



## Effect of *Azolla filiculoides* on removal of reactive red 198 in aqueous solution

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### Original Article

#### Abstract

The textile dyes are considered as major environmental problems. The dyes can be removed by various methods. Therefore, this study aimed to evaluate the adsorption rate of Reactive Red 198 (RR198) from aqueous solution by activated *Azolla filiculoides*. This was an empirical-lab study. The *Azolla* was used as an adsorbent to remove Reactive Red 198 dye. The effect of various parameters was investigated on adsorbent performance and the adsorption isotherms were determined. The dye concentration was measured by spectrophotometer (DR4000) in  $\lambda_{\max} = 518$  nm. The results indicated that *A. filiculoides* biosorbent had a large specific surface area (36 m<sup>2</sup>/g). Using the Langmuir equation, the biosorption capacity ( $q_m$ ) for RR198 was 12.2 mg/g. The results showed that the removal ratio of RR198 reached to 97.3% from wastewater containing 10 mg/l RR198. The biomass could be used as a potential biosorbent for the removal of RR198 from industrial wastewater.

**KEYWORDS:** Biosorption, *Azolla Filiculoides*, Reactive Red 198 Dye

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#### Introduction

Textile dyes are considered as one of the major environmental problems because the dyes can be toxic by decomposition.<sup>1-3</sup> The dye production amount<sup>4-8</sup> is estimated between  $7 \times 10^5$ - $10^6$  which is used in various industries such as production of cosmetic, leather, paper and textile.<sup>9,10</sup> Among this industries, the textile have high dye consumption and can generate high volume wastewater with dye concentration in range of 10-200 mg/l.<sup>7,11</sup> The dyes have carcinogenic and mutagenic properties and can cause to allergy and dermatitis.<sup>12,13</sup> Mainly, the dyes have one or more benzene molecular structure which due to

toxicity and slow degradation, can affect the environment seriously. Therefore, these wastewaters must be treated by suitable methods. Various methods such as biological processes, membrane processes, advanced oxidation processes (AOPs) and etc. were used to treat textile effluents.<sup>14,15</sup> Most studies which conducted on dye removal were based on AOPs that despite high efficiency in dye removal, the formation of by-products and their cost were consider as a major problem.<sup>11</sup> Adsorption process is performed on activated carbon which the carbon has high capacity and adsorption surface; however it is expensive and utilizing it requires to expertise.<sup>16,17</sup> Therefore, using natural and low cost adsorbents instead of commercial carbon has been considered by researchers.

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Today, many researchers use the various natural adsorbents including Chitosan, fly ash, peach kernel, olive, charcoal, barley and wheat straw, sawdust to remove organic and inorganic pollutants.<sup>9,10</sup> Other methods such as biosorption, bioaccumulation, and biodegradation were suggested to textile effluent treatment.<sup>18,19</sup> *Azolla filiculoides* is a floating aquatic fern which is growing rapidly in stagnant wetlands and cover the surface of water. Therefore, it is a risk for aquatic life<sup>20,21</sup> especially in Anzali wetlands in north of Iran. The researchers were seeking a method to eliminate this plant from water and reuse.<sup>21</sup> In many countries of world, it is used as high efficiency and inexpensive adsorbent to remove organics such as dyes and heavy metals with regarding to its adsorbing properties.<sup>18,20,22-25</sup> Because there was no study on reactive red 198 (RR198) removal by *Azolla filiculoides*; Therefore, this research aimed to investigate the removal of a textile dye RR198 from aqueous solutions by dried *Azolla filiculoides* as an effective and low cost biosorbent. The effects of various operating parameters were studied including pH, biosorbent dosage and contact time.

