# The application of Azolla filiculoides biomass in acid blue 15 dye (AB15) removal from aqueous solutions

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## Abstract

**Introduction:** Industrial wastewater is one of the most important environmental pollutants. Discharging the colorful industrial effluents into receiving waters can lead to eutrification which has many adverse effects on human health. Therefore, the present study aimed at evaluatingacid blue 15 dye removal from aqueous solution by dried Azolla.
**Materials and methods:** Azolla biomass was dried in the sunlight, and then crushed and sieved to particle sizes in range of 1-2 mm. Next, it was treated with 0.1 M HCl for a period of 5 hours. The Azolla was washed with distilled water and used as absorbent. The effect of operating parameters such as pH, contact time, AB 15 concentration and adsorbent dose on the AB15 removal efficiency was investigated. The dye concentration was measured by spectrophotometer (DR4000) at λmax =565nm.
**Results:** In optimum condition (pH 3, contact time 90 min , absorbent dose 10 g/l and AB15 concentration 10 ppm), application of Azolla removed 98% of AB15 from aqueous solutions. The equilibrium data was best fitted on Langmuir isotherm and the adsorption kinetic model followed a pseudo-second model.
**Conclusion:** The obtained results showed that the dried Azolla can be used as a high efficiency and low-cost absorbent to treat textile effluents.

**Keywords:** Azolla filiculoides, AB15 dye, isotherm's model, adsorption, water treatment

## Introduction

Synthetic dye is one of the most serious problems for environment because it may become toxic due to decomposition (1, 2). The amount of generated dye is estimated in the range of 7×105-106 ton/year which is used in many industries such as production of cosmetic, leather, paper and textile (3-5). Maximum dye consumption is used in textile industry and these industries can produce high volume wastewater with dye concentration in the range of 10-200 mg/l(3, 6). Approximately, 10-20% of total world production of dyes is lost during the painting process and is released into wastewater streams (7, 8). The dyes are formed with different chemical structures such as acidic, basic, reactive, disperse, azo, anthraquinone and metal dyes (9, 10). Discharging the wastewaters into receiving waters leads to eutrification and interference in the ecology (11). Most dyes have carcinogenic and mutagenic properties and can cause allergy and dermatitis (11). Various methods were used to treat the textile effluents such as biological, membrane process, advanced oxidation process, etc. (12-14). Most conducted studies on dye removal are based on advanced oxidation process; however, the formation of by-product and their high cost is considered as a major problem (9). Adsorption process is one of the most common processes used in water and wastewater treatment (15, 16). Typically, adsorption process is performed by activated carbon. Although the advantages of activated carbon are the high capacity and adsorption surface, it is expensive and requires expertise (17, 18). Therefore, researchers have attempted to use the natural and low cost adsorbents instead of commercial carbon (11, 18, 19). Nowadays, different natural adsorbents such as chitosan, fly ash, peach kernel, olive, charcoal, barley and wheat straw, sawdust are used to remove organic and inorganic pollutants (11, 18, 20-22). A number of studies suggest the using of biosorption methods such as plant biomass to treat these wastewaters (23). Azolla is a flouting aquatic fern which has a rapid growing rate in stagnant waters and wetlands and can rapidly cover the surface of water (24, 25). Therefore, it can be a serious problem for aquatic life and many studies are conducted to eliminate this plant in the Anzali wetlands. Dried Azolla is used as high efficiency and inexpensive adsorbent to remove the organic substances such as dyes and heavy metal in many countries of the world due to its adsorbing properties. Table 1 shows the sorption capacity for Azolla adsorbent used to remove pollutants (26-31). Therefore, the purpose of this study was to use dried Azolla as an effective and low cost adsorbent to remove reactive Acid Blue15 from aqueous solutions.

Table 1. The removal efficiency of pollutant by using the Azolla.

| Author | Pollutant | Removal efficiency |
|---|---|---|
| Balarak D | Pyrocatechol | 97% |
| Balarak D | Phenol | 99% |
| Padmesh TVN | Acid red 88, acid green 3, acid orange 7 | 99% |
| Pandey VC | Heavy metals | 96% |

## Material and method

**Adsorbent preparation:** Azollafiliculoides was collected from rice fields of Sari. It was sun dried then crushed and finally sieved to particle sizes in the range of 1–2 mm. The biomass was treated with 0.1 M HCl for 5 h followed by washing with distilled water and then dried in shade (32). The resultant biomass was subsequently used in absorption experiments. The specific surface area of adsorbent was determined by the BET method using the Gemini2357 of micrometrics Co. Scanning electron microscopy (SEM ) of the modified Azollafiliculoides were carried out using Philips, Eindhoven.

