Equilibrium and kinetics studies for adsorption of direct blue 71 from aqueous solution by wheat shells

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Abstract

This paper deals with the application of wheat shells (WS), an agricultural by-product, for the removal of direct blue 71 (DR) from aqueous solution. The characteristics of WS surface, such as surface area, Bohem titration and scanning electron microscopy (SEM) were obtained. The removal of direct blue 71 onto WS from aqueous solution was investigated by using parameters, such as pH, temperature, adsorbent dose, contact time and initial concentration. The adsorption process attains equilibrium within 36 h. The extent of dye removal decreased with increasing adsorbent dosage and also increased with increasing contact time, temperature, in solution concentration. Optimum pH value for dye adsorption was determined between 6 and 8. The experimental data were analysed by the Langmuir and Freundlich models of adsorption. It was found that the Langmuir equation fit better than the Freundlich equation. Maximum adsorption capacity (Q_m) was calculated as at different temperatures (293, 303 and 313 K) 40.82, 45.66 and 46.30 mg g^{-1}, respectively. In addition, the adsorption data obtained at different temperatures of DR by WS were applied to pseudo first-order, pseudo second-order and Weber–Morris equations, and the rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and intraparticle diffusion rate constants (k_3) at these temperatures were calculated, respectively. The rates of adsorption were found to conform to pseudo second-order kinetics with good correlation ($R^2 \geq 0.9904$). Also, free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were determined to predict the nature of adsorption. Furthermore, the results indicate that WS could be employed as a low-cost alternative to other adsorbents in the removal of direct blue 71 from aqueous solution.
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Keywords: Adsorption; Kinetics; Thermodynamics; Dyes; Direct dyes; Wheat shells

1. Introduction

Dyes are important water pollutants, which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. Synthetic dyes usually have a complex aromatic molecular structure, which possibly comes from coaltar-based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. The wordwide high level of production and extensive use of dyes generate coloured wastewaters that cause environmental pollution. For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can colour large water bodies [1,2]. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and reducing the photosynthetic reaction. Some dyes are also toxic and even carcinogenic. Therefore, it is highly necessary to reduce dye concentration in the wastewater [3].

Precipitation, ion exchange, solvent extraction, biosorption, filtration, electrochemical treatment and adsorption are the conventional methods for the removal of dyes from aqueous solutions. All these methods have significant disadvantages such as incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal. Therefore, these methods do not suit the needs of developing countries [4]. There are the advantages and disadvantages of some methods of dye removal from wastewaters [5,6].

Among the above-mentioned methods, adsorption is considered to be relatively superior to other techniques because low cost, simplicity of design, viability and ability to treat dyes in more concentrated form [7]. Activated carbon is the most widely used adsorbent because it has excellent adsorption efficiency for

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organic compounds, but its use is usually limited due to its high cost [5].

This has led many researchers to search for cheaper substitutes such as coal, fly ash, silica gel, wool wastes, biomass, agricultural wastes, wood wastes, and clay materials. They have been applied with varying success in dye removal [8]. To find an effective and ideal adsorbent, researchers have exploited many low cost and biodegradable substitutes obtainable from natural resources for the removal of different dyes from aqueous solutions at different operating conditions [4,7–14].

Wheat is one of the cereals used for the preparation of bread and other bakery products, and wheat shell is the by-product of wheat bread production industries. Wheat shell is a rich source of dietary fibre and contains carbohydrates, proteins, starch, sugar and celluloses [15,16].

The aim of this work is to investigate the effect of several parameters such as initial concentration, contact time, temperature, adsorbent dosage and pH on the adsorption efficiency of direct blue 71 from aqueous solutions by wheat shells, which is a very cheap and readily available material in most countries.

2. Materials and methods

2.1. Materials

WS were obtained from local wheat mills. The collected materials (the last hard layer of wheat) were then washed several times with distilled water to remove all dirt particles. The washing process was continued till the wash water contained no colour. The washed materials were then dried in a hot oven at 50 °C for 12 h. The dried materials were then ground, using a steel mill. The adsorbent was sieved through 0.6 mm sieve and used as such without any pretreatment. Characteristics of the WS were determined, and results are summarized in Table 1. An elemental analysis (C and H content) was carried out with an EA 1108 Fisons instruments. Direct blue 71 (DR) (CI = 34,140; molecular weight = 1029.88 g mol^{-1}; maximum wavelength = 587 nm) supplied by Aldrich was used as adsorbate and was not purified prior to use (Fig. 1). A stock solution of DR 1000 mg L^{-1} was prepared, which was diluted to required initial concentrations.