### Materials and Methods

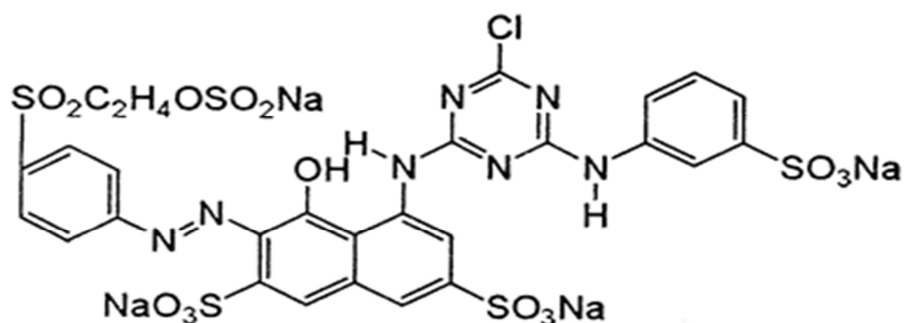
The RR198 dye was supplied from Alvan Sabet Co. The stock solution (1000 mg/l) was prepared and desired concentration of dye solution was prepared by dilution of stock solution. General characteristics and chemical structures of RR198 are presented in table 1 and figure 1, respectively. All the chemicals used were analytical grade.

**Table 1. The characteristics of Reactive Red 198 dye<sup>17</sup>**

Name	Molecular weight	$\lambda_{max}$ (nm)	Molecular formula
Reactive Red198	967.5	518	$C_{27}H_{18}ClN_7Na_4O_{15}S_5$

*Azolla filiculoides* was obtained from paddies surrounding Sari, Iran. It was dried in the sun. They were then powdered and sieved to select 1-2 mm particle sizes for using as a biosorbent. The biomass was treated with 0.1M HCL for 5 hours followed by washing with distilled water and then dried.<sup>18</sup>

The literature review indicated that the most important effective variables on adsorption were including pH, adsorbent dose, contact time and dye concentration. Because the dye concentration in textile effluent was 10-200, therefore the initial dye concentration was selected 10, 25, 50, 100, and 200. Adsorbent dosage (0.2-1.4 g), contact time (10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes) and pH (3, 5, 7, 9 and 11) were investigated. The experiments in batch system were carried out in a 250 ml erlenmeyer flask. In each adsorption experiment, the specific concentrations of dye solution were added into the flask. The desired condition was adjusted and then the specific dosage of adsorbent was added. The samples were mixed by a magnetic stirrer with 180 rpm for 60 min. After the requirement time, the samples were centrifuged at 3,600 rpm for 10 min. Finally, the residual concentrations were measured using spectrophotometer (DR4000) in  $\lambda_{max} = 518$  nm.<sup>13,18</sup>



**Figure 1. The chemical structure of Reactive Red 198<sup>17</sup>**

## Results and Discussion

The specific surface area of adsorbent was one of the most important parameters on adsorption ability. The more surface area of material was, the greater the porosity of the material could be. Therefore, it will have higher contact surface with the adsorption. The surface area of dried *Azolla* was 36 m<sup>2</sup>/g.

