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Biosorption of indigo from aqueous solution by dead fungal biomass *Aspergillus alliaceus*

Eltaief Khelifi*, Youssef Touhami, Hassib Bouallagui, Moktar Hamdi

Laboratoire d'Ecologie et de Technologie Microbienne, Institut National des Sciences Appliquées et de Technologie (INSAT), Université de Carthage, 2 Boulevard de la terre, B.P. 676, 1080 Tunis, Tunisie
Tel. +216 71 703 829; *Fax*: +216 71 704 329; *email:* khelifi.eltaief@yahoo.fr

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ABSTRACT

The capacity of a nonviable *Aspergillus alliaceus* to remove the textile indigo dye from aqueous solution was investigated using different parameters such as pH and temperature. The effects of pH (at a pH range from 1 to 8) and temperature (at 30, 40 and 50˚C) on dye biosorption were studied. The indigo dye bioremoval reached its maximum with 99% after 240 min, at pH 4. In batch experiments, the biosorption capacity increased with the increase of the temperature, and the maximum dye uptake capacity of the biosorbent was 195 mg/g at 500 mg/l dye concentration at 50˚C. The modeling of the experimental data at equilibrium was performed with Langmuir and Freundlich isotherms. On the basis of regression coefficient values, the Freundlich model is almost more successful in representing experimental isotherm data for the biosorption of indigo on inactive *A. alliaceus* than the Langmuir model.

Keywords: *Aspergillus alliaceus*; Biosorption; Dead fungus; Decolourization; Indigo

1. Introduction

Dyes are widely used in various industries such as textile, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, solvent, rubber, plastic, pesticide, wood preserving chemicals, and pharmaceutical industry. Over 10,000 of different commercial dyes and pigments exist and more than 7×10^5 tonnes are produced annually worldwide [1,2]. Indigo (C.I. Vat Blue 1) is one of the oldest vat dyes used by people. The current consumption of this dye is enormous due especially to the popularity of blue jeans, which are dyed with indigo. The consumption of indigo and other vat dyes reaches about 120,000 t annually [3]. This dye is expected to have moderate persistence and low bioaccumulation potential. The acute toxicity to humans is low via the oral, inhalation, and the dermal routes. It is not irritating to skin or eye and is not a skin sensitizer in humans. In fact, most reports relating to the biological and toxicological properties of indigo concluded that indigo has a very low order of both acute and chronic toxicity, but it is quite recalcitrant and difficult to degrade [4]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters [5,6]. For this purpose, some conventional methods such as biological [7–9], physical and chemical have been used [10–13].

It is now well established that for the wastewater treatment, adsorption has several advantages over other methods. However, adsorption has been found

*Corresponding author.

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 [14–18]. In the last 20 years, studies concerning the adsorption on biomass (biosorption) have highlighted its potentiality as a suitable method for water remediation [19]. Biosorption is defined as the passive uptake of organic or inorganic species from aqueous solutions by microbial biomasses (bacteria, yeasts, filamentous fungi and algae) [20]. The process encompasses a number of metabolism-independent phenomena (physical and chemical adsorptions, electrostatic interaction, ion exchange, complexation, chelation and micro-precipitation) that mainly take place at the cell wall level [21].

Dead cells are obviously preferable for dyes removal since they are not affected by chemicals and toxic wastes and do not pollute the environment by releasing propagules and/or toxins. Fungal biomass holds distinct advantages over other micro-organisms with respect to industrial exploitation due to the large-scale availability, ability to grow in cheap medium and ease of harvesting. Among the fungi, *Aspergillus* is the most widespread saprophytic fungus in the terrestrial environment [13]. Some researchers have studied the removal of dyes by various species of *Aspergillus*: *A. niger* [22]; *A. wenti* [23]; and *A. foetidus* [24]. The recent studies show that inactive *Aspergillus* species exhibit excellent adsorption capacities in removing dyes. But, according to our knowledge, no studies in the literature have been focused until now on the biosorption capacity of *A. alliaceus* neither dead nor alive for any dyes. Furthermore, our previous works proved firstly that this fungus presents a high ability to decolorize indigo dye. When this fungus was grown in liquid medium, more than 98.6% of color removal was obtained for the indigo dye. The detection of enzymatic activities in the culture indicated that laccase and LiP may play an important role in the degradation of this dye [25]. Secondly, it was shown that the microbial consortium developed by the mixture of *Aspergillus alliaceus*, *Bacillus cereus* and *Bacillus pumilus* presented a significant improvement of textile wastewater decolorization (100%) and COD removal yields (98%) due to the synergetic reaction of bacterial and fungal strains [8]. This ability indicated its potential use in antipollution treatments. However, only a better understanding of the mechanisms used by the fungi will allow applying this fungus to clean up aquatic terrestrial environments.

