudo-first-order</td>
<td>$\log(q_e - q) = \log q_e - k_1 t / 2.3$</td>
</tr>
<tr>
<td>pseudo-second-order</td>
<td>$t/q = 1/k_2 q_e^2 + 1/q_e t$</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>$q_t = k_{ad} t 0.5 + c$</td>
</tr>
</tbody>
</table>

**Results**

**Characterization of adsorbent:**
The SEM images of the dried Lemna minor are presented in Fig 1. It is evident from these images that the surface of dried Lemna minor is the porous with heterogeneous surface. In addition, the specific surface area of the dried Lemna minor was calculated to be 30 m²/gram.

**The effect of contact time:**
The effect of contact time on RB19 dye removal by dried Lemna minor was studied by varying the contact time from 10 to 180 min and keeping constant of other parameters. Fig 2 illustrates the effect of this parameter. The dye removal efficiency increases by increasing the contact times. As it can be seen in Fig 2, the removal efficiency was 41% in contact time of 10 min but it was increased up to 96.1 in contact time.

**The effect of pH:**
The effect of pH on RB19 dye removal efficiency is illustrated in Fig 3. This figure shows the range of pH for investigation of this variable effect selected from 3 to 11. In addition, the obtained results indicate that the dye removal efficiency decreases by an increase in pH. The best results were obtained at pH = 3 and in acidic condition. As can be observed, the dye removal efficiency decreased from 96.1% to 54.4% by increasing the pH from 3 to 11.
The application of low-cost adsorbent for reactive dyes removal

As can be observed, the RB19 dye adsorption increased from 1.918 to 25.84 mg/g with the increase of initial concentrations of RB19 dye from 10 to 200 mg/L, whereas the RB19 removal efficacy declined from 95.9 to 64.6 percentage.

Figure 4) Effect of AR88 concentration on of RB19 dye removal efficiency (time =75 min, dosage: 5 g/L, pH=3)

The effect of adsorbent dosage

The effect of adsorbent dosage on dye removal efficiency was evaluated in different values of adsorbent dosage and constant amount of other parameters with the results shown in Fig 5. As it is obvious from this figure, although the RB19 dye removal efficiency is developed by increasing the adsorbent dosage, the RB19 dye adsorption amount is decreased.
The isotherm and kinetic studies

The results of the isotherm and kinetic studies are presented in Tables 3 and 4. As it was mentioned earlier, 4 isotherm models and 3 kinetic models were used.

| Table 4) Equilibrium constants for RB 19 dye adsorption |
|---------------------------------|----------------|----------------|----------------|
| Langmuir Model                  | Freundlich Model | Temkin Model   | BET Model      |
| $q_m$                           | $K_L$           | $R^2$          | n              |
| 9.45                            | 0.324           | 0.998          | 0.432          |
|                                 | 0.214           | 0.982          | 0.832          |
|                                 | 41.7            | 2.19           | 0.923          |
|                                 | 24.4            | 0.998          | 0.814          |

| Table 5) Kinetic parameters for the adsorption of reactive blue 19 onto Lemna at various concentrations |
|---------------------------------|----------------|----------------|----------------|
| Con (mg/L)                      | $q_e$           | Pseudo-first order | Pseudo-second order | Intra-particle diffusion |
|                                 | exp            | $K_1$           | $q_e$           | $R^2$        | $K_2$           | $q_e$           | $R^2$        | $K_{dif}$    | C              | $R^2$        |
| 10                              | 1.91           | 0.341           | 6.19            | 0.965        | 0.0021         | 2.24           | 0.999        | 2.18         | 1.39           | 0.835        |
| 50                              | 9.11           | 0.574           | 13.24           | 0.941        | 0.0043         | 7.36           | 0.998        | 3.42         | 3.65           | 0.842        |
| 100                             | 17.25          | 0.922           | 18.45           | 0.972        | 0.0072         | 11.14          | 0.999        | 5.24         | 2.66           | 0.872        |

Discussion

Adsorbent characterization:
The determination of adsorbent characteristics indicates that the dried leman minor has porous and heterogeneous surface. It is also observed that the surface of adsorbent varied after adsorption of RB19 dye, which may be due to the saturation of the adsorbent surface. In addition, it was found that the size of specific surface area of this adsorbent is 30 m$^2$/gr, which can verify the high ability of this adsorbent in dye adsorption (14) However, the specific surface area of Canola and Azolla are greater than the studied adsorbent (35).

