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Low cost removal of reactive dyes using wheat bran

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Abstract

In this study, the adsorption of Reactive Blue 19 (RB 19), Reactive Red 195 (RR 195) and Reactive Yellow 145 (RY 145) onto wheat bran, generated as a by-product material from flour factory, was studied with respect to initial pH, temperature, initial dye concentration, adsorbent concentration and adsorbent size. The adsorption of RB 19, RR 195 and RY 145 onto wheat bran increased with increasing temperature and initial dye concentration while the adsorbed RB 19, RR 195 and RY 145 amounts decreased with increasing initial pH and adsorbent concentration. The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data depending on temperature and the isotherm constants were determined by using linear regression analysis. The monolayer covarage capacities of wheat bran for RB 19, RR 195 and RY 145 dyes were obtained as 117.6, 119.1 and 196.1 mg/g at 60 °C, respectively. It was observed that the reactive dye adsorption capacity of wheat bran decreased in the order of RY 145 > RB 19 > RR 195. The pseudo-second order kinetic and Weber–Morris models were applied to the experimental data and it was found that both the surface adsorption as well as intraparticle diffusion contributed to the actual adsorption processes of RB 19, RR 195 and RY 145. Regression coefficients (R^2) for the pseudo-second order kinetic model were higher than 0.99. Thermodynamic studies showed that the adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran was endothermic in nature.

Keywords: Reactive Blue 19 (RB 19); Reactive Red 195 (RR 195) and Reactive Yellow 145 (RY 145); Wheat bran; Isotherm; Kinetic models; Adsorption

1. Introduction

Colored wastewater, particularly associated with those reactive azo dyes that are used for dyeing cellulose fibres, is a consequence of batch processes both in the dye manufacturing industries and in the dye consuming industries [1]. The discharge of these wastewaters into receiving streams not only affects the aesthetic nature but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity [2]. In addition, there are more than 100,000 dyes available commercially, most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic orgin [3]. Furthermore, the expanded uses of azo dyes have shown that some of them and their reaction products such as aromatic amines are higly carcinogenic [4]. Therefore, removal of dyes before disposal of the wastewater is of significant environmental technical and commercial importance. Physical and/or chemical methods such as chemical coagulation and/or ozonation, electrochemical treatment and biological treatment have been used to achieve decolorization of the wastewater. However, the decolorization process using these methods may be economic unfeasibility because a significant amount of toxic sludge may be due to excessive chemical usage [5,6]. A conventional biological treatment process is not very effective in treating a dye wastewater due to low biodegrability of dyes [7,8].

Adsorption of pollutants from aqueous solution plays an important role in wastewater treatment since it eliminates the need for huge sludge-handling processes [9]. Activated carbon is the most commonly used adsorbent for the treatment of dye bearing wastewaters. However, this process is proved to be uneconomic due to the high cost of activated carbon and also the additional cost involved in regeneration [10]. Therefore, the potential exists for the process of dye removal by adsorption to be more economically feasible by looking at the use of lower cost adsorbents. Different adsorbents have been used for removal of various dyes from aqueous solutions. These include sepiolite [11], cross-linked chitosan beads [12], vermiculite [13], sawdust [8], activated clay [14], rice husk [2], dolomitic sorbents [15], bagasse fly ash [2,16], perlite [17], apple pomace and wheat straw [18], algae [10,19] and powdered peanut hull [20].

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Nomenclature

C_0	initial dye concentration (mg/L)
C_t	the dye concentration at any time t (mg/L)
C_{ad}	the adsorbed dye concentration (mg/L)
C_{eq}	unadsorbed dye concentration in solution at equilibrium (mg/L)
ΔG	free energy change (kJ/mol)
ΔH	enthalpy change (kJ/mol)
k_1	pseudo-first order rate constant of (1/min)
k_2	pseudo-second order rate constant (g/mg.min)
K_a	constant related to the affinity of the binding sites (L/mg)
K_F	adsorption capacity
K_i	intraparticle rate constant (mg/g.min$^{1/2}$)
M	adsorbent amount (g)
MW	molecular weight (g/g mol)
n	adsorption intensity
q	amount of adsorbed dye per unit weight of adsorbent (mg/g)
q_t	amount of adsorbed dye per unit weight of adsorbent at any time t (mg/g)
q_{eq}	the amount of adsorbed dye per unit weight of adsorbent at equilibrium (mg/g)
q_{exp}	experimental amount of adsorbed dye per unit weight of adsorbent at equilibrium (mg/g)
$q_{cal,1}$	calculated amount of adsorbed dye per unit weight of adsorbent at equilibrium (mg/g) from the pseudo-first order kinetic model (mg/g)
$q_{cal,2}$	calculated amount of adsorbed dye per unit weight of adsorbent at equilibrium from the pseudo-second order kinetic model (mg/g)
q_{max}	maximum amount of the dye per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/g)
R	the universal gas constant, 8.314 (J/mol K)
R^2	correlation coefficient
ΔS	entropy change (kJ/mol K)
T	absolute temperature (K)

This study presents results on the adsorption of RB 19, RR 195 and RY 145 by wheat bran. Reactive dyes are extensively used for dyeing and printing in industries and dye effluents have resulted in serious environmental problems [21]. For this reason, RB 19, RR 195 and RY 145 dyes have been selected as model compounds to determine the adsorption capacity of wheat bran, as a cheap adsorbent, to uptake reactive dyes from their wastewaters.

