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Direct dye biosorption by immobilized barley husk

Moin ud Din*, Haq Nawaz Bhatti, Muhammad Yasir, Aisha Ashraf

Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan, Tel. +92 321 7805005; Fax: +92 419 200193; emails: moingenious@yahoo.com, moingenious@gmail.com (M. ud Din), Tel. +92 333 6528455; email: hnbhatti2005@yahoo.com (H.N. Bhatti), Tel. +92 321 7539910; email: yasirchemist@yahoo.com (M. Yasir), Tel. +92 344 7878172; email: aisha_ashraf43@yahoo.com (A. Ashraf)

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ABSTRACT

The potential of low-cost adsorbent–barley husk to remove direct dye, namely Actarus Red BWS through biosorption process has been investigated in both continuous and batch modes. A series of experiments have been performed to evaluate the optimum biosorption conditions such as pH (2–5), biosorbent dosage (0.2–0.8 g), initial dye concentration (50–200 ppm), equilibrium time, and temperature (303–333 K). The adsorption efficiency decreased with increase in pH and increased with increase in biomass dose. Equilibrium isotherms have been developed by applying data to Langmuir, Freundlich, and Flory–Huggins models. The highest correlation coefficient ($R^2 = 0.99$) related to Langmuir isotherm indicated good fitness of this model, explaining the sorption as monolayer process. The process followed pseudo-second-order kinetic model. The negative ΔG° and positive ΔH° values indicated the spontaneous and endothermic nature of process. The continuous mode of biosorption has been tested as the function of flow rate and bed height too.

Keywords: Biosorption; Barley husk; Actarus Red BWS; Isotherm; Kinetics

1. Introduction

Discharge of colored waste into aquatic streams without any proper treatment poses serious threat towards environment and human health [1]. Dyes are classified according to their use in dying process like acidic, basic, mordant, direct, disperse, vat, reactive, azo dyes, etc. Synthetic dyes are being used in all industries such as textile, paper, craft mills, dye manufacturing, food and cosmetic industries [2] as these are simple to handle, inexpensive, and have much stability. In addition, their availability in variety of new colors and better imparting properties in comparison with natural dyes make their use so frequent. Nearly, 10,000 different dyes and pigments are available commercially worldwide and 5–10% of these are being excreted as waste [3].

Water pollution is due to discharge of colored effluents by various dye manufacturing units and textile dye mills into water bodies. Even their little quantity is sufficient to pollute large water bodies which not only reduces the light penetration but also inhibits the process of photosynthesis and thus disturbing the aquatic systems [4]. Dye poses significant toxicity towards humans and animals. Their prolonged contact with eyes and skin causes severe irritation, while ingestion may result in gastrointestinal irritation with nausea, vomiting, and diarrhea [5]. Cellulose is being dyed using direct dyes for more than 100 years. Dyes

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*Corresponding author.

in this group have various planar, highly conjugate molecular structures with one or more anionic sulfonate group due to which these dyes become water soluble [6].

In general, dyes are poorly degradable and conventional treatment processes have shown little effect towards their removal. These methods can be divided into three groups: biological, physical, and chemical [7]. The search of new methods for the removal of noxious materials has directed the consideration towards biosorption which is based on dye-binding capacities of various materials having biological origin. The research has clearly proved that adsorption is the most convenient and economic method for the removal of toxic metals and dyes from the wastewater. Adsorption of toxic chemicals from the effluent using a waste material and its recovery by desorption process has further broadened the role of adsorption technique in environmental science [8]. Adsorbents still used include wastes like banana and orange peel [9], sawdust [10], seaweeds [11], wheat straw [12], wheat bran [13], etc.

Barley, a member of grassy family Poaceae, is an annual cereal grain which is serving as a major feed crop for large number of animal population with little quantity used in malting and health food. It is widely dispersed in Turkey, Syria, Egypt, Pakistan, India, and Western China.

The intension behind present study has been the evaluation of cheap and suitable method for dye removal from an artificial effluent. Barley husk has been studied for its effectiveness in removal of Actarus Red BWS, which belongs to the class of direct dyes.

