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Biosorption of Turquoise Blue dye from aqueous solution by dried fungal biomass (*Trichoderma harzianum*) – kinetic, isotherm and thermodynamic studies

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ABSTRACT

The removal of Turquoise Blue dye by the dried biomass of *Trichoderma harzianum* has been investigated through equilibrium, kinetics and thermodynamic studies. The parameters such as the effect of dye concentration, temperature, contact time, adsorbent dosage and pH are studied in batch experiments. A maximum decolourization of 94% was achieved at pH 4 at the temperature of 37°C, a dye concentration of 50 mg/L and 0.4 g/L biosorbent dose. In addition, characterization of biosorbent was performed by scanning electron microscopy and Fourier transform infrared (FTIR) analysis. The FTIR spectral analyses showed the involvement of hydroxyl, carbonyl and carboxyl groups in biosorption process. These results indicated that *T. harzianum* could be used as a novel biosorbent for the removal of Turquoise Blue dye from aqueous solution. The experimental biosorption equilibrium data for Turquoise Blue dye are processed with various isotherm like Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models. For the present system, high correlation coefficients favour the Freundlich isotherm model. Similarly, pseudo-second-order model seems to best fitted from the interpretation of biosorption kinetics data. The biosorption was found to be endothermic in nature. To our knowledge, this is the first report to confirm the effective use of *T. harzianum* biosorbent to remove Turquoise Blue dye from industrial effluents in wastewater treatment process.

Keywords: Biosorption; Turquoise Blue dye; Kinetic; Thermodynamics; Isotherm; Characterization; Decolourization

1. Introduction

Chemically different dyes are prepared in large number for decades. These are mainly used in paint, textile, packed food, tannery, pharmaceutical, pulp and electroplating industries [1,2]. Industries leaving coloured wastes into water not only affect the aesthetic nature but also resist the passage of sunlight and reduce the photosynthetic action. Moreover, the chemicals in dye wastes cause toxic effects to the microbial populations and carcinogenic to mammals [3,4]. Based on physiochemical processes, the technologies commonly used for colour removal are coagulation, flocculation, chemical precipitation, ion exchange, reverse osmosis, biosorption and ultrafiltration. But the applications of the above-stated technologies remain limited due to technical and economic constraints [5,6]. Also, synthetic dyes have a complex aromatic molecular structure, which makes them stable and resistant to biological degradation [7–9].

The search for alternative and innovative wastewater treatment techniques has focused attention on the use of natural and/or biological materials such as sugarcane bagasse [10,11], peanut husk [12], agricultural waste [13],

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algae [14], fungi [15], bacteria [16], yeast [17] and for the dye removal and recovery technologies, and has gained importance during recent years. Some of the fungal biosorbents are *Aspergillus* [18–20], *Rhizopus* [21,22], *Penicillium* [23–25], etc. that have been previously studied for the removal of different types of dyes, but highly operative and more economical biosorbent remains to be uncovered (Table 4). The present study has investigated the effect of pH, temperature, biosorbent dose and initial dye concentration on biosorption of dyes using dead fungal biomass. Studies have been carried out to fit the obtained equilibrium data from batch studies to suitable isotherm. The biosorption capacity of the dyes was investigated using the biosorption isotherms.

2. Materials and methods

2.1. Biosorbent cultivation and preparation

The species *Trichoderma harzianum* used in this study was obtained from IMTECH, Chandigarh, India. The species was grown in Sabouraud Dextrose Broth medium composed of peptone, dextrose and distilled water, and maintained at a pH of 5.6. The species was allowed to grow at 28°C for 7 d in a shaker. After 7 d of growth the dead biomass was obtained by autoclaving at 121°C for 15 min. The dead fungal biomass was then filtered by adding distilled water to remove the traces of the medium and dried overnight in an hot air oven at 50°C–60°C. The dried biomass obtained were powdered in a mortar and pestle, and used for the biosorption study without any further size reduction.