2. Materials and methods

2.1. Preparation of wheat bran

The wheat bran used in this study is a by-product of a flour factory in Elazığ, Turkey. The wheat bran was sieved at different mesh adsorbent sizes and was directly added to the dye solutions.

2.2. Chemicals

The stock solutions of RB 19, RR 195 and RY 145 dyes were prepared in 1.0 g/L concentration and then diluted to an appropriate concentration. The initial pH of each run solution was adjusted to the required value with concentrated and diluted H_2SO_4 and NaOH solutions before mixing with the wheat bran.

2.3. Experimental

In the first section of the study, the experiments were conducted in a 1000 mL vessel containing 500 mL of synthetic dye solution. For this, 0.5 g of wheat bran with 50–100 mesh, except for the adsorbent dose and adsorbent size experiments, was mixed with the adsorption solution of known initial dye concentration and initial pH and then the adsorption solution was mixed magnetically at a constant temperature and rate. Samples were taken at predetermined time intervals for the dye concentration remaining in the solution. They were centrifuged at 10,000 rpm for 5 min and the supernatant was analysed. The experiments were repeated for different parameters such as initial pH, initial dye concentration, adsorbent dose, adsorbent size and temperature.

For the second part of the study, the isotherm experiments were carried out in 150 mL Erlenmeyer flasks containing 100 mL of adsorption solution. The flasks were agitated at a constant temperature and shaking rate for 24 h. Samples were taken at 24th hour. The centrifugation and dye analysis was repeated as in the first section experiments.

2.4. Dye analysis

The analysis of dye remaining in the solution was done colourimetrically using a spectrophotometer (Bausch & Lomb Spectronic 20). The absorbance values for RB 19, RR 195 and RY 145 were read at 592, 540 and 420 nm, respectively. Then, dye concentration was calculated from a calibration curve. The adsorbed dye amount (mg/g) and adsorption yield (%) at any time were computed as follows, respectively:

$$q_t\,(\mathrm{mg/g}) = \frac{(C_0 - C_t) \times V}{M} \quad (1)$$

$$\text{Adsorption yield}\,(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 and C_t are the initial and any time t dye concentration (mg/L), V is the solution volume (L) and M is the adsorbent mass (g).

3. Results and discussion

3.1. Determination of optimum adsorption conditions

3.1.1. The effect of initial pH

Initial pH is one of the most important factors affecting the adsorption process. Fig. 1 shows the effect of initial pH on the

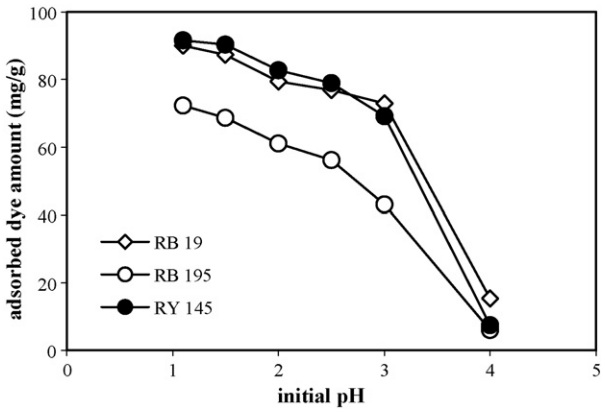

Fig. 1. The effect of initial pH on the uptake capacity of wheat bran for RB 19, RR 195 and RY 145 (initial dye concentration 100 mg/L, adsorbent dose 0.5 g, temperature 20 °C, contact time 24 h, adsorbent size 50–100 mesh).

adsorption of RB 19, RR 195 and RY 145 onto wheat bran at 20 °C, adsorbent concentration of 1.0 g/L and initial dye concentration of 100 mg/L. As can be seen from Fig. 1, the adsorbed amounts of RB 19, RR 195 and RY 145 dyes decreased with increasing initial pH and the optimum pH value for the studied dyes was found to be 1.0. Reactive and acid dyes have anionic characters. Higher uptake values obtained at lower pH values may be due to electrostatic attractions between negatively charge dye anion and positively charged wheat bran surface. As the initial pH of the solution increases, the number of negatively charged sites increases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion [4,9,12]. Similar result was also obtained for the adsorption of RR 189 onto chitosan at an initial pH 1.0 [22].