2. Experimental Section

2.1. Adsorbent

Barley husk was collected from local fields of Faisalabad, washed with water, cut into small pieces, and dried in shade for several days. The dried biomass was crushed in an electrical ball mill. Powdered biosorbent was sieved using Octagon sieve (OCT-DIGITAL 4527-01) to obtain uniform particle size fraction <0.250 mm.

2.2. Immobilization of biomass

Dried and sieved barley husk was immobilized by making its solution with sodium alginate in water. The mixture was shaken well until it became homogeneous and viscous. Then, it was trickled drop wise from burette into 0.1 M $CaCl_2$ solution to get fine spherical beads [14].

2.3. Artificial effluent

The direct dye used in this study was Actarus Red BWS. A stock solution (1,000 ppm) of dye was prepared in deionized water and further dilutions were made to get different concentrations (50–200 mgL^{-1}). The desired pH of solutions was adjusted by adding appropriate quantity of 0.1 M HCl and NaOH solutions.

2.4. Apparatus

A U-2001 model UV–vis spectrophotometer having a tungsten lamp was used to analyze the dye concentrations in solution at λ_{max} 520 nm. pH of solutions was measured using HI-8104 HANNA digital pH meter.

2.5. Batch biosorption studies

Batch studies were carried out in conical flasks by mixing the pre-weighted quantity of immobilized biosorbent in aqueous dye solution of particular concentration and pH. The conical flasks were shaken at constant temperature in orbital shaker (PA 250/25. H) for a predetermined time interval at a fixed speed i.e. 125 rpm. The contact time between dye and biomass was 10–90 min with temperature range 30–60°C.

2.6. Continuous biosorption studies

Continuous flow sorption experiments were conducted in a packed glass column. Glass wool was kept at base and top of column whereas packing was done with known quantity of biomass to provide a desired bed height. The flow rate was regulated using a variable peristaltic pump for proper percolation of effluent through a bed of biomass. The flow rates were altered in a range between 3 and 15 mL/min. Column study was performed at room temperature (30 ± 0.5°C) which was periodically checked during the course of operation. The dye samples were collected at different time intervals in 10 mL volume and analyzed at λ_{max} 520 nm.

3. Results and discussion

3.1. Effect of pH

The pH of solution is an important factor for determining the biosorption process of dyes. Synthetic effluents from different industries contain dyes with varying extent of ionization at different values of pH. Similarly biosorbents have different biopolymers of varying net charge with the change in pH. So, pH is a significant factor for removal of dyes from aqueous solution [15,16].

The pH profile for Actarus Red BWS for both continuous and batch studies using barley husk is depicted in Fig. 1. The maximum removal in both cases was at pH 1 i.e. 19.82 and 24.70 mg/g for continuous and batch modes, respectively. The reason was the availability of more cationic sites on the surface of biosorbent at lower pH providing more binding sites for anionic dye molecules. On the other hand, the increase in OH^- ions with the increase in pH of solution developed a competition among dye anions for the adsorption sites resulting in decrease biosorption [17].

3.2. Effect of biosorbent dose

Fig. 2 represents the effect of biosorbent dose on the sorption capacity of barley husk. Dose of sorbent was varied from 0.2 to 0.8 g and equilibrated for 3 h. An increase in the sorption capacity was observed from 0.2 to 0.8 g biomass dosage as 19.70–31.18 mg/g and 24.15–36.47 mg/g for both continuous and batch mode, respectively. This could be contributed to increase in surface area and sorption sites with increase in biomass concentration [18].

3.3. Effect of initial dye concentration

The dye concentration has a significant effect in biosorption process. With the increase in dye concentration, biosorption increased up to a limit followed by stabilization shown in Fig. 3. In continuous mode, adsorption capacity was increased from 19.92 to 40.19 mg/g, whereas in case of batch study, it increased as 22.42–48.46 mg/g, as initial dye concentration increased from 50–150 mg/L. This could be attributed to increase in competition of ions for the binding sites at higher concentration. But after achieving maximum point in all these experiments, there stabilization was seen for further increase in dye concentration or even decrease indicating saturation of all binding sites [19].

