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Research article/Araştırma makalesi

Removal of Acid Blue 294 (AB294) dye from aqueous solutions by using lichen *Umbilicaria decussata* biomass

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Abstract

This research presents the investigation of binding behaviour of the lichen *Umbilicaria decussata* biomass toward AB294 in aqueous solutions. The effects of various variables such as pH, initial AB294 concentration, time and temperature on the AB294 binding were tested. The Langmuir and Freundlich binding isotherm models were applied for the characterization of interactions between AB294 and lichen *Umbilicaria decussata* biomass. The obtained results showed that AB294 binding to the lichen *Umbilicaria decussata* biomass is well described by the Langmuir binding isotherm. The Langmuir constant K_L for AB294 was calculated as 0.337 Lmg^{-1}. The maximum binding capacity of the lichen bimass toward AB294 was calculated to be as 25.6 mgg^{-1} biomass at pH 1.0 within 2 h. The pseudo-first-order pseudo-second-order kinetic and intraparticle diffusion models were also used to investigate the AB294 binding mechanism. The mechanism of AB294 binding to the lichen *Umbilicaria decussata* biomass is well suited to the pseudo-second-order kinetic model. The obtained results showed that lichens are potentially efficient biomaterials for the removal of dye compounds from contaminated water samples.

Key words: lichens; acid blue 294; umbilicaria; biomass; binding isotherms

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Liken *Umbilicaria decussate* ile sulu çözeltilerden Asit Mavisi 294 (AB294) uzaklaştırılması

Özet

Bu çalışmada liken *Umbilicaria decussata* biyokütlesinin sulu çözeltilerde AB294'e karşı bağlanma davranışı araştırılmıştır. AB294 bağlanmasına pH, başlangıç AB294 konsantrasyonu, zaman ve sıcaklığın etkisi incelenmiştir. Liken *Umbilicaria decussata* biyokütlesi ve AB294 arasındaki etkileşimin karakterizasyonu Langmuir ve Freundlich bağlanma izotermleri kullanılarak gerçekleştirilmiştir. Elde edilen sonuçlar liken *Umbilicaria decussata* biyokütlesi ve AB294 arasındaki etkileşimin Langmuir bağlanma izotermine uyduğunu göstermiştir. AB294 için Langmuir sabiti 25.6 mgg^{-1}biyokütle olarak hesaplanmıştır. Ayrıca, AB294 bağlanma mekanizmasının araştırılması amacıyla yalancı birinci-derece, yalancı ikinci-derece kinetik ve intra-partikül difüzyon modelleri de uygulanmıştır. Liken *Umbilicaria decussata* biyokütlesine AB294 bağlanmasının yalancı ikinci-derece kinetik modele uyduğu tespit edilmiştir. Elde edilen sonuçlar kontamine su numunelerinden boyar bileşiklerin uzaklaştırılmasında likenlerin potansiyel etkili biyomateryaller olduğunu göstermiştir.

Anahtar kelimeler: Likenler; Asit Mavisi 294; Umbilicaria; Biyokütle; Bağlanma izotermleri

1. Introduction

Dyes such as Acid Blue 294 are commonly used in different application areas such as textile industry, rubber industry, paper industry and plastics industry (Hunger, 2003; Kusic et al., 2013). Wastes contaminated with dye pigments and toxic compounds lead to environmental pollution which is a serious problem. Thus, these contaminants should be efficiently removed from the wastes. It is a challenging process in the industry and cheap, enviromentally-friendly and efficient approaches are required for this purpose.

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Removal of dye compounds from contaminated water involves biological and chemical processes. Various microorganisms such as fungi, bacteria, algea etc are commonly used in biological processes (Tan et al., 2013; Gül, 2013; Kelewou et. al., 2013). This approach is cheap and environmentally friendly. However, it is technically ineffective and challenging (Szpyrkowicz et al., 2001). Traditional adsorbents such as activated carbon are commonly used for the removal of dye (Hazzaa and Hussein, 2015; Aguiar et. al., 2016; Silvia et. al., 2016; Regti et. al., 2017) due to its high binding capacity toward target compound. But, it has also some limitations such as high cost and regeneration problems compared to other cheap natural materials such as clays and lichens (Hsu et. al., 1997; Nassar et al., 1991; Rytwo et. al., 2000; Kulkarni et. al., 2014; Ozcan et. al., 2005).

