



## Batch Removal of Acid Blue 292 dye by Biosorption onto *Lemna minor*: *Equilibrium and Kinetic Studies*

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### ABSTRACT

**Background:** Recently, there has been a great concern about the consumption of dyes because of their toxicity, mutagenicity, carcinogenicity, and persistence in the aquatic environment. Therefore, the aim of this study was to determine the feasibility of using *Lemna minor* for Acid Blue 292 (AB292) dye removal from aqueous solution and to determine the optimal conditions.

**Methods:** This experimental study was conducted in the batch systems to investigate the effects of parameters such as contact time, initial concentration of dye, pH and *Lemna minor* biomass dose. Isotherms and kinetic studies of dye adsorption were performed using equilibrium data.

**Results:** According to the results, a maximum removal efficiency of 98.5% was obtained at pH of 3 and the contact time of 90 min; initial dye concentration 10 mg/L and adsorbent dose 3g/L. The adsorption data was best fitted to the Langmuir isotherm and pseudo-second order kinetic model.

**Conclusion:** The results showed that *Lemna minor* could be used as a cost-effective adsorbent for removing AB292 dye from textile wastewater efficiently.

## 1. Introduction

The textile industries are recognized as the main industry to use a great amount of water and synthetic dyes which ends in generating a high volume of colorful wastewater (1-3). It is stated that 1000000 kg/yr of dyes is discharged into the effluents by textile industries (4). The synthetic dyes are classified as anionic, cationic and nonionic (in which the acid replaces anionic dye group) (2). The toxicity and harmful impacts of the dyes have been confirmed by many studies conducted throughout the world (5). The dyes can

threaten the human health by their carcinogenic and mutagenic properties; also, the aquatic life can be influenced by the blocking of sunlight penetration and the reduction of oxygen in water bodies (6-8).

Since the textile dyes have complex aromatic structure, they are resistant against the conventional biological treatment methods indicating the necessity to use the effective and promising methods to remove these dyes (9-10).

The previous studies have indicated that the adsorption onto activated carbon is a reliable, inexpensive and significantly effective technique to remove the dyes; however, the high cost of activated carbon limits its use (11-14).

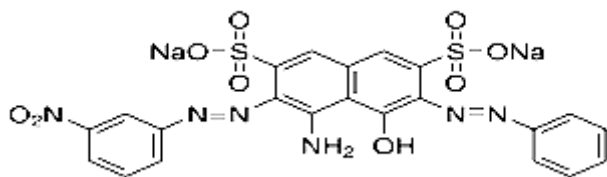
In the recent decades, various materials such as Azolla, fly ash, wheat straw, apple pomace, fungi, orange peels, soy meal hull, eggshell, and etchas have been applied to develop low-cost and effective adsorbents (15-17). *Lemna minor* is one of wide-spread aquatic plants, which is classified as duckweed species group, with special characteristics including rapid growth, high nutritional value, and high water purification capabilities, also used to remove the pollutants from water and wastewater. A number of studies have been conducted by the scientists to remove the heavy metals, dyes, etc by *Lemna minor* (18-20).

Therefore, the purpose of the present study was to assess *Lemna minor* capability to remove the AB292 dye. Also, the effects of several parameters including contact time, pH, adsorbent dose and initial dye concentration were investigated.

## 2. Materials and Methods

### 2.1. Chemicals and experiments

All chemicals used in this work were of GR grade obtained from Merck (Darmstadt, Germany). The chemical structure of Azo Dye Acid Blue 292 (molecular weight: 616.49 and Molecular Formula  $C_{22}H_{14}N_6Na_2O_9S_2$  and CAS Number: 5850-35-1) is shown in Fig. 1. The pH of the solution was adjusted by 0.1M  $H_2SO_4$  or NaOH. All experiments were conducted in batch mode in 250 mL conical flasks.