3.1.2. The effect of the temperature

Fig. 2 shows the effect of temperature on the adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran at initial pH 1.5, adsorbent dose 0.5 g and initial dye concentration of 100 mg/L. While the optimum pH was obtained as 1.0, the initial pH of adsorption solution was adjusted to 1.5 since the decrease of pH values from 1.5 to 1.0 requires too much reagent to use. The adsorbed RB 19, RR 195 and RY 145 amounts increased with increasing temperature from 20 to 50 °C, resulting endothermic adsorption process. In general, an increase in temperature is followed by an increase in the diffusivity of dye ion, and consequently by an increase in the adsorption rate if diffusion is the rate-controlling step [23]. An increase in the uptake of RB 19, RR 195 and RY 145 dyes with temperature may also be due to the enhanced rate of particle diffusion of dye because the diffusion is an endothermic process [14].

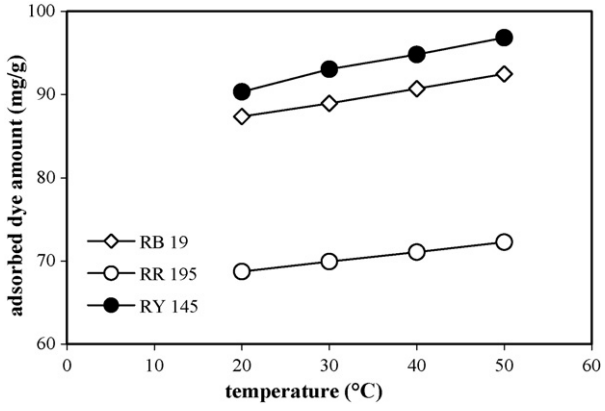

Fig. 2. The effect of temperature on the uptake capacity of wheat bran for RB 19, RR 195 and RY 145 (initial dye concentration 100 mg/L, adsorbent dose 0.5 g, initial pH 1.5, contact time 24 h, adsorbent size 50–100 mesh).

3.1.3. The effect of the contact time and initial dye concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases [9]. The effect of initial dye concentration on adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran was investigated in the range of 50–150 mg/L of the initial dye concentrations while the temperature, initial pH, adsorbent dose and adsorbent size values were kept at 20 °C, 1.5, 0.5 g and 50–100 mesh, respectively. Time course of uptake for the studied dyes is presented in Fig. 3. It was observed that the adsorption equilibrium for the studied dyes was established for 300 min and was not depending on the initial dye concentrations and dye species (Fig. 3). The contact time is of significant importance in the wastewater treatment by adsorption [2]. Strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium [2]. As a result, the adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran is the chemical adsorption since 5 h contact time for the adsorption equilibrium is much higher. Fig. 4 shows the variation with the initial dye concentration of the adsorbed dye amounts for the studied dyes. The adsorbed RB 19, RR 195 and RY 145 amounts (mg/g) increased with increasing initial dye concentration up to 100–150 mg/L and then they did not change with further increase in the dye concentration since it has reached to saturation of the adsorption, as can be seen from Fig. 4. The adsorption yields of RB 19, RR 195 and RY 145 onto wheat bran for different initial dye concentrations are also given in Table 1. The adsorption yields of wheat bran for RB 19, RR 195 and RY 145 dyes for 50 and 100 mg/L of initial dye concentrations were found as 97.5 and 94.2, 98.9 and 87.4, 68.7 and 90.3%, respectively (Table 1). Lower adsorption yields at higher dye concentrations are due to the saturation of adsorption sites. The results showed that the dye adsorption capacity of wheat bran decreased in the order of RY 145 > RB 19 > RR 195.

3.1.4. The effect of the adsorbent dose and adsorbent size

The effect of adsorbent dose on RB 19, RR 195 and RY 145 uptake capacity of wheat bran was investigated, with different adsorbent dose in the range of 0.5–3.0 g at 20 °C temperature, initial pH 1.5 and initial dye concentration 100 mg/L. The variation of the adsorbed RB 19, RR 195 and RY 145 amounts with adsorbent dose is given in Fig. 5 and the adsorption yields (%) of wheat bran for RB 19, RR 195 and RY 145 are also presented in Table 1. It was observed that the adsorption yields