Table 1
Physical and chemical properties of WS used in the experiments

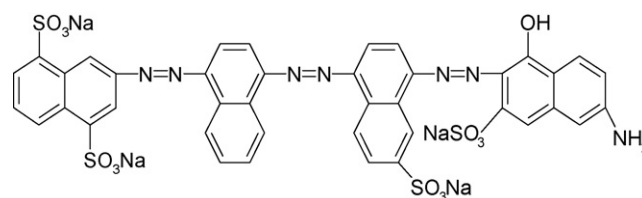| Chemical characteristic	
Moisture content (%)	6.40
Water soluble components (%)	20.89
Insoluble components (%)	72.34
Ash (%)	2.58
Total loss of ignition (%)	88.45
C content (%)	44.59
H content (%)	6.56
pH	6.05
Physical characteristic	
Surface area (BET) (m^2 g^{-1})	0.67
Bulk density (g mL^{-1})	0.36
Particle size (mm)	0.60

Fig. 1. The structure molecular of direct blue 71: (a) wheat shells and (b) dyed wheat shells.

2.2. Methods

The effect of contact time and initial concentration on the amount of dye adsorbed were investigated at 50–250 mg L^{-1} initial concentration of dye and at different temperatures (293, 303 and 313 K). A weighed sample of WS (0.5 g) was mixed with a 50 mL of dye solution known initial concentration at desired temperature and at 150 rpm for 60 h. For the other adsorption experiments, 50 mL of dye solution of known initial concentration was shaken with a certain amount of adsorbent at desired temperature for 36 h. Constant bath was used to keep the temperature constant. At the end of the adsorption period, the mixture was centrifuged for 10 min at 4000 rpm. After centrifugation, it was the analyzed by using a UV Spectrophotometer (Shimadzu UV-160) by monitoring the adsorbance changes at a wavelength maximum absorbance (587 nm). The samples were pipetted from the medium reaction by the aid of a very thin point micropipette, which prevented the transition to the solution of the WS samples. The amount of dye adsorbed was calculated, using the following equation

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where q_e is the amount adsorbed per gram of adsorbent, C_i and C_e the concentration of dye (mg L^{-1}) at initial and equilibrium, respectively. V is volume solution of dye (L) and m is adsorbent dosage (g).

3. Result and discussion

3.1. SEM analysis

Scanning electron microscopy (SEM) has been a primary tool for characterising the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of WS and adsorbed WS with DR are shown in Fig. 2. From Fig. 2, it is clear that, WS has considerable numbers pf pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores [7,17].

3.2. Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity [3]. The effect of pH on the removal of DR is shown
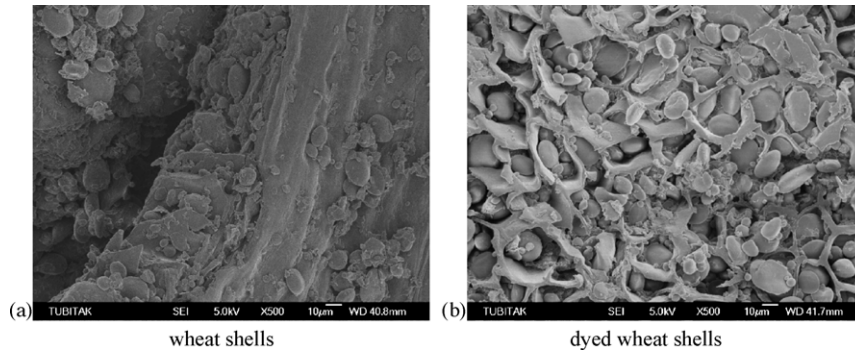
Fig. 2. Scanning electron microscope of original WS (a) and dye adsorbed with DR (b).
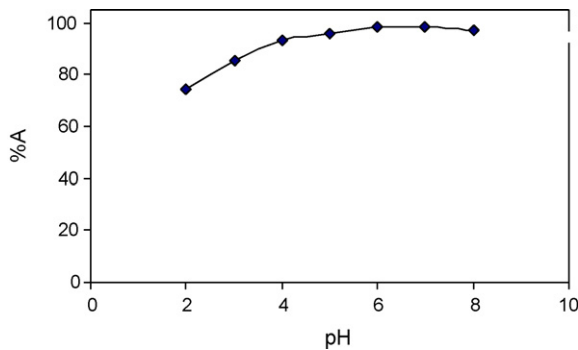

