Desalination and Water Treatment
www.deswater.com
1944-3994/1944-3986
doi: 10/5004/dwt.2012.2928

37 (2012) 169–177
January

Taylor & Francis
Taylor & Francis Group

Removal of textile dyes from aqueous solutions with eco-friendly biosorbent

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Received 19 April 2011; Accepted 4 July 2011

ABSTRACT

Inexpensive and eco-friendly biosorbent wheat bran has been successfully utilized for the removal of textile dyes from aqueous solutions. Remazol Red F3B (Reactive red 180) was initially used as a model textile dye. The effects of contact time, pH, initial dye concentration, biosorbent dose and temperature were investigated. The optimum biosorption conditions were found as following: contact time 4 h, initial pH 2.0, initial dye concentration 200 mg/l, biosorbent dose 0.25 g and temperature 20°C. The results indicate that acidic pH supported the biosorption of dyes on the wheat bran. The biosorption capacity was 39.42 mg/g for this dye. Using optimum biosorption conditions, five other dye types with reactive, direct and acidic structures were also investigated for biosorption capacity. The Langmuir and Freundlich models were evaluated using the experimental data and the experimental results showed that the Langmuir equation fit better than the Freundlich equation. Different thermodynamic parameters i.e., changes in standard free energy, enthalpy and entropy have also been evaluated and it has been found that the reaction was spontaneous and exothermic in nature. Finally, the effect of biosorbent surface was analyzed by scanning electron microscope (SEM). SEM images showed reasonable agreement with adsorption measurements.

Keywords: Wheat bran; Biosorption; Kinetic study; Reactive dye; Direct dye; Acidic dye

1. Introduction

There are more than ten thousand type of commercially available dyes with over seven hundred tons of dyestuff produced annually worldwide and used extensively in textile, dyeing and printing industries [1–3]. It is estimated that about 10–15% of the dyes were lost in industrial effluents [4].

Textile dye wastewater is well known to contain strong color, high pH, presenting large amount of suspended solids, COD and low bio-degradable chemicals especially the effluent from the dyeing stages of the dyeing and finishing processes [5]. The removal of dye color is therefore a challenge to both the textile industry and the wastewater-treatment facilities. Apart from being aesthetically displeasing, they are toxic to some aquatic organisms and are of serious health risk to human beings. Therefore, these synthetic dyes cause considerable environmental pollution. They bring greater public concern and present legislation problems. A very small amount of dye in water (10–50 mg/l) is highly visible and reduces light penetration, gas solubility in water systems thus causing a negative effect on photosynthesis [6,7].

Recently, dye removal became a research area of increasing interest, as government legislation concerning the release of contaminated effluent has become more stringent. Physical and chemical methods such as biological oxidation, adsorption, foam flotation, electrolysis, coagulation-flocculation, ozonation, oxidation,

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filtration, membrane separation, photo catalysis and electrochemical methods have been used for wastewater decolourisation [8–23].

The adsorption process is one of the most efficient methods of reactive, acidic and direct dyes in neutral solutions removing pollutants from wastewater and provides an attractive alternative treatment, especially if the biosorbent is inexpensive and readily available [24]. Granular activated carbon is the most popular biosorbent and has been used with great success, but it is expensive [25,26].

Many studies have been made on the possibility of biosorbents using activated carbon, peat, chitin, silica, fly ash, clay, apple pomace, wheat straw, orange peel, banana peel, maize cob, maize stalk, rice husk, peanut hull barley husk, wood chip, palm fruit bunch, sawdust, eucalyptus bark, neem leaf powder, coir pith, banana pith, bagasse pith, aquatic plants, hen feather, sunflower stalk and others [6, 27–53].

Recent studies have shown that different bran species posses impressive adsorption capacities for a range of heavy metal ions but there is a few studies on the colour removal [54,55]. Every year, large amounts of straw and bran from wheat, a major food crop of the world, are produced as by-products/waste materials. The purpose of this article is to investigate rather scattered information on the utilization of wheat bran for the removal of dyes from waters.