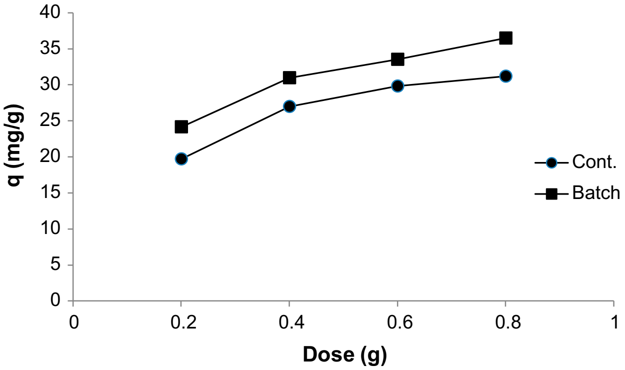

Fig. 2. Effect of dose on biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

3.4. Effect of time

The effect of time to establish equilibrium is represented in Fig. 4. Removal efficiency was quite rapid during initial stage which gradually stabilized to achieve equilibrium. Equilibrium established in 60 min for both modes of operation. The rapid rate of dye biosorption could be attributed to the availability of large number of sites for adsorption which decreased gradually due to their saturation [20].

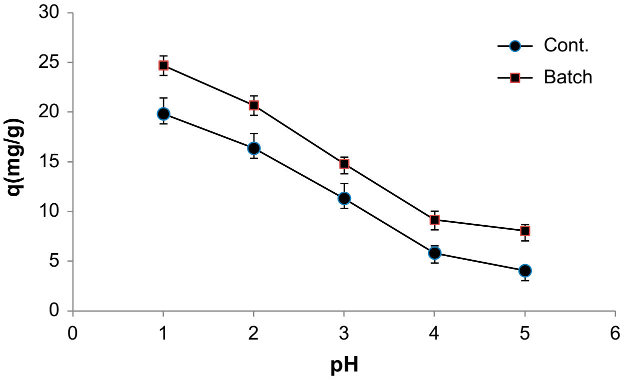

Fig. 1. Effect of pH on biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

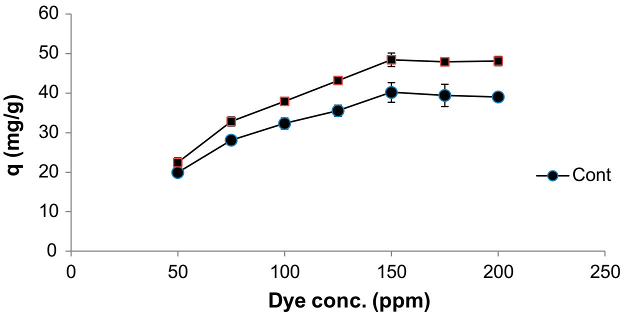

Fig. 3. Effect of initial dye concentration on biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

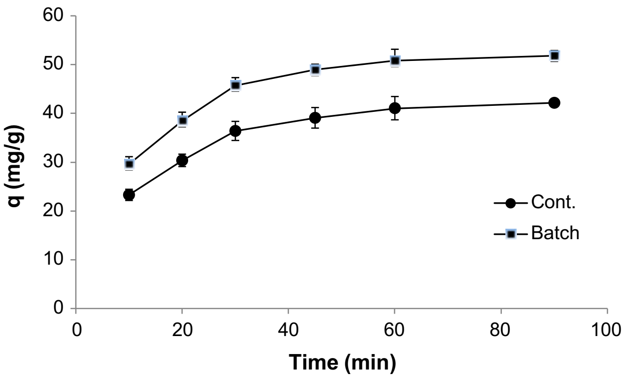

Fig. 4. Effect of time on biosorption of Actarus Red BWS by immobilized Barley husk waste biomass.

3.5. Effect of flow rate

In column, the rate of flow of effluent was varied from 3 to 15 mL/min to determine the effect of flow rate on uptake capacity of barley husk. The result is shown in Fig. 5. It is clear that flow rate effectively influenced the uptake capacity of dye and inverse relationship was found among them [21]. This is because at lower rates the contact of dye with biomass was for longer period of time which resulted in greater removal and vice versa [22]. Therefore, Actarus Red BWS biosorption was reduced from 48.27 to 14.09 mg/g with an increase in flow rate from 3 to 15 mL/min.

