Original Article

Application of Azolla filiculoides Biomass for Acid Black 1 Dye Adsorption from Aqueous Solution

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Abstract

Background and purpose: The textile dyes are considered as important pollutants due to the toxicity on human and environment. Therefore, the dye removal from industrial effluents is necessary. This study evaluates the ability of Azolla for the adsorption of acid black 1 (AB1) dye from aqueous solution.

Materials and Methods: This was an experimental-laboratory study. The Azolla biomass was sun dried, crushed and sieved to particle sizes in the range of 1-2 mm. Then, it treated with 0.1 M HCl for 5 h, followed by washing with distilled water, and it used as an adsorbent. The effect of study parameter was investigated, and the residues AB1 concentration was measured by DR2800 spectrophotometer at in λ_{max} = 622 nm.

Results: The results indicated that the efficiency of AB1 adsorption decreased with increased initial dye concentration. It increased with increased contact time and adsorbent. The highest adsorption efficiency was occurred at pH = 2. The equilibrium data were the best fitted on Langmuir isotherm and pseudo-second-order kinetic model.

Conclusion: The Azolla could present high ability in dye removal. Therefore, it can be used as inexpensive and effective adsorbent in textile effluent treatment.

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Key words: Adsorption, Acid Black 1, Azolla, Isotherm

1. Introduction

The application of dyes is common in many industries such as textile, paper, leather, food, plastic, cosmetic industries, etc. (1, 2). The textile industries are known as significant dye consumer and major colorful wastewater producer (3). The dyes are defined as organic molecules with complex aromatic structure (4, 5). Owing to their properties, the dyes can create an esthetic issues and many risks to public health (6, 7). Some health risks can imply to mutagenic and carcinogenic activity, dermatitis and, etc. (8). Therefore, the treatment of textile effluent and especially dye removal is necessary. It has been reported that the acid and reactive dyes are resistant against the conventional treatment methods (5, 9). Consequently, the many techniques such as membrane separation, electrochemical, flocculation-coagulation, reverse osmosis, ozone oxidation, biological treatments, etc. were assessed for dye removal (10). However, it discovered that the mentioned techniques are faced with many limitations such as high cost, formation of hazardous by-products and intensive energy requirements. For that reason, it is a significant need to find a simple, inexpensive and efficient method to remove the dyes (11). The literature review indicated that the adsorption process is a cost-effective technique to dye removal (12). Although the activated carbon is a promising adsorbent, however it is an expensive adsorbent, which leads the researchers try to find a low-cost and effective adsorbents (13). The several researches have been conducted on different material such as chitosan, banana peel, coconut shell, rice husk, canola etc (14-20). Meanwhile, researchers are studying an another adsorbent that derived from an algae called Azolla. Azolla filiculoides has been used in many studies for pollutant removal. Table 1 shows the results of previous studies on pollutant removal by Azolla
(21, 22). It can be found in northern of Iran, particularly in Anzali wetland. The algae grow quickly and cover the surface of stagnant water and lakes. The rapid growth of this algae produce negative effects on the environment if Azolla is used as an adsorbent, it can control their growth (23, 24). The purpose of this study are to investigate of the ability of Azolla biomass for acid black 1 (AB1) adsorption; to assess, the effect of several parameters, including contact time, pH, initial dye concentration, adsorbent dose on dye adsorption; and to study the isotherm and kinetics of adsorption.

2. Materials and Methods

2.1. Materials

The AB1 dye was purchased from Alvan Sabet Co (Iran). The desired concentration of dye solution was prepared by dilution of stock solution (1000 mg/L). Table 2 presents the general characteristics and chemical structures of AB1 by manufacturer. All chemicals used in this research were of analytical reagent grade, which were supplied from Merck. Co (Germany). Deionized water was used for all dilutions.

Table 1. The pollutant removal efficiency using Azolla

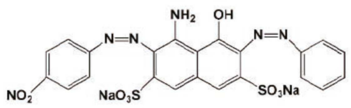
Author	Pollutant	Removal percentage (%)
Zazouli et al. (21)	Pyrocathechol	97
Zazouli et al. (29)	Bisphenol A	99
Present work	AB1	96

AB1: Acid black 1

2.2. Adsorbent preparation

A. filiculoides was collected from the rice paddies of Sari, Iran. It was dried in the sun and then were crushed and sieved to 1-2 mm particle sizes for using as an adsorbent. The biomass were treated with 0.1 M HCl for 5 h, followed by washing with distilled water and then dried (25). The surface morphology of adsorbent was observed with a scanning electron microscope (SEM) before and after adsorption process.

