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Biosorption of C.I. Direct Blue 199 from aqueous solution by nonviable *Aspergillus niger*

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ABSTRACT

The capacity and mechanism with which nonviable *Aspergillus niger* removed the textile dye, C.I. Direct Blue 199, from aqueous solution was investigated using different parameters, such as initial dye concentration, pH and temperature. In batch experiments, the biosorption capacity increased with decrease in pH, and the maximum dye uptake capacity of the biosorbent was 29.96 mg g^{-1} at 400 mg L^{-1} dye concentration and 45 °C. The Langmuir and Freundlich models were able to describe the biosorption equilibrium of C.I. Direct Blue 199 onto the fungal biomass. Biosorption followed a pseudo-second order kinetic model with high correlation coefficients ($r^2 > 0.99$). Thermodynamic studies revealed that the biosorption process was successful, spontaneous and endothermic in nature.

1. Introduction

The discharge of dye wastewater can adversely affect the aquatic environment by impeding light penetration. Moreover, some dyes (as well as their breakdown products) are highly toxic and potentially carcinogenic, mutagenic or allergenic to aquatic life [1]. The traditional methods for color removal, including chemical precipitation, adsorption, reverse osmosis, and solvent extractions are limited because of the excessive usage of chemicals, accumulation of concentrated sludge, expensive plant requirements, and high operational costs [2].

Adsorption has been found to be superior to the other techniques for dye wastewater treatment in terms of cost, simplicity of design, ease of operation and insensitivity to toxic substances. Therefore, there is a growing interest in using low cost, easily available materials for the adsorption of dyes. Biosorption encompasses a number of metabolism-independent processes (physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation and micro precipitation) that mainly take place in the cell wall [3]. The main attractions of biosorption are its high selectivity and efficiency, cost effectiveness and efficient removal from large volumes. Activated carbon has been widely used as an adsorbent for the removal of textile dyes from wastewater. However, this technique was found to be ineffectual due to its cost and poor regeneration. Low-cost materials have also been extensively studied as alternative adsorbents for dyes, and recent studies show that waste biomass [3], shells of bittim [4], rice husk ash [5] and fungi [6] may be used effectively as adsorbents in decolorization. Dead cells are obviously preferable for wastewater treatment since they are not affected by toxic wastes and chemicals and do not pollute the environment by releasing toxins and/or propagules [7,8].

Among the fungi, *Aspergillus niger* is the most widespread saprophytic fungus in the terrestrial environment and recent studies show that both active and inactive *A. niger* exhibit excellent adsorption capacities in removing heavy metal ions [9], and also dyes such as the anionic diazo direct dye Congo red [10], reactive black 8 [6], and the reactive dyes red HF6BN and yellow HF2GR [11].

The phthalocyanine dye C.I. Direct Blue 199, widely used in the textile industry, contains a copper ion in its structure, and could possibly be removed from aqueous solution by inactive *A. niger*, which has a high adsorption ability for copper ions [9]. However, no study has so far been focused on the biosorption ability of inactive *A. niger* for this dye. In this study, nonviable *A. niger* powder was used for the biosorption of C.I. Direct Blue 199 in a batch system. The major objective of the present study was to investigate the influences of pH, reaction time, temperatures and initial dye concentration on the biosorption capacity of *A. niger* powder. The biosorption behavior was analyzed based on the Langmuir, Freundlich and Temkin adsorption isotherms. The experimental data were also analyzed using the pseudo-first and pseudo-second order kinetic models and the kinetic constants were calculated. Furthermore, the thermodynamics of this process were studied.

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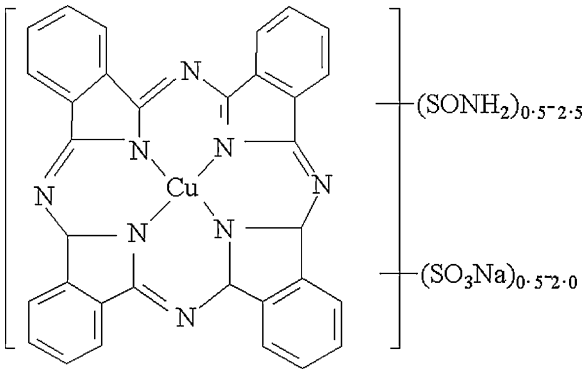

Fig. 1. Chemical structure of FBL.