3.6. Effect of bed height

The beds of varying heights ranging from 2.5 to 18.5 cm of immobilized barley husk were used to evaluate its effect on biosorption of Actarus Red BWS in continuous flow packed column at pH 1 with flow rate 3 mL/min and the initial dye concentration 150 mg/L. The results are shown in Fig. 6. Direct relationship was found between bed height and dye uptake capacity of biomass which is due to fact that uptake capacity is depends on amount of biomass available for sorption [23]. The sorption capacity of Actarus Red BWS was found maximum i.e. 47.21 mg/g at bed height 18.5 cm.

3.7. Equilibrium modeling

Equilibrium data are the basic requirement to apply different designs related to adsorption system. In order to find out the sorption capacity of barley husk waste biomass for Actarus Red BWS, three, two parameter models were used and their results are shown in Table 1.

3.7.1. Langmuir isotherm

It assumes that there is present fixed number of binding sites distributed homogeneously over the entire surface of biosorbent. The equation can be written as [24]

$$q_e = \frac{Q_o.b.C_e}{1 + b.C_e} \tag{1}$$

where C_e is the residual dye concentration (mg/L), Q_o (mg/g) and b (L/mg) are the Langmuir constants representing the monolayer adsorption capacity and adsorption energy, respectively, and quantity of dye adsorbed is given by q_e (mg/g). The plots of $1/C_e$ vs. $1/q_e$ (Fig. 7(a)) at temperature 303 K in continuous mode and three different temperatures (303, 313 and 323 K) in batch mode were used to calculate these

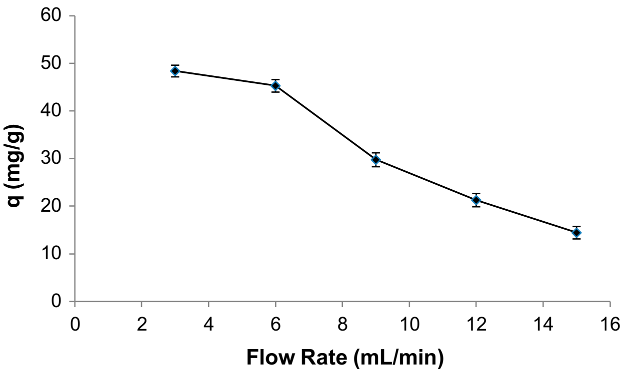

Fig. 5. Effect of flow rate on biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

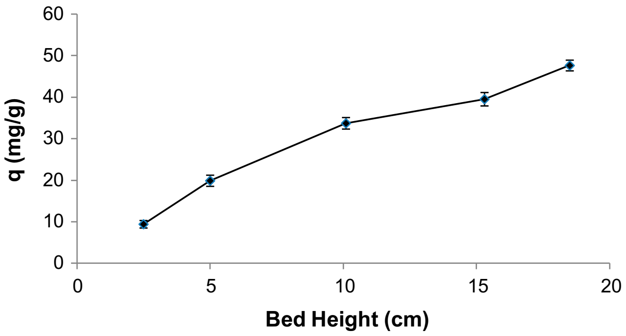

Fig. 6. Effect of bed height on biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

Table 1
Langmuir, Freundlich, and Flory–Huggins isotherm constants and correlation coefficients for the biosorption of Actarus Red BWS onto immobilized barley husk waste biomass

Isotherm	Temp. (K)	Batch	Continuous
Langmuir	303	Q_o (mg/g) = 71.87 K_L (L/mg) = 2.02 $R^2 = 0.97$ $b = 0.016$	Q_o (mg/g) = 53.26 K_L (L/mg) = 2.77 $R^2 = 0.98$ $b = 0.020$
	313	Q_o (mg/g) = 83.11 K_L (L/mg) = 1.77 $R^2 = 0.99$ $b = 0.015$	
	323	Q_o (mg/g) = 90.60 K_L (L/mg) = 1.73 $R^2 = 0.97$ $b = 0.016$	
Freundlich	303	K_f (mg/g) = 10.37 $n = 2.93$ $R^2 = 0.89$	K_f (mg/g) = 8.53 $n = 3.03$ $R^2 = 0.89$
	313	K_f (mg/g) = 10.53 $n = 2.78$ $R^2 = 0.93$	
	323	K_f (mg/g) = 12.67 $n = 3.01$ $R^2 = 0.95$	
Flory–Huggins	303	$K_{FH} = 0.0296$ $n_{FH} = 3.02$ $R^2 = 0.95$	$K_{FH} = 0.036$ $n_{FH} = 2.82$ $R^2 = 0.96$
	313	$K_{FH} = 0.0295$ $n_{FH} = 3.23$ $R^2 = 0.95$	
	323	$K_{FH} = 0.027$ $n_{FH} = 3.28$ $R^2 = 0.96$	

constants (Table 1). The isotherms at all temperatures were found linear over the whole range of concentration studied and the correlation coefficients were extremely high which strongly supported that Actarus Red BWS biosorption data closely followed the Langmuir model.