**Materials:** The AB15 dye was supplied from Alvansabet Co. the stock solution (1000mg/l) was prepared and desired concentration of dye solution was prepared by dilution of stock solution. The General characteristics and chemical structures of AB15 are presented in Table 2 and Figure 1, respectively.

Table 2. Properties of AB15(33).

| C.I. name | Molecular weight | λmax (nm) | Molecular formula |
|---|---|---|---|
| Acid Blue15 | 775.96 | 565 | $C_{42}H_{46}N_3NaO_6s_2$ |

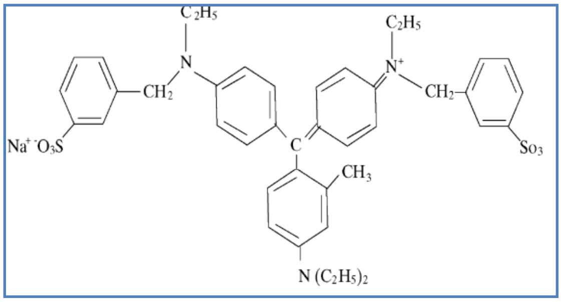


Figure 1. The chemical structures of AB15 (33).

**Batch adsorption experiments:** The literature review indicated that the most important effective variables on adsorption are pH, adsorbent dose, contact time, and pollutants concentrations. Therefore, the initial AB15 concentration was selected (10-200 mg/l). The effect of absorbent dosage (0.2-1.4 g/100 ml), contact time (10 - 180 min) and pH (3- 11) were investigated. The experiments in batch system were carried out using 100ml in a 250 ml Erlenmeyer flask Meyer. In each adsorption experiment, certain concentration of AB15 solution was added into the flask. In every experiment, a certain concentration of AB15 and specific dose of absorbent poured into the Flask and completely mixed with magnetic stirrer at 3600 rpm for 60 minutes. Then, the sample was centrifuged at 3600 rpm for 10 minutes. Finally, the residual concentrations were measured using spectrophotometer at λmax of 565 nm (33). The amount of adsorbed AB15 was calculated according to the following Eq 1(34).

$$q_e = (C_O - C_e) V/m \qquad \text{Eq1}$$

Where qe is the amount of adsorbed (mg/g), $C_0$ and $C_e$ are the initial and equilibrium concentrations of liquid phase (mg/L), respectively. V is the volume of the solution (L), and m is the mass of the adsorbent (g).

**Adsorption isotherms:** The equilibrium adsorption isotherm is an important parameter for the design of adsorption systems. Although several isotherm equations are available, two important isotherms of Langmuir and Freundlich isotherms were selected. The Langmuir isotherm is presented in the Eq2 (34, 35).

$$Ce / q_e = 1/q_m K_L + Ce / q_m \qquad \text{Eq2}$$

Where qe is the amount of sorbatebiosorbed at equilibrium (mg/g); $C_e$ is the equilibrium concentration of the sorbate or the sorbateunadsorbed in the solution (mg/L); $q_m$ (mg/g) is the maximum theoretical biosorption capacity and $K_L$ (L/mg) is a measure of biosorption energy that is indicated on the affinity between biosorbent and sorbate.

The Freundlich equation is given by the following Eq3 (36, 37):

$$\text{Log } x/m = 1/n \log Ce + \log KF \qquad \text{Eq3}$$

Where $q_e$ is the sorbatebiosorbed at the equilibrium (mg/g); $C_e$ is the equilibriumconcentration of the sorbate or the unabsorbed sorbate in the solution (mg/L); $K_F$ is a constant, indicative of biosorptioncapacity(36). Table 2 shows the Freundlich and Langmuir equation obtained for the biosorption of AB15 onto dried A. filiculoides.

**Adsorption kinetics:** Kinetic models are used to examine the rate of the adsorption process and potential rate controlling step. In the present study, obtained kinetic data were analyzed from batch studies using the pseudo second-order and pseudo First-order model.

The pseudo-first-order rate equation is expressed as Eq 4 (38):

$$\log (q_e - q) = \log q_e - k_1 t / 2.3 \qquad \text{Eq4}$$

Where $q_e$ and q are the amounts of AB15 adsorbed (mg/g) at equilibrium and at time t (min), respectively, k1 is the rate constant of adsorption ($min^{-1}$). Values of $k_1$ were calculated from the plots of log ($q_e$-q) versus (t) for different concentrations.
Also, equation 5 provides the pseudo-second-order rate equation:

$$dq / dt = k_2 (q_e - q)^2 \quad Eq5$$

Where $K_2$ is the second order rate constant (g mg −1min−1), q and qe are the amount of the adsorbed on the adsorbent (mg/g) at equilibrium and at time t. The integration fromEq 6is as follows:

$$t/q = 1/k2qe2 + 1/ qet \quad Eq6$$

If the second-order kinetic equation is applicable, the plot of t/q against t of Eq (6) will give a linear relationship. The qe and K2 can be determined from the slope and the intercept of the plot.