Lichens are symbiotic organisms consisting of a fungal partner and at least one photosynthetic partner (algea or cyanobacteria) (Sanders, 2001; Ahmadjian, 1993; Lutzoni and Miadlikowska, 2009). It has been reported that more than 20,000 species of lichens are known in the World (Feuerer and Hawksworth, 2007). Lichens exhibit biosorption behavior toward heavy metals, dyes etc. and their applications for the removal of these environmental pollutants have been reported in the literature Uluözlü et al. (Uluözlü et. al., 2010) used lichen *Physcia tribacia* for the biosorption of Sb(III). They obtained 81.1 mgg^{-1} biosorption capacity within 30 min. In another study performed by Altınışık and co-workers (Altınışık et. al., 2010), malachite green biosorption from aqueous solutions were carried out by using lichen *Luffa cylindrica*. In their study, maximum biosorption capacity of the lichen *Luffa cylindrica* was 29.4 mgg^{-1} at 34.8 ^{0}C. Kulkarni et al.,(Kulkarni et. al., 2014) used lichen *Permelia perlata* for the removal of textile dye Red 24 from aqueous solutions. The obtained results showed that 250 pm dye was efficiently removed at pH 8.0. In another study, Haas and his colleagues used lichen *Peltigera membranacea* for uranium biosorption (Haas et. al., 2010). They removed 42.0 $mgmL^{-1}$ uranium at pH 4.5 for 24 h. Tay et al., (Tay et. al., 2009) used lichen *Ramalina frexinea* for the removal of cadmium ions from aqueous solutions. The maximum biosorption capacity of the lichen *Ramalina frexinea* was found to be as 7.0 $mgmL^{-1}$ at pH 6.0.

In this work, the efficient removal of AB294 from aqueous solutions by using lichen *Umbilicaria decussata* biomass was investigated. For this purpose, the experiments were performed to evaluate the effects of different factors such as pH, initial AB294 concentration, time and temperature on the AB294 binding. The Langmuir and Freundlich binding isotherm models were applied for the characterization of interactions between AB294 and lichen *Umbilicaria decussata* biomass. The pseudo-first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were also used to investigate the binding behaviour of the lichen *Umbilicaria decussata* biomass toward AB294 in details.

2. Materials and methods

2.1. Materials

The biomass of lichen *Umbilicaria decussata* was provided from TEMA Forest, Eskişehir, Turkey. Collected samples were stored at the Herbarium of Biology Department, Anadolu University, Eskişehir. The lichen biomass was washed with deionized H_2O several times. Then it was allowed to dry at 60 ºC for 20 h. Finally, the dried lichen bimass was ground and sieved into the different particle sizes (0-75, 75-125, 125-250 and 250-500 μm). The lichen biomass with 125-250 μm particle size was used for all AB294 binding experiments. The picture of the *Umbilicaria decussata* is given in Figure 1.

Figure 1. The picture of the lichen *Umbilicaria decussata*

2.2. Instrumentation

An Orion 420A pH meter was used to measure pH values of the prepared solutions. All spectrophotometric analyses were performed by using a Shimadzu UV-2450 spectrophotometer.

2.3. AB294 binding onto the lichen Umbilicaria decussata biomass

The studies for AB294 binding were performed in batch-mode. For this purpose, 100 mg of lichen *Umbilicaria decussata* biomass was put into glass beaker. Then, 10 mL of 50 ppm AB294 in pH 1.0 was added and the solutions

were stirred for 4 h. The binding of AB294 to the lichen *Umbilicaria decussata* biomass was evaluated by measuring the absorbance of AB294 at 605 nm.