**Fig.1: Chemical structure of the used Acid blue 292.**

### 2.2. Preparation of adsorbent

The *Lemna minor* biomass was collected from the wetlands of Sari, Iran. It was sun dried and then crushed and sieved to 1-2 mm particle sizes. Then the biomass was treated with 0.1 M HCl for 5 hr, followed by washing with distilled water and drying (17). The prepared adsorbent was stored to use in experiments. The BET- $N_2$  method using an ASAP 2000 apparatus- based nitrogen adsorption-desorption isotherms at 77K was applied to determine the specific surface area of the resultant adsorbent. The surface morphology of adsorbent was observed with a Philips XL30 scanning electron microscope (SEM) before and the after adsorption process.

### 2.3. Sorption studies

Adsorption experiments were carried out by agitating 0.3 g of adsorbent with 100 ml of desired concentration of AB292 dye solution in a thermostated rotary shaker (ORBITEK, Chennai, India) at 200 rpm and 25°C in various contact times (10, 20, 30, 45, 60, 75, 90, 120, 150 and 180 min). Dye concentration was estimated by monitoring the absorbance at 632 nm using a UV-vis spectrophotometer (DR-5000). pH was measured using a pH meter (300 Hanna Instrument, USA). The samples were removed from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 4000 rpm for 10 min. The absorbance of supernatant solution was measured. The effect of pH on the adsorption of AB 292 dye was studied by conducting equilibrium sorption tests at different pH values (3-11) using 3 g of powdered biomass for 90 min.

The pH was adjusted by using dilute NaOH and HCl solutions. Effect of adsorbent dosage was studied with different adsorbent doses (0.5-5 g/L) and 100 ml of 100 mg/L AB 292 dye solutions at equilibrium time and pH 3. The experiments were carried out using 3 g of biomass for 90 min. Langmuir, Freundlich and Temkin isotherms were employed to study the adsorption capacity of the adsorbent. The amount of AB 292 dye adsorbed by

biomass was calculated from the differences between the amount added to the biomass and the dye content after adsorption using the following equation (21-23):

$$q_e = \frac{(C_0 - C_e) \times V}{M}$$

Where  $q_e$  is the dye uptake (mg/g),  $C_0$  and  $C_e$  are the initial and final dye concentrations in the solution respectively (mg/L),  $V$ , the solution volume (L) and  $M$  is the mass of biosorbent (g).

### 3. Results and Discussion

#### 3.1. Adsorption characterization

Figures 2a and b show the SEM images of adsorbent in both before and after use. The SEM images show the texture and porosity of adsorbent. The difference between the adsorbent surfaces can be concluded by the comparison of the images. Before the use of adsorbent, the porous surface of adsorbent was obvious, however, they are saturated and unclear after using the adsorption experiments. Also, the specific surface area was  $30 \text{ m}^2/\text{g}$  which was greater than the surface of adsorbents probably due to potent and effective adsorbent.