The present work deals with a series of experiments to assess the utility of wheat bran as a biosorbent for the removal of textile dyes from aqueous solution. The aim of the study is to investigate the effect of wheat bran biosorption capacity for different type of dyes. Therefore the optimum conditions of contact time, pH, initial dye concentration, biosorbent dose, temperature were determined using Remazol red F3B (Reactive red 180) as an initial dye model. Based on optimum conditions obtained five other different dye types were performed for the maximum removal of these dyestuff by wheat bran from aqueous solutions. With this in mind, wheat bran was examined as a biosorbent, which is low cost, biodegradable and poses no disposal problems. For this purpose, some known kinetic equations have also been evaluated.

2. Materials and methods

2.1. Biosorbent

Wheat bran was supplied from commercial market in Turkey and used for the preparation of biosorbent. It was washed with distilled water and then dried. The particle size distribution of the wheat bran was determined by Mastersizer 2000. According to the obtained values from the equipment, at least 50% of the size distribution was approximately between 490–505 μm.

2.2. Adsorbate

An accurately weighed quantity of the dyes was dissolved in double-distilled water to prepare stock solutions (1000 mg/l). Experimental solutions of the desired concentration were obtained by dilutions with double-distilled water. The pH of each solution was adjusted to the required value with 0.1 M HCI and NaOH solutions before mixing the wheat bran. Remazol red F3B (Reactive red 180), Remazol brillant orange 3R (Reactive orange 16), Remazol black B (Reactive black 5), Sirius red F3B (Direct red 80), Telon red BN (Acid red), Telon yellow 4R (Acid yellow 199) was supplied by Dystar company. Table 1 presents the selected dyes and their characteristics as reported in the color index [58].

2.3. Batch adsorption studies

The removal of textile dyes on wheat bran was studied using a batch technique. 50 ml of the dye solution was taken in 100 ml erlenmayer flasks containing wheat bran. The flasks were agitated on a shaker at 180 rpm for a pre-determined time. After equilibration, 10 ml of the suspension was centrifuged in a stopped tube for 5 min at 3000 rpm and 4 ml of the dye solution was taken from the tube by a filtered syringe for measurement. The color of dye concentrations were measured with a Cintro model UV/VIS spectrophotometer using maximum absorbance wavelength values (λ_{max}) for each dye. To determine the optimum conditions of the several parameter such as contact time, pH, initial dye concentration, biosorbent dose, temperature were studied for the model dye compound Reactive red 180. Using optimum conditions dye removal capacity, equilibrium values and kinetic studies were performed for all other dyes.

Table 1
Selected dyes and their characteristics, taken from the color index Ref [56]

	Initials	Commercial name	Generic name	λ_{max}
Reactive	RR	Remazol Red F3B	Reactive red 180	539
Reactive	RO	Remazol Brillant Orange 3R	Reactive orange 16	498
Reactive	RB	Remazol Black B	Reactive black 5	597
Direct	SR	Sirius Red F3B	Direct red 80	525
Acid	TR	Telon Red BN	Acid red	510
Acid	TY	Telon Yellow 4R	Acid yellow 199	446

Decolourisation of dyes sorbed by the wheat bran was calculated using the following equation:

$$\text{Removal percentage} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

C_0 and C_t (mg/l) are the initial and final concentration of dye solutions

Biosorption capacity of the wheat bran was calculated using the following equation:

$$q = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where q (mg/g) is the amount of dye sorbed by wheat bran, C_0 and C_e (mg/l) are the initial and equilibrium liquid phase concentration of dye solutions, respectively, V (l) is the initial volume of dye solution, W (g) is the weight of the wheat bran.

3. Results and discussion

3.1. Effect of different parameters

3.1.1. Effect of contact time

For the biosorption processes, biosorption experiments were carried out for different contact times with a fixed biosorbent dose 1.0 g, initial dye concentration 50 mg/l at solution pH 5.80 and at 20°C (Fig. 1). It is observed that the uptake of the dye increases with time. It was established that at 20°C, within the first hour of contact, almost 59% of dye removal was achieved for wheat bran. In the case of wheat bran, 4 h of reaction was found to be sufficient to attain equilibrium.

3.1.2. Effect of pH

The pH of the dye solution plays an important role in the whole biosorption process and especially on the biosorption capacity. Experiments were performed at different pH (2.0, 3.0, 5.80, 7.0 and 10.0). It was clear from Fig. 2 that the removal of dye was lower in alkaline pH. However, the removal was higher in the acidic range and reached a maximum at pH 2.0. The removal was increased from 52.67% to 96.05% with decrease of pH from 10.0 to 2.0 at 20°C.