In this study, nonviable *A. alliaceus* was used for the biosorption of indigo (widely used in the textile industry) in a batch system. The major objective of the present study was to investigate the influences of pH, temperatures and initial dye concentration on the biosorption capacity of dead *A. alliaceus*. The biosorption behavior was analyzed based on Langmuir and Freundlich adsorption isotherms.

2. Materials and methods

2.1. Dye solution preparation

The indigo dye, supplied by Sigma Chemical Company, St Louis, MO, USA was used in this study. Its chemical structure is shown in Fig. 1. Dye solution was prepared by dissolving accurately weighted dye in distilled water at different concentrations. The concentration of dye solution was determined by a UV–vis spectrophotometer (Jenway UV visible spectrophotometer) at the wavelength $\lambda_{max} = 620$ nm in which maximum absorbance spectra were obtained. Absorbance values were recorded at the corresponding maximum absorbance wavelength (λ_{max}) and dye solution was initially calibrated for concentration in terms of absorbance units [26].

2.2. Preparation of the dead biomass A. alliaceus

A laboratory strain of *A. alliaceus* strain 121 C (previously identified by Khelifi et al. [25]) was used in this work. This strain was maintained by transferring colonies at approximately monthly intervals onto potato dextrose agars stored at 4°C. For bio-adsorbent preparation, single colonies from potato dextrose agar plate stock cultures were subcultured in 250 ml conical flasks at 30°C and shaken at 150 rpm in the liquid medium for 7 days. All culture work was conducted aseptically. The mycelial pellets were harvested through filtering. The biomass was then washed thoroughly with distilled water to remove the growth medium adhering on its surface. For excluding the biodegradation of indigo by living mycelia, the mycelial pellets, which were autoclaved at 121°C for 30 min, were used in the adsorption experiments [22,27].

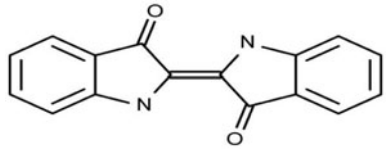

Fig. 1. Chemical structure of indigo.

2.3. Effect of pH and temperature on indigo biosorption

Batch pH studies were conducted by shaking 0.2 g of the dead biomass in 100 ml of indigo solution at a concentration of 100 mg/l, for 240 min over a range of initial pH values from 1 to 8. For pH adjustment 1 N HCl or 1 N NaOH was used. The pH value corresponding to the highest biosorption capacity will be considered as the effective (optimum) pH for the following biosorption studies.

The effects of temperature and initial dye concentration were investigated by repeating the biosorption experiments using dye solutions of different concentrations ranging from 50 to 500 mg/l at different temperatures of 30, 40, and 50˚C. The other factors involved in the biosorption process including pH 4 (the pH considered as the effective pH for the biosorption), dead biomass, agitation rate, and time were kept fixed.

2.4. Batch biosorption studies

Equilibrium adsorption isotherm was determined by placing 0.2 g of dead biomass in 100 ml of the dye solution, at 50˚C and at initial dye concentrations ranging from 50 to 500 mg/l for 240 min at the effective (optimum) pH 4 for three different temperatures (30, 40, and 50˚C).

The residual dye concentration was determined at the wavelength $\lambda_{max} = 620$ nm. Biomass dye mixture was filtered (0.45 μm) for analysis of residual dye concentrations in solutions. The decolorization of the dye was determined by measuring the absorbance of the residual dye concentration against the original color of the medium. 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 and Freundlich isotherm equations [13,28].