2.2. Preparation of dye solution

The Turquoise Blue dye (99.9% pure) used in this study was purchased from a textile industry, Tirupur, Tamil Nadu, and used without any further purification. The stock solution was prepared by dissolving 0.2 g of the dye in 1,000 mL of distilled water from which different concentrations of the dye solution were prepared. All the solutions were freshly prepared, and the pH of these dye solutions were adjusted using 0.1 N HCl and 0.1 N NaOH. All the chemicals used were of analytical grade.

2.3. Batch biosorption experiments

The biosorption experiments were carried out in batch mode by mixing 0.2 g of the dried biomass with 20 mL of the dye solutions of known concentrations. The system was placed in a 100-mL glass conical flask, which was sealed and agitated with a rotary shaker at 125 rpm. The desired initial pH (range 1–12) of the adsorbate solution was adjusted using 0.1 N HCl and 0.1 N NaOH before mixing them. The biosorption kinetics was investigated with a biomass dosage of 0.5 g/L and the initial dye concentration at 50 mg/L for 5 h. The samples were withdrawn at a time interval of 10 min for the first 1 h and a time interval of 30 min for the next 4 h. The kinetic experiments were carried out in an orbitary shaker at a temperature of 310 K. The equilibrium experiments were carried out at 300, 303, 310 and 318 K in an orbital shaker using eight different initial concentrations (10, 20, 30, 40, 50, 100, 150 and 200 mg/L) with a contact time of 4 h in order to estimate the parameters of isotherm models. The biosorption yield was calculated by:

Removal percentage (% R) =
$$\frac{C_i - C_o}{C_i} * 100$$
 (1)

The biosorption capacity can be calculated by:

$$q_e = \frac{C_i - C_o}{m} * V \tag{2}$$

2.4. Analytical methods

For the determination of the amount of dye left unadsorbed in the solutions, samples were withdrawn at the specified time and centrifuged at 10,000 rpm for 10 min after which the supernatant was collected and the absorbance of the dye left unadsorbed in the solution was determined using a UV–visible spectrophotometer (Schimadzu, Japan, Model UV-1600PC) at a wavelength of 507 nm, and the corresponding concentration was calculated using a standard plot.

2.5. Characterization of biosorbent

The surface morphologies of the *T. harzianum* biomass with dye before and after biosorption were visualized using scanning electron microscope (SEM) (Hitachi, Japan, S-3000H). Fourier transform infrared (FTIR) spectroscopy spectra of dried fungal biomass with dye before and after biosorption were collected in 500–4,000 cm⁻¹ using FTIR spectrophotometer (Schimadzu, Japan, FTIR 8400S). Thermal stability of the adsorbents was performed using a thermogravimetric analyzer (SDT Q600).

2.6. Determination of point of zero charge

The point of zero charge (pH_{PZC}) was determined by solid addition method [26]. A series of 0.1 M KNO₃ solutions (50 mL each) were prepared, and their pH values were adjusted in the range of 1.0–12.0 by addition of 0.1 mol/L HCl and 0.1 mol/L NaOH. To each solution, 0.1 g of dried biomass of *T. harzianum* was added, and the suspensions were shaken manually, and the solution was kept for a period of 48 h with intermittent manual shaking. The final pH of the solution was recorded, and the difference between initial and final pH (Δ pH) was noted. The point of this curve yielded pH_{PZC}.

3. Results and discussion

3.1. Effect of pH

The effect of pH of the dye solution on biosorption of Turquoise Blue dye was studied at pH values ranging from 1 to 12. Biosorption of Turquoise Blue dye on dead fungal biomass was greatly affected by change in pH of the aqueous solution. Amount of dye adsorbed on *T. harzianum* in acidic pH was higher at all concentrations as compared with biosorption in a lesser acidic and alkaline environment. The result (Fig. 1) shows that maximum biosorption occur at pH 4, and the percentage of the biosorption decreases from

93% to 52% when the pH increases from 5 to 9. The abovementioned data proves that the biosorption of Turquoise Blue dye on the fungal biomass is more at acidic pH. This reveals that at higher pH levels, excess OH⁻ ions compete with the anions of the dye for biosorption sites on the biomass surface resulting in decreased biosorption [26]. For pH from 2 to 6, biosorption percentages are around 90%. There is no significant change in increasing the pH after 6; hence, pH 4 is found to be the optimum. The decrease in percentage removal of Turquoise Blue dye with increasing pH was studied [27,28].