This variation is also reported as similar on elsewhere [59,60]. It is known that ionic dyes upon dissolution release colored dye anions/cations into solution. The biosorption of these charged dye groups onto the biosorbent surface is primarily influenced by the surface charge on the biosorbent, which is in turn influenced by the solution pH.

3.1.3. Effect of dye concentration

Different Reactive red 180 dye concentrations (50, 100, 200, 300 and 400 mg/l) were used to determine the effect of dye concentration. The increase in the dye concentration over 100 mg/l did not affect the uptake capacity significantly (Fig. 3).

3.1.4. Effect of biosorbent dose

In order to evaluate the maximum biosorption capacity of the wheat bran, the effect of biosorbent dose was investigated. For wheat bran biosorption

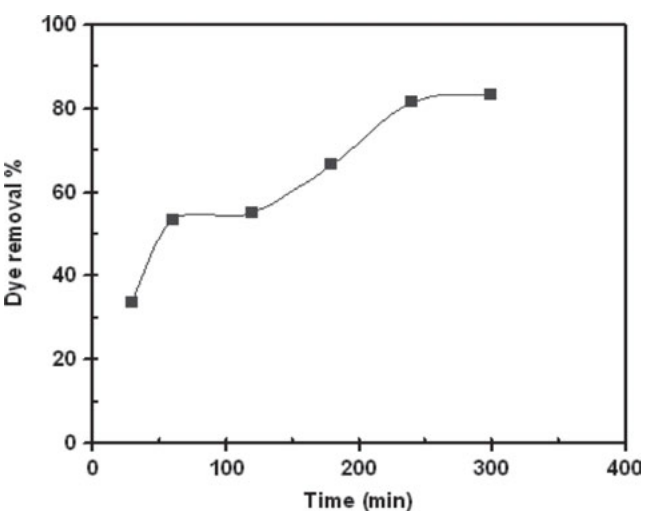

Fig. 1. Effect of contact time on the removal of Reactive red 180 by wheat bran (Biosorbent dose 1.0 g, initial concentration of dye 50 mg/l, pH 5.80 and 20°C).

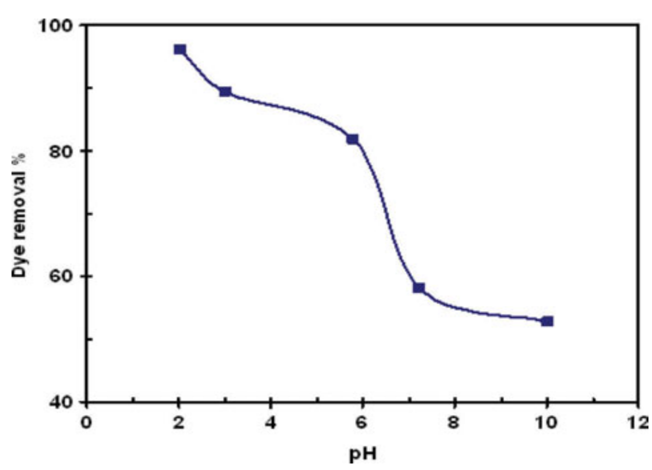

Fig. 2. Effect of pH on the removal of Reactive red 180 by wheat bran (Contact time 4 h, biosorbent dose 1.0 g, initial concentration of dye 50 mg/l and 20°C).

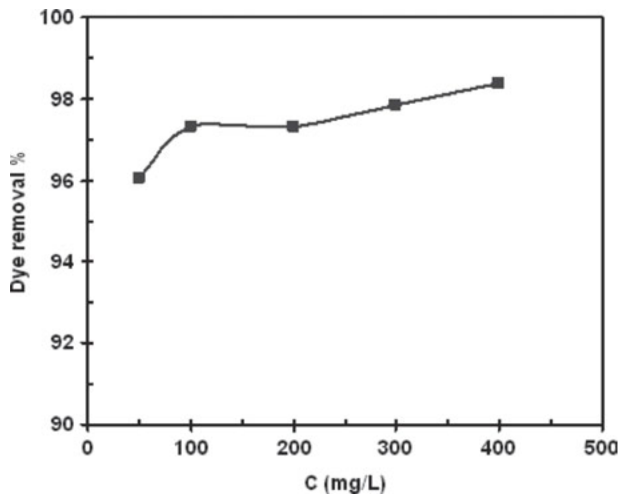

Fig. 3. Effect of dye concentration on the removal of Reactive red 180 by wheat bran (Contact time 4 h, biosorbent dose 1.0 g, pH 2.0 and 20°C).