3. Results and discussion

3.1. Effect of pH on indigo biosorption

The effect of pH in the range 1–8 on the biosorption of indigo was investigated with dye concentration fixed at 100 mg/l. Fig. 2 shows the effect of pH on the biosorption capacity of dead *A. Alliaceus*. It can be seen that when pH was in the range of 3–4, biosorption capacity of dead *A. Alliaceus* increased and tended to reach an equilibrium value of 45–50 mg/g after 240 min. The optimum biosorption capacity was observed at pH 4 with 50 mg/g. A decrease in pH from 3 to 1, and its increase from 5 to 8, caused a significant reduction in the amount of indigo biosorbed by the dead biomass. The optimum adsorption was observed at pH 2–4. Similar results have also been reported in the literature [21].

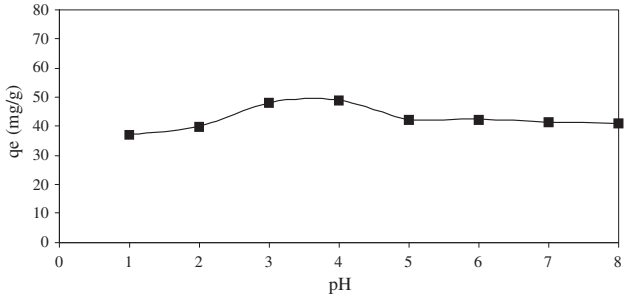

Fig. 2. The effect of initial pH on the equilibrium biosorption of dead *A. alliaceus*. Experimental conditions: C_0: 100 mg/l, dead biomass: 2 g/l, temperature: 30˚C, agitation rate: 150 rpm, and time: 240 min.

The pH solution usually plays a major role in biosorption, and seems to affect the solution chemistry of dyes and the activity of the functional groups of the biomass. The change in pH solution may indicate an ion exchange mechanism. Low pH has been found to favor the biosorption of dyes by the fungal biomass [29]. In fact, at acidic conditions, binding sites of the biomass would be closely associated with the hydrogen ions which act as bridging ligands between the biomass surface and the dye molecule. Acidic conditions cause a positive surface charge to develop on the adsorbent, resulting in higher biosorption of anionic species [30]. Under alkaline conditions (at higher pHs), the high negatively charged adsorbent surface sites did not favor the biosorption of the dye. However, 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 [22].

3.2. Effect of temperature on indigo biosorption

The effect of temperature on biosorption was studied at fixed pH 4 using dye solutions at different concentrations ranging from 50 to 500 mg/l, at different temperatures of 30, 40, and 50˚C. Fig. 3 shows the effect of the initial dye concentration (C_0) on the biosorption capacity of the dead biomass at these various temperatures. The biosorption capacity increased linearly with increasing C_0 from 50 to 400 mg/l at all the studied temperatures, indicating that the biosorption process was more affected by C_0 than by

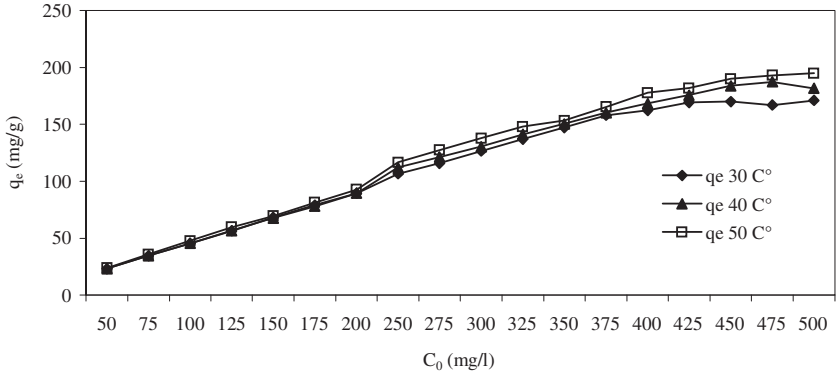

Fig. 3. Effect of temperature on equilibrium of indigo biosorption capacity of dead *A. alliaceus* at various temperatures of 30, 40, and 50°C. Experimental conditions: dead *A. alliaceus*: 2 g/l; pH: 4 (effective pH corresponding to the highest biosorption capacity); agitation rate: 150 rpm; and time: 240 min.