### Effect of Contact Time and Initial Dye Concentration

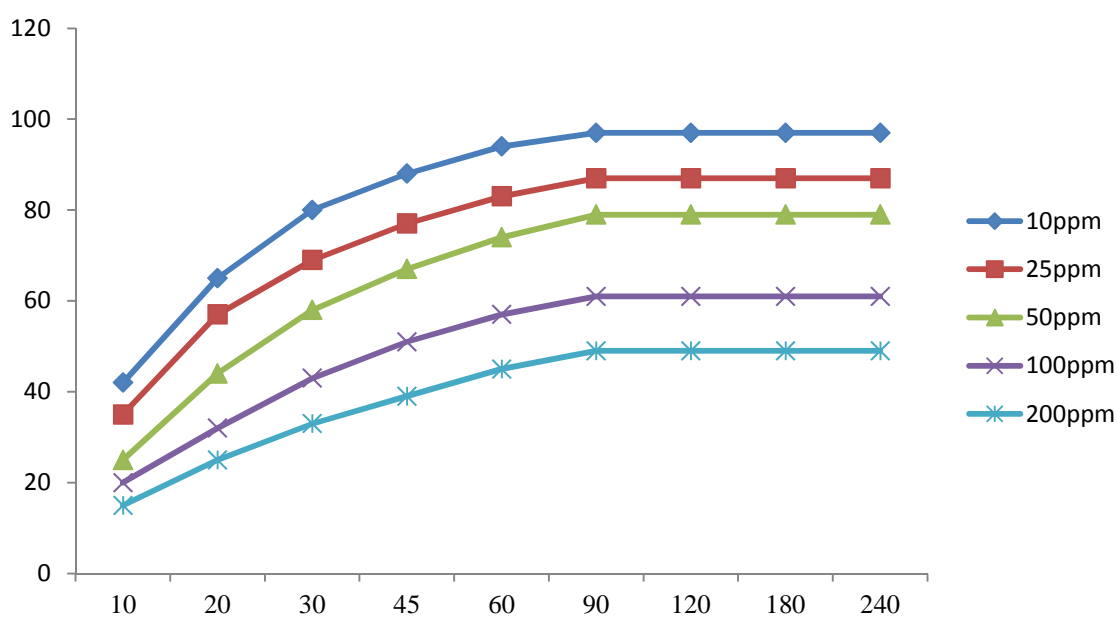
The adsorption percentage increases by increasing of contact time; however adsorption ratio reached to equilibrium after 90 minutes. With regarding to present study, the dye removal efficiency increased by increasing contact time which was due to more contact between pollutants and adsorbent. In the initial minutes of process, the dye adsorption was rapidly done. Adsorption rate decreased with time which was due to declining of dye concentration and decreasing active points on adsorbent surface area. There were a lot of empty spaces in the early stages of absorption and they were occupied by dye molecules with time. It was in accordance with several studies

that conducted on dye removal by *Azolla*.<sup>3,20</sup>

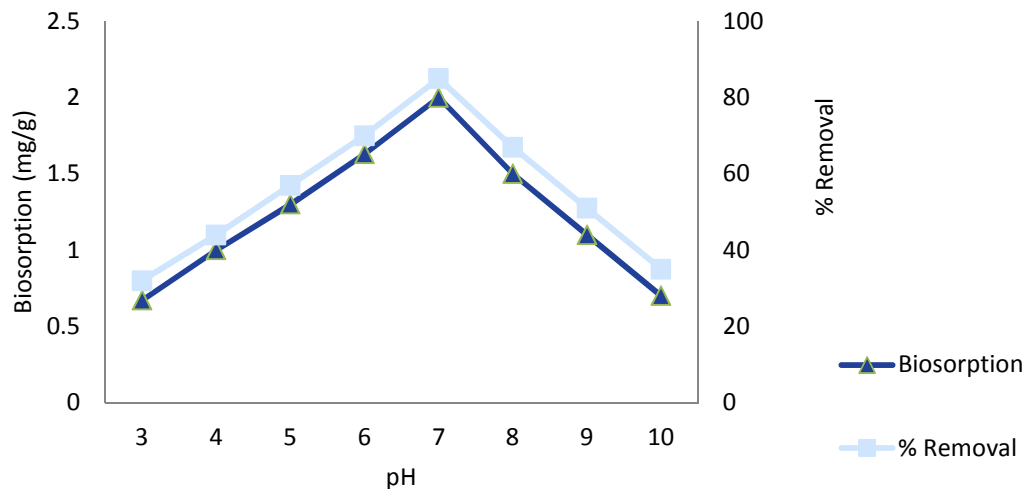
The dye removal efficiency decreased by increasing initial concentration, so that adsorption rate in concentration of 10 mg/l was double than 200 mg/l. When the initial RR198 concentration increased, the adsorbent sites was filled earlier and the dye removal efficiency decreased. The results of this study were agreed with previous studies. The results of this study were in accordance with previous studies.<sup>3,26</sup> Figure 2 illustrates the effect of contact time and initial dye concentration on removal efficiency.