The pH_{PZC} gives very significant information about the biosorption of Turquoise Blue by dried biomass of *T. harzianum*. The pH_{PZC} of fungal biomass was found to be 6. This shows that below this pH, the fungal biomass acquires a positive charge due to protonation of functional groups, and above this pH, negative charge exists on the surface of dried biomass. The biosorption of Turquoise Blue is favoured at pH < pH_{PZC} where the surface becomes positively charged [26].

3.2. Effect of contact time

The effect of contact time on the biosorption of Turquoise Blue dye by the fungal biomass was studied at constant experimental conditions such as concentration, temperature



Fig. 1. Effect of pH on the adsorptive removal of Turquoise Blue dye by *T. harzianum*.



Fig. 2. Effect of contact time on the adsorptive removal of Turquoise Blue dye by *T. harzianum*.

and pH. The results (Fig. 2) show that the biosorption of Turquoise Blue dye by *T. harzianum* initially occurs at 10 min and reaches a maximum of 94% at 120 min. Beyond 120 min, the biosorption remains constant. Therefore, 120 min is determined to be the optimum contact time. Initially, the biosorption occurs due to film diffusion from the bulk to the surface due to the availability of all the biosorption sites. As equilibrium is reached, the concentration of the leftover dye molecules remains a constant irrespective of the duration of the exposure of the sorbent to the dye solution because of the exhaustion of the biosorption sites. Therefore, 120 min is determined to be the optimum contact time. Similar results were observed in the decolourization of Reactive Red 198 by *Aspergillus parasiticus* [28] and bioremoval of direct red by *Pseudomonas putida* [29].

3.3. Effect of biosorbent dose

From this study, optimum biosorbent dose for dye removal was determined. The dye solutions were treated with different dosage (0.1-0.5 g/L) of dried fungal biomass under 120 rpm; after the equilibrium period the biosorbent was separated; and percentage removal of dye was calculated. From several experiments, it was found that the dye removal percentage gradually increased from 44% to the maximum of 76% at the biosorbent dose of 0.4 g/L (Fig. 3). Nevertheless, additional rise in the biosorbent dosage does not affect the dye removal percentage. It is readily understood that the number of available biosorption sites increases with an increase in biosorbent concentration and it, therefore, results in the increase of dye concentration. Sometimes further increment in biosorbent concentration may not cause an improvement in biosorption. This may be due to that almost all ions will be bound to the biomass as an equilibrium will be reached between the dye molecules bound to the biomass and those remaining unadsorbed in the solution [30]. Another reason may be due to the particle interaction, such as aggregation, which may result from high biosorbent concentration. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length [31].



Fig. 3. Effect of biosorbent dose on the adsorptive removal of Turquoise Blue dye by *T. harzianum*.

3.4. Effect of initial dye concentration

Fig. 4 presents the removal percentage of Turquoise Blue dye against various dye concentrations (10–50 mg/L)l the percentage of removal of Turquoise Blue dye increases and reaches maximum removal for 50 mg/L and decreases with increasing dye concentration. This shows that the removal of dye by biosorption depends on the concentration of the initial dye solution. Similar results were obtained in the biosorption of Methylene blue by *Aspergillus wentii* [32] and *Aspergillus niger* [33].