temperature at lower dye concentrations. At 50°C, the dye biosorption capacity increased linearly with increasing C_0 from 400 to 500 mg/l. At 30 and 40°C, a linear increase in the adsorption capacity was observed as C_0 increased up to 400 mg/l, but tended to reach an equilibrium value of 160 and 175 mg/g, respectively, when C_0 was above 400 mg/l, indicating that the biosorption capacity was significantly affected by the temperature at the higher dye concentrations. The adsorption capacity increased from 175 to 195 mg/g when the temperature rose from 40 to 50°C at a C_0 of 500 mg/l.

Higher temperatures usually enhance biosorption. This finding implied that the higher temperatures were responsible for an increase in active sites due to bond rupture. This result was proved by Solis et al. [31], which showed that some pretreatment processes can modify the biosorption capacity of the biomass, such as autoclaving, as high temperature causes cell rupture with a consecutive increase in surface area which changes the surface of the micro-organism and increases the capacity of the binding sites. However, physical damage to the biosorbent can be expected at very higher temperatures. Due to the exothermic nature of some adsorption processes, an increase in temperature has been found to reduce the biosorption capacity of the biomass [32].

3.3. Adsorption isotherms

The equilibrium adsorption isotherm model, which is the number of mg adsorbed per gram of adsorbent vs. the equilibrium concentration of adsorbate $q_e = f(C_e)$ (Fig. 4), is fundamental in describing the interactive behavior between adsorbate and adsorbent. Analysis of isotherm data is important for predicting the biosorption capacity of the biosorbent, which is one of the main parameters required for the design of an adsorption system. Equilibrium isotherm studies were carried out with different concentrations of indigo ranging from 50 to 500 mg/l at different temperatures and at pH 4. Two models were used to analyse the equilibrium adsorption data: Langmuir [33] and Freundlich and Heller [34]. Langmuir's model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface [35]. The general form of the Langmuir isotherm is:

$$q_e a_L / K_L = K_L C_e / (1 + K_L C_e) \quad (1)$$

where C_e is the equilibrium concentration of the indigo in the solution (mg/l), q_e is the amount of indigo adsorbed per unit mass of adsorbent (mg/g), at equilibrium concentration, C_e, a_L (l/mg) and K_L (l/g) are the Langmuir constants with a_L related to the adsorption energy, and q_m [= K_L/a_L] signifies the maximum adsorption capacity (mg/g), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of anions adsorbed increases as the concentration increases up to a saturation point. As long as there are available sites, adsorption will increase with increasing indigo concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of indigo solutions does not increase the amount of indigo on adsorbents. After linearization of the Langmuir isotherm, Eq. (2), we obtain:

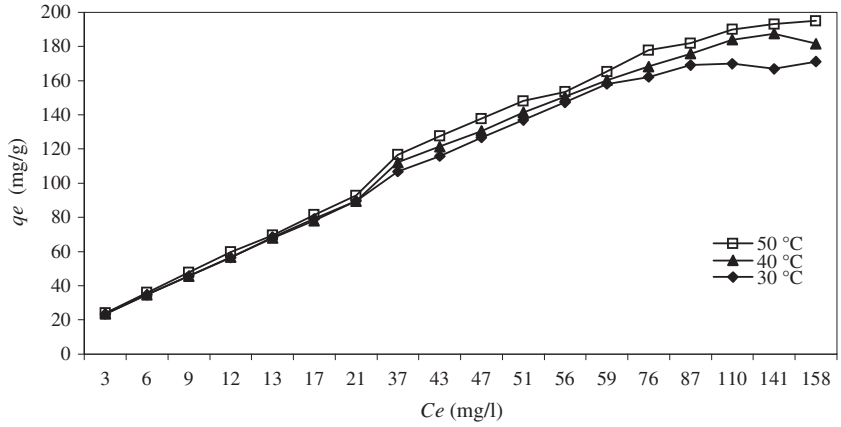

Fig. 4. Plots of $q_e = f(C_e)$ for the biosorption of indigo using dead *A. alliaceus*. Experimental conditions: dead *A. alliaceus*: 2 g/l; pH: 4 (effective pH corresponding to the highest biosorption capacity); agitation rate: 150 rpm; and time: 240 min.