2. Materials and methods

2.1. Absorbate

The dye used in this study was C.I. Direct Blue 199 (FBL), obtained from the Xiamen Jutai Chemical Reagent Factory, China. This dye is phthalocyanin and contains Cu cations. The chemical structure of FBL is given in Fig. 1.

2.2. Organism, media and culture conditions

The *A. niger* strain used in this work was maintained by the Department of Life Sciences, Xiamen University, China. The biomass was maintained by transferring colonies at approximately monthly intervals onto potato dextrose agar stored at 4 °C. For the preparation of biosorbent, single colonies from potato dextrose agar plate stock cultures were subcultured at 30 °C and shaken at 150 rpm in a liquid medium for 7 days. The liquid medium was Czapek Dox medium of composition (in g L^{-1}); sucrose; 30, $NaNO_3$; 3, K_2HPO_4; 1, KCl; 0.5, $MgSO_4{\cdot}7H_2O$; 0.5, $FeSO_4$; 0.01[12]. The cells were then autoclaved at 121 °C for 30 min, harvested by filtration, rinsed several times with generous amounts of deionized water and then oven-dried at 80 ± 1 °C for 24 h. For the biosorption studies, the dried biomass was ground to powder in a disintegrator (GJ-1, China) and sieved to a diameter of 0.07–0.154 mm.

2.3. Batch adsorption experiments

To measure the biosorption characteristics of *A. niger* on the dye, batch experiments were carried out in 250 mL Erlenmeyer flasks with 50 mL dye solution and 0.3 ± 0.002 g biosorbent. The mixtures were shaken on an orbital shaker at 150 rpm at 35 ± 1 °C for 4 h. After shaking, the mixtures were filtered and the supernatants were measured for the remaining dye. Each flask was capped to avoid evaporation at high temperature. All decolorization experiments were performed in triplicate, one without being inoculated as a control; and the mean values were used in data analysis. The characteristic of the adsorption equilibrium was estimated using Langmuir, Freundlich and Temkin isotherm equations.

2.4. Effect of pH on biosorption

The effect of pH on biosorption was studied at pH 3, 5, 7 and 9, adjustments being made using 1 M HCl or NaOH solution at an initial dye concentration of 50 mg L^{-1}. The adsorption conditions (temperature, biosorbent dosage and agitation rate) were the same as those used in the batch adsorption experiments. Samples were intermittently taken in order to measure the amount of dye retained in solution.

2.5. Effect of temperature and initial dye concentration

The effects of temperature and initial dye concentration were investigated by repeating the adsorption experiments using dye solutions of different concentration (25–400 mg L^{-1}) at 25, 35, and 45 °C. The adsorption conditions (time, pH, biosorbent dosage and agitation rate) were the same as those used in the batch adsorption experiments.

2.6. Biosorption dynamics

In order to determine the contact time required to reach biosorption equilibrium, the biosorbents were suspended in 50 mL of dye solutions at different concentrations (25, 50, 100 and 150 mg L^{-1}) in glass containers. The adsorption conditions (temperature, biosorbent dosage, pH and agitation rate) were the same as those used in the batch adsorption experiments. Samples were taken from the vessels at set time intervals for analyzing the FBL concentration.

2.7. Analysis

The residual amount of FBL in each medium was monitored using an HP-8453 UV–vis spectrophotometer at λ_{max} of 608 nm, and the amount of dye adsorbed per unit *A. niger* (mg dye per g dry biomass) was calculated using the equation:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t are the amounts of initial and retained dye in the solution at time t (mg L^{-1}), respectively, V is the solution volume (L), and m is the weight of adsorbent (g).

To solve kinetic and isotherm equations, a minimization procedure was adopted by minimizing the sum of the error squared (SSE) between the predicted values and the experimental data [13]:

$$\mathrm{SSE} = \sqrt{\frac{\sum (Q_{exp} - Q_{cal})^2}{N}} \quad (2)$$

where the subscripts "exp" and "cal" are the experimental and calculated values of Q, respectively, and N is the number of measurements.