Moreover, to test the adsorption favorability separation factor R_L was also calculated as

$$R_L = \frac{1}{(1 + b\ C_o)} \tag{2}$$

where C_o is the initial metal concentration (mg/L).

This parameter explains the isotherm as follows

$R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$ reversible.

The values of R_L for the tested biosorbent were in range 0–1 which showed favorable uptake of dye that is also depicted from the shape of the curve (Fig. 7(b)).

3.7.2. Freundlich isotherm

It considers the sorption surface to be heterogeneous. The linear form of the model [25] is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \cdot (\log C_e) \tag{3}$$

where K_f is the constant relating biosorption capacity (mg/g dry weight), n is the Freundlich exponent relating biosorption intensity and it varies with heterogeneity of the material. The values of K_f and $1/n$ (Table 1) were calculated by plotting log C_e vs. log q_e (Fig. 7(c)). However, coefficients of correlation indicated that data were not well correlated to Freundlich isotherm.

3.7.3. Flory–Huggins Isotherm

This model was applied to evaluate the extent of surface coverage of dye on sorbent [26]:

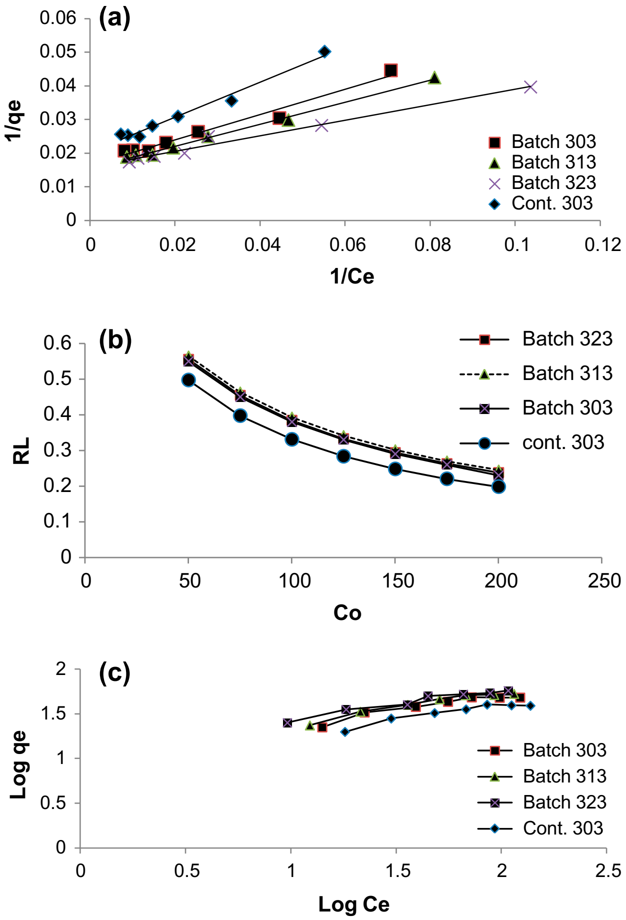

Fig. 7. Langmuir isotherm plot (a), Freundlich (b), and separation factor plot (c) for biosorption of Actarus Red BWS onto immobilized barley husk waste biomass.

$$\log \frac{\theta}{C_o} = \log K_{FH} + n_{FH} \cdot \log(1-\theta) \tag{4}$$

where K_{FH} is the Flory–Huggins model equilibrium constant, n_{FH} is model exponent for the said model, and θ is the degree of surface coverage. The isotherm showed the linear plot and values of K_{FH} and n_{FH} calculated from the slope and intercept of the plot for both batch and continuous modes are shown in Table 1. The high value of R^2 shows good applicability of the model for this biosorbent.