Fig. 3. Effect of pH on DR adsorption (*conditions*: $V = 50$ mL, $m = 0.5$ g, contact time = 36 h, agitation speed = 150 rpm, $C_i = 100$ mg L^{-1}).

in Fig. 3, where it is seen that biosorption efficiencies increased from 74.15% at pH 2 to 98.95% at pH 6–7. The DR adsorption by WS was significantly affected over the pH range of 2–5. The surface of WS may contain a large number of active sites, and the solute (dye ions uptake can be related to the active sites and also to the chemistry of the solute in the solution. At higher pH (6–8), the surface of WS particles may become negatively charged, which enhances the positively charged DR through electrostatic forces of attraction [8].

3.3. The activation energy

The activation energy of adsorption was also calculated from the linearized Arhenius equation [8]:

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \tag{2}$$

where k_2 is the rate constant second-order of adsorption (g mol^{-1} h^{-1}), k_0 the independent temperature factor (g mol^{-1} h^{-1}), E_a the activation energy of adsorption (J mol^{-1}), R the gas constant (J mol^{-1} K^{-1}) and T is the solution temperature (K). A plot of $\ln k_2$ versus $1/T$ gives a straight line, and the corresponding activation energy was determined from the slope of the linear plot. The results obtained were 98.81, 88.24 and 31.30 kJ mol^{-1} for the adsorption of DR on WS, respectively, at initial concentration 50, 100 and 250 mg L^{-1}. The activation energy of adsorption decreases with increasing initial concentration of adsorbate.

3.4. Adsorption isoterm studies

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [8]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents and thus is critical in optimizing the use of adsorbents. Adsorption isotherms expressing the adsorbed amounts as a function of equilibrium concentration for different temperatures are presented in Fig. 4.

Several isotherm equations are available, and two important isotherms are selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation is represented as follows [18]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{3}$$

where b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L mg^{-1}) or (L mol^{-1}) and Q_m represents a particle limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance. Q_m and b are calculated from the slope and intercept of the straight lines of plot C_e/q_e versus C_e.

The Freundlich isotherm an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm is
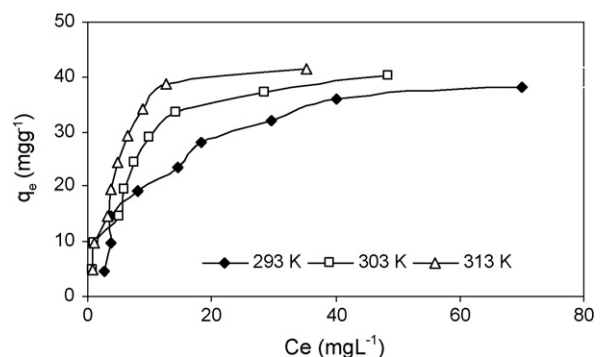

Fig. 4. Isotherm for adsorption of DR on WS (*conditions*: $V = 50$ mL, $m = 0.5$ g, contact time = 36 h, agitation speed = 150 rpm).

given in logarithmic form as [18]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where K_F is roughly indicates of the adsorption and $(1/n)$ of the adsorption intensity. K_F and n can be determined from the linear plot of $\log q_e$ versus $\log C_e$.