## Results

Scanning electron microscopy (SEM) images were used to analyze the surface structure of A. Filiculoides (Fig. 2). It was found that the adsorbent has Heterogeneous surface structure with deep pores. The specific surface area of modified Azolla was determined in the size of 36 $m^2$/g.

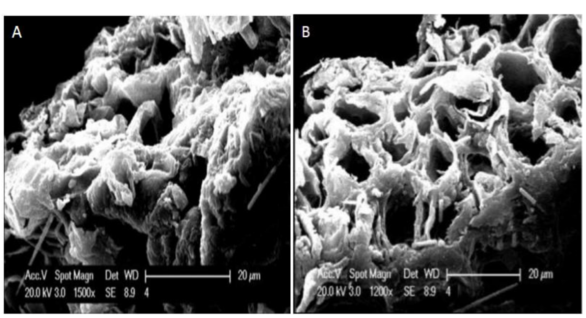


Figure 2. SEM photographs of adsorbent: (A) before use,(B) after use.

**The effect of contact time and initial dye concentration:** Increasing the contact time raised the adsorption percentage; however, adsorption ratio reached equilibrium after 90 min. The dye removal efficiency was decreased by increasing initial concentration. Figure 3 presents the effect of contact time and initial dye concentration on dye removal. As can be observed,in dye concentration of 200 and 10 mg/l, the dye removal efficiency is 49 and 98%, respectively.

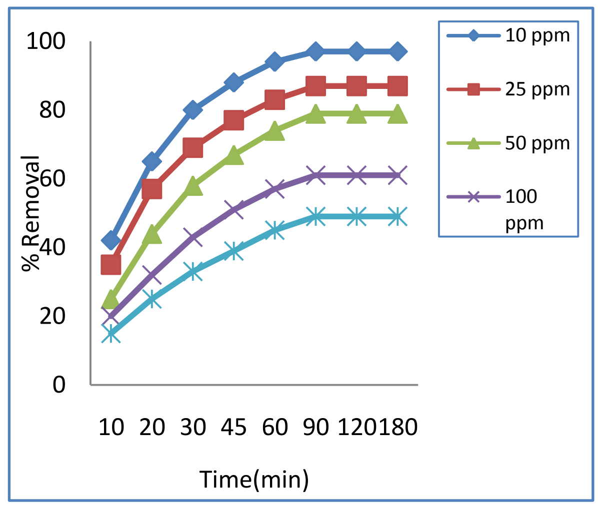


Figure 3. Effect of contact time and initial dye concentration on removal efficiency (pH = 3, adsorbent dosage 1 g/100cc).

**The effect of pH and adsorbent dosage:** Figures 3, 4 and 5 shows the effect of pH and adsorbent dosage on adsorption rate. As it is seen, the maximum adsorption rate was performed in acidic pH and it is decreased in alkaline pH. The adsorption rate was raised by increasing the adsorbent dosage up to the concentration of 10 g/L, and then reached to equilibrium. As a result, adsorption rate was also enhanced by increasing the adsorbent dosage.
**Adsorption kinetics and isotherms:** Table 2 and 3 show the isothermal models and adsorption kinetics.

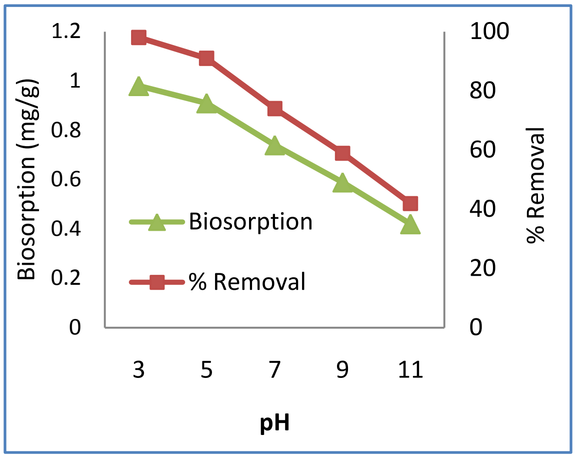


Figure 4. Effect of pH on removal efficiency of AB15 (contact time = 90min, dose: 10g/l, AB15 concentration: 10ppm).