system, the dose of respective biosorbent was varied from 0.25, 1.0, 2.0, 3.0 g respectively at a fixed pH, temperature and adsorbate concentration. It was observed that the uptake of the dye increased with increased biosorbent dose from 0.25 to 3.0 g (Fig. 4). However, the removal efficiency was already around 93% for 0.25 g dose and increased only around 5% more while the biosorbent dose was increased to 3.0 g which is 12 times of the initial value of 0.25 g. Hence, all subsequent studies were carried out with 0.25 g biosorbent dose as an optimum value.

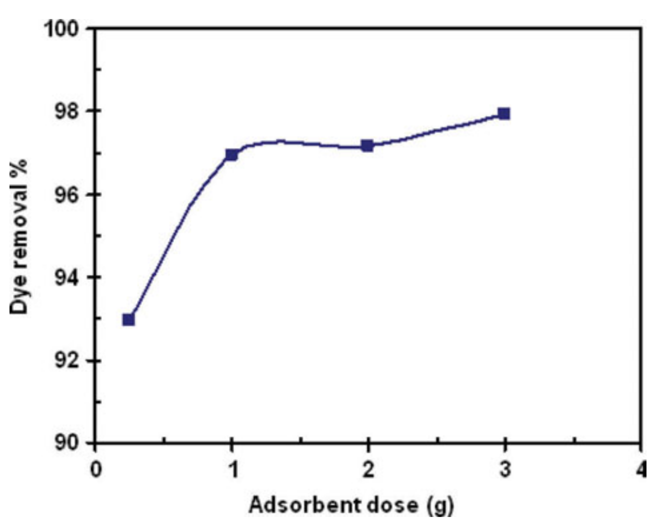

Fig. 4. Effect of biosorbent dose on the removal of Reactive red 180 by wheat bran (Contact time 4 h, initial concentration of dye 200 mg/l, pH 2.0 and 20°C).

3.1.5. Effect of temperature

Biosorption experiments were carried out at three different temperatures, i.e. 20, 35, 45 and 50°C, and at a constant Reactive red 180 concentrations of 200 mg/l, biosorbent dose 0.25 g and pH 2.0. It was observed that the uptake of Reactive red 180 by the wheat bran decreased with the increase in temperature (Fig. 5).

The thermodynamic parameters for the biosorption process, ΔH, ΔS and ΔG^0, were evaluated using the equation [40,41]:

$$\Delta G^0 = -RT \ln K \tag{3}$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H}{RT} \tag{4}$$

where K, known as the distribution coefficient of the adsorbate, is equal to (q_e/C_e). R is the gas constant (8.314 J/mol K) and T is the temperature in Kelvin. The plot of ln$K$ vs $1/T$ is linear with the slope and the intercept giving values of ΔH and ΔS (Fig. 6). These values could be used to compute ΔG^0 from the Gibbs relation, $\Delta G^0 = \Delta H - T\Delta S$ at constant temperature.

All these relations are valid when the enthalpy change remains constant in the temperature range.

These thermodynamic parameters are given in Table 2. Generally, the change of free energy for physical biosorption is smaller than that of chemical biosorption. From Table 2, the standard free energy change, ΔG^0, for the biosorption of Reactive red 180 onto wheat bran

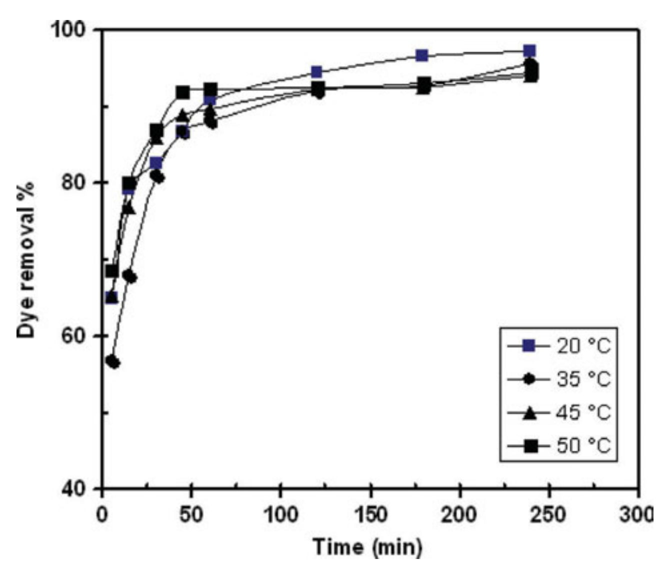

Fig. 5. Effect of temperature on the removal of Reactive red 180 by wheat bran (Contact time 4 h, initial concentration of dye 200 mg/l, pH 2.0 and biosorbent dose 0.25 g).