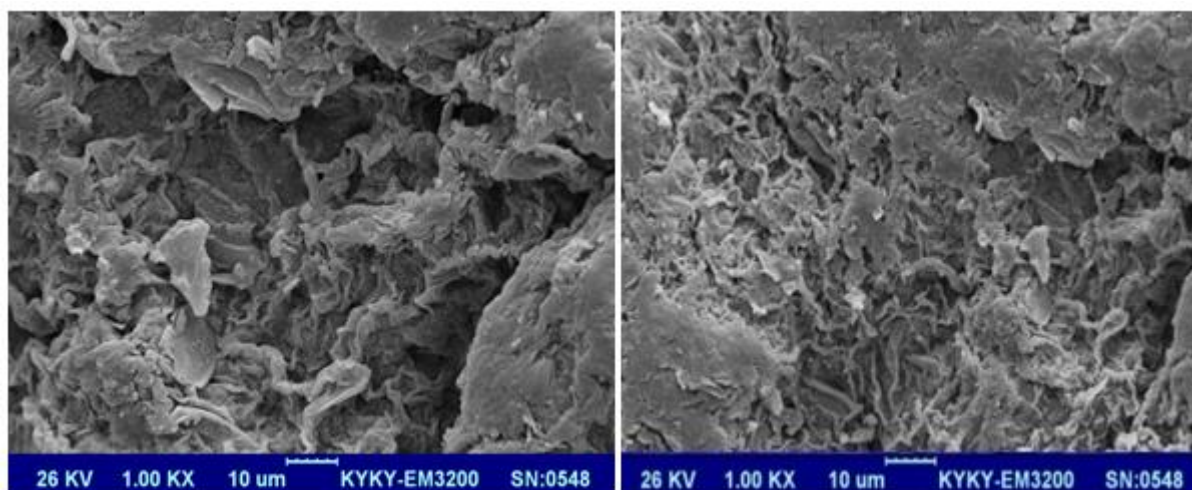
#### 3.2. Effect of pH

The effect of pH for the adsorption of AB292 dye onto *Lemna minor* is shown in Fig. 3. It can be seen that the adsorption of AB292 dye was pH-dependent. The results show that the amount of adsorbed dye onto *Lemna minor* decreases as the pH increases from 3 to 11.

#### 3.3. Effect of Contact Time and Initial Concentration of AB292

The experiments to study the effect of contact time were carried out in various concentrations of AB292 dye at constant value of pH=3, and the results are shown in Fig. 4. As seen in Fig. 4, the removal efficiency of AB292 increased with time until reaching an equilibrium constant value after 90 min for all concentrations.

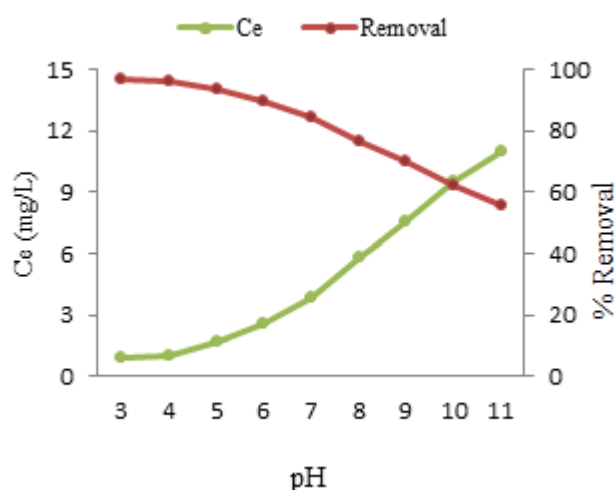
The percentage removal efficiency for AB292 dye decreased with increasing AB292 dye concentration in the aqueous solutions. Thus, in the concentration of 10 mg/L the highest adsorption percentage was observed and with increasing the concentration amount from 10 to 200 mg/L, adsorption percentage decreased from 98.9% to 74.4%.



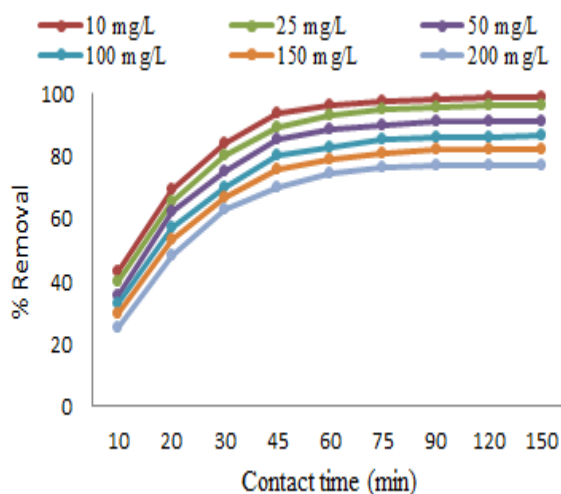
**Fig.2:** The SEM image of modified *Lemna minor* a: before use b: after used.