3.8. Biosorption kinetic study

The Lagergren's pseudo-first- and second order was applied to evaluate the biosorption kinetics of Actarus Red BWS onto immobilized biomass for both continuous and batch mode performed at 303 K. The experimental data which were used here at initial concentrations 150 mg/L for both modes (Fig. 8).

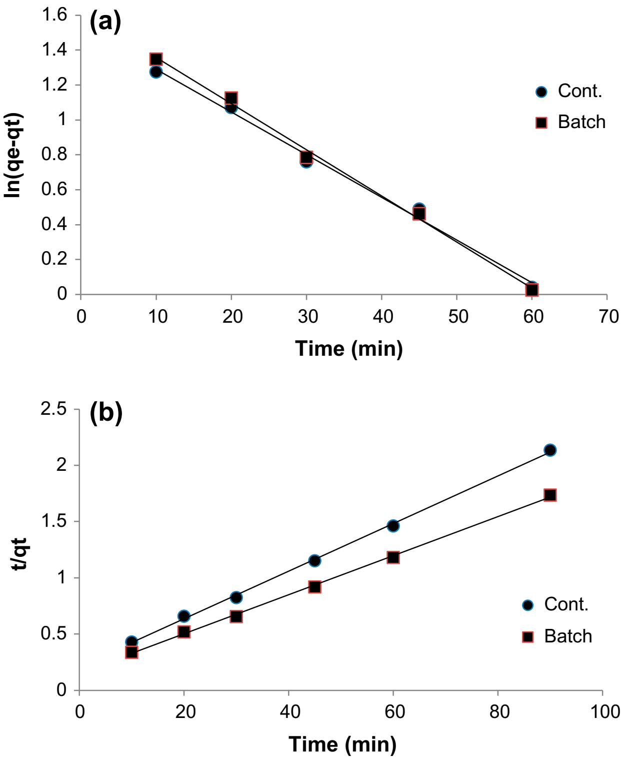

Fig. 8. Pseudo-first-order plot (a) and Pseudo-second-order plot (b) for biosorption of Actarus Red BWS onto immobilized barley husk waste biomass.

The linear form of pseudo-first-order rate equation [27] is given as

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \tag{5}$$

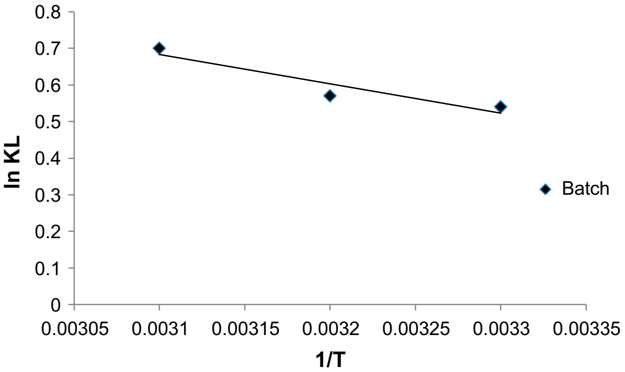

Fig. 9. Plot of K_L vs. $1/T$ for biosorption of Actarus Red BWS by immobilized barley husk waste biomass.

Table 2
Pseudo-first-order and pseudo-second-order models for the biosorption of Actarus Red BWS onto immobilized barley husk waste biomass

		Pseudo first order			Pseudo second order		
Mode	q_{exp} (mg/g)	q_{cal} (mg/g)	K_1 (min^{-1})	R^2	q_{cal} (mg/g)	K_2 (min^{-1})	R^2
Batch	50.77	41.84	−0.061	0.99	57.47	0.0019	0.99
Continuous	41.03	34.19	−0.056	0.98	47.17	0.0021	0.99

Table 3
Values of thermodynamic parameters for the biosorption of Actarus Red BWS onto immobilized barley husk biomass

Dye	Temperature (K)	ΔG° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})
Actarus Red BWS	303	−1.378	26.26	6.64
	313	−1.483		
	323	−1.877		

where q_e (mg/g) and q_t are the amounts of metal ions sorbed at equilibrium time and at t (min), respectively, and K_1 is the first-order-rate constant (min^{-1}).