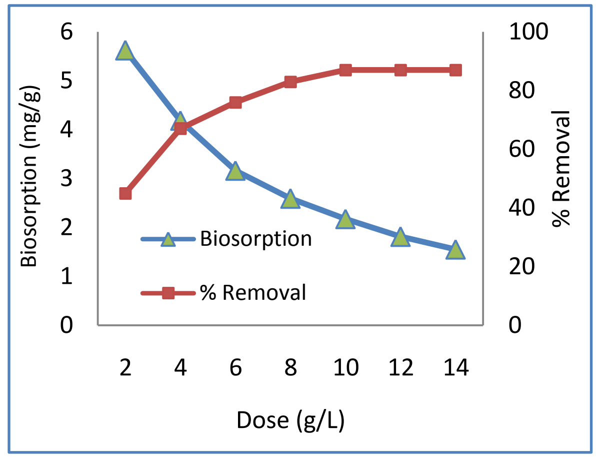


Figure 5. Effect of adsorbent dose on removal efficiency of AB15 (contact time = 90 min, PH = 3, AB15 concentration: 25 ppm).

Table 3. The isotherms constants for the removal AB15 dye.

| Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|
| b(ml/g) | $R^2$ | $q_m$ | $K_F$ | $R^2$ | 1/n |
| 1.11 | 0.998 | 7.1 | 51.2 | 0.963 | 1.02 |

Table 4. The kinetic model constants for the removal AB15 at 10, 25, 50 mg/L dye concentrations

| Pseudo second-order model | | | | Pseudo First-order model | | |
|---|---|---|---|---|---|---|
| co(mg/L) | $K_2$(g/mg min) | $R^2$ | q(mg/g) | $k_1$(1/ min) | $R^2$ | q(mg/g) |
| 10 | 0.07 | 0.988 | 1.84 | 0.060 | 0.948 | 1.45 |
| 25 | 0.10 | 0.992 | 3.90 | 0.075 | 0.964 | 3.40 |
| 50 | 0.114 | 0.998 | 5.90 | 0.088 | 0.978 | 5.60 |

## Discussion

The specific surface area is related to the number of active adsorption sites of dried A. filiculoides.The adsorption was increased with the specific surface area and pore volume of the sorbent. The specific surface area of themodified Azolla was determined in the size of 36 $m^2$/g. This situation indicated that the modified Azolla has a relatively good ability to remove the pollutants (9).

With regard to the present study, the dye removal efficiency enhances by increasing contact time which is due to more contact between pollutant and adsorbent. The dye adsorption was rapidly performed in initial minutes of the sorption process. Adsorption rate decreases with time which can decline the dye concentration and lower active points on adsorbent surface area. There are a lot of empty spaces in the early stages of adsorption and they were occupied by dye molecules with time. This situation is consistent with several studies that were conducted on dye removal by Azolla (29, 39).

The greater adsorption occurs in low concentrations and dye removal efficiency reduces with increasing initial concentration of dye. Since the adsorbents have little adsorption sites, their adsorption capacity is therefore saturated by increasing the pollutant concentration and the removal efficiency will reduce.

The results of this study are in line with previous studies (30, 36). pH plays an important role in all processes and adsorption capacity. It can influence various aspects of adsorption including adsorbent surface charge, the degree of ionization, and separation of functional groups on the active sites of adsorbent and solution chemistry. Many researchers have reported that pH plays a main role in electrostatic force between adsorbent and AB15. In this study, the maximum AB15 removal was obtained in pH=3 which is similar to previous studies on dye removal by azolla. This is probably due to the binding group between adsorbent and adsorbate (9, 29).The adsorption rate enhances by an increase in adsorbent dose which is due to increasing the active surface of adsorbent. The results show that although efficiency rises with increasing adsorbent dose, the dye adsorbed per gram of adsorbent decreases and active sites of adsorbent are not saturated because of it. So, when the adsorbent dose increases, the total capacity of the adsorbent surface points is not completely used and this reduces the adsorption rate per unit mass of the adsorbent (3, 12).

The Freundlich equation is based on the hypothesis of multi-layer biosorption and the linear form is given by the following equation and Langmuir isotherm assumes monolayer coverage of a sorbent on the solid surface of adsorbent, uniform energy of sorption, and no transmigration of sorbate in the surface of plant. The obtained equilibrium data from AB15 adsorption by this plant indicated that the data is better fitted on Langmuier isotherm (R2=0.998) than Freundlich isotherm (R2=0.963) which is in line with the studies that are performed by this plant for dye removal (6, 28, 30). Kinetics of adsorption was well described by pseudo-second order model. The result of this study is consistent with other studies(19, 29, 32).

## Conclusion

According to the obtained results, Azolla can be used as an effective, inexpensive, and available adsorbent to treat the effluents with organic compound (dye) such as textile wastewater. The dye removal efficiency depends on various parameters such as contact time, pH, adsorbent dose, and initial dye concentration.

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