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Utilization of walnut shells (*Juglans regia*) as an adsorbent for the removal of acid dyes

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ABSTRACT

The removal of acid red 183 and acid green 25 onto walnut shells (*Juglans regia*) (WS) from aqueous solutions was investigated by using parameters such as contact time, temperature, pH, adsorbent doses and initial dye concentration. Adsorption equilibrium was reached within 30 min. The adsorption isotherms were described by means of the Langmuir and Freundlich isotherms. It was found that the Langmuir isotherm appears to fit the isotherm data better than the Freundlich isotherm. The maximum adsorption capacities for acid red 183 and acid green 25 on WS at 308, 313, and 318 K were found to be 45, 37, and 37; 21, 14, and 7 mg g^{-1}, respectively. The data obtained from adsorption isotherms at different temperatures were used to calculate some thermodynamic quantities such as free energy of adsorption (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0). That G^o is negative, indicating that the nature of adsorption process for dyes is spontaneous. The positive value of H^o indicates that the adsorption of dyes onto WS is an endothermic process. The positive value of S^o reflects the affinity of the adsorbent for dyes. The kinetics and the factors controlling the adsorption process were also studied. The adsorption process followed a second-order model. WS, being a cheap, and easily available material, can be an alternative for more costly adsorbents used for dye removal in wastewater treatment processes.

Keywords: Adsorption; Adsorption isotherms; Adsorption of dyes; Walnut shells; Acid dyes

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1. Introduction

Many industries use dyes and pigments to colour their products [1]. In addition, textile industries use large amounts of water and chemicals for finishing and dying processes. The chemical structures of dyes vary enormously, and some have complicated aromatic structures that resist degradation in conventional wastewater treatment processes because of their stability to sunlight, oxidizing agents, and microorganisms [2]. Coloured effluents are not only aesthetically displeasing, but they also impede light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms and may cause direct destruction of aquatic communities; therefore, some form of treatment is necessary [3]. Removal techniques for dyes include coagulation, ozonation, membrane process, filtration with coagulation, ozonation with coagulation and adsorption. Among these, the adsorption process gives the best results as it can be used to remove different types of colouring materials. Although activated carbon is a preferred adsorbent for colour removal, its widespread use is restricted due to high cost [4]. Accordingly, alternative adsorbents, including palm-fruit bunch particles [3], quaternized rice husk [6], silica fumes [7], magnesium chloride [8], shale oil ash [9], manganese mineral [10], alum sludge [2], natural zeolite [11], cotton [12], treated sawdust [13], spent

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brewery grains [14], wheat shells [15], modified bentonite [16], bittim shells (*Pistacia khinjuk* Stocks) [17], etc. and various industrial wastes [4], have been previously investigated. However, the results have not been promising and cannot be compared with activated carbon which shows high removal efficiencies. Thus, efforts are still going on to develop alternative low-cost materials. In the present study, walnut shell (*Juglans regia*) (WS) were tried as an adsorbent for the removal of acid red 183 and acid green 25, which are toxic and are used in textile industries. The effect of solution contact time, temperature, pH, adsorbate doses, and initial dye concentration on the removal of dyes by WS was studied. The thermodynamic parameters for the adsorption dyes were computed and discussed. The kinetics and the factors controlling the adsorption process were also investigated.

2. Materials and methods

2.1. Adsorbents

The adsorbent was sieved through 100-mesh sieve and used as such without any pretreatment. The WS used as the adsorbent were supplied from the southeastern Anatolia region of Turkey. The chemical and physical characteristics of the adsorbent are presented in Table 1. For the experimental studies only, the adsorbent was washed several times with twice distilled water to remove surface impurities. The process was followed by air drying at 308 K for 24 h.