Table 2. Chemical structure and characteristics of AB1 (26)

Chemical structure	
Chemical formula	$C_{22}H_{14}N_6Na_2O_9S_2$
M.W	616.5 g mol^{-1}
λ_{max}	622 nm

2.3. Batch adsorption experiments

By reviewing of performed studies, it was discovered that contact time, pH, initial dye concentration and adsorbent dose can attribute as the effective parameter on the adsorption process. It is reported that the dye concentration in textile effluent is between 10 and 200 mg/l; therefore, the initial dye concentration was selected 25, 50, 75,100, 125, 150, 175, and 200. The effect of adsorbent dosage, contact time and pH were studied in a range of (0.2-2 g), (10-240 min) and (2-11), respectively. The pH of dye solution was regulated by NaOH and H_2SO_4. The experiments in a batch system were carried out in a 250 ml Erlenmeyer flask. In each adsorption experiment, certain amount adsorbent was added to the Erlenmeyer with known concentration of dye. The samples were mixed by shaker with 180 rpm for 120 min. Then the samples were centrifuged at 3600 rpm for 10 min. This study was done according on optimization of each parameter. For example to obtain the optimum contact time, all parameters assumed constant except contact time. The contact time was varied between 10 and 240 min and the time with maximum dye removal is considered as optimum contact time. This time was constant in next steps. This is continued in the next experiments to find the other optimum parameters. The experiments repeated 2 times, and the number of samples was 78. Samples were measured using a spectrophotometer (DR2800) at 622 nm. The dye removal percentage (R) and the amount of adsorbed dye on adsorbent, qe (mg/g), were calculated by equations 1 and 2, respectively.

$$R=\frac{C_0-C_e}{C_0}\times 100 \quad (1)$$

$$qe=\frac{(C_0-C_e)V}{M} \quad (2)$$

Where qe is the amount of adsorbed dye per unit mass of adsorbent (mg/g), C0 and Ce are the initial and the equilibrium concentrations of dye solution (mg/L), respectively. V is the volume of the dye solution (L), and M is the mass of the adsorbent (27).

2.4. Adsorption isotherms and kinetics

The equilibrium adsorption isotherm is used to design of adsorption systems. Among the several isotherm models, the Langmuir and Freundlich isotherm were selected isothermic studies. The equations of these isotherms described in the previous studies. The Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites. Furthermore, the kinetic mechanism in the AB1 adsorption process was investigated using the pseudo-first-order and pseudo-second-order model that was described in other research (20, 28).

3. Results

3.1. SEM analysis

The SEM provides the surface information. The surface structure of the adsorbent was observed with SEM at different magnifications. The SEM images show in figure 1. The images clearly depicted that surface topography/morphology and internal architecture of adsorbent were different before and after using adsorption processes. The adsorbent had irregular and porous structure before using (Figure 1a); however, remarkable dye adsorption was indicated in figure 1b as it can be seen the adsorption surface of the adsorbent is saturated after dye adsorption that it mentioned in previous studies, also (17).

3.2. The effect of contact time

The AB1 adsorption efficiency increases by increasing the contact time. As it has shown in figure 2, there is a sharp slope in the initial time of the adsorption process. It decreases after 120 min, and the dye removal efficiency is constant over this time. This time is considered as equilibrium time.