To evaluate the applicability of isotherm equations and adsorption kinetic models, the nonlinear correlation coefficient and relative error (ΔQ) were calculated:

$$\Delta Q\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{[Q_{cal} - Q_{exp}]}{Q_{exp}}\right| \times 100 \quad (3)$$

3. Results and discussion

3.1. Effect of pH on dye decolorization

Fig. 2 shows the effect of pH on the biosorption capacity of dried *A. niger*. It can be seen that when pH was in the range of 3.0–7.0, biosorption capacity of dried *A. niger* increased rapidly within 1 min and tended to reach an equilibrium value of 7.50–8.24 mg g^{-1} after 40 min. When pH increased to 9.0, the biosorption process reached equilibrium after 40 min; however, the equilibrium value fell to 2.0 mg g^{-1}. These results were in agreement with the finding that the removal of Congo red by electro-coagulated metal hydroxide sludge increases remarkably as pH decreases [14].

As Fig. 1 shows, FBL contains a sulphonate, which could cause a dye anion to dissociate in aqueous solution according to the following equation [4]:

$$\text{Dye-}SO_3Na \rightarrow \text{Dye-}SO_3^- + Na^+ \quad (4)$$

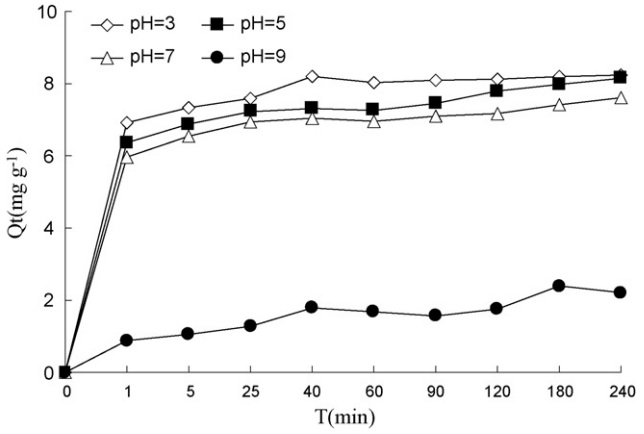

Fig. 2. Effect of pH on the biosorption capacity of dried *A. niger*. Experimental conditions: initial FBL conc., 50 mg L^{-1}; dried *A. niger* conc., 6.0 g L^{-1}; *T*, 35 °C.

Since the dye molecule has net negative charges in aqueous solution, the positive sites of the fungal biomass are favorable for biosorption of the dye. Acidic conditions cause a positive surface charge to develop on the adsorbent, resulting in higher adsorption of anionic species [5]. Under alkaline conditions, the decrease of biosorption capacity could be due to the increasing number of negative charges distributed on the fungal biomass surface, which would result in electrostatic repulsion between the adsorbent and dye molecules.

3.2. Effects of temperature and initial dye concentration

Fig. 3 shows the effect of the initial dye concentration (C_0) on the adsorption capacity of the biomass at various temperatures. The adsorption capacity increased linearly with increasing C_0 from 25 to 200 mg L^{-1} at all the temperatures studied, indicating that the adsorption process was more affected by C_0 than by temperature at lower dye concentrations. At 35 and 45 °C, the dye adsorption capacity increased linearly with increasing C_0 from 200 to 400 mg L^{-1}. At 25 °C, a linear increase in the adsorption capacity was observed as C_0 increased up to 200 mg L^{-1}, but tended to reach an equilibrium value of 18.0 mg g^{-1} when C_0 was above 200 mg L^{-1}, indicating that the adsorption capacity was significantly affected by the temperature at the higher dye concentrations. The adsorption capacity increased from 18.34 to 29.96 mg g^{-1} when the temperature rose from 25 to 35 °C at a C_0 of 400 mg L^{-1}. This finding implied

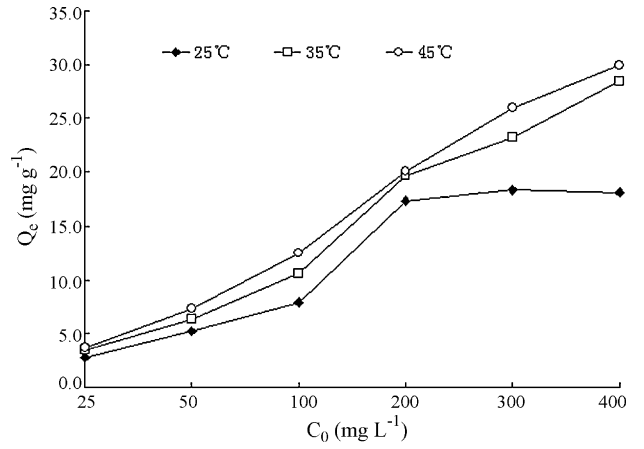

Fig. 3. Effect of temperature and initial dye concentration on equilibrium FBL biosorption capacity of dried *A. niger* at various temperatures. Experimental conditions: dried *A. niger* conc., 6.0 g L^{-1}; pH, 3.0.