To investigate the pH effect on AB294 binding to the lichen *Umbilicaria decussata* biomass, 10 mL of 50 ppm AB294 at various pH values in the range of 1.0 to 8.0 was added to 100 mg of lichen *Umbilicaria decussata* biomass and the solution was stirred for 4 h. Then, spectrophotometric analysis of 2 mL of each sample was done.

To test the effect of initial AB294 concentration on AB294 binding to the lichen *Umbilicaria decussata* biomass, 10 mL of different concentrations of AB294 in pH 1.0 were prepared and added to 100 mg of lichen *Umbilicaria decussata* biomass. The AB294 solutions were then stirred for 4 h and analysis of 2 mL aliquots of each sample were performed by UV-VIS spectrophotometer.

The experiments for the effect of temperature and time on AB294 binding to the lichen *Umbilicaria decussata* biomass were also carried out. Firstly, 10 mL of 50 ppm AB294 in pH 1.0 was added to 100 mg of lichen *Umbilicaria decussata* biomass in a glass baker. Then, of AB294 solutions in pH 1.0 were allowed to stirr for 4 h and 2 mL of each sample was taken a different interaction time in the range from 5 min to 240 min and analyzed at 605 nm. On the other hand, different temperature values in the range between 10°C and 40°C were used to obtain optimum temperature on AB294 binding.

3. Results

3.1. Effect of pH on AB294 binding

pH is a crucial paramater that controls the binding of target compound onto biomass. The experiments for the AB294 binding onto the lichen *Umbilicaria decussata* biomass were carried out in a pH range of 1.0 and 8.0. Figure 2 shows the effect of pH on AB294 binding onto the lichen *Umbilicaria decussata* biomass. As seen from the figure, maximum AB294 binding was achieved at pH 1.0. This could be explained by the electrostatic interactions between AB294 which is negatively charged and positively charged binding groups of the *Umbilicaria decussata* biomass surface. At more acidic pH values, electrostatic interactions increase and this lead to an increase in AB294 binding onto the lichen *Umbilicaria decussata* biomass.

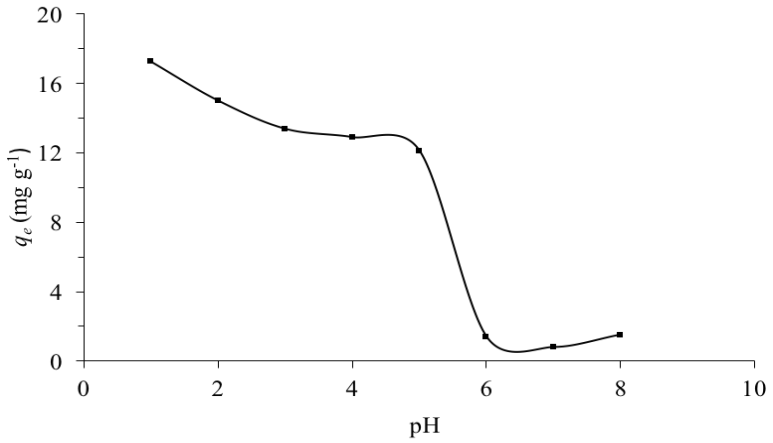

Figure 2. The effect of pH on AB294 binding onto the lichen *Umbilicaria decussata* biomass (C_o=50 ppm, m_{lichen}=100 mg, t=240 min, V=10 ml)

3.2. Effect of initial AB294 concentration on binding

Figure 3 shows the initial AB294 concentration effect on AB294 binding onto the lichen *Umbilicaria decussata* biomass. As seen from the Figure 3, AB294 binding increased by increasing AB294 concentration (10–300 ppm). At 250 ppm AB294 which is saturation point, all binding sites of lichen *Umbilicaria decussata* biomass were occupied with AB294. After 250 ppm concentration value, binding capacity of the lichen *Umbilicaria decussata* biomass towards AB294 was the same value for higher concentrations of AB294. The maximum AB294 binding of the *Umbilicaria decussata* biomass was calculated to be as 25.6 mgg^{-1} biomass.