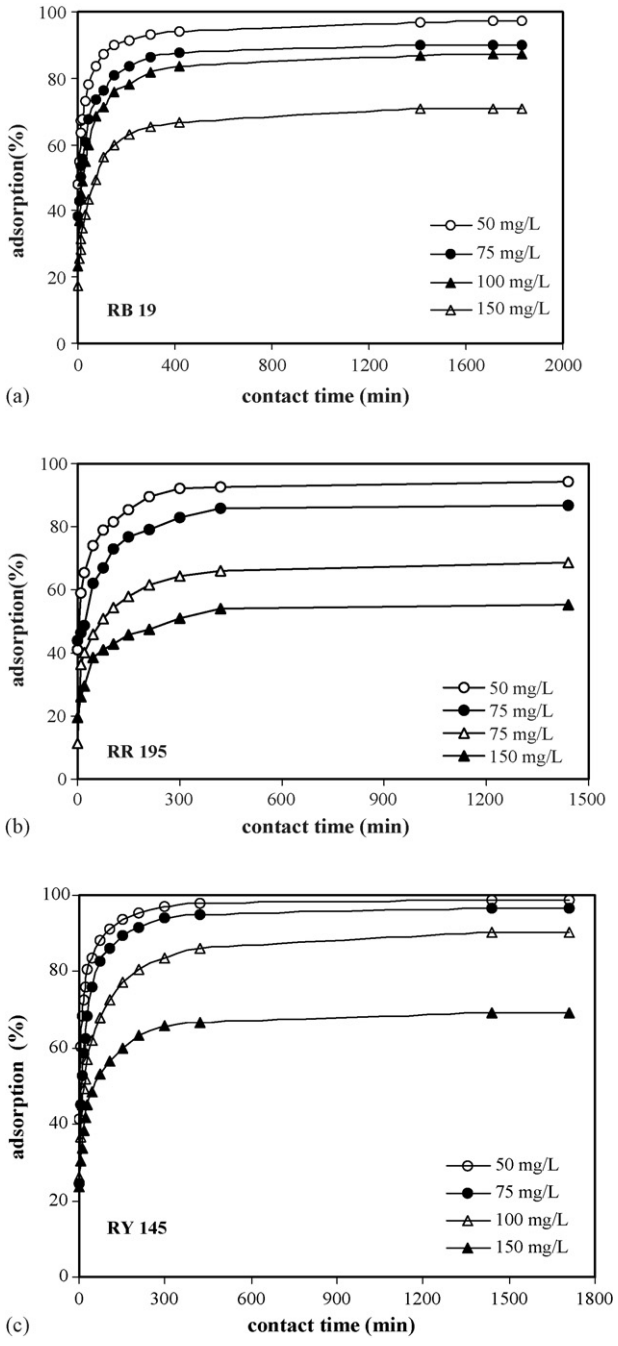

Fig. 3. The effect of contact time on the uptake capacity of wheat bran for (a) RB 19, (b) RR 195, (c) RY 145 (temperature 20 °C, adsorbent dose 0.5 g, adsorbent size 50–100 mesh).

of wheat bran for RB 19, RR 195 and RY 145 increased with increasing adsorbent dose while the adsorbed RB 19, RR 195 and RY 145 amounts per unit adsorbent weight decreased by increasing the adsorbent dose from 0.5 to 3.0 g. At higher wheat bran to solute concentration ratios, there is a very fast superficial sorption onto the adsorbent surface that produces a lower solute concentration in the solution than when the adsorbent to solute concentration ratio is lower [24]. Increase in the adsorption yield at low adsorbent dose can be explained by the availability of more adsorption sites. The decrease in uptake amounts (q, mg/g)

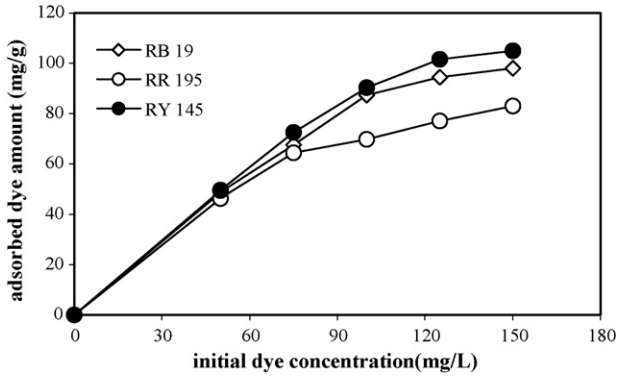

Fig. 4. The effect of initial dye concentration on the uptake capacity of wheat bran for RB 19, RR 195 and RY 145 (temperature 20 °C, adsorbent dose 0.5 g, temperature 20 °C, contact time 24 h, adsorbent size 50–100 mesh).

Table 1
The adsorption yields obtained from the adsorption of the studied reactive dyes onto wheat bran (initial pH 1.5, temperature 20 °C)

Initial dye concentration (mg/L)	Percentage adsorption		
	RB 19	RR 195	RY 145
50	97.5	94.2	99.0
75	90.2	86.8	96.7
100	87.4	68.7	90.3
125	75.6	59.6	81.3
150	70.6	55.3	69.1
Adsorbent size (mesh)			
−100	90.0	70.5	92.4
−50 + 100	87.4	68.7	90.3
−30 + 50	83.8	62.0	86.0
−16 + 30	75.3	56.2	81.0
−8 + 16	71.0	45.0	74.6
Adsorbent dose (g)			
0.5	53.0	57.6	60.2
1.0	68.4	78.7	90.3
1.5	89.13	91.3	95.84
2.0	91.31	97.8	98.2
3.0	94.4	95.6	99.3