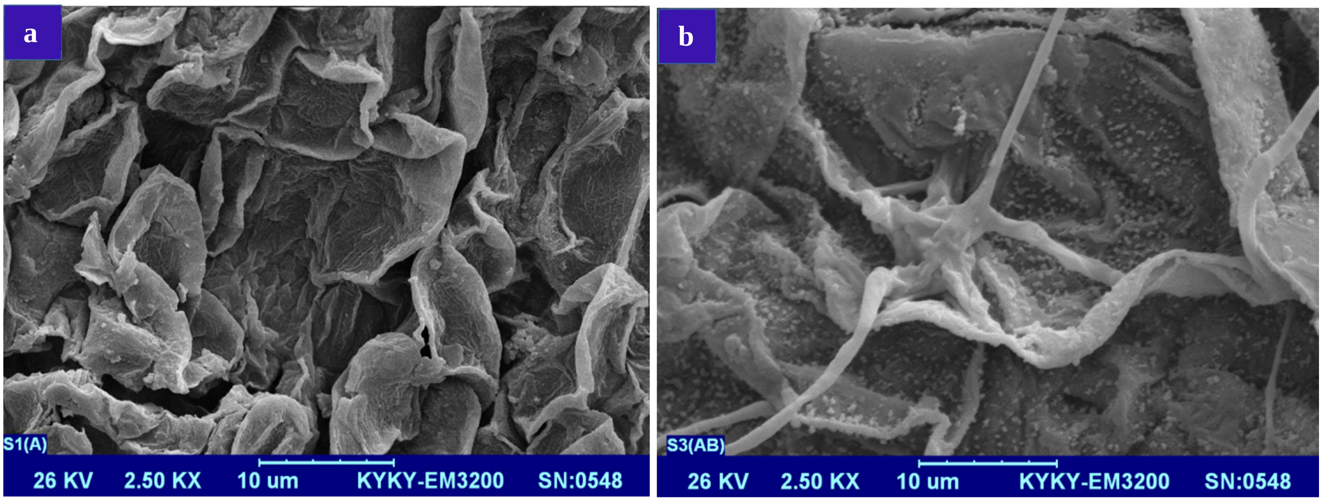


Figure 1. The scanning electron microscope images: (a) before used (b) after used

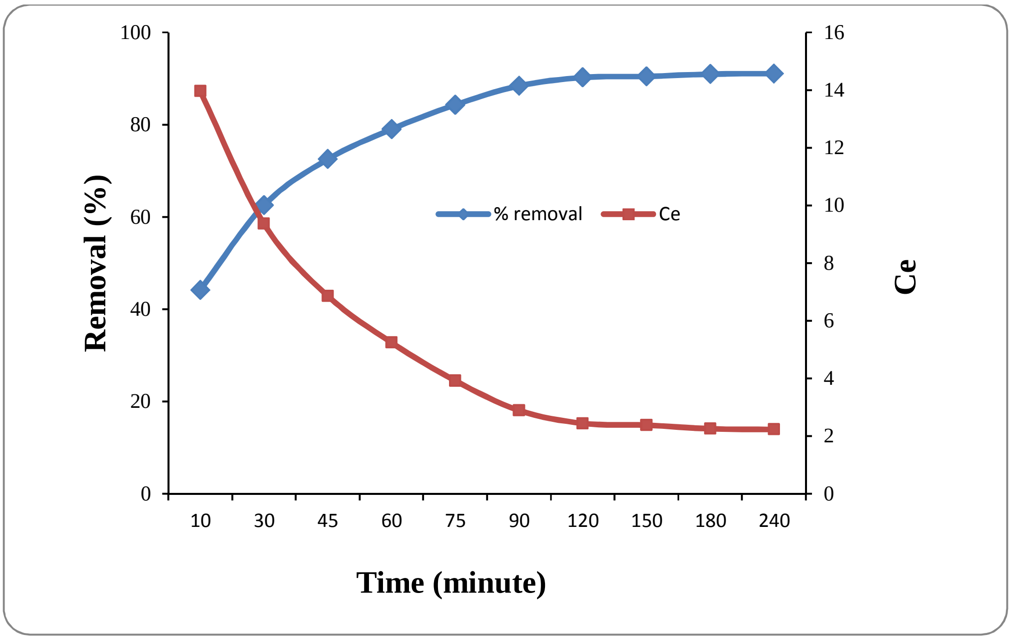


Figure 2. The effect of contact time on acid black 1 removal efficiency

3.3. The effect of pH

Figure 3 shows that the pH can influence on AB1 removal percentage. As it is observed an increase of pH leads to decreasing the dye removal efficiency. This indicated that maximum removal efficiency dye was observed in acidic condition and in pH =2.

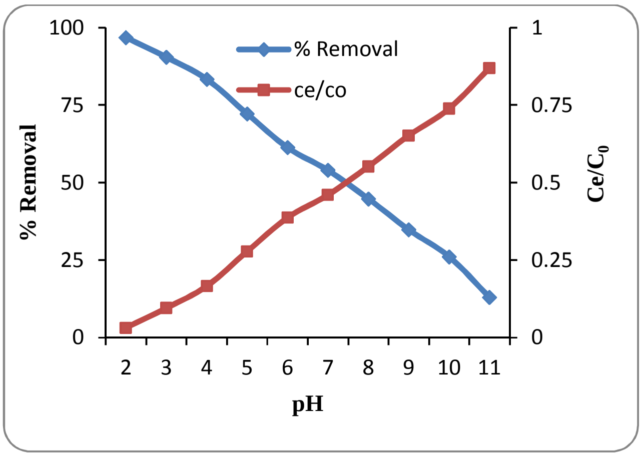


Figure 3. The effect of pH on acid black 1 removal efficiency

3.4. The effect of adsorbent dose

The adsorption efficiency increases by an increase in adsorbent dose up to 10 g/L. It reaches equilibrium after those doses. Although the adsorption efficiency increases by increasing in adsorbent dose, however the adsorption rate per unit mass of adsorbent (qe) decreases. The effect of adsorbent dose is presented in figure 4.