$$C_e/q_e = C_e(a_L/K_L) + (1/K_L) \quad (2)$$

The values of a_L and K_L are calculated from the slope and intercept of the plot of $C_e/q_e = f(C_e)$ (Fig. 5). The amount of indigo adsorbed (mg/g) was calculated based on amass balance equation as given below:

$$q_e = V(C_0 - C_e)/m \quad (3)$$

where C_0 is the initial concentration of indigo in mg/l, V is the volume of experimental solution in litre (l), and m is the weight of dead *A. alliaceus* in g. The parameters of the Langmuir equation were calculated and are given in Table 1. Table 1 indicates that the maximum adsorption capacity of dead *A. alliaceus* ($q_m = 198$ mg/g) for indigo is very higher than other adsorbents used by Adetuy and Jabar [36] for the adsorption of indigo such as algae-activated carbon (182 mg/g) and elephant grass-activated carbon (167 mg/g), and lower than of those obtained by Aber and Sheydaei [37], who studied the adsorption of industrial effluent containing indigo dye using adsorption method by activated carbon cloth ($q_m = 500$ mg/g) (Table 2). The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor.

R_L given by the following equation:

$$R_L = 1/(1 + a_L C_0) \quad (4)$$

The constants such as a_L and C_0 are obtained from the Langmuir isotherm. Values of R_L greater than 1 indicate unfavorable adsorption, whereas $0 < R_L < 1$ indicates favorability of the adsorption process [38,39].

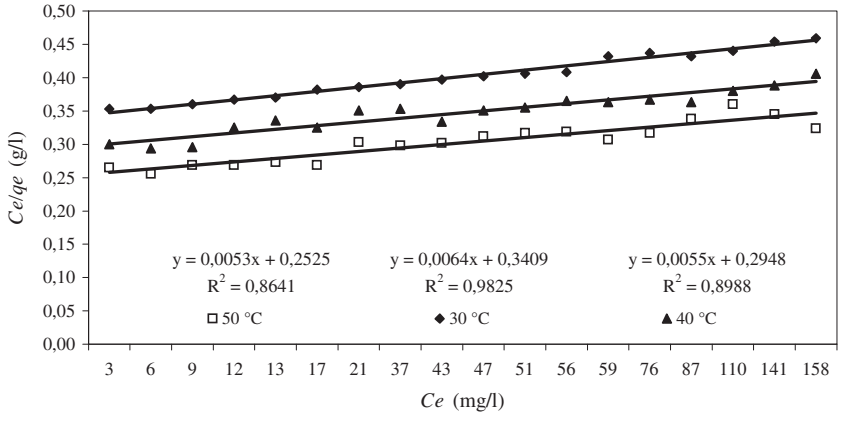

Fig. 5. Linearization of the Langmuir isotherm. Experimental conditions: dead *A. alliaceus*: 2 g/l; pH: 4 (effective pH corresponding to the highest biosorption capacity); agitation rate: 150 rpm; and time: 240 min.

Table 1
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) for the biosorption of indigo on dead *A. alliaceus* at 30, 40, and 50°C and at pH 4 (effective pH and temperature corresponding to the highest biosorption capacity)

Langmuir constants	$a_L \times 10^3$ (l/mol)	a_L (l/mg)	K_L (l/g)	q_m [=K_L/a_L] (mg/g)	R_L*	r
50°C	5.52	0.02	3.96	198	0.33	0.8641
40°C	4.854	0.0186	3.321	181.78	0.349	0.8988
30°C	4.88	0.0187	2.9334	156.28	0.348	0.9825
Freundlich constants		K_f ($mg^{1-1/n}\ l^{1/n}/g$)	$1/n$	n		r
50°C		38.7178	0.3767	2.654		0.9197
40°C		15.4591	0.5287	1.891		0.9478
30°C		13.2077	0.6031	1.658		0.961

*For indigo concentration of 100 mg/l.