3.5. Effect of temperature

To ascertain the effect of temperature on Turquoise Blue dye removal percentage, the experiments were carried out at different temperatures ($25^{\circ}C-45^{\circ}C$), initial dye concentration 50 mg/L, biosorbent dose 0.4 g/L and pH 4. From Fig. 5, increasing temperature from $25^{\circ}C$ to $45^{\circ}C$ shows that notable increase in the dye removal percentage of Turquoise Blue dye onto dried fungal biomass of *T. harzianum* was observed at $35^{\circ}C$. It means that when the temperature rises, diffusion rate of dye molecules increases within the biosorbent pores due to decreasing solution viscosity. Similar observation was also found in [34,35].

3.6. Characterizations of biosorbent

SEM micrograph of *T. harzianum* (Figs. 6(a) and (b)) presents the surface morphology. From the figures one can clearly



Fig. 4. Effect of initial dye concentrations on the adsorptive removal of Turquoise Blue dye by *T. harzianum*.

see that surface is full of macropores developed by inter- and intra-mycelial dead fungal biomass and which were filled by the Turquoise Blue dye after biosorption. FTIR spectrum was observed in the range 500–4,000 cm⁻¹ in order to distinguish the modifications in the functional groups (Fig. 7). The peak observed between 3,414.03 and 3,423.52 cm⁻¹ informs that the presence of –OH groups associated with it. Peaks in between 2,810.55 and 2,856.11 cm⁻¹ noted stretching vibrations due to the presence of –CH groups. Due to the presence of the –C–C groups, significant peaks were observed at the region of 1,646.17–1,640.55 cm⁻¹. Also at 1,231.11–1,243.33 cm⁻¹ peaks indicates –CO groups. The band observed between 1,027.3 and 1,036.5 cm⁻¹ was due to the presence of –C–C groups. The stretching vibrations of –CN groups lead to the peaks between 573.37 and 563.09 cm⁻¹.

Thermogravimetric analysis was carried out to determine the thermal stability of the biosorbent. A total of three decomposition steps were observed from Fig. 8. The first one being noted at 40°C–90°C, unbound moisture because of the water evaporation. Between the temperature 251.72°C and 440.21°C, the second decomposition was detected due to the degradation of the saccharide structure of the dead fungal biomass. The third decomposition witnessed between the temperature 440.21°C and 660.27°C due to the breakdown of the acetylated and deacetylated units of dead fungal biomass. The remaining residual mass



Fig. 5. Effect of temperature on the adsorptive removal of Turquoise Blue dye by *T. harzianum* (experimental conditions: pH 4, biosorbent dose of 0.4 g/L, dye concentration of 50 mg/L and contact time of 120 min).



Fig. 6. (a) SEM diagram of dead *T. harzianum* after biosorption and (b) SEM diagram of dead *T. harzianum* before biosorption.



Fig. 7. (a) FTIR spectra of dried *T. harzianum* before biosorption and (b) FTIR spectra of dried *T. harzianum* after biosorption.



Fig. 8. Thermogravimetric analysis of *T. harzianum* with dye.

after heating just before 800°C was 12.76% because of the presence of some minerals.

3.7. Thermodynamic studies

To determine the feasibility and spontaneity of biosorption, both energy and entropy factors should be considered. The Gibb's free energy change (ΔG°) is the measure of spontaneity. If ΔG° is a negative, then reactions is spontaneous. The Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are evaluated using the following equations [36]:

$$\Delta G^{\circ} = -RT \ln k_{c} \tag{3}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{4}$$

where *R* is the gas constant (8.314 J/mol K), and *T* is the absolute temperature in K. The values of ΔH° and ΔS° were obtained from the slope and intercept of the linear plot of ΔG° vs. temperature *T* [37], and the results are shown in the Table 1. ΔH° and ΔS° for the biosorption were determined to be 26.895 and 0.108 KJ/mol, respectively. The negative value of ΔG° shows the spontaneous and favourable condition of biosorption. The positive value of ΔH° confirms that the

Table 1 Thermodynamic parameters for the biosorption of Turquoise Blue dye at optimal conditions

| Temperature (K) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (J/mol K) |
|-----------------|-----------------------------|-----------------------------|------------------------------|
| 300 | -5.01 | 20.96 | 110.91 |
| 303 | -6.02 | | |
| 310 | -9.13 | | |
| 318 | -8.71 | | |

biosorption reaction is endothermic. The positive value of ΔS° indicates the increasing randomness at the solid/liquid interface during the biosorption process [38].