### 3.4. Effect of *Lemna minor* dosage on the adsorption capability

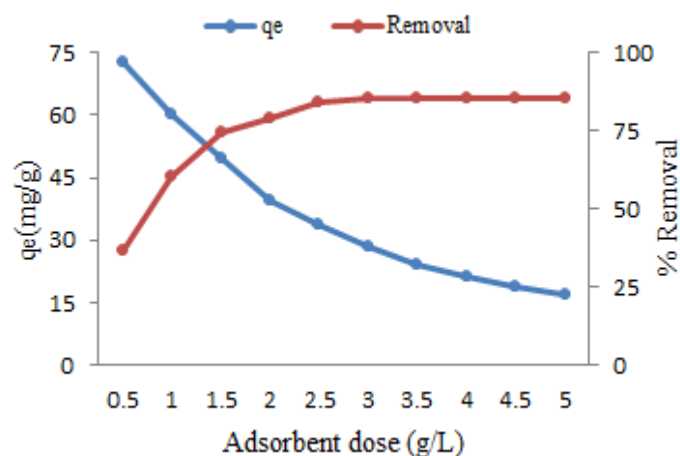
The effect of biomass dosage on removal rate of AB292 dye was investigated in different activated carbon doses (0.5-5 g/L), while other parameters were kept constant. As can be seen from Fig. 5, the adsorption capability and the adsorption rate dramatically increased with the amount of biomass used.



**Fig.3:** Effect of pH on AB292 dye removal efficiency ( $C_0=25$  mg/L, contact time= 75 min, adsorbent dose=3 g/L).



**Fig.4:** Effect of Contact time and initial dye concentration on AB292 dye removal efficiency (pH=3, adsorbent dose=3 g/L).



**Fig.5:** Effect of adsorbent dose on AB292 dye removal efficiency (contact time= 75min,  $C_0=100$  mg/L, pH=3).

### 3.5. Adsorption isotherm

The existence of adsorbate equilibrium between the liquid and solid phase is well described by adsorption isotherms. Experimental isotherm data were fitted on Langmuir, Freundlich, and Temkin adsorption isotherm models. The Langmuir isotherm can be expressed as (24, 25).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} K_L}$$

Where  $q_m$  is a constant related to adsorption capacity (mg/g) and  $K_L$  is Langmuir constant related to energy of adsorption (L/mg). The constants  $q_m$  and  $K_L$  can be calculated from the slope and intercept of the plot of  $C_e/q_e$  vs  $C_e$ .

The Langmuir plot of  $C_e/q_e$  vs  $C_e$  is shown in Fig. 5. The results calculated from the plot are given in Table 1. The Langmuir adsorption capacity was determined to be 29.25 mg/g. The essential characteristics of Langmuir isotherm can be expressed by dimensionless separation factor,  $RL$ .

The value of separation factor  $RL$  indicates the nature of the adsorption process as given below

(26, 27):

$$R_L = \frac{1}{1 + C_0 K_L}$$

$R_L > 1$  Unfavorable,  $R_L = 1$  Linear,  $0 < R_L < 1$  Favorable and  $R_L = 0$  Irreversible.

Where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration (mg/L). The  $R_L$  value was obtained to be 0.554 which was between 0 and 1 indicating the favorable adsorption process.

**Freundlich model** is the most popular model for a single solute system, based on the distribution of solute between the solid phase and aqueous phase at equilibrium. The Freundlich equation is expressed as (28, 29):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where  $K_F$  is the measure of adsorption capacity and  $n$  is the adsorption intensity:

A plot of  $\log q_e$  vs  $\log C_e$  gives a linear trace with a slope of  $1/n$  and intercept of  $\log K_F$ . The values of  $1/n$  and  $K_F$  are given in Table 1 (Fig not shown). When  $1/n$  is  $>1.0$ , the change in adsorbed dye concentration is greater than the change in the dye concentration in solution. The Temkin isotherm is applied in the following form (30, 31):

$$q_e = \frac{RT}{b} \ln(K_t) + \frac{RT}{b} \ln(C_e)$$

Where  $b$  is the Temkin constant related to heat of sorption (J/mg) and  $K_t$  the equilibrium binding constant corresponding to the maximum binding energy (L/g).

The Temkin constants  $K_t$  and  $b$  are calculated from the slopes and intercepts of  $q_e$  vs  $\ln C_e$  are given in Table 1 (Fig not shown). Out of three isotherm models studied for this adsorbent-adsorbate system, Langmuir model shows the best fit with a correlation coefficient of 0.995.