### Effect of pH and Adsorbent Dosage

Figures 3 and 4 suggest the effect of pH and adsorbent dosage on adsorption ratio. Many researchers expressed that the pH plays an essential role in the electrostatic attraction between the adsorbent and the dye. In this study, the maximum dye removal was observed in neutral pH. The efficiency was decreased in acidic or alkaline pH, which it was inconsistent with the Mahvi study on dye removal by activated carbon and the study of Wang on dye removal by Red mud.<sup>3,27</sup>

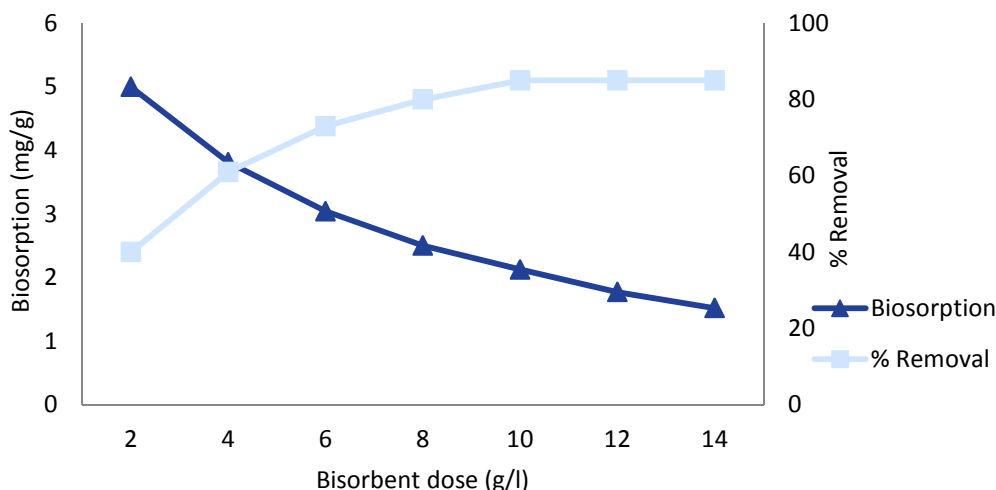


**Figure 2. Effect of contact time and initial dye concentration on removal efficiency**  
(pH = 3, adsorbent dosage 1 gr/100 cc)



**Figure 3. Effect of pH on adsorption**

(Initial dye concentration of 25mg/l, contact time = 90 minutes, adsorbent dosage 1 gr/100 cc)



**Figure 4. Effect of adsorbent dose on adsorption**

(Dye initial concentration 25mg/l, contact time = 90 min, pH = 3)

The dye removal efficiency increased by increasing adsorbent dosage up to concentration of 10 g/l; however thereafter, it reached to equilibrium. The adsorption rate increased by adsorbent dosage increasing which was due to increasing the active surface of adsorbent. The results showed that although efficiency increased with increasing adsorbent dose, the dye adsorbed per gram of adsorbent decreases and it was because the active sites of adsorbent

were not saturated. So that, when the adsorbent dose was increasing, the total capacity of the adsorbent surface points were not used completely and this reduced the absorption rate per unit mass of the adsorbent.<sup>20,28</sup>

#### Adsorption Isotherms

The adsorption of adsorbate (RR198) onto the adsorbent (*A. filiculoides*) was modeled using the Langmuir and Freundlich equations. The Langmuir isotherm assumed monolayer

coverage of an adsorbate onto the solid surface of adsorbent, uniform energy of sorption, and no transmigration of adsorption in the plane of the surface.<sup>29</sup> At equilibrium, the Langmuir isotherm can be expressed as equation 1:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \frac{1}{C_e} + \frac{1}{q_m}$$

where  $q_e$  is the amount of adsorbate adsorbed at equilibrium (mg/g);  $C_e$  is the equilibrium concentration of the adsorbate or the adsorbate unadsorbed in the solution (mg/L);  $q_m$  (mg/g) is the maximum theoretical biosorption capacity and  $K_L$  is a measure of biosorption energy, indicating the affinity between adsorbent and adsorbate.<sup>30</sup>