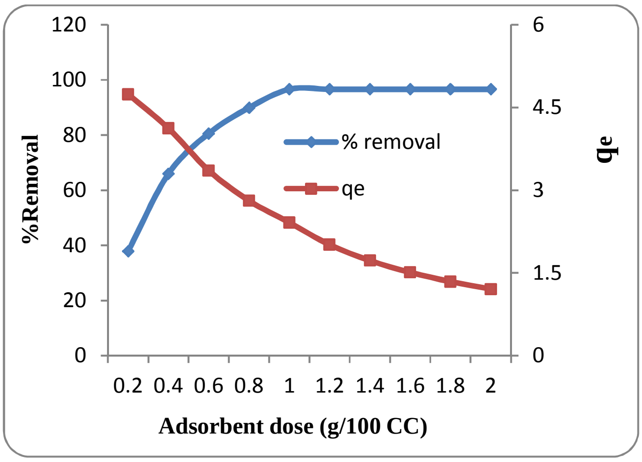


Figure 4. The effect of adsorbent dose on acid black 1 removal efficiency

3.5. The effect of initial dye concentration

The results show that the dye removal efficiency decreases by increasing dye concentration from 25 to 200 mg/L. the effect of initial dye concentration on removal efficiency is shown at figure 5. As shown in this figure, the dye removal percentage is 96% for dye concentration of 25 mg/L. It decreases to 30% for the concentration of 200 mg/L.

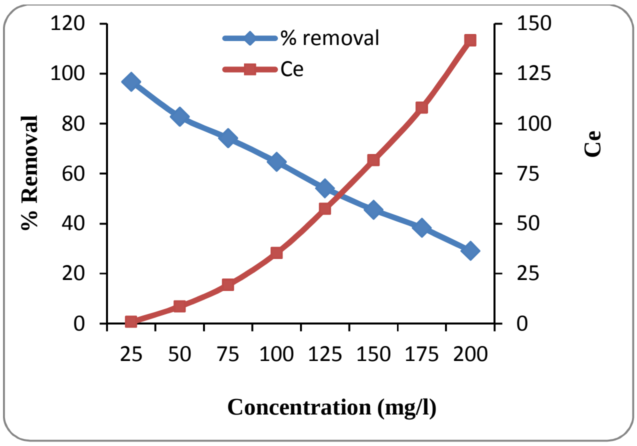


Figure 5. The effect of initial dye concentration on removal efficiency

3.6. Adsorption kinetics and isotherms

The results of isothermal and kinetics studies of dye adsorption are presented in figures 6 and 7. As can be observed, the equilibrium data were the best fitted on Langmuir isotherm and pseudo-second-order kinetic model.

4. Discussion

As it implied in previous studies, the absorbent specific surface area is an important parameter in adsorption efficiency. There is a direct relationship between the amount of surface area and dye removal efficiency. The adsorbent surface area of Azolla is 36 m^2/g, which it is greater than some other studied adsorbents (8, 15).

The results indicated that the AB1 removal efficiency increased with increasing of contact time. The greater contact between dye molecules and adsorbent surface is attributed as this event reasons which this agrees with many studies (15, 29).