### 3.6. Kinetics of Adsorption

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption are controlled

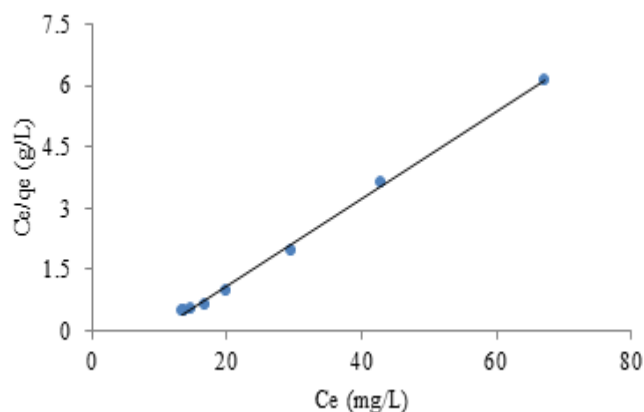


Fig.6: Langmuir isotherms ( $C_0=100$  mg/L,  $pH=3$ ).

by various factors like physical and/or chemical properties of adsorbent, ambient temperature, solution pH and nature of adsorbate. These kinetic models are useful for the design and optimization of effluent-treatment process. In order to investigate the mechanism of AB292 dye adsorption by biomass the following three kinetic models were considered.

### Pseudo first-order kinetic model

The pseudo first-order kinetic model was proposed by Lagergren. The integrated linear form of the model is (32, 33):

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

Where  $q_e$  is the amount of dye adsorbed at equilibrium (mg/g),  $q_t$  is the amount of dye adsorbed at time  $t$  (mg/g),  $K_1$  is the first-order rate constant (1/min) and  $t$  is time (min).

Hence, a linear trace is expected between the two parameters,  $\log (q_e - q_t)$  and  $t$ , provided that the adsorption follows the first order kinetics. The values of  $k_1$  and  $q_e$  can be determined from the slope and intercept.

The results of pseudo first-order plot for the adsorption of AB292 dye by biomass are given in Table 2 (Fig not shown). The calculated and



**Table 1: Isotherm parameters for AB292dye adsorption onto Lemna minor.**

Langmuir			Freundlich			Temkin		
R <sub>L</sub>	q <sub>max</sub> (mg/g)	R <sup>2</sup>	K <sub>F</sub> (mg/g)	n	R <sup>2</sup>	K <sub>t</sub> (L/g)	B	R <sup>2</sup>
0.554	29.25	0.998	0.784	2.94	0.894	0.811	9.47	0.822

experimental  $q_e$  values show a reasonable correlation in the case of pseudo first-order kinetics. Even though  $q_{ecal}$  (calculated value) and  $q_{exp}$  (experimental value) are closer, the  $R^2$  values suggest that the adsorption data fitted poorly to pseudo first-order kinetics. Hence, the adsorption of AB292 dye onto Lemna minor does not follow the pseudo first-order rate expression.

### Pseudo second-order kinetics

The adsorption may also be described by pseudo second-order kinetic model, if the adsorption does not follow the first order kinetics.

The linearized form of the pseudo second-order model is (34, 35):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where  $K_2$  is the second-order rate constant (g/mg min) and  $q_e$  is the equilibrium adsorption capacity (mg/g). A plot of  $t/q_t$  and  $t$  should give a linear relationship if the adsorption follows second order.  $q_e$  and  $K_2$  can be calculated from the slope and intercept of the plot.

Fig. 7a shows the pseudo second-order plot for the adsorption of AB292dye by biomass at various initial dye concentrations and the results are given in Table 2. The pseudo second-order rate constant decreases from 0.0045 to 0.0014 (g/mg min) with the increases in initial dye concentration. The correlation coefficient  $R^2$  ranges from 0.995 to 0.999, which is higher than pseudo first-order values. From the results, it can be suggested that pseudo second-order describes the adsorption of AB292dye much better than pseudo first-order model.