Table 1
Adsorption isotherm constants and statistical comparison values.

	25 °C	35 °C	45 °C
Langmuir			
Q^0 (mg g^{-1})	20.8	30.77	30.67
K_b (L mg^{-1})	0.033	0.032	0.061
SSE	1.695	2.337	3.452
ΔQ (%)	19.17	23.95	35.07
r^2	0.975	0.950	0.970
Freundlich			
K_F (L g^{-1})	2.508	2.741	5.040
n	2.632	2.263	2.981
SSE	2.124	1.173	0.822
ΔQ (%)	18.63	11.10	5.95
r^2	0.893	0.983	0.993
Temkin			
K_T (L g^{-1})	1.648	1.908	7.441
b_T (kJ mol^{-1})	0.516	0.661	0.397
SSE	8.678	3.939	21.225
ΔQ (%)	100.01	39.65	199.91
r^2	0.89	0.92	0.84

that the higher temperatures were responsible for an increase in active sites due to bond rupture [15].

3.3. Adsorption isotherms

The experimental data obtained at 25, 35 and 45 °C were analyzed using the Langmuir, Freundlich and Temkin adsorption isotherms. The adsorption isotherm constants were determined using linear regression. The isotherm constants, SSEs, average relative errors (ΔQ) and correlation coefficients (r^2), based on the actual deviation between the experimental and predicted values, are given in Table 1.

3.3.1. Langmuir isotherm

The Langmuir isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent [16], and is expressed in the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 K_b} + \frac{C_e}{Q^0} \quad (5)$$

where C_e is the equilibrium dye concentration in the solution (mg L^{-1}), Q_e is the equilibrium dye concentration on the biosorbent (mg g^{-1}), Q^0 is the maximum adsorption capacity of the dye (forming a monolayer) per unit weight of adsorbent (mg g^{-1}), and K_b is a constant related to the affinity of the binding sites (L mg^{-1}).

As Table 1 shows, Q^0 and K_b reached maximum values of 30.77 mg g^{-1} at 35 °C and 0.061 L mg^{-1} at 45 °C, respectively, demonstrating that the dye molecules exhibited highest affinity for the adsorbent above 35 °C.

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor R_L [17], which is defined in the following equation:

$$R_L = \frac{1}{1 + K_b C_0} \quad (6)$$

The R_L value shows the nature of the adsorption process to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

As Table 2 shows, all the R_L values obtained at 25, 35 and 45 °C were in the range 0–1, indicating that the experimental conditions in this work were favorable for the adsorption process [17,18].

3.3.2. Freundlich isotherm

The Freundlich isotherm assumes a heterogeneous surface with a nonuniform distribution of heat of adsorption [19], which is

Table 2
R_L at various temperatures.

C_0 (mg L^{-1})	R_L		
	25 °C	35 °C	45 °C
25	0.55	0.56	0.40
100	0.23	0.24	0.14
200	0.13	0.14	0.08
400	0.07	0.07	0.04

expressed in the following equation:

$$\ln Q_e = n \ln C_e + \ln K_F \quad (7)$$

where K_F and n are indicative isotherm parameters of adsorption capacity and intensity, respectively. Both K_F and n in the range 1–10 are required for beneficial adsorption.

As Table 1 shows, K_F increased with increasing temperature and reached its maximum of 5.04 at 45 °C, implying that the adsorption process may be endothermic in nature. All n values were in the range 1–10, indicating that the biosorption process was favorable at all the temperatures studied [19].

3.3.3. Temkin isotherm

The Temkin isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [20], which is expressed in the following equation:

$$Q_e = \frac{RT}{b_T} \ln C_e + \frac{RT}{b_T} \ln K_T \quad (8)$$

where K_T is the constant of the Temkin isotherm (L g^{-1}), and b_T is the Temkin isotherm constant related to the heat of adsorption (kJ mol^{-1}). R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

As Table 1 shows, at 25, 35 and 45 °C, the values of K_T were 1.648, 1.908 and 7.441 L g^{-1}, and the values of b_T were 0.516, 0.661 and 0.397 kJ mol^{-1}, respectively. The higher K_T indicated a stronger interaction between the dye and the adsorbent surfaces. Since the regression coefficient r^2 was less than 0.92, the Temkin isotherm model did not fit well with the experimental data.