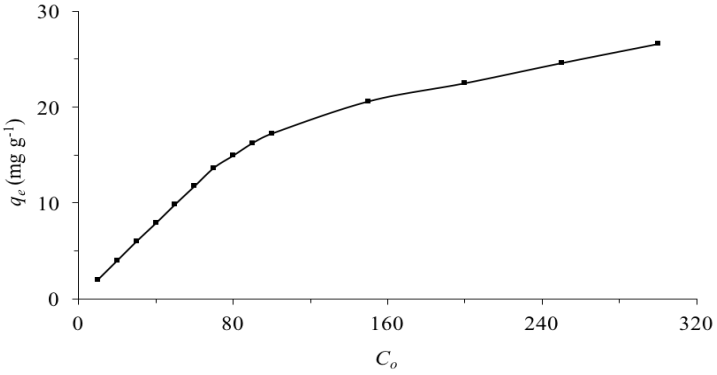

Figure 3. The effect of initial AB294 concentration on AB294 binding onto the lichen *Umbilicaria decussata* biomass (m_{lichen}=100 mg, t=240 min, V=10 ml, pH 1.0)

3.3. Effect of time on AB294 binding

The binding kinetics for AB294 was performed to investigate how the binding capability of the lichen *Umbilicaria decussata* toward AB294 changes over time. The AB294 binding studies were performed using 50 ppm AB294. The obtained results from these studies were given in Figure 4. The results showed that binding capacity of the lichen *Umbilicaria decussata* toward AB294 increased until the value at 120 min where the maximum binding was obtained. After 120 min, binding process reached equilibrium.

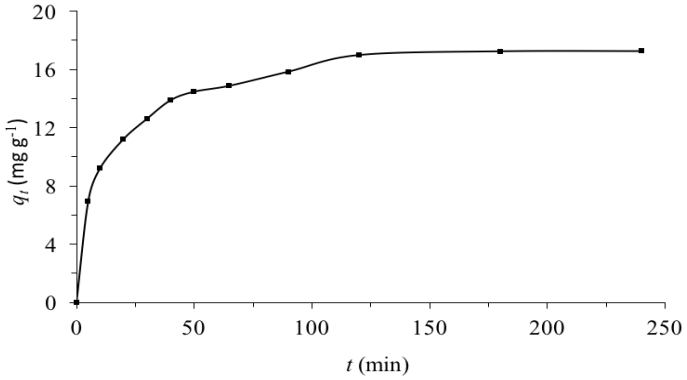

Figure 4. The effect of contact time on AB294 binding onto the lichen *Umbilicaria decussata* biomass (C_o=50 ppm, m_{lichen}=100 mg, V=10 ml, pH 1.0)

3.4. Effect of temperature on AB294 binding

The effect of temperature on AB294 binding to the lichen *Umbilicaria decussata* biomass is shown in Figure 5. As can be seen from the figure, AB294 binding slightly increased with the temperature until 20°C. But, there were no remarkable changes in the binding capacity of the *Umbilicaria decussata* biomass toward AB294 at 30°C and 40°C.

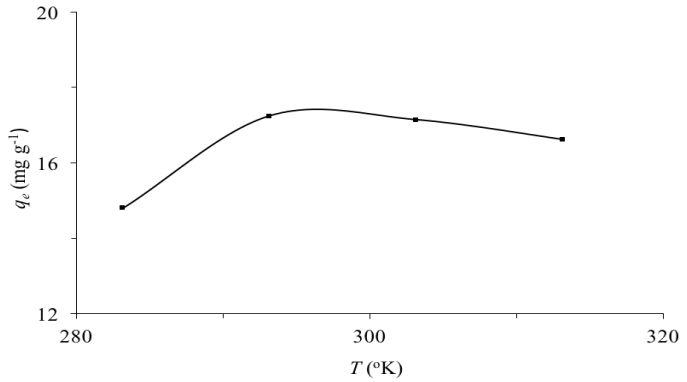

Figure 5. The effect of temperature on AB294 binding onto the lichen *Umbilicaria decussata* biomass (C_o=50 ppm, $_{lichen}$=100 mg, t=240 min, V=10 ml, pH 1.0)