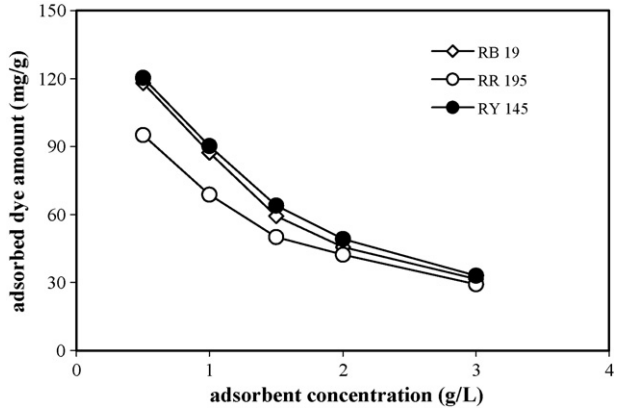

Fig. 5. The effect of adsorbent dose on the uptake capacity of wheat bran for RB 19, RR 195 and RY 145 (initial pH 1.5, initial dye concentration 100 mg/L, temperature 20 °C, contact time 24 h, adsorbent size 50–100 mesh).

may be due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent with increasing adsorbent dose causing a decrease in amount of dye adsorbed onto unit weight of adsorbent [24]. Another reason may be due to the particle interactive behavior, such as aggregation, resulted from high adsorbent dose. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length. Similar phenomena were also observed for Malachite Green adsorption on sawdust [8] and reactive dyes onto the cross-linked chitosan beads [12].

Table 1 shows the effect of adsorbent size on the adsorption of RB 19, RR 195 and RY 145 onto wheat bran at temperature 20 °C, initial pH 1.5, adsorbent dose 0.5 g and initial dye concentration of 100 mg/L. It was observed that the adsorption yields increased with decreasing adsorbent size as expected.

3.2. Equilibrium modelling

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, and is important in the design of adsorption system [22]. The most widely used isotherm equation for modelling equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules [25]. The linearised Langmuir isotherm model is given by Eq. (3):

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_a q_{max}} + \frac{C_{eq}}{q_{max}} \quad (3)$$

where q_{eq} (mg/g) and C_{eq} (mg/L) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. q_{max} is the maximum amount of the dye per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/L) and K_a (L/mg) is a constant related to the energy of adsorption. q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and it assists in the comparison of adsorption performance, particularly in cases where the adsorbent did not reach its full saturation in experiments.

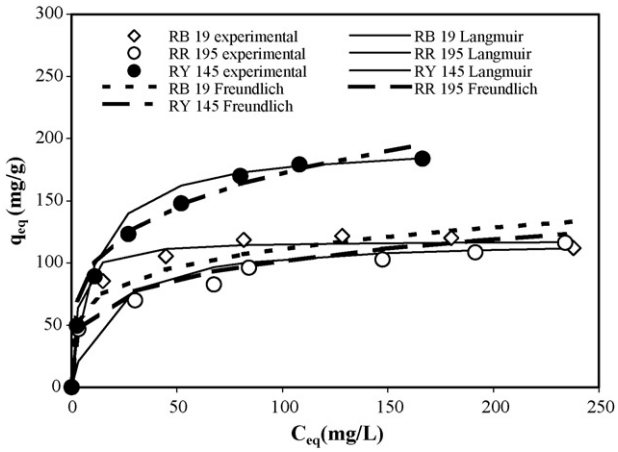

Fig. 6. Comparison of the experimental and predicted isotherms for the adsorption of RB 19, RR 195 and RY 145 onto wheat bran (initial pH 1.5, adsorbent size 50–100 mesh).

The Freundlich isotherm (1906) is the earliest known relationship describing the sorption equation [26]. The Freundlich isotherm model is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. Theoretically using this expression, an infinite amount of adsorption can occur [26]:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (4)$$

In this equation, K_F and $1/n$ are the Freundlich constants indicating adsorption capacity and intensity, respectively.

The Langmuir and Freundlich isotherm models were applied to the adsorption data of RB 19, RR 195 and RY 145 onto wheat bran. The experimental and predicted isotherms for the studied dyes at different temperature values are given in Fig. 6 and the isotherm constants calculated with linear regression analysis are also presented in Table 2. As can be seen from Table 2, the maximum monolayer covarage capacities (q_{max}) of wheat bran for RB 19, RR 195 and RY 145 dyes at 60 °C were determined to be 117.7, 119.1 and 196.1 mg/g, respectively. According to q_{max} value, the adsorption of RY 145 was believed to be more favorable than RB 19 and RR 195, leading to the highest decolorization efficiency of RY 145 among the studied dyes during

Table 2
The Langmuir and Freundlich isotherm constants at different temperatures for the adsorption of the reactive dyes onto wheat bran