### Intra particle diffusion model

In the batch systems of adsorption process, initial adsorption occurs on the surface of the adsorbent. In addition, there is a possibility of the adsorbate to diffuse into the interior pores of the adsorbent. Weber and Morris suggested the following kinetic model to explore if the adsorption is intra-particle diffusion or not. According to this theory (36, 37):

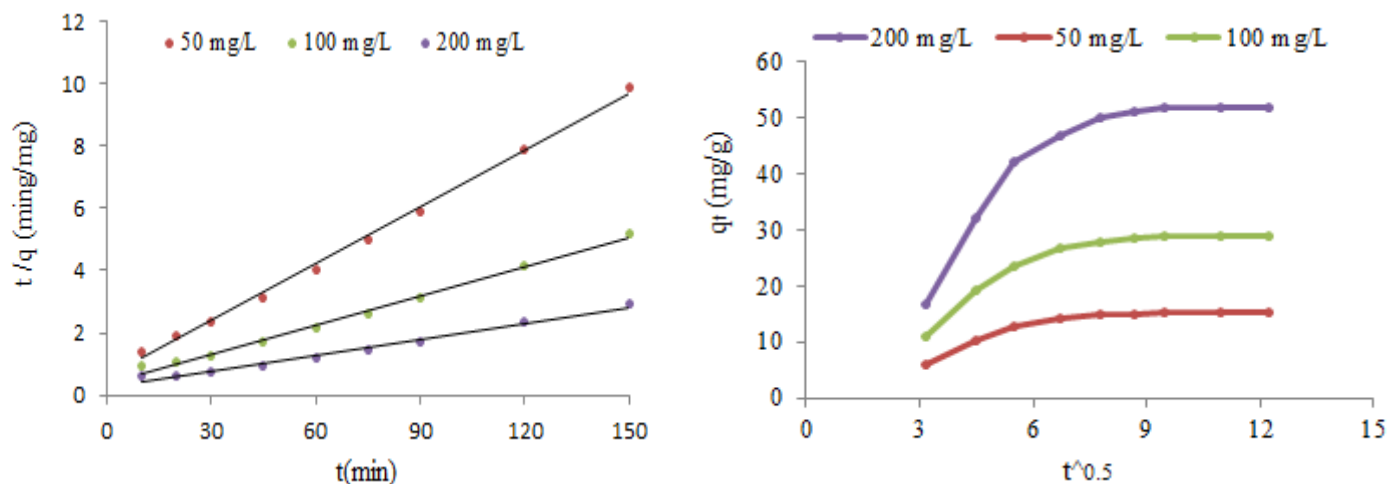
$$q_t = K_d \cdot t^{1/2}$$

Where  $K_d$  is the intra particle diffusion rate constant and is calculated by plotting  $q_t$  against  $t^{1/2}$  (Fig. 7b) and the results are given in Table 2. The linear portion of the plot for wide ranges of contact time between adsorbent and adsorbate does not pass through the origin. This deviation from the origin or near saturation may be due to the variation of mass transfer in the initial and final stages of adsorption.

In the process of absorption, pH plays a key role in absorptive capacity and effects the adsorbent surface features (functional groups on the active sites), degree of ionization and removal efficiency.

The results show that the amount of adsorbed dye onto Lemna minor decreases as the pH increases from 3 to 11. This situation can be attributed to the surface charge of the adsorbent. Lemna minor has negatively charged adsorption sites, but it is positively charged at low pH values.

Therefore, the electrostatic interactions between negatively charged  $-SO_3^-$  groups in the dye molecule and the positively charged adsorbent increase (28-40). As a result, the amount of dye molecules onto the modified bentonite increases at lower pH values.