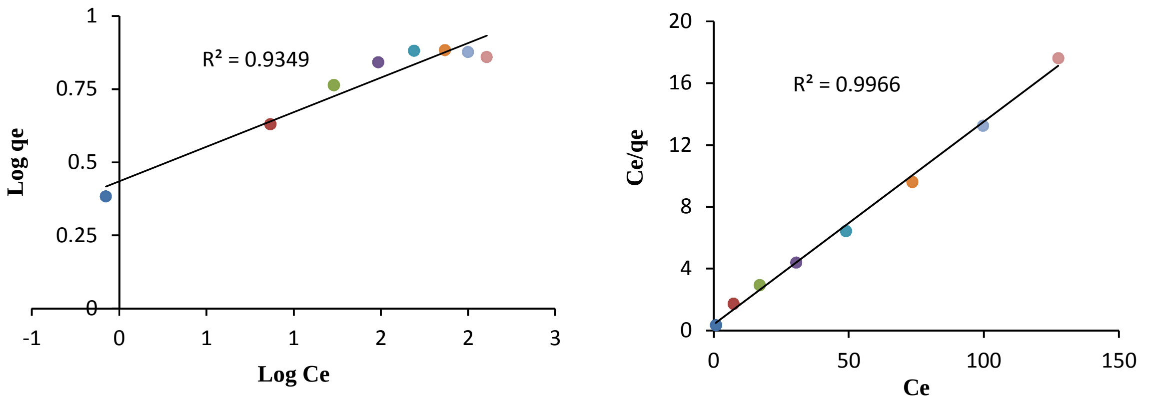


Figure 6. The isotherms model: (a) Freundlich (b) Langmuir

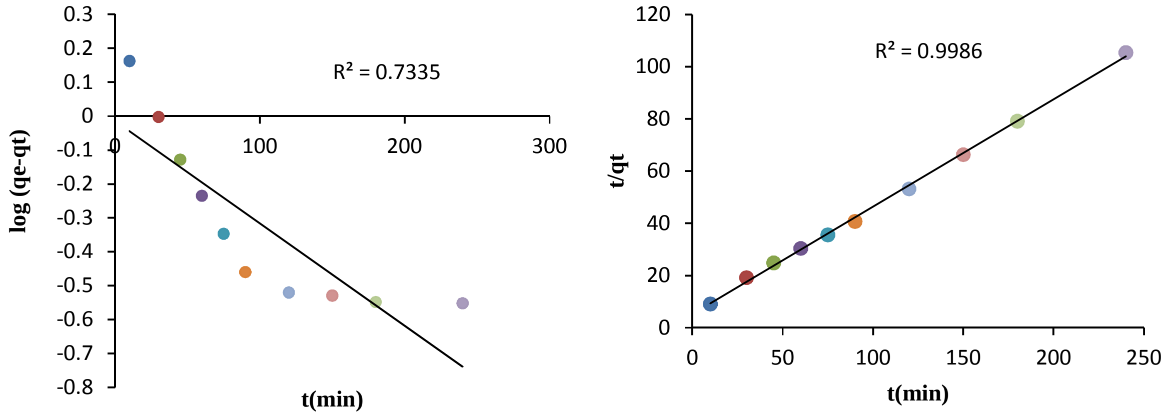


Figure 7. The kinetics model: (a) pseudo-first-order (b) pseudo-second-order

Also, it is observed that the adsorption process is rapidly at the beginning. However, it decreases and reaches equilibrium after 90 min which this can be described by the presence of the most active sites on the surface area of the adsorbent and the saturation of these sites by AB1 molecules with time. This is consistent with the Zazouli et al study on RR198 removal by Azolla (8). The pH is a significant parameter in adsorption process which it can affect on the adsorbent characteristics and dye chemistry (25). The highest AB1 removal efficiency is obtained in pH = 2 and it decreases with an increase in pH value. The results of this study are confirmed by several previous studies on dye removal. The electrostatic interaction between the surface of the adsorbent and the dye can attribute as the greater dye removal in acidic pH. Since the adsorbent surface is positive in acidic pH, therefore, the AB1 (an anionic dye) has better interaction with the adsorbent surface and the dye removal increases. The negative charge of adsorbent in alkali pH will reduce the anionic dye removal (30, 31). The adsorbent dose is another parameter that can influence the dye removal efficiency. As it mentioned, the dye removal increased with increasing the adsorbent dosage up to 10 mg/L which it can be due to the increasing the available adsorption sites for dye molecules; however the amount of adsorbed AB1 per unit mass of adsorbent (qe) decreased which it is observed in several studies (8, 15, 32). As it was observed the AB1 removal efficiency decreased from 96% to 30% for initial dye concentration of 25 and 200 mg/L, respectively. This indicates that there is an inverse relationship between initial dye concentration and dye removal percentage which it is agreed with the previous studies (33, 34). This can be due to that there is greater competition between the dye molecules to adsorb on limited active surface of the adsorbent with increasing the dye concentration (35). The kinetic studies indicated that the AB1 adsorption onto Azolla is better fitted on the pseudo-second-order kinetic (R^2= 0.9986) model than the pseudo-first-order model (R^2 = 0.7335). These results are similar to other studies on dye removal (36). Furthermore, the compression between the correlation coefficient of Langmuir and Freundlich indicated that the equilibrium data are better followed on Langmuir isotherm, which it is consistent with the conducted study by Zazouli et al (28).

The study indicated that the Azolla has significant ability in AB1 dye removal and can be used to treat the textile effluent. The studied parameter can affect on dye removal efficiency.

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