The value of distribution coefficient, k_c , can be calculated by:

$$k_c = \frac{q_e}{C_e} \tag{5}$$

where q_e and C_e is the adsorption capacity and concentration at equilibrium, respectively.

4. Isotherm modelling

The interactions between dye and biosorbent until a state of equilibrium can be studied using isotherms. In fact, it is important to investigate and obtain a fitting isotherm model for present Turquoise Blue biosorption system on *T. harzianum*. Therefore, the biosorption equilibrium data were fitted to the Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherm models.

The Langmuir isotherm parameters were determined by converting the following Langmuir equation:

$$q_e = \frac{Q_o b_L C_e}{1 + b_I C_e} \tag{6}$$

into the linearized form, where Q_o (mg/g) is the maximum monolayer adsorption capacity, and b_L (L/mg) is the Langmuir isotherm constant related to the affinity and binding energy. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_{L'}$ which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = \frac{1}{1 + b_L C_i} \tag{7}$$

where C_i is the initial concentration; b_L is the constant related to the energy of biosorption (Langmuir constant) [39]. If $R_L > 1$, the biosorption is unfavourable; if $R_L = 1$, the biosorption is linear condition; the biosorption is favourable when $0 < R_L < 1$ and $R_L = 0$ for irreversible condition. The values of maximum biosorption capacity, Langmuir isotherm constants, are listed and tabulated in Table 2. From the table, it is known that Langmuir isotherm model does not fit the equilibrium data. The maximum dye biosorption capacity of *T. harzianum* is found to be 14.14 mg/g. R_L (1.672) indicates the favourable biosorption.

The Freundlich isotherm model is commonly used to describe the adsorption characteristics for heterogeneous group. The equation is of the following linearized form:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{8}$$

where C_{i} is the equilibrium concentration of dye (mg/L); q_e is the amount of Turquoise Blue dye adsorbed per gram of the biosorbent at equilibrium (mg/g). The constant k_{f} is an approximate indicator of biosorption capacity, while 1/n is the indication of the strength of biosorption process [40]. The k_{t} and *n* values for *T. harzianum* can be achieved from the intercept and the slope of plot of $\log q_{e}$ against $\log C_{e'}$ as shown in Fig. 9. In accordance, the high correlation coefficient in Freundlich equation ($R^2 > 0.94$) depicts that Freundlich isotherm has the best fit on experimental data than the Langmuir model. Considering the result, it is concluded that the biosorption of Turquoise Blue on T. harzianum takes place through heterogenous surface by multilayer sorption. In Freundlich model, when *n* values lie between 1 and 10, the removing process will be beneficial biosorption.

The effect of indirect dye-biosorbent interactions on biosorption isotherm is exhibited by Temkin isotherm. While the Freundlich isotherm states that the fall in the heat of biosorption is logarithmic, the Temkin isotherm

 Table 2

 Biosorption isotherms parameter by *T. harzianum*

| Isotherm models | Parameters | Values |
|--------------------------------------|------------------------------------|----------------------|
| Langmuir | $Q_{o}(mg/g)$ | 14.14 |
| | b_L (L/mg) | 10.87 |
| | R^2 | 0.9867 |
| Freundlich | $k_f(mg/g)(L/mg)^{1/n}$ | 0.628 |
| | n | 1.56 |
| | R^2 | 0.9923 |
| Temkin | A_{T} (L/mg) | 0.3001 |
| | b_{T} (kJ/mol) | 3,541.1 |
| | R^2 | 0.8382 |
| Dubinin-Radushkevich | Q_m (mg/g) | 22.67 |
| | $K (\text{mol}^2 \text{ kJ}^{-2})$ | 2 × 10 ⁻⁵ |
| | E (kJ/mol) | 0.0045 |
| | R^2 | 0.6059 |
| 4 3.5 3 2.5 50 2 - | | *** |