**Fig.7: Adsorption kinetics of AB292 dye on Lemna minor: a) pseudo-second-order b) intra-particle diffusion.**

**Table 2: Kinetic parameters for the adsorption of AB292 dye onto Lemna minor biomass in various concentrations.**

C <sub>0</sub> (mg/L)	q <sub>exp</sub> (mg/g)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
		K <sub>1</sub>	q <sub>e</sub>	R <sup>2</sup>	K <sub>2</sub>	q <sub>e</sub>	R <sup>2</sup>	k	C	R <sup>2</sup>
50	15.18	0.0445	11.29	0.825	0.0045	14.48	0.995	0.171	1.479	0.794
100	28.86	0.0563	23.14	0.841	0.0027	27.86	0.998	0.184	2.728	0.831
200	51.22	0.0712	45.96	0.869	0.0014	50.12	0.999	0.213	3.449	0.852

Adsorption process of AB292 dye consists of two stages. At the first stage, rapid initial adsorption was observed in 45 min and at the second stage, adsorption process was slow and performed during 45-90 min. At this stage, the removal rate was slower than the first stage.

Obviously, increasing the time up to 90 min had no significant effect on removal rate. This effect is due to the availability of the initial abundant number of active sites on the sorbents at the beginning of the process, whereas, with the gradual increase of time, these sites are occupied by AB292 dye molecules and the adsorption process has become less effective with increasing time (41- 43).

As in Fig. 4 was seen, by increasing the initial concentration of AB292 dye in aqueous solution, removal percentage was decreased. At a constant Lemna minor biomass dose, the decrease in the

adsorption percentage was seen which is probably due to the saturation of the active sites on the biomass surface at higher AB292 dye concentrations (44, 45). On the other hand, by increasing the initial AB292 dye concentration, the actual amount of AB292 dye adsorbed per unit mass of the biomass was increased. The higher initial concentration of AB292 dye provides an important driving force to overcome the mass transfer resistance for AB292 dye transfer between the solution and the surface of the biomass.

Similar results were observed by Azarpira (2016) who investigated the effect of initial concentration on removal of Acid Orange 7 from aqueous solution by *Cyperus rotundus* biomass and indicated that adsorption decreases with increasing the initial concentration of metals (42).

The adsorbent dose is another important parameter because it has a direct relationship with

the uptake capacity of an adsorbent for a given concentration of dye under the optimum conditions. As can be observed from Figure 5, removal efficiency was increased by increasing the amount of Lemna minor biomass from 0.5 to 5 g. This is mainly due to the greater available sites or surface area for the adsorption at the higher amount of the Lemna minor biomass (45, 46). A similar phenomenon has also been shown in the adsorption of Acid violet 17 from water with Orange peel (38).

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species (36). The Langmuir model was originally developed to describe the adsorption of gas onto solid surface. It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous (38). The Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption (39). The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich expression. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions (36). The correlation coefficients ( $R^2$ ) for Langmuir, Freundlich, and Temkin models were 0.998, 0.894 and 0.822 respectively. The proper agreement between the adsorption data and Langmuir model implies that the adsorption of AB292 dye onto the Lemna minor biomass occurred as a single monolayer.

#### 4. Conclusion

The prediction of adsorption rate gives crucial information for designing sustainable batch adsorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch processes (38). In order to evaluate the kinetic mechanism

that controls the adsorption process, the experimental data was analyzed using pseudo-first-order, pseudo-second-order models and Intra particle diffusion. The correlation coefficients ( $R^2$ ) for pseudo-second-order model are all higher than for the pseudo-first-order model and Intra particle diffusion and the experimental data fit the pseudo-second-order model better than the pseudo-first-order model and Intra particle diffusion. Also,  $q_e$  value agreed with the calculated values ( $q_{eexp}$ ), indicating a good fit of the adsorption process to this model. The results indicate that chemical adsorption might be the rate-limiting step. The results obtained were similar and supported by other researchers (16-18).

This study focused on the biosorption of AB292 dye onto Lemna minor biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time and initial dye concentration were found to be effective on the biosorption efficiency of AB292 dye. The kinetic data signified that the biosorption of AB292 dye onto Lemna minor followed the pseudo-second-order kinetic model. It could be finally concluded that Lemna minor biomass, an inexpensive and easily available adsorbent, can be an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

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