3.5. Binding isotherms

For the characterization of interactions between AB294 and lichen *Umbilicaria decussata* biomass, binding isotherm models such as Langmuir and Freundlich were used. In the Langmuir isotherm (Langmuir, 1918), binding data can be obtained using the equation 1. This binding isotherm model indicates the monolayer binding onto the adsorbent surface having identical binding sites for the target compound.

$$\frac{C_e}{q_m} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad (1)$$

where q_m **(mgg^{-1})** and C_e **(mgL^{-1})** represent the AB294 amount onto the lichen *Umbilicaria decussata* biomass (per gram) any time and the unbound AB294 concentration at equilibrium, respectively. K_L **(Lmg^{-1})** represents the measure of the binding process intensity. q_{max} **(mgg^{-1})** is the maximum AB294 amount bound to the lichen *Umbilicaria decussata* biomass. Figure 6 shows the Langmuir binding isotherm for AB294 binding onto the lichen *Umbilicaria decussata* biomass.

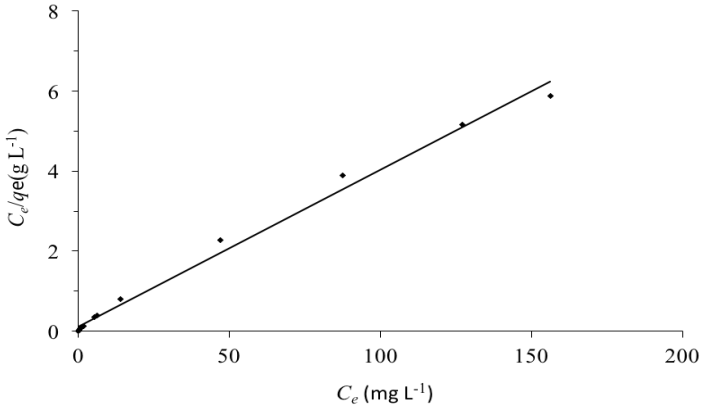

Figure 6. The Langmuir binding isotherm for AB294 binding onto the lichen *Umbilicaria decussata* biomass

The other binding isotherm model Freundlich (Freundlich, 1906) is an empirical equation and expressed in the following:

$$\log q_m = \log K_F + \frac{1}{n} \log C_e \qquad (2)$$

Where ***Ce*** is the AB294 concentration in equilibrium (mgL^{-1}) K_F represents the Freundlich constant and ***n*** represents the Freundlich exponent. **1/n** is a measure of heterogeneity of the binding sites of the lichen *Umbilicaria decussata* biomass ranging between 0 and 1. When this value gets closer to 0, heterogeneity increases. he Freundlich binding isotherm for AB294 binding to the lichen *Umbilicaria decussata* biomass is shown in Figure 7. The obtained results from Langmuir and Freundlich binding isotherms showed that AB294 binding to the lichen *Umbilicaria decussata* biomass is well suited the Langmuir binding isotherm. The Langmuir constant K_L for AB294 was calculated as 0.337 Lmg^{-1}.

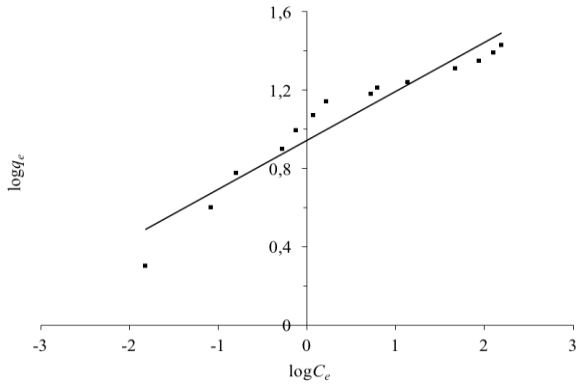

Figure 7. The Freundlich binding isotherm for AB294 binding onto the lichen *Umbilicaria decussata* biomass

Table 1 shows the parameters obtained from the Langmuir and Freundlich binding isotherms for AB294 binding to lichen *Umbilicaria decussata* biomass.