0 0.5 1 1.5 2 2.5 logCe

1.5

1

0.5

0

onto T. harzianum.

shows that it is linear. This model considers that the biosorption is characterized by a uniform distribution of binding energies and the heat of biosorption of all the molecules decreases linearly. The experimental data were applied to Temkin isotherm equation [41], and the values of the constants were evaluated from the plots of q_e vs. $\ln C_e$ at different temperatures.

$$q_e = \frac{RT}{b_T} \ln A_T C_e \tag{9}$$

The constant *B*, which is related to the heat of biosorption, rises with an increase in temperature thereby proving that the biosorption is endothermic. The values of Temkin isotherm constants are listed and tabulated in Table 2. From the table, the data obtained does not fit Temkin isotherm model, which is inferred from its poor correlation coefficients.

The mean free energy of biosorption was calculated by applying the obtained data to D–R isotherm model. The equation related to this model is given as:

$$q_e = Q_m \exp^{-\kappa \epsilon^2} \tag{10}$$

where q_e is the amount of dye adsorbed per gram of biosorbent at equilibrium (mg/g); Q_m is the maximum biosorption capacity (mg/g); and *K* is the coefficient related to the mean free energy of biosorption (mol² kJ⁻²). ε is referred to as the Polanyi potential that can be estimated by the equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{11}$$

Mean biosorption energy E (kJ/mol) was calculated by means of the following equation [42]:

$$E = \sqrt{2K} \tag{12}$$

This model does not assume a constant biosorption potential or homogeneous surface. The saturation biosorption capacity can also be estimated by using D–R model for the sorption of Turquoise Blue. If the value of *E* is lesser than 8 kJ/mol, then the biosorption is of physical nature; if the value of *E* is between 8 and 16 kJ/mol, the biosorption follows by chemical ion exchange, and if the value is >16 kJ/mol, then chemisorption prevails. The values of the parameters present in the D–R model equation are listed in Table 2. From the Table 2, it confirmed that D–R isotherm model does not fit the equilibrium data.

5. Kinetic studies

It is extremely desirable to conduct a study of kinetics of the biosorption process as it provides information about the mechanism of biosorption and the rate of biosorption. Knowing the mechanism of biosorption is vital to estimate the efficiency of the process. Prediction of the rate of the biosorption process is one of the most important factors in the design of the biosorption system. This is the reason for conducting a series of kinetic calculations for the biosorption experiment. The linearized form of the pseudo-first-order model is given by the following equation [43]:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t$$
(13)

where k_1 is the pseudo-first-order rate constant.

The linearized form of second-order rate equation is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(14)

where k_2 is the pseudo-second-order rate constant [44].

From Table 3 and Fig. 10 we can clearly understood that the data obeys pseudo-second-order kinetic model rather than pseudo-first-order kinetic model. From the correlation coefficient values, the pseudo-second-order model hereby confirms that kinetic behaviour of biosorption is chemisorptions and not physisorption [45].

6. Conclusion

The toxic textile dye Turquoise Blue in aqueous phase is removed using dead fungal biomass of *T. harzianum*. The influence of the parameters such as pH (1–12), temperature (25°C–45°C), dye concentration (10–200 mg/L), contact time (10–150 min) and biosorbent dose (0.1–0.5 g/L) on biosorption process of dye onto dried *T. harzianum* was investigated. The maximum dye removal was achieved at pH (4), temperature (45°C), dye concentration (50 mg/L), contact time (120 min) and biosorbent dose (0.4 g/L). The isotherm studies indicate that equilibrium data fit well to Freundlich model. The pseudo-second-order kinetic equation interprets the biosorption kinetics reasonably. Thermodynamic studies reveal that the biosorption of Turquoise Blue dye onto dried *T. harzianum* is spontaneous and endothermic in nature.