	RB 19			RR 195			RY 145		
Langmuir isotherm constants									
T (°C)	20	40	60	20	40	60	20	40	60
q_{max} (mg/g)	97.1	104.2	117.7	103.4	116.3	119.1	125.0	147.1	196.1
K_a (L/mg)	0.162	0.246	0.394	0.046	0.056	0.064	0.086	0.089	0.092
K_a (L/g mol)	101501.1	154131.3	246860.7	52271.0	63634.2	72724.8	88258.4	91337.1	94415.9
R^2	0.999	0.999	0.996	0.988	0.983	0.985	0.997	0.997	0.989
Freundlich isotherm constants									
T (°C)	20	40	60	20	40	60	20	40	60
K_F	39.6	42.1	43.4	28.9	31.4	35.7	37.1	42.0	55.0
n	5.831	5.999	4.878	4.531	4.241	4.589	4.400	4.200	4.03
R^2	0.864	0.853	0.870	0.970	0.915	0.913	0.972	0.984	0.980

Table 3
Comparison of adsorbent capacities for different dyes

Adsorbent	Adsorbate	q_{max} (mg/g)	References
Coir pith carbon	Congo Red	6.72	[7]
P. oxalicum pellets	Reactive Blue 19	159	[21]
	Reactive Blue 241	122	
	Reactive Yellow 145	137	
C. lipolytica	Remazol Blue	250	[27]
Cross-linked chitosan beads	Reactive Blue 2	2498	[12]
	Reactive Red 2	2422	
	Reactive Yellow 89	1911	
Spent brewery	Acid Orange 7	30.5	[28]
Rice husk	Methylene Blue	40.6	[24]
Powdered peanut hull	Amaranth	14.90	[20]
	Sunset Yellow	13.99	
	Fast Green FCF	15.60	
$TiO_2 + SiO_2$ Photocatalytic degradation	Reactive Yellow 145	5.13	[29]
Bagasse fly ash	Orange G	18.8	[2]
	Methyl Violet	26.2	
Wheat bran	Reactive Blue 19	117.6	This study
	Reactive Red 195	119.1	This study
	Reactive Yellow 145	196.1	This study

the adsorption experiments. Table 3 lists the comparison of maximum monolayer adsorption capacity of some dyes on various adsorbents. As can be seen from Table 3, the wheat bran has relatively high adsorption capacity of RB 19, RR 195 and RY 145 dyes.

High K_F and n values indicate easy separation of RB 19, RR 195 and RY 145 from aqueous solutions with high adsorptive capacity of wheat bran. Values of n higher than one show the favorable nature of adsorption of RB 19, RR 195 and RY 145 onto wheat bran. According to linear regression coefficients (R^2), the Langmuir isotherm model defined best the adsorption data of RB 19, RR 195 and RY 145 dyes onto wheat bran at studied temperatures. The predicted Langmuir and Freundlich isotherm equations for RB 19, RR 195 and RY 145 dyes onto wheat bran which can be useful for predicts are given by Eqs. (5)–(7), respectively.

Langmuir isotherm model	Freundlich isotherm model	Dyes	
$q_{eq} = 46.4 * C_{eq}/(1+0.394* C_{eq})$;	$q_{eq} = 43.4* C_{eq}^{1/4.9}$	**RB 19**	(5)
$q_{eq} = 7.6* C_{eq}/(1+0.064* C_{eq})$;	$q_{eq} = 35.7* C_{eq}^{1/4.4}$	**RR 195**	(6)
$q_{eq} = 18.1* C_{eq}/(1+0.092* C_{eq})$;	$q_{eq} = 55.0* C_{eq}^{1/4.0}$	**RY 145**	(7)

3.3. Adsorption kinetic study

In order to investigate the mechanism of RB 19, RR 195 and RY 145 adsorption and potential rate-controlling steps such as external mass transfer, intraparticle diffusion and adsorption processes and also for design purposes, mass transfer model (Weber–Morris model) and kinetic models (the pseudo-first and second order kinetic model) have been used to test the experimental data.

3.3.1. Intraparticle diffusion model (Weber–Morris model)

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber–Morris, plot, rather than with the contact time, t [30].

$$q = K_i t^{1/2} \tag{8}$$

where K_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$). According to this model, the plot of uptake (q) versus the square root of time should be linear if intraparticular diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step. In many cases, an initial steep-sloped portion indicating external mass transfer is followed by a linear portion to the intraparticle diffusion and plateau which represents the final equilibrium stage where the intraparticular diffusion starts to slow down due to exteremely low solute concentration in the solution and surface.

In this part of study, Weber–Morris model was applied to the adsorption of RB 19, RR 195 and RY 145 onto wheat bran as a function of the initial dye concentration and the constants obtained from the intercepts and slopes of their plots are given in Table 4. As can be seen from Table 3, each adsorption process have an intercept, indicating that the Weber–Morris model curves do not pass through the origin, leading to the conclusion that the removal mechanisms of RB 19, RR 195 and RY 145 dyes onto wheat bran are complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process. Values of intercept give an idea about the thickness of the boundary layer, that is, the larger intercept the greater is the boundary layer effect [16]. In this state, Weber–Morris equation can be written as $q = K_i t^{1/2} + I$. It shows clearly that the uptake values are composed of two contributions, intraparticle and external diffusion [19]. As can be seen from Table 4, the K_i values and intercepts increased with increasing the initial dye concentrations and the R^2 values are close to unity indicating the applicability of this model. The observed increase in K_i values with increasing initial dye concentration can be explained by the growing effect of driving force, the concentration gradient. It is clear that the external mass transfer resistance cannot be neglected although this resistance is only significant for the initial period of adsorption time.