Table 2
Summary of indigo adsorption capacities of various adsorbents

Type of adsorbent	q_m (mg/g)	Reference
Cattle bone-activated carbon	571	[36]
Algae-activated carbon	182	[36]
Water lettuce-activated carbon	235	[36]
Elephant grass-activated carbon	167	[36]
Commercially available powder0-activated carbon	1,000	[36]
Activated carbon cloth	500	[37]
Dead *A. alliaceus*	198	Present work

The R_L values computed for the adsorption system are 0.348, 0.349, and 0.33 at 30, 40, and 50°C, respectively, indicating thereby the favorability of the ongoing process.

The Freundlich isotherm model is an empirical equation that describes the surface heterogeneity of the sorbent. It considers multi-layer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [35]. The Freundlich empirical model is represented by:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), and K_f ($mg^{1-1/n}\ l^{1/n}/g$) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple. n is related to the adsorption energy distribution, and K_f indicates the adsorption capacity. The linearized form of the Freundlich adsorption isotherm equation is:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{6}$$

The values of K_f and $1/n$ calculated from the intercept and slope of the plot of Fig. 6 which represented $\ln q_e = f(\ln C_e)$ are listed in Table 1. Table 1 shows that the values of correlation coefficient, r, for the fit of experimental isotherm data to Freundlich equation is more close to 1 than that for Langmuir equation. These r values are 0.961, 0.9478, and 0.9197 at 30, 40, and 50°C, and 0.9825, 0.8988 and 0.8641 at 30, 40, and 50°C, respectively, for Freundlich and Langmuir models. Therefore, the Freundlich model represents the experimental data better on the basis of values of regression coefficients.

3.4. Thermodynamic parameters

Using the Freundlich and Langmuir constants, thermodynamic parameters like change in enthalpy (ΔH°), Gibb's free energy (ΔG°), and changes in entropy (ΔS°) have been calculated [38] by using the following mathematical expressions:

$$\Delta G^\circ = -RT \ln a_L \tag{7}$$

$$\Delta H^\circ = -R(T_2 T_1/(T_2 - T_1)) \times \ln (a_{L2}/a_{L1}) \tag{8}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{9}$$

Here, a_L, a_{L1}, and a_{L2} are Langmuir constants at different temperatures, R the universal gas constant,

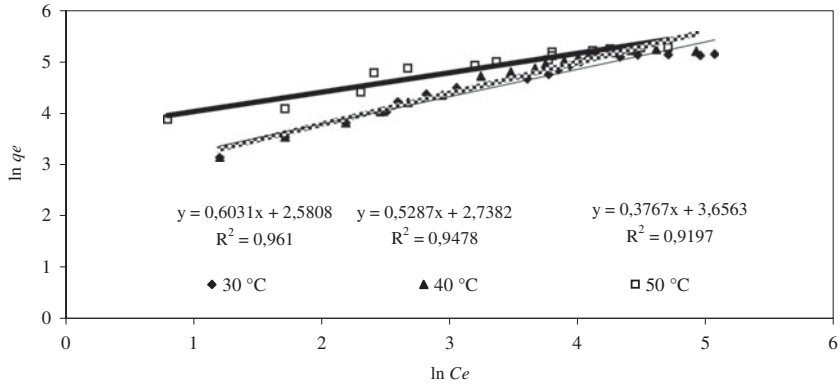

Fig. 6. Linearization of the Freundlich adsorption isotherm. Experimental conditions: dead *A. alliaceus*: 2 g/l; pH: 4 (effective pH corresponding to the highest biosorption capacity); agitation rate: 150 rpm; and time: 240 min.

and T the temperature in Kelvin. Calculated values of the thermodynamic parameters are presented in Table 3. The positive value obtained for entropy change indicates an increase in randomness, whereas the exothermic nature of the process is further confirmed by the negative value of enthalpy (−10.758 (kJ/mol)). The feasibility of the process is further supported by negative value of free energy. Moreover, the increasing values of the negative free energy with elevation in temperature supported the better adsorption process at high temperatures [38].