Adsorption isotherms were obtained in terms of Eqs. (3) and (4) by using experimental adsorption results in these equations. The values Q_m, b, K_F, and n are summarized in Table 2. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 2, the Langmuir equation represents the adsorption process very well; the R^2 values were all higher than 0.9856, indicating a very good mathematical fit. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto WS surface, since the Langmuir equation assumes that the surface is homogenous [3]. Also, as seen in Table 2, the maximum adsorption capacities for DR onto WS at 293, 303 and 313 K were found to be 40.82, 45.66 and 46.30 mg g^{-1}, respectively. Maximum adsorption capacities of WS increase with the rice increasing in temperature.

K_F is an Freundlich constant that shows adsorption capacity of adsorbent, n is a constant which shows greatness of relationship between adsorbate and adsorbent [8]. The value K_F of WS for DR at 293, 303 and 313 K are 5.73, 8.14 and 9.36, respectively. It is generally reported that the values of n in the range 1–10 represent good adsorption [19]. In the present work, the exponent was $1 < n < 10$, indicating favourable adsorption.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which is defined by the following relationships [8] given by:

$$R_L = \frac{1}{1 + bC_i} \tag{5}$$

According to the value of R_L the isotherm shape may be interpreted as follows:

Value of R_L	Type of adsorption
$R_L > 1.0$	Unfavourable
$R_L = 1.0$	Linear
$1 > R_L > 0$	Favourable
$R_L = 0$	Irreversible

The results given in Table 2 show that the adsorption of DR onto WS is favourable. As also seen in Table 2, the maximum adsorption of capacities WS for DR varied between 40.82 and

46.30 mg g^{-1}. Previously some researchers investigated several adsorbents such as soy meal hull [7], orange peel [10], rice hull ash [12], banana pith [13] and red mud [14] for the removal of direct dyes. By comparison of the results obtained in this study with those in the previously reported works on adsorption capacities of various low-cost adsorbent in aqueous solution for dyes, it can be stated that our findings are good.

3.5. Effect of temperature

To determine the effect of temperature on the adsorption of dye, experiments were also conducted at 293, 303 and 313 K and are shown in Fig. 4. The degree of adsorption increases with increased temperature, indicating that the adsorption is endothermic [1]. The values of free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$), for the adsorption process were calculated, using the following equations [1,8]:

$$\Delta G° = -RT \ln b \tag{6}$$

$$\ln b = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{7}$$

Thus, a plot of $\ln b$ versus $1/T$ should be a straight line. $\Delta H°$ and $\Delta S°$ values were obtained from the slope and intercept of this plot, respectively [8].

The estimated values of $\Delta G°$ for adsorption of DR onto WS were -28.147, -30.567 and -32.987 kJ mol^{-1} at 293, 303 and 313 K, respectively. Negative $\Delta G°$ values indicate the spontaneous nature of the adsorption process and positive $\Delta S°$ values indicate (242 J mol^{-1} K^{-1}) the affinity of the adsorbent for DR. Also the positive values of $\Delta H°$ (42.759 kJ mol^{-1}) indicate that the adsorption of DR on WS is an endothermic process.

3.6. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate [8].

The adsorption of DR on WS was studied by changing the quantity of adsorbent (0.25, 0.5, 1.0 and 2.0 g 100 mL^{-1}) in the different initial concentrations of DR (50, 100, 250 and 500 mg L^{-1}) at 293 K for 36 h (Table 3). After equilibrium, the samples were centrifuged and the concentration in the supernatant dye solution was analyzed. As seen from Table 3, the amount adsorbed per unit mass of the adsorbent decreases with increasing adsorbent dosage and also increases with increasing

Table 2
Langmuir and Freundlich constants for adsorption of DR on WS

T (K)	Langmuir isotherm constants					Freundlich constants		
	Q_m (mg g^{-1})	b (L mg^{-1})	b (L mol^{-1})	R_4^2	R_L	K_F	n	R_5^2
293	40.82	0.10	102,988	0.9856	0.166–0.039	5.73	2.17	0.7811
303	45.66	0.15	154,482	0.9946	0.118–0.026	8.14	2.27	0.8772
313	46.30	0.22	226,574	0.9960	0.083–0.018	9.36	2.17	0.8339

Table 3
Effect of adsorbent dose on DR removal

Adsorbent dosage (g)	q_e (mg/g)			
	$C_i = 50$ (mg L^{-1})	$C_i = 100$ (mg L^{-1})	$C_i = 250$ (mg L^{-1})	$C_i = 500$ (mg L^{-1})
0.25	8.49	16.94	29.35	36.67
0.5	4.68	9.57	23.00	36.14
1.0	2.34	4.80	12.15	24.03
2.0	1.18	2.42	6.12	12.38

Conditions: $V = 50$ mL, $T = 293$ K, contact time = 36 h. Agitation speed = 150 rpm.

initial concentration of DR. The decrease in unit adsorption with increasing dose of adsorbent is basically due to adsorption sites that remain unsaturated during the adsorption reaction [8].