Pseudo-second-order kinetic model was also applied on the experimental data given below [28]

$$\frac{t}{q_t} = \frac{1}{K_2.q_e^2} \cdot \frac{t}{q_e} \tag{6}$$

where K_2 (mg g^{-1} min^{-1}) is the rate constant for second-order reaction, q_t and q_e (mg/g) are the biosorption at time t (min) and at equilibrium, respectively.

The rate constants and correlation coefficient values for different models are given in Table 2. Pseudo-second-order equation showed best fit rather than pseudo-first-order equation with high correlation coefficient ($R^2 = 0.99$) and closer q_{exp} value to theoretical value. It made clear that not only biosorbent amount affected the biosorption rate but also contributed the other factors like pH, temperature, initial dye concentration, etc. [29].

3.9. Biosorption thermodynamics

Thermodynamic parameters such as Gibbs free energy ΔG°, enthalpy ΔH°, and entropy ΔS° were calculated to describe the thermodynamic behavior of biosorption of Actarus Red BWS onto barley husk biomass using following equations:

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

where R is the general gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the temperature (K), and K_L is the Langmuir constant.

The values of enthalpy (ΔH°) and entropy (ΔS°) were calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{9}$$

The values of ΔG° were calculated from Eq. (7). The values of ΔH° and ΔS° were calculated from slope and intercept of the plot of K_L vs. $1/T$, respectively (Fig. 9). The negative values of ΔG° indicated that the process was spontaneous and feasible and adsorption favorability increased with temperature. Positive value of ΔH° confirmed the endothermic nature of biosorption process. The positive change in entropy indicated increase in randomness at solid–liquid interface during the process of adsorption. It also suggested some structural changes in dye and the adsorbent [30]. The values of thermodynamic parameters for the biosorption of Actarus Red BWS onto barley husk are given in Table 3.

4. Conclusions

Biosorption of direct dye, Actarus Red BWS, onto immobilized barley husk biomass from aqueous solution in both batch and continuous mode was tested.

Various parameters like pH of solution, biomass dosage, contact time, initial metal concentration, and temperature were tested. The experimental data were analyzed using Langmuir, Freundlich, and Flory-Huggins isotherm models. The equilibrium data were well described by the Langmuir isotherm model with maximum monolayer biosorption capacity 57.52 and 39.04 mg g^{-1} for batch and continuous mode, respectively. The analysis of kinetic data revealed that pseudo-second-order model was the best applicable for the description of biosorption process. Thermodynamic parameters indicated that biosorption process was feasible, endothermic, and spontaneous.

Acknowledgments

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References

[1] I.K. Tonlé, E. Ngameni, H.L. Tcheumi, V. Tchiéda, C. Carteret, A. Walcarius, Sorption of methylene blue on an organoclay bearing thiol groups and application to electrochemical sensing of the dye, Talanta 74 (2008) 489–497.

[2] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061–1085.

[3] S.V. Mohan, S.V. Ramanaiah, P.N. Sarma, Biosorption of direct azo dye from aqueous phase onto *Spirogyra* sp. *I02*: Evaluation of kinetics and mechanistic aspects, Biochem. Eng. J. 38 (2008) 61–69.

[4] I.A. Rahman, B. Saad, S. Shaidan, E.S. Sya Rizal, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical–thermal process, Bioresour. Technol. 96 (2005) 1578–1583.

[5] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 52 (2014) 227–237.

[6] J.S. Bae, H.S. Freeman, Synthesis and evaluation of non-genotoxic direct dyes, Fibers Polym. 3 (2002) 140–146.

[7] Y. Wang, Y. Mu, Q.B. Zhao, H.Q. Yu, Isotherms, kinetics and thermodynamics of dye biosorption by anaerobic sludge, Sep. Purif. Technol. 50 (2006) 1–7.

[8] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desalin. Water Treat. 53 (2015) 214–220.

[9] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. 92 (2002) 263–274.

[10] S.P. Raghuvanshi, R. Singh, C.P. Kaushik, A.K. Raghav, Removal of textile basic dye from aqueous solutions using sawdust as bio-adsorbent, Int. J. Environ. Stud. 62 (2005) 329–339.

[11] V. Murphy, H. Hughes, P. McLoughlin, Comparative study of chromium biosorption by red, green and brown seaweed biomass, Chemosphere 70 (2008) 1128–1134.