The Freundlich equation is also often used as an empirical relationship between the concentration of an adsorbate on the surface of an adsorbent and the concentration of the adsorbate in the solution at equilibrium.<sup>30</sup> The Freundlich equation is based on the hypothesis of multi-layer adsorption and the linear form is given by the equation 2:

$$\log q_e = \log k + \frac{1}{n} \log c_e$$

where  $q_e$  is the adsorbate adsorbed at the equilibrium (mg/g);  $C_e$  is the equilibrium concentration of the adsorbate or the unadsorbed adsorbate in the solution (mg/L); and  $K$  is a constant, indicative of adsorption

capacity.<sup>29</sup> Figure 5 shows the Freundlich and Langmuir equation obtained by the adsorption of RR198 onto dried *A. filiculoides*.

With regarding to obtained equilibrium, data of using this plant to RR198 adsorption indicated that the data were better fitted on Langmuir isotherm ( $R^2 = 0.999$ ) than Freundlich isotherm ( $R^2 = 0.932$ ) which was in agreement with the studies that were performed by this plant to dye removal.<sup>18,20,31</sup>

## Conclusion

Based on the results, the dried *Azolla* can be used as an effective and low cost adsorbent to treat effluent containing dye. The removal efficiency depends upon parameters such as initial dye concentration, adsorbent dose, pH, and contact time. The data were best fitted on Langmuir isotherm.

## Conflict of Interests

Authors have no conflict of interests.

## Acknowledgements

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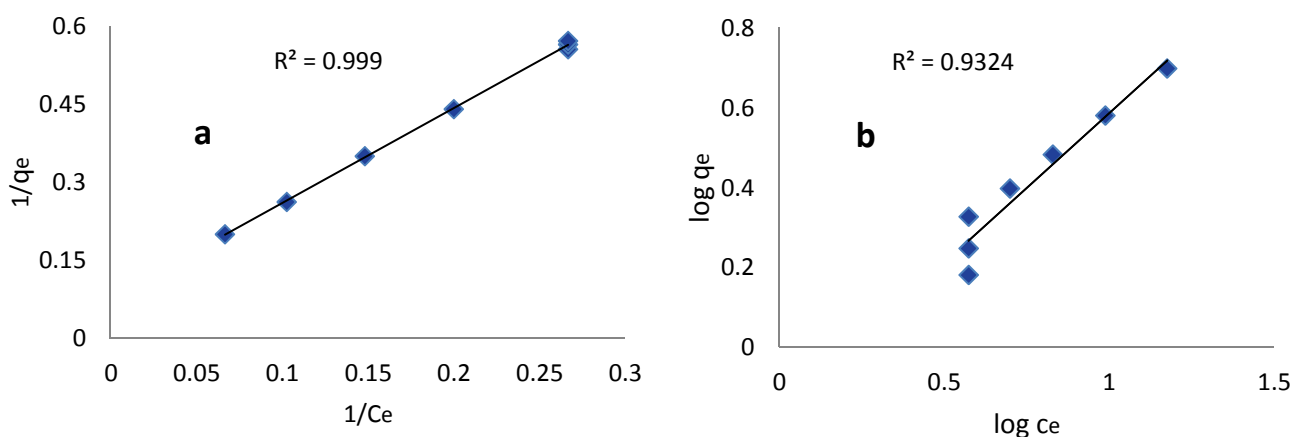


Figure 5. Isotherm models: (a) Langmuir (b) Freundlich



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