3.7. Adsorption kinetics

It is important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an adsorption treatment plant. In order to investigate the mechanism of adsorption, characteristic constants of adsorption rate were determined using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase adsorption and an intraparticle diffusion model [7,18,20,21].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2303}\right)t \qquad (8)$$

where q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (h), respectively, and k_1 is the equilibrium rate constant of pseudo first-order sorption (h^{-1}). The values of the rate constant, k_1, equilibrium adsorption capacity, q_e, and the correlation coefficient, R_1^2, were calculated from the plots of $\log(q_e - q_t)$ versus t (plots are not shown). Although the correlation coefficients, R_1^2, for the application of the pseudo first-order model are reasonably high in some cases, all of the intercepts of the straight line plots do not yield predicted q_e values equal, or even values reasonably close to experimental q_e values (Table 4) [21]. Any reaction occurring is therefore not likely to be a first-order reaction.

Kinetic data were further treated with pseudo second-order kinetic model [22]. The differential equation is as follows:

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \left(\frac{1}{q_e}\right)t \qquad (9)$$

where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g mg^{-1} h^{-1}). If pseudo second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship (Fig. 5). The correlation coefficients (R_2^2) for the second-order rate kinetic model are higher than 0.99. The second-order rate constant, k_2, and equilibrium adsorption capacity, q_e, were calculated from the intercept and slope of the plots of t/q_t versus t.

The calculated q_e values agree very well with the experimental data (Table 4). These indicate that the adsorption of DR from aqueous solution on WS obeys pseudo second-order kinetic
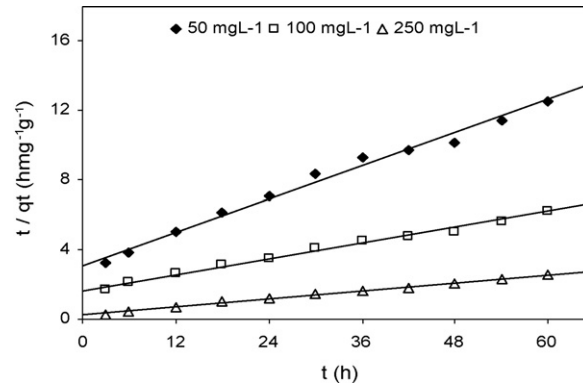

Fig. 5. Pseudo second-order kinetics for adsorption of DR on WS at 293 K.

Table 4
Comparison of the pseudo first-order and second-order and intraparticle diffusion adsorption constants at different initial concentrations and temperatures

T (K)	C_i (mg L^{-1})	q_e^* (mg g^{-1})	Pseudo first-order			Pseudo second-order			Intraparticle diffusion		
			q_e (mg g^{-1})	k_1 (h^{-1})	R_1^2	q_{eq} (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	R_2^2	k_3 (mg g^{-1} h$^{-1/2}$)	C	R_3^2
293	50	4.72	6.16	0.070	0.9258	6.26	0.0083	0.9912	0.611	0.18	0.9673
	100	9.62	14.38	0.081	0.9113	13.05	0.0035	0.9904	1.278	0.06	0.9651
	250	23.55	27.16	0.093	0.8959	25.32	0.0081	0.9951	1.847	10.06	0.9179
303	50	4.91	3.79	0.057	0.4865	5.13	0.0484	0.9922	0.324	2.52	0.8281
	100	9.85	4.55	0.041	0.6001	10.82	0.0135	0.9950	0.914	3.16	0.8440
	250	24.24	16.25	0.080	0.7122	26.18	0.0078	0.9989	1.861	10.80	0.8970
313	50	4.93	1.90	0.102	0.8661	5.10	0.1098	0.9990	0.262	3.16	0.6130
	100	9.88	4.03	0.119	0.8888	10.37	0.0353	0.9955	0.702	5.13	0.5670
	250	24.62	16.15	0.105	0.9562	25.64	0.0186	0.9920	1.733	12.66	0.7440

q_e^* = experimental; q_e = calculated.