Table 1. Parameters for the Langmuir and Freundlich binding isotherms for AB294 binding to lichen *Umbilicaria decussata* biomass

Langmuir Equation	
q_{max} (mg/g)	25.28
K_L (L/mg)	0.337
R^2	0.992
Freundlich Equation	
K_F (L/mg)	8.77
n	4.0
R^2	0.921

3.6. Binding Kinetics

Binding kinetics is very important to obtain more information abaout the mechanisms of binding and rate-controlling steps in the binding process. For this purpose, the pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to explore binding mechanism of AB294 binding to the lichen *Umbilicaria decussata* biomass (Figure 8 and Figure 9). The pseudo-first-order kinetic model is described by the equation 3:

$$\ln (q_1 - q_t) = \ln q_1 - k_1 t \qquad (3)$$

Where q_1 (mg/g) is the amount of AB294 bound to the lichen *Umbilicaria decussata* biomass at equilibrium and q_t (mg/g) is the amount of AB294 bound to the lichen *Umbilicaria decussata* biomass at time t (min), and k_1 (min^{-1}) represents the rate constant of first-order binding.

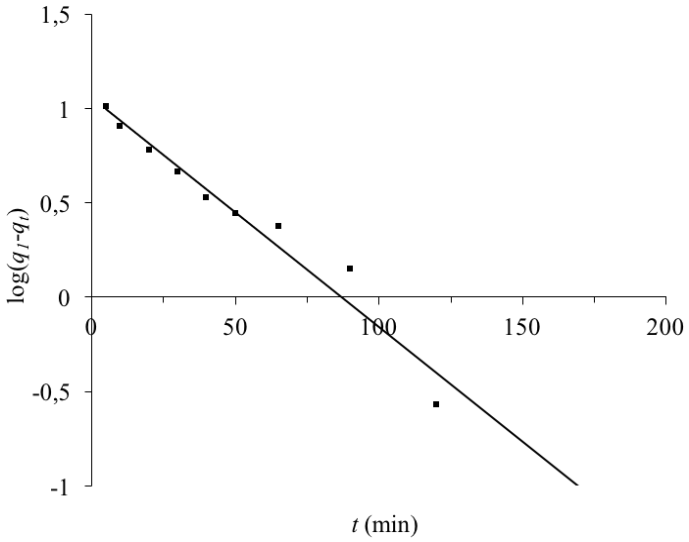

Figure 8. Pseudo-first-order kinetic plot for AB294 binding onto the lichen *Umbilicaria decussata* biomass

The pseudo-second-order kinetic model is described by the equation 4.

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \qquad (4)$$

If the binding process is well described by the pseudo-second-order kinetic model, a straight line is obtained by plotting t/q_t versus t and q_2 and k_2 can be calculated using the slope and intercept of the plot, respectively.

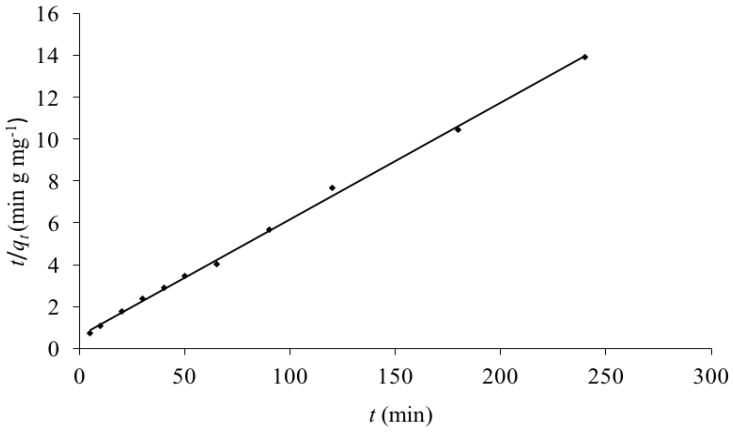

Figure 9. Pseudo-second-order kinetic plot for AB294 binding onto the lichen *Umbilicaria decussata* biomass