3.3.4. Comparison of the three isotherms

Table 1 shows the Q^0 and K_b values for the Langmuir isotherm, the K_F and n values for the Freundlich isotherm, the K_T and b values for the Temkin isotherm, and also SSE, ΔQ and r^2 values obtained from the linear regression equation between the values of C_e/Q_e and C_e, $\ln Q_e$ and $\ln C_e$, and Q_e and $\ln C_e$, respectively. Comparing the SSE, ΔQ and r^2 values obtained from the three models, it was found that the isotherm was closer to the Freundlich model than the other models at temperatures above 35 °C, whereas it was closer to the Langmuir model at 25 °C.

Comparison of the experimental equilibrium data with the theoretical equilibrium data obtained from Langmuir, Freundlich and Temkin adsorption isotherms is shown in Figs. 4–6. The observed applicability of the Langmuir and Freundlich isotherm models to the FBL-biomass system at various temperatures implied that either homogeneous or heterogeneous surface conditions existed under different experimental conditions [20].

3.4. Adsorption kinetics

As shown in Fig. 7, the biosorption capacity of biomass increased significantly in the initial 30 min and then gradually increased over 50 min. The time required for attaining the maximum uptake depended on the initial FBL concentration.

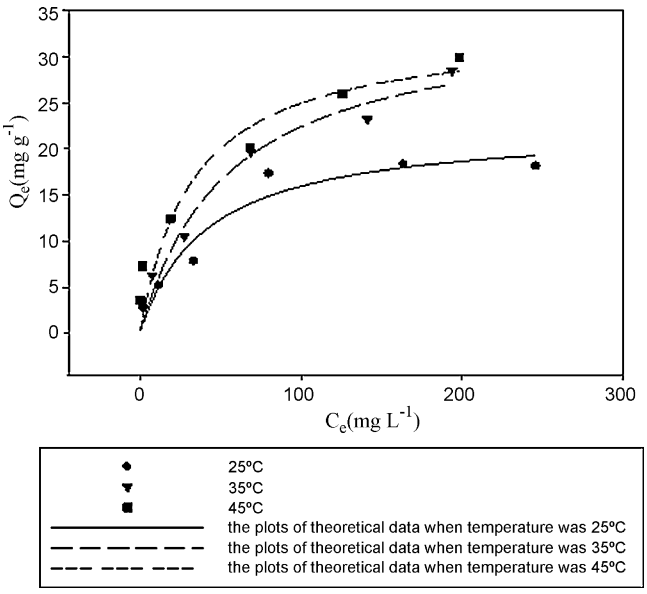

Fig. 4. Comparison of the experimental isotherm data with the theoretical isotherm data obtained from the Langmuir isotherm model at various temperatures.

In order to characterize the kinetics involved in the process of biosorption, pseudo-first order and pseudo-second order rate equations were proposed and the kinetic data were analyzed based on the regression coefficient (r^2) and the amount of dye adsorbed per unit weight of *A. niger* (Q_e) [21].

3.4.1. The pseudo-first order model

The pseudo-first order model can be written as [22]:

$$\frac{1}{Q_t} = \left(\frac{k_1}{Q_e}\right)\left(\frac{1}{t}\right) + \frac{1}{Q_e} \quad (9)$$

where Q_e and Q_t are the amount of dye adsorbed per unit weight of the adsorbent (mg g^{-1}) at equilibrium and at a certain time; t is the contact time; and k_1 is the rate constant for the first order kinetics.