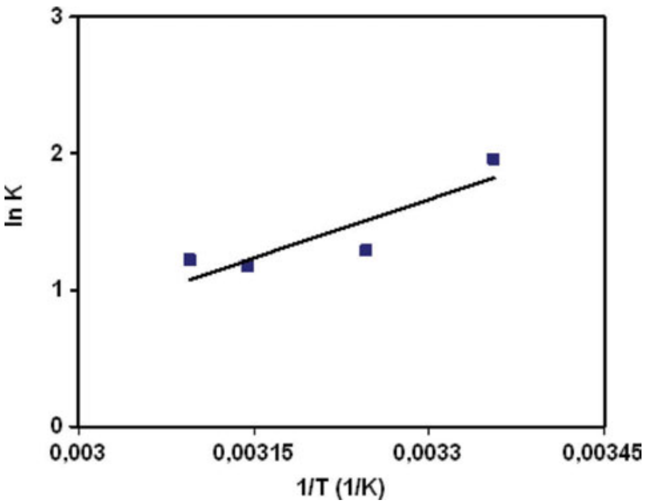

Fig. 6. Plot of ln K versus $1/T$ for estimation of the thermodynamic parameters.

Table 2
Thermodynamic parameters for biosorption of Remazol Red F3B on wheat bran at different temperatures

Temperature (20°C)	$-\Delta G^0$ (k J/mol)	$-\Delta H^0$ (k J/mol)	$-\Delta S^0$ (k J/mol)
20	4.79	23.545	0.064
35	3.83		
45	3.19		
50	2.87		

was from –4.79 to –2.57 kJ/mol. It is obvious from this table that the negative and small value of free energy change (ΔG^0) was an indication of spontaneous nature of the biosorption process. The negative values of standard enthalpy change (ΔH^0) at different temperatures were indicating the exothermic nature of the biosorption process and the negative values of (ΔS^0) suggested the probability of a favorable biosorption [62].

3.1.6. SEM analysis

Scanning electron micrographs of wheat bran and adsorbed wheat bran with Remazol Red 180 are shown in Fig. 7. From Fig. 7, it is clear that, the SEM pictures of wheat bran samples show considerable numbers of holes and spots where there is a good possibility for dyes to the trapped and adsorbed into these spaces.

3.2. Effect of different structure of dye types

Using the optimum conditions based on the model dye (Reactive red 180) results, five other dye types were also evaluated for biosorption capacity of the wheat