The pseudo-first-order and pseudo-second-order kinetic models can not be used for the investigation of diffusion mechanism. Therefore, the obtained data should be analyzed by another model. The intraparticle diffusion model proposed by Weber and Morris (Weber and Morris, 1963) is used for this purpose. In this model, intra-particle diffusion is calculated by using the following equation:

$$q_t = k_{id} t^{0.5} \qquad (5)$$

Where ***qt*** (mg/g) is the AB294 amount bound to the lichen *Umbilicaria decussata* biomass at time ***t*** (min) and k_{id} (mg/g $min^{0.5}$) is the rate constant for the intraparticle diffusion. Figure 11 shows the Intraparticle diffusion plot for the biosorption of AB 294 onto *Umbilicaria decussata*.

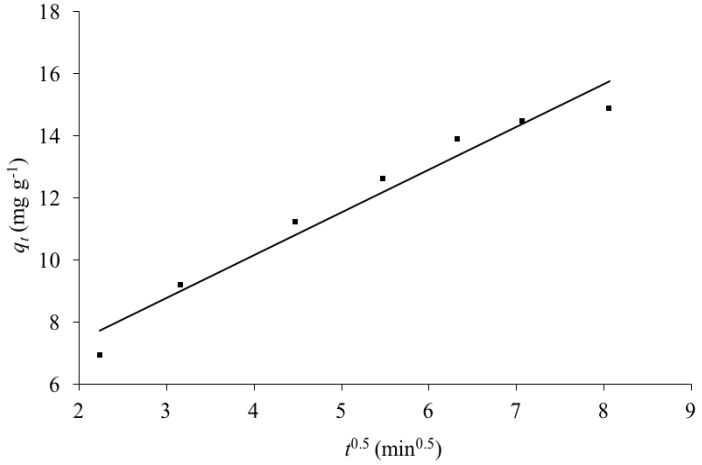

Figure 10. Intraparticle diffusion plot for the AB294 binding onto the lichen *Umbilicaria decussata* biomass

The pseudo-first order, second-order and intraparticle diffusion kinetic parameters for AB294 binding to the lichen *Umbilicaria decussata* biomass are shown in Table 2. As seen from the data in the table, biosorption of AB 294 onto *Umbilicaria decussata* is well suited to the pseudo-second order kinetic model.

4. Conclusions and discussion

In this study, binding behavior of the lichen *Umbilicaria decussata* biomass toward AB294 in aqueous solutions was investigated. The obtained results showed that efficient removal of AB294 from aqueous solutions by using *Umbilicaria decussata* biomass depends on various paramaters such as pH, initial AB294 concentration and interaction time. The binding experiments showed that AB294 binding capacity of the lichen *Umbilicaria decussata* biomass is 25.6 mgg^{-1} biomass. The results obtained from the studies of binding kinetics and binding isotherms showed that the mechanism of AB294 binding to the lichen *Umbilicaria decussata* biomass is well described by the pseudo-second-order kinetic model and Langmuir binding isotherm.

Table 2. Kinetic parameters obtained from the pseudo-first-order, pseudo-second-order and intra-particle diffusion models for AB294 binding to lichen *Umbilicaria decussata* biomass

Pseudo-first-order	
k_1 (1/min)	12.2×10^{-3}
q_1 (mg/g)	11.43
R_1^2	0.956
Pseudo-second-order	
k_2 (g/(mg.min))	5.06×10^{-3}
q_2 (mgg^{-1})	17.99
R_2^2	0.998
Intraparticle diffusion	
k_p ($mg.g.min^{-1/2}$)	1.377
C	4.64
R_p^2	0.961

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