Fig. 7 shows a plot of the nonlinear form of pseudo-first order equation at various concentrations. The values of the rate constants

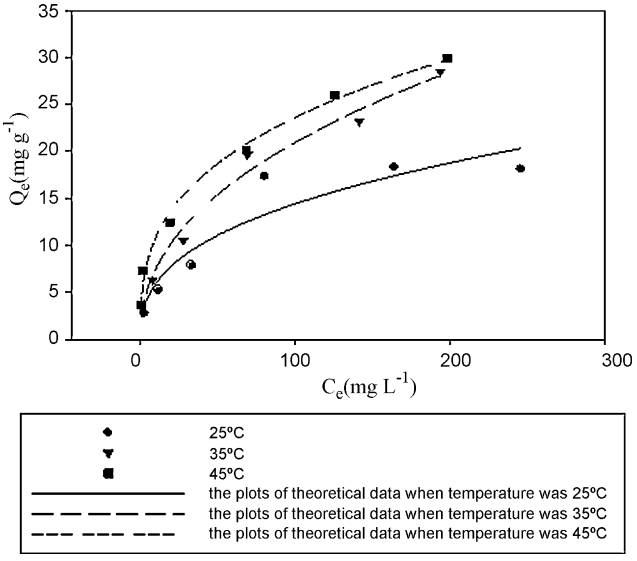

Fig. 5. Comparison of the experimental isotherm data with the theoretical isotherm data obtained from the Freundlich isotherm model at various temperatures.

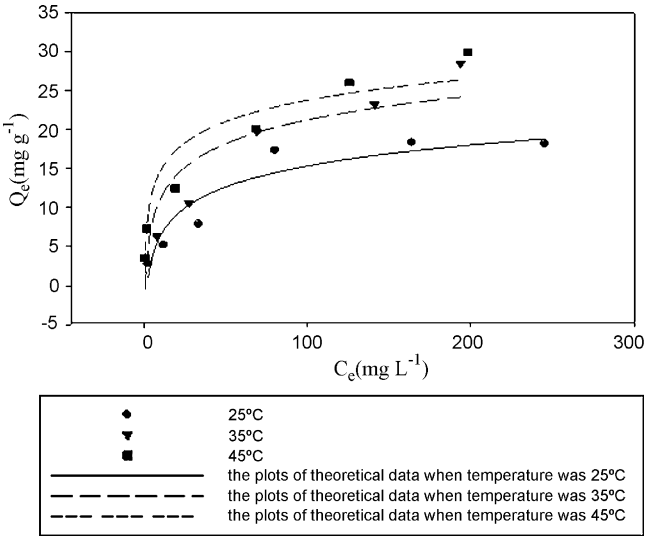

Fig. 6. Comparison of the experimental isotherm data with the theoretical isotherm data obtained from the Temkin isotherm model at various temperatures.

Q_e and k_1, and the correlation coefficients are presented in Table 3. In Fig. 7, the nonlinearity of the plots at various initial concentrations of FBL suggested that the adsorption process did not follow first order kinetics. The correlation coefficients for the first order kinetic model obtained at all of the concentrations studied were relatively low ($r^2 < 0.9$), and the calculated Q_e values obtained from this equation have not given reasonable values (Table 3), since they were too low when compared with the experimental Q_e values [23].

3.4.2. The pseudo-second order model

The pseudo-second order equation is based on the adsorption capacity of the solid phase. Contrary to other models, it predicts the behavior over the whole range of adsorption [24].

The pseudo-second order rate equation is expressed as follows:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k_2} \tag{10}$$

where k_2 is the rate constant for the second order kinetics.

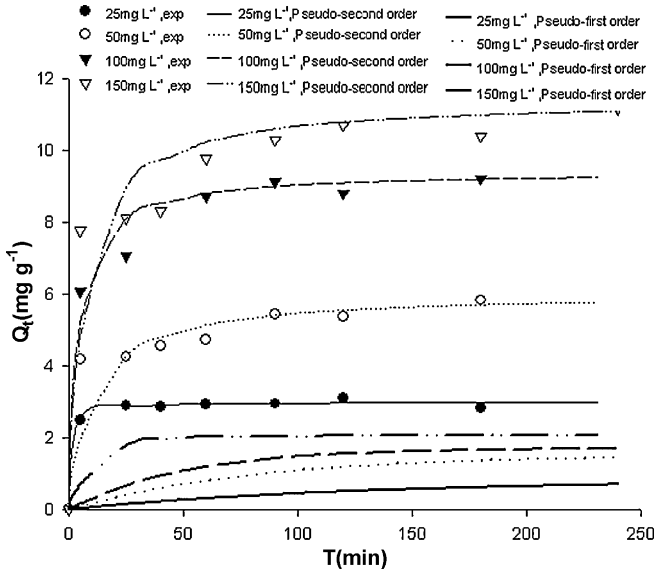

Fig. 7. Effect of agitation time and initial dye concentration on the adsorption of FBL. Experimental conditions: initial pH, 3.0; dried *A. niger* conc., 6.0 g L^{-1}; contact time, 4 h.