3.5. Color removal efficiency of indigo by nonviable A. alliaceus

To assess the biosorption potential of the dead fungal biomass (*A. alliaceus*), the color removal efficiencies were measured. As shown in Fig. 7, nonviable *A. alliaceus* exhibited high biosorption efficiency. The color removal reached the maximum values of 99% after 240 min, at pH 4 and at a temperature of 50˚C. The obtained results showed the importance of initial media pH and temperature on the bioremoval process. The results were in agreement with those obtained by other researchers. Fu and Viraraghavan [40–42] investigated the removal of various dyes like, basic blue 9, acid blue 29, Congo red, and disperse red 1 by biosorption on dead and pretreated *A. niger* fungus. The authors found that *A. niger* is capable of removing dyes from an aqueous solution and suggested that three major functional groups: carboxyl, amino, and phosphate, and the lipid fraction in the biomass of *A. niger* plays an important role in the biosorption of these dyes. *A. niger* was also used by Khalaf [43], who studied the biosorbent for removal of a reactive dye synazol from its multi-component textile. The obtained results revealed that autoclaved biomass of *A. niger* exhibited maximum dye removal of 88%, with conditions of pH 3, temperature 30˚C and 8 g/l (w/v) of biomass concentration after 18 h of contact time [43]. Gimba et al. [44] studied the adsorption of indigo blue dye by activated carbons from coconut shells, and proved that activated carbon was most effective

Table 3
Thermodynamic parameters for the uptake of indigo

−ΔG˚ (kJ/mol)				
30˚C	40˚C	50˚C	−ΔH˚ (kJ/mol)	ΔS˚ (J/K mol)
21.398	22.087	23.137	10.758	38.32

Note: Adsorbent dose (dead *A. alliaceus*) = 0.2 g, pH 7.0.

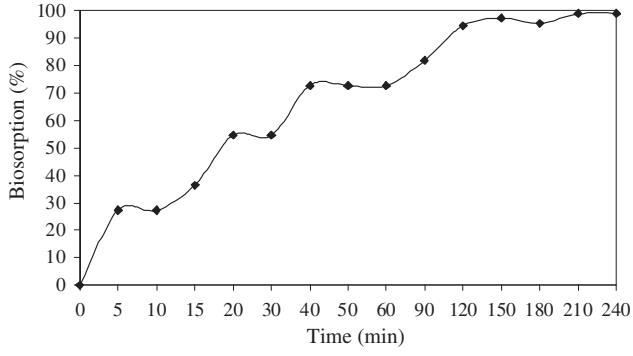

Fig. 7. Biosorption efficiency of indigo by nonviable *A. alliaceus*. Experimental conditions: dead *A. alliaceus*: 2 g/l; pH: 4 (effective pH corresponding to the highest biosorption capacity); temperature: 50˚C (effective temperature corresponding to the highest biosorption capacity); and agitation rate: 150 rpm.

adsorbent with dye removal up to 98%. Fu and Viraraghavan [40] demonstrated that biosorption capacity of fungal biomass could be increased by some pretreatments such as autoclaving, as high temperature causes cell rupture with a consecutive increase in surface area which changes the surface of the micro-organism and increases the capacity of the binding sites [45]. The effectiveness of biosorption depends on the following conditions: pH, temperature, ionic strength, time of contact, adsorbent and dye concentration, dye structure, and type of micro-organism [46–49].

4. Conclusions

It was found that inactive *A. alliaceus* could be applied as a biosorbent for the removal of indigo from aqueous solutions. The results showed that the highest biosorption ability of the dead *A. alliaceus* for indigo was at pH 4, and a temperature of 50˚C. The isotherm of indigo biosorption was described by Langmuir and Freundlich isotherm models. The values of correlation coefficient, *r*, for the fit of experimental isotherm data to Freundlich equation is more close to 1 than that to Langmuir equation. Therefore, the Freundlich model is almost more successful in representing experimental isotherm data for the biosorption of indigo on inactive *A. alliaceus* than the Langmuir model on the basis of values of regression coefficients.

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