[12] H.D. Doan, A. Lohi, V.B.H. Dang, T. Dang-Vu, Removal of Zn^{+2} and Ni^{+2} by adsorption in a fixed bed of wheat straw, Process Saf. Environ. Prot. 86 (2008) 259–267.

[13] Y. Bulut, Z. Baysal, Removal of Pb(II) from wastewater using wheat bran, J. Environ. Manage. 78 (2006) 107–113.

[14] S.K. Nadavala, K. Swayampakula, V.M. Boddu, K. Abburi, Biosorption of phenol and *o*-chlorophenol from aqueous solutions on to chitosan–calcium alginate blended beads, J. Hazard. Mater. 162 (2009) 482–489.

[15] M.Y. Arıca, G. Bayramoğlu, Biosorption of reactive red-120 dye from aqueous solution by native and modified fungus biomass preparations of *Lentinus sajor-caju*, J. Hazard. Mater. 149 (2007) 499–507.

[16] B.E. Wang, Y.Y. Hu, L. Xie, K. Peng, Biosorption behavior of azo dye by inactive CMC immobilized *Aspergillus fumigatus* beads, Bioresour. Technol. 99 (2008) 794–800.

[17] M.C. Ncibi, B. Mahjoub, M. Seffen, Investigation of the sorption mechanisms of metal-complexed dye onto *Posidonia oceanica* (L.)bres through kinetic modelling analysis, Bioresour. Technol. 99 (2007) 5582–5589.

[18] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desalin. Water Treat. 52 (2014) 4508–4519.

[19] H. Salehizadeh, S.A. Shojaosadati, Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*, Water Res. 37 (2003) 4231–4235.

[20] E. Pehlivan, A.M. Özkan, S. Dinç, Ş. Parlayici, Adsorption of Cu^{2+} and Pb^{2+} ion on dolomite powder, J. Hazard. Mater. 167 (2009) 1044–1049.

[21] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Bioresour. Technol. 99 (2008) 2938–2946.

[22] M.G.A. Vieira, R.M. Oisiovici, M.L. Gimenes, M.G.C. Silva, Biosorption of chromium(VI) using a *Sargassum* sp. packed-bed column, Bioresour. Technol. 99 (2008) 3094–3099.

[23] K. Vijayaraghavan, M. Thilakavathi, K. Palanivelu, M. Velan, Continuous sorption of copper and cobalt by crab shell particles in a packed column, Environ. Technol. 26 (2005) 267–276.

[24] U. Farooq, J.A. Kozinski, M.A. Khan, M. Athar, Biosorption of heavy metal ions using wheat based biosorbents—A review of the recent literature, Bioresour. Technol. 101 (2010) 5043–5053.

[25] O.S. Lawal, A.R. Sanni, I.A. Ajayi, O.O. Rabiu, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*, J. Hazard. Mater. 177 (2010) 829–835.

[26] M.H. Jnr, I. Spiff, Equilibrium sorption study of Al^{+3} and Ag in aqueous solution by fluted pumpkin (*Telfairia occidentalis* HOOK f) waste biomass, Acta. Chim. Slov. 52 (2005) 174–181.

[27] M.V. Subbaiah, Y. Vijaya, A.S. Reddy, G. Yuvaraja, A. Krishnaiah, Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto *Trametes versicolor* biomass, Desalination 276 (2011) 310–316.

[28] Y. Prasanna Kumar, P. King, V.S. Prasad, Equilibrium and kinetic studies for the biosorption system of copper(II) ion from aqueous solution using *Tectona grandis* L.f. leaves powder, J. Hazard. Mater. 137 (2006) 1211–1217.

[29] R. Herrero, P. Lodeiro, R. Rojo, A. Ciorba, P. Rodríguez, M.E. Sastre de Vicente, The efficiency of the red alga *Mastocarpus stellatus* for remediation of cadmium pollution, Bioresour. Technol. 99 (2008) 4138–4146.

[30] R. Jain, P. Sharma, S. Sikarwar, J. Mittal, D. Pathak, Adsorption kinetics and thermodynamics of hazardous dye Tropaeoline 000 unto Aeroxide Alu C (Nano alumina): A non-carbon adsorbent, Desalin. Water Treat. 52 (2014) 7776–7783.