Table 3
Constants in the two kinetic models.

	25[a]	50[a]	100[a]	150[a]
$Q_{e,exp}$(mg g^{-1})	3.20	6.00	9.30	12.00
Pseudo-first order model				
Q_e (mg g^{-1})	0.83	1.53	1.70	2.05
k_1 (min^{-1})	0.008	0.012	0.020	0.083
SSE	2.379	3.916	6.780	7.350
ΔQ (%)	87.62	83.57	86.70	80.94
r^2	0.34	0.86	0.88	0.75
Pseudo-second order model				
Q_e (mg g^{-1})	2.98	6.02	9.38	11.17
k_2 (min^{-1})	0.423	0.016	0.026	0.013
h_0 (mg g^{-1} min^{-1})	3.756	0.580	2.288	1.622
SSE	0.079	0.765	0.474	1.163
ΔQ (%)	2.25	9.24	4.74	10.06
r^2	0.998	0.997	0.999	0.996

[a] C_0: initial concentration, mg L^{-1}.

The initial adsorption rate h_0 is expressed as follows:

$$h_0 = k_2 Q_e^2 \text{ mg g}^{-1} \text{ min}^{-1} \tag{11}$$

As Table 3 indicates, the maximum predicted initial adsorption rate of 3.756 mg g^{-1} min^{-1} was achieved at a C_0 of 25 mg L^{-1}. Since a relatively lower error ($\Delta Q < 11\%$) and a high correlation coefficient ($r^2 > 0.99$) were gained from the pseudo-second order model, and since the theoretical $Q_{e,max}$ calculated using the pseudo-second order model was much closer to the experimental value, it can be reasonably assumed that the process of FBL adsorption followed pseudo-second order kinetics [25]. Meanwhile, the nonlinearity plots at various initial concentrations of FBL shown in Fig. 7 suggested that the experimental data well fitted pseudo-second order kinetics.

Since dye adsorption follows pseudo-second order kinetics, this suggested that boundary layer resistance was not the rate limiting step [25]. The rate of dye adsorption may be controlled largely by a chemisorption process, in conjunction with the chemical characteristics of the biomass and dye [26]. Similar modeling results are also found in the kinetic studies on biosorption of Brilliant Green by rice husk ash [5] and Direct Blue 71 by palm ash [27].

3.5. Determination of thermodynamic parameters of biosorption

The Gibbs free energy change (ΔG°) is the fundamental criterion of the spontaneity of a process [28], and is determined using the following equations [28,29]:

$$\Delta G^\circ = -RT \ln K_b \tag{12}$$

$$\ln\left(\frac{K_{b2}}{K_{b1}}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature (K); K_{b1}, K_{b2} are the Langmuir constants at temperatures of T_1 and T_2; ΔH° is the change in enthalpy; and ΔS° is the change in entropy.

The thermodynamic parameters of biosorption are summarized in Table 4. The ΔG° values were negative, suggesting that the biosorption process was favorable and spontaneous in nature. The positive value of ΔH° confirmed the endothermic nature of the biosorption process, which may explain the fact that the biosorption capacity was enhanced by increasing the temperature. The positive value of ΔS° suggested that good affinity, either physical or chemical, between FBL and the adsorbent occurred spontaneously [30].

Table 4
Thermodynamic parameters of the adsorption.

C_0 (mg L^{-1})	T (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
50	25	−8.662		−0.179
	35	−8.875	2.348	−0.174
	45	−10.869	44.59	−0.174

4. Conclusions

It was found that inactive *A. niger* could be applied as an adsorbent for the removal of FBL from aqueous solutions. The results showed that the highest biosorption ability of dried *A. niger* for FBL was at pH 3.0–7.0, at a fairly high dye concentration and a temperature above 35 °C. The isotherm of FBL adsorption was well described by Langmuir and Freundlich isotherm models, which implied that either homogeneous or heterogeneous surface conditions existed under different experimental conditions. Adsorption kinetics followed the pseudo-second order equation, which suggested that chemisorption significantly contributed to the adsorption process. The negative ΔG° and positive ΔH° values obtained using thermodynamic analysis revealed that the biosorption process of FBL by inactive *A. niger* was favorable, spontaneous and endothermic in nature.

Acknowledgements

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