Table 3 Parameters of kinetic models of biosorption of the Turquoise Blue by *T. harzianum*

| Concentration (mg/L) | Pseudo-first order | | | Pseudo-second order | | |
|----------------------|--------------------|-----------------------|--------|------------------------|-------------|-----------------------|
| | k_1 (cal) (min) | $q_e (\mathrm{mg/g})$ | R^2 | k_2 (cal) (g/mg/min) | $q_e(mg/g)$ | <i>R</i> ² |
| 10 | 8.522 | 1.79 | 0.8787 | 9.9 | 9.1 | 0.9958 |
| 20 | 9.726 | 1.8 | 0.9195 | 10.31 | 9.5 | 0.9986 |
| 30 | 10.829 | 1.87 | 0.9195 | 10.41 | 10.7 | 0.9986 |
| 40 | 10.901 | 1.93 | 0.9017 | 11.86 | 17.8 | 0.9856 |
| 50 | 11.097 | 2.10 | 0.8737 | 14.2 | 21.1 | 0.9959 |
| 100 | 12.546 | 2.47 | 0.7206 | 14.45 | 32.1 | 0.9934 |
| 150 | 13.655 | 2.52 | 0.9783 | 15.31 | 34.8 | 0.9954 |
| 200 | 14.788 | 2.56 | 0.8979 | 15.5 | 35.1 | 0.9923 |



Fig. 10. Pseudo-second-order kinetic model plot.

Table 4 Comparison of biosorption capacities *T. harzianum* over other adsorbents

| Adsorbent | Biosorption | References |
|------------------------|-----------------|---------------|
| | capacity (mg/g) | |
| Afsin–Elbistan fly ash | 7.936 | [46] |
| Surfactant-modified | 12.93 | [47] |
| zeolite | | |
| Sunflower seed shells | 1.075 | [48] |
| Eichhornia crassipes | 5.6 | [49] |
| Rice husk | 11.39 | [50] |
| Borassusaethiopum | 4.9 | [51] |
| flower | | |
| Biochar | 6.08 | [52] |
| Neem leaf powder | 7.43 | [53] |
| Ficus auriculata leaf | 13.33 | [54] |
| powder | | |
| T. harzianum | 14.14 | Present study |

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Symbols

- ΔG° Gibbs free energy, kJ/mol
- ΔH° Enthalpy, kJ/mol
- $\Delta S^{\circ} -$ Entropy, J/mol K
- Temkin isotherm equilibrium binding constant, A_{T} L/mg
- Temkin isotherm constant, J/mol
- dye concentration in solution at equilibrium, mg/L _
- Initial dye concentration, mg/L
- Exit dye concentration, mg/L
- Mean Biosorption energy, kJ/mol _
- 8 Polanyi potential
- Κ Coefficient related to the mean free energy of biosorption, mol²/kJ²
- k_1 pseudo-first-order constant, min
- k_2^1 pseudo-second-order constant, g/mg/min
- k, Distribution coefficient
- k_f K_f Freundlich isotherm constant, (mg/g)/(mg/L)^{1/n}
- Langmuir isotherm constant, L/mg
- Amount of biosorbent, g т _
- **Biosorption intensity** п _
- Amount of dye adsorbed per unit mass of q_e biosorbent, mg/g
- Q_m Maximum biosorption capacity in D-R model, mg/g _
- Maximum biosorption capacity, mg/g $q_{\rm max}$
- Amount of dye adsorbed at any time t, mg/g q_t
- Ŕ Atmospheric gas constant, 8.314 J/mol K
- \mathbb{R}^2 Coefficient of determination
- R_{I} _ Separation factor
- _ time, min or s t
- Т Temperature, K
- VVolume of the solution, L

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