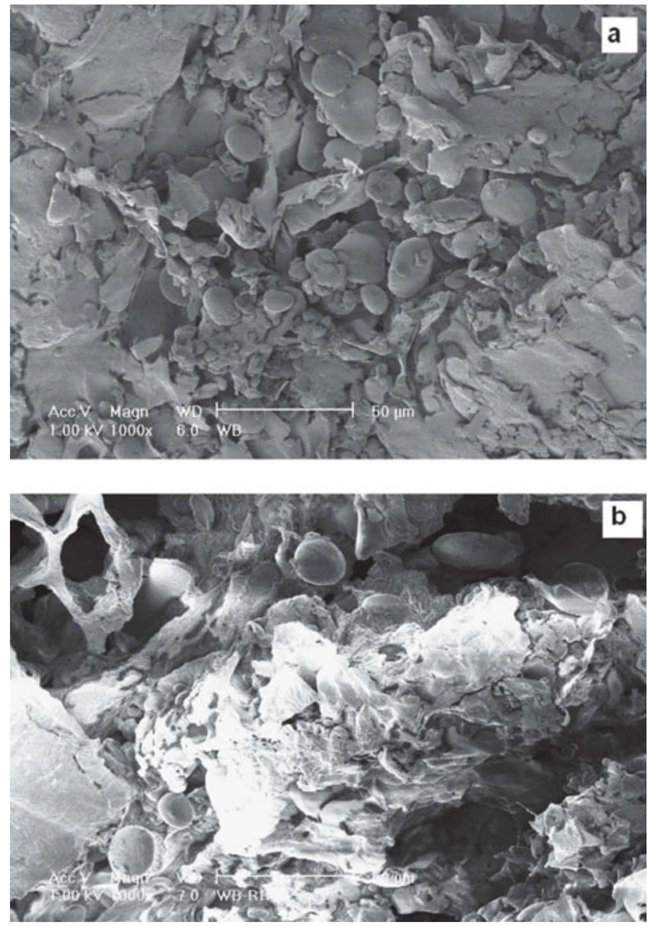

Fig. 7. SEM micrograph of sample: (a) wheat bran; (b) dye biosorbed wheat bran with Remazol Red 180.

bran. The other dye types are also listed on Table 1. The results are indicated in Fig. 8 as dye removal percents and in Table 3 as biosorbent capacity of wheat bran for different dyes. The results showed almost similar values for biosorption capacity and the difference between values and different initial percent yields can be related to chemical structure, molecular size and stereo-chemistry of the dyes, this is also stated elsewhere [63].

3.3. Biosorption isotherms

Biosorption isotherms are the most important information for analyzing and designing a biosorption process [64,65]. Several isotherm equations are available and two important isotherms are selected in this study, the Langmuir and Freundlich isotherms [66,67]. The Langmuir biosorption isotherm assumes that adsorption takes place at specific homogeneous sites within the biosorbent and has found successful applications for too many biosorption processes of monolayer adsorption. The Langmuir isotherm can be written in the form

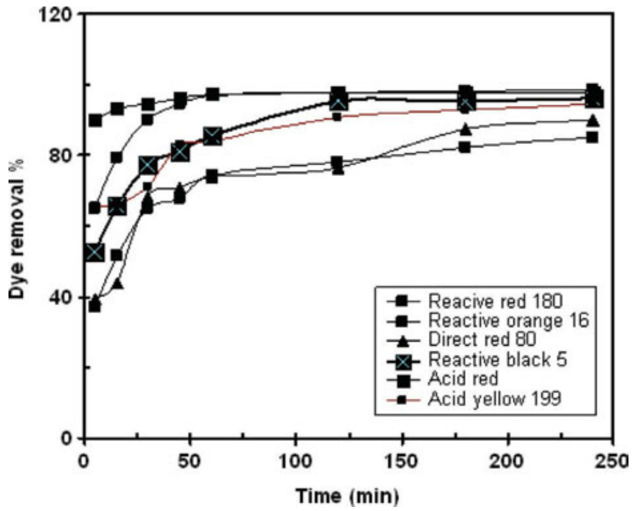

Fig. 8. Dye removal percent for the biosorption of different type of dye structure by wheat bran (Contact time 4 h, initial concentration of dye 200 mg/l, pH 2.0 and biosorbent dose 0.25 g, 20°C).

Table 3
Biosorbent capacity of wheat bran for different type of dyes

	RR	RO	RB	SR	TR	TY
q_e	39.42	34.03	38.44	36.03	39.15	37.76

$$q_e = \frac{Q_m K C_e}{1 + K C_e} \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m}\left(\frac{1}{C_e}\right) \tag{6}$$

where q_e (mg/g) is the adsorbed amount of the dye, C_e (mg/l) is the equilibrium concentration of the dye in solution, Q_m (mg/g) and b (l/mg) are Langmuir isotherm constants related to maximum biosorption capacity and energy of biosorption, respectively. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equations are

$$q_e = K_F C_e^{1/n} \tag{7}$$

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

where, K_F is biosorption capacity at unit concentration and $1/n$ is biosorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) and unfavorable ($1/n>1$).

The biosorption capacity depends on the properties of adsorbate and biosorbent. All constants obtained by both Langmuir and Freundlich models are listed in Table 4. From Table 4, it can be concluded that the biosorption isotherms of RR, RB, RO, SR, TR and TY exhibit Langmuir behavior. The suitability of Langmuir model shows that the biosorption process is monolayer and has a constant adsorption energy. The Langmuir isotherm yields the best fit for all dyes. The results also showed that besides the Langmuir model, Freundlich model is also suitable for describing the biosorption of RR, RB, RO, SR, TR and TY.