3.3.2. Pseudo-first order kinetic model

The pseudo-first order kinetic equation is [31]:

$$\frac{dq_t}{dt} = k_1(q_{eq} - q_t) \tag{9}$$

where k_1 is the pseudo-first order rate constant (1/min) and t is the time (min). After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes:

$$\log(q_{eq} - q_t) = \log q_{eq} - k_1 t/2.303 \tag{10}$$

The pseudo-first order rate constant values for the adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran

Table 4
Weber–Morris model constants (initial pH 1.5, temperature 20 °C, adsorbent dose 0.5 g, adsorbent size 50–100 mesh)

	RB 19			RR 195			RY 145		
Initial dye concentration (mg/L)	50	100	150	50	100	150	50	100	150
K_i (mg/g min$^{1/2}$)	1.69	4.20	5.01	1.26	2.32	2.93	1.54	3.81	4.56
I (mg/g)	26.8	30.4	32.3	27.9	30.2	34.5	30.6	34.8	40.3
R^2	0.983	0.981	0.987	0.967	0.994	0.911	0.951	0.983	0.960

are determined from the plots of $\log(q_{eq} - q_t)$ against t (data not shown) at different temperatures. The rate constants, experimental and predicted q_{eq} values are presented in Table 5. It was observed that the experimental adsorption data of RB 19, RR 195 and RY 145 dyes onto wheat bran did not fit to the predicted ones although their regression coefficients were high.

3.3.3. Pseudo-second order kinetic model

If the rate of adsorption is a second-order mechanism, the pseudo-second order kinetic model is expressed as [32]:

$$\frac{dq}{dt} = k_2(q_{eq} - q_t)^2 \quad (11)$$

where k_2 is the pseudo-second order biosorption rate constant (g/mg min), q_{eq} and q_t are the adsorbed amount per unit mass at equilibrium and any time, respectively. For the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ the integrated and linear form of Eq. (11) becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (12)$$

If the pseudo-second order kinetic model is applicable, the plot of t/q_t against t of Eq. (12) should give a linear relationship, from which q_{cal} and k_2 can be determined from the slope and intercept of the plot.

The pseudo-second order kinetic model were applied to the adsorption data of RB 19, RR 195 and RY 145 dyes onto wheat bran at the different temperatures and the rate constants, the experimental and calculated q_{eq} values and correlation coefficients are given in Table 5. As can be seen from Table 5, the pseudo-second order rate constant values increased with increasing temperature and the correlation coefficients of all temperatures studied were also found very high. For the adsorption of RB 19, RR 195 and RY 145 dyes onto wheat bran, the variation of experimental and predicted q_t values with contact time is given in Fig. 7. The adequate fitting of calculated (q_{cal}) and experimental (q_{exp}) values suggests the applicability of pseudo-second order kinetic model to these adsorption systems.

3.4. Determination of thermodynamic parameters

The Langmuir isotherm constant, K_a (L/mol), values for different temperatures can be used for the thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of RB 19, RR 195 and RY 145 dyes-wheat bran adsorption processes. The free energy change of the adsorption reaction is given by the following equation:

$$\Delta G = -RT \ln K_a \quad (13)$$

where ΔG is free energy change (J/mol); R is universal gas constant (8.314 J/mol K) and T is absolute temperature (K). In

Table 5
The pseudo-first and second order kinetic model constants at different temperatures for the adsorption of the reactive dyes onto wheat bran (initial pH 1.5, initial dye concentration 100 mg/L, adsorbent dose 0.5 g, adsorbent size 50–100 mesh)

	Pseudo-first order kinetic model				Pseudo-second order kinetic model			
	$q_{eq,exp}$ (mg/g)	$q_{eq,cal1}$ (mg/g)	$k_{1ad} \times 10^3$ (L/min)	R^2	$q_{eq,exp}$ (mg/g)	$q_{eq,cal2}$ (mg/g)	$k_{2ad} \times 10^4$ (g/mg min)	R^2
RB 19								
$T = 20$ °C	87.38	41.79	6.50	0.927	87.38	87.72	6.62	0.999
$T = 30$ °C	89.13	42.16	7.14	0.939	89.13	90.09	7.00	0.999
$T = 40$ °C	90.87	43.33	7.83	0.962	90.87	91.74	7.38	0.999
$T = 50$ °C	92.62	41.69	7.83	0.950	92.62	93.46	7.92	0.999
RR 195								
$T = 20$ °C	68.71	33.75	6.68	0.943	68.71	69.44	7.15	0.999
$T = 30$ °C	69.90	31.30	6.68	0.925	69.90	70.42	8.24	0.999
$T = 40$ °C	71.04	28.19	6.68	0.917	71.04	71.43	9.66	0.999
$T = 50$ °C	72.29	26.04	6.22	0.907	72.29	72.99	9.90	0.999
RY 145								
$T = 20$ °C	90.31	43.29	6.22	0.939	90.31	90.91	6.12	0.999
$T = 30$ °C	93.05	39.54	6.00	0.919	93.05	93.46	6.88	0.999
$T = 40$ °C	94.82	34.21	6.22	0.898	94.82	95.24	8.66	0.999
$T = 50$ °C	96.86	30.89	6.45	0.898	96.86	97.09	10.40	0.999