model [22]. A similar phenomenon was observed in the adsorption of direct red 12 B and methylene blue onto Fe(III)/Cr(III) hydroxide [18], direct and acid dyes on soy meal hull [7], basic dyes on kudzu [21], direct red 23 and direct red 80 on orange peel [20].

The nature of the rate-limiting step in a batch system can also be assessed from properties of the solute and adsorbent. Weber and Morris [19] stated that if intraparticle diffusion is the rate-controlling factor, uptake of the adsorbate varies with the square root of time. Thus, rate of adsorption are usually measured by determining the adsorption capacity of the adsorbent as a function of the square root of time [19].

Intraparticle diffusion model can be represented in the form:

$$q_e = k_3 t^{1/2} + C \tag{10}$$

where C is the intercept and k_3 is the intraparticle diffusion rate constant (mg g^{-1} h$^{1/2}$) [8]. Best-fit straight (plots are not shown) that do not pass through the origin indicating that there are an initial boundary layer resistance. The result also indicates that adsorption of DR on WS is not diffusion controlled [19].

3.8. Effect of contact time and concentration

There are many factors, which can contribute to the adsorbate concentration effect. The first and important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause can be the aggregation/agglomeration of adsorbent particles at higher concentrations. Such aggregation would lead to a decrease in the total surface area of the sorbent particles available for dye adsorption and an increase in the diffusional path length [16]. The effect of the initial adsorbate concentration (namely 50, 100 and 250 mg L^{-1}) and contact time is shown Fig. 6 for 293 K (for 303 and 313 K are not shown plots). The amount of dye adsorbed (mg g^{-1}) increased with increase in contact time and initial concentration. It is seen that nearly 36 h are required for the equilibrium adsorption to be attained for different initial concentrations and temperatures. Hence, for all adsorption studies, the equilibration time was kept as 36 h.

It is further seen from Fig. 6 that adsorption is very fast initially, showing that 50% adsorption in the case of different temperature is completed in 12 h, then it slowly attains equi-
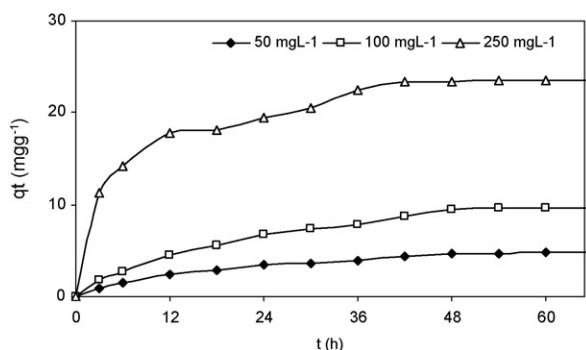
librium adsoption. A similar phenomenon was observed for the adsorption dyes from aqueous solution on peanut hull [2].

4. Conclusions

The present study shows that WS prepared from low-cost material is considerably efficient for removal of DR from aqueous solution. The adsorption is highly dependent on contact time, adsorbent dosage and initial concentration. The kinetics of DR adsorption on WS follows the pseudo second-order model. The equilibrium data fit well in the Langmuir model of adsorption, showing monolayer coverage of dye molecules at the outer surface of WS. The dimensionless separation factor (R_L) showed that WS could be used for removal of DR from aqueous solutions. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as ΔG°, ΔH° and ΔS°. The adsorption of DR on WS is spontaneous and physical in nature. WS, which is an inexpensive and easily available material, can be an alternative for more costly adsorbents used for dye removal in waste-water treatment processes.

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Fig. 6. Effect of contact time and initial concentration on adsorption of DR at 293 K (conditions: $V = 50$ mL, $m = 0.5$ g, agitation speed = 150 rpm).

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