The effect of contact time:
The contact time has a significant effect in dye adsorption studies. As was mentioned above, the dye removal efficiency is enhanced by increasing the contact time up to 75 min and significant change can't be seen after this time. This result can be supported by results of various studies (32,36). In addition, it can be seen that the dye removal is quickly performed in the initial step of the study which is gradually decreased with time. This is consistent with the results of another study (37). Tan et al have assessed the dye adsorption efficiency by dried Azolla filiculoides. Their results agreed with the results of the present work. Furthermore, they stated that the high availability of binding sites on the surface of adsorbent can be considered the result of greater dye removal efficiency at beginning of adsorption process (38).

The effect of pH:

pH has been introduced as the most effective parameter on dye adsorption process. In the
present study, maximum dye removal was obtained in pH=3 and it was observed that the dye removal decreased by increasing pH. This result has been observed in other studies which were conducted on dye removal by adsorption (39-40). Bayramoğlu and et al have assessed the ability of fungus Phanerocheate chrysosporium for reactive dye removal efficacy in adsorption process and have found that the maximum dye removal efficiency was observed at pH=3. The reason for this phenomenon may be because of the –SiO-3 group which is in dye structure and the positive surface of adsorbent in acidic pH. This difference between surface charge of adsorbent and dye molecule lead to the enhancement of the dye removal efficiency (41).

**The effect of initial dye concentration:**
Another effective parameter on dye removal adsorption is the initial dye concentration which has been studied in this work. As was observed in Fig 4, the RB19 dye removal efficiency can be drastically affected by the initial dye amount. The dye adsorption amount increases by increasing the initial dye concentration but increasing this parameter led to the decrease of dye removal efficiency. These results can be confirmed by other studies (42-43). Increasing the initial dye concentrations leads to develop the driving force in order to overcome the resistance of the mass transfer of dye between the solution and the adsorbent surface, which increases the dye adsorption (35). Grag et al have studied the dye removal efficiency and observed that an increase in initial dye concentration led to an increase in dye adsorption amount and a decrease in dye removal efficiency (44).

The effect of adsorbent dosage
Adsorbent dosage is another effective variable in dye adsorption studies. In this work, it was observed that the increase of adsorbent dosage improved the dye removal efficiency but it led to a reduction in the dye adsorption amount, which is confirmed by other dye adsorption studies (45-46). The increase of dye removal efficiency can be described by the increase of available adsorption site (47). Madrakian et al. have observed the above results in their study on dye removal and stated that their dye removal efficiency increased by increasing the adsorbent dosage due to the increase in contact surface of adsorbent with investigated dyes and the greater availability of the adsorbent (48).

**Isotherm studies:**
The isotherm studies were conducted with respect to four known models including Langmuier, Freundlich, Tekmin and BET. The constant and parameters of the applied model in this study have been presented in table 4. The comparison of the R² values can help to determine the effective isotherm model in RB19 dye removal. As it can be observed, the correlation coefficient (R²) of Langmuir isotherm was greater than that of the models, which indicates that the obtained data from the isotherm studies are better described by the current model. The monolayer adsorption onto a surface with a finite number of identical and homogeneous sites is assumed by the Langmuir adsorption isotherm. Several dye adsorption studies verify the results of this study (26,49).

**Kinetic studies**
The kinetics of RB19 dye adsorption on Lemna minor were studied in different initial concentrations. Three common kinetic models e.g. pseudo-first-order and pseudo-second-order kinetic models and intra-particle diffusion were utilized in this study. The variables and the constant related to each model were calculated according to the equation which is presented in table 3 and the obtained values which are shown in table 5. By comparing R² values of each model, it can be concluded that the most appropriate model for describing RB19 dye adsorption process mechanism was the pseudo second-order kinetic model, which can be validated by the results of other studies (50-51).

**Conclusion**
The potential of dried Lemna natural biosorbent for RB19 dye removal from aqueous solution was surveyed in the batch system. The detailed results were so clear that each of studied parameter could influence the dye removal efficiency. The development of RB19 dye removal was observed by increasing contact time and adsorbent dosage. In contrast, the increase of pH and RB19 dye concentration decreased the dye removal efficiency. The equilibrium data were best fitted with the Langmuir isotherm. The kinetic data were best described by the pseudo-second order model. The results indicated that the Lemna minor could be an effective adsorbent for removal of RB19 dye from aqueous solution.

### Footnotes

**Conflict of Interest:**

The authors declared no conflict of interest.

### References

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