4. Conclusion

The biosorption of textile dyes from aqueous solution onto wheat bran has been studied. Biosorption tests were carried out as a function of contact time, biosorbent dose, pH, dye concentration and temperature. The biosorption experiments indicated that wheat bran was effective in removing textile dyes such as Reactive red 180, Reactive black 5, Reactive orange 16, Direct red 80, Acid red, Acid yellow 199 from aqueous solutions. The percentage of removal increased with the increasing concentration of dye in the solution and increased with the increasing biosorbent dose. Thermodynamic studies confirmed that process was spontaneous and exothermic. The fitness of the biosorption data into Langmuir isotherm confirmed the monolayer adsorption. The biosorption data was described by the Langmuir isotherm equation.

The results of this study and the comparison of recent studies are both given at Table 5. There are numerous studies on the removal of heavy metals by the means of

Table 4
Isotherm parameters for different type of textile dyes at 20°C

Isotherms	Parameters	RR	RB	RO	SR	TR	TY
Langmuir	Q_m	65.79	70.4	76.3	27.3	166.6	96.15
	b	0.154	0.04	0.017	5.40	0.085	0.03
	R^2	0.989	0.989	0.982	0.949	0.981	0.903
Freundlich	K_F	10.84	6.59	2.15	19.02	18.77	4.02
	n	2.40	2.21	1.49	10.73	1.91	1.46
	R^2	0.805	0.877	0.899	0.785	0.958	0.890

Table 5
Comparison of adsorbent capacities for different dyes

Biosorbent/non-biosorbent	Dyes	q_{max} (mg/g)	References
Wheat bran	Reactive red 180	39.42	This study
	Reactive orange 16	34.03	
	Reactive black 5	36.03	
	Direct red 80	39.15	
	Acid red	37.76	
	Acid yellow 199		
Natural zeolite with cetyltrimethylammonium bromide	Reactive black 5	12.9	[68]
Sunflower seed shells	Reactive black 5	0.87	[69]
Fly ash	Reactive black 5	7.9	[70]
Titania	Reactive black 5	23.7	[71]
Laminaria biomass	Reactive black 5	41.9	[72]
Waterworks sludge	Reactive Orange 16	47	[73]
Crosslinked poly (N-vinylpyrrolidone)	Reactive Orange 16	0.5	[74]
Bagasse fly ash	Orange G	18.8	[75]
	Methyl Violet	26.2	
Rice husk	Methylene Blue	40.6	[76]
Spent brewery	Acid Orange 7	30.5	[77]
Barley straw	Reactive black 5	25.4	[78]
	Acid blue 40	47	
Activated carbon	Reactive black 5	58.8	[70]
Glass powder	Acid red 4	4.03	[79]
Red mud	Direct red 28	4.05	[80]

wheat bran. We not only found out that there are only one or two studies on this subject one of which is, in fact, our group study, but also that there exists no other study examining reactive, direct, and acid dyes concurrently. Furthermore, this study indicates that the biosorption capacity of the wheat bran is better than many other bio and non-bio adsorbents explored in the literature. Given the facts that wheat bran necessitates no pretreatment; it is eco-friendly and low-cost, and that it has a satisfying biosorption capacity, it might well be used in different types of removal activities where textile dyes, phenolics, pesticides, and the like are concerned.

Appendix A. List of symbols

C_0 — Initial dye concentration (mg/l)
C_t — Final dye concentration (mg/l)
C_e — Equilibrium liquid phase concentration of dye solutions (mg/l)
K_F — Freundlich biosorption constant (mg/g)
N — Freundlich biosorption constants
q — Amount of dye sorbed per gram of biosorbent at any time (mg/g)
q_e — Amount of dye per gram of biosorbent at equilibrium (mg/g)
Q_m — Langmuir biosorption constant (mg/g)
b — Langmuir biosorption constant (l/mg)
R — Gas constant (8.314 J mol/K)
R^2 — Correlation coefficient
W — Amount of biosorbent (g)
t — Time (min)
T — Solution temperature (^{0}C, K)
V — Initial volume of dye solution (l)
K — Equilibrium constants (l/mol)
ΔG^0 — Standard free energy change (kJ/mol)
ΔH^0 — Enthalpy change (kJ/mol)
ΔS^0 — Entropy change (kJ/mol)

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