Table 6
Thermodynamic parameters (initial pH 1.5, initial dye concentration 100 mg/L, adsorbent dose 0.5 g, adsorbent size 50–100 mesh)

	RB 19			RR 195			RY 145		
T (°C)	20	40	60	20	40	60	20	40	60
ΔG (kJ/mol)	−28.4	−31.1	−34.4	−26.5	−28.8	−31.0	−27.7	−29.7	−31.7
ΔH (kJ/mol)		19.69			6.72			1.37	
ΔS (J/mol K)		162.3			113.2			99.3	

principle, K_a in Eq. (13) should be in terms of molar unit (L/mol). The values of ΔG and ΔS can be calculated only if molar mass of the dye is known. The free energy change can be represented as follows:

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

The change with temperature of the free energy change and the equilibrium constant can be represented as follows.

$$\ln K_a = \frac{-\Delta H}{R(1/T)} + \frac{\Delta S}{R} \tag{15}$$

According to Eq. (15), a plot of ln K_a versus $1/T$ is linear and the enthalpy and entropy change values can be determined from the slope and intercept of this plot. The enthalpy and entropy change values for the adsorption of RB 19, RR 195 and RY 145 onto wheat bran were presented in Table 6. The effect of temperature on the equilibrium constant K_a is determined by the sign of ΔH. The positive value of ΔH shows that the adsorption processes of RB 19, RR 195 and RY 145 onto wheat bran are endothermic in nature, an increase in T causes an increase in K_a. The positive value of ΔS reflects the affinity of wheat bran for RB 19, RR 195 and RY 145 anions and suggested some structural changes in dye and adsorbent [29]. The free energy changes for RB 19, RR 195 and RY 145-wheat bran adsorption processes are also given in Table 6. The negative ΔG values confirm the feasibility of the adsorption of RB 19, RR 195 and RY 145 onto wheat bran and the spontaneous character of adsorption with high preference of RB 19, RR 195 and RY 145 onto wheat bran.

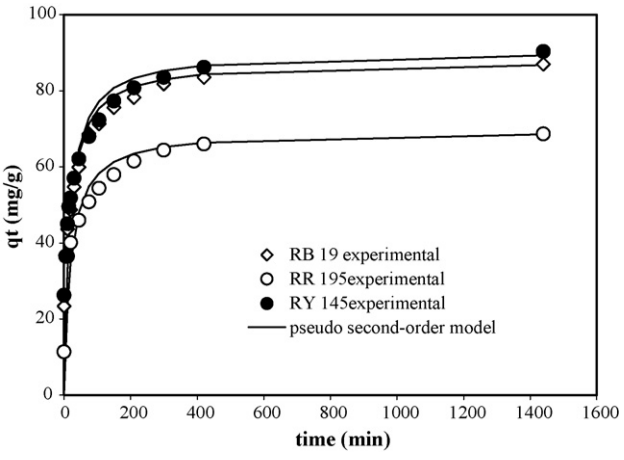

Fig. 7. Comparison of the experimental and pseudo-second order kinetic model for the adsorption of RB 19, RR 195 and RY 145 onto wheat bran (initial pH 1.5, temperature 20 °C, initial dye concentration 100 mg/L, adsorbent size 50–100 mesh).

4. Conclusion

The optimum adsorption of RB 19, RR 195 and RY 145 onto wheat bran was observed at low initial pH and 60 °C of temperature. Higher uptake values obtained at lower pH values may be due to electrostatic attractions between negatively charged dye anion and positively charged wheat bran surface. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The monolayer adsorption capacity of wheat bran was obtained as 117.6, 119.1 and 196.1 mg/g for RB 19, RR 195 and RY 145, respectively. It was observed that the biosorption data of RB 19, RR 195 and RY 145 fitted well to the Langmuir model according to R^2. It was observed that the dye adsorption capacity of wheat bran decreased in the order of RY 145 > RB 19 > RR 195. The pseudo-second order kinetic and Weber–Morris models were applied to the experimental data and it was found that both the surface adsorption as well as intraparticle difussion. Determination of thermodynamic parameters such as enthalpy, entropy and Gibb's free energy changes showed the reversible and endothermic nature of the adsorption of RB 19, RR 195 and RY 145 onto wheat bran.

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