2.2. Chemicals

Acid red 183 (CI = 18,800; molecular weight (MW) = 587.87 g mol^{-1}; maximum wavelength = 493 nm molar absorption coefficient= 9013 L mol^{-1} cm^{-1}) and acid green 25 (CI = 61,570 MW = 622.59 g mol^{-1}; maximum wavelength = 641 nm; molar absorption coefficient = 9687 L mol^{-1} cm^{-1}) were obtained from Aldrich and used without any further purification. All of the compounds used to prepare reagent solutions were of analytic reagent grade.

Table 1
Physical and chemical properties of WS in the experiments

Moisture content, %	90.00
Bulk density, g/mL^{-1}	0.6305
Total loss of ignition, %	97.00
Organic and inorganic components, %	89.77
Insoluble components, %	10.23
Surface area (BET), m^2 g^{-1}	0.72
C content, %	47.07
H content, %	5.65

The stock solution of dyes were prepared (100 mg L^{-1}) by dissolving it in double distilled water.

2.3. Apparatus

A pH meter (Jenway 3010) and shaker (Nuve ST 400) were used for pH adjustment and shaking, respectively. Absorbance values were measured with a Shimadzu-160 UV spectrophotometer. Elemental analysis was carried out with EA 1108 Fisons instruments. The surface area was determined by a single-point N_2 gas adsorption method using Micromeritics model Flow Sorb 11.2300.

2.4. Procedure

Batch adsorption studies were performed at different pH, temperature, initial dye concentration and adsorbent doses to obtain equilibrium isotherms. For isotherm studies, adsorption experiments were carried out by shaking 1.0 g of WS samples with 50 mL aqueous solution in a series of 100 mL flasks closed with teflon caps. Each flask was filled with 50 mL of a dye solution of varying concentrations (30–60 mg L^{-1}) and adjusted to the desired pH, temperature, initial dye concentration and adsorbent doses. A given amount of adsorbent was added to each flask and agitated for the desired time periods, up to a maximum of about 30 min. Equilibration requires longer times practically for some uptakes. Therefore, a contact period of 45 min, which is more than sufficient time to reach equilibrium was finally selected for all of the equilibrium tests. At the end of the adsorption process, the solution was centrifuged for 10 min at 3000 rpm and then the concentrations of the residual, C_{eq}, were determined through an UV spectrophotometer. The measurements were made at the wavelength λ= 493 nm (for acid red 183) and λ =641 nm (for acid green 25), which amounted to maximum absorbance. The effect of pH was observed by studying the adsorption of dye over a pH range of 2–8. The pH of the solution was adjusted with 0.1 M NaOH or HCl solution by using Jenway 3010 pH meter equipped with a combined pH electrode. The pH meter was standardized with NBS buffers before every measurement. The adsorption studies were also carried out at different temperatures (308, 313, and 318 K) to determine the effect of temperature and to evaluate the adsorption thermodynamic parameters. A thermostated shaker bath was used to keep the temperature constant. The amounts of dyes adsorbed were calculated from the concentrations in solutions before and after adsorption. All the experiments were carried out in duplicate. The amount of dyes adsorbed (mg g^{-1}) ,(q_{eq}), onto WS was calculated from the mass balance equations as follows:

$$q_{eq} = (C_i - C_{eq})\, V/W \tag{1}$$

where C_i and C_{eq} are the initial and equilibrium concentrations of dye solution (mg L^{-1}), respectively; V the volume of dye solution (L), and W the mass of adsorbent sample used (g).

3. Results and discussion

3.1. Elemental analysis of adsorbent (C and H)

Elemental analysis was carried out with EA 1108 Fisons instruments. A sample of adsorbent was put in an oven at 1273 K under oxygen in order to obtain quick and complete combustion; H_2O and CO_2 were released and conducted in a copper oven at 923 K, then passed through a 2 m column with helium vector gas, and analyzed with a katharometer detector. The results of analysis are shown in Table 1.

3.2. Other physicochemical characteristics

The characteristics of the adsorbents such as moisture content, bulk density and solubility in water (inorganic and organic matter) were determined. The results are summarized in Table 1.

3. 3. Effect of temperature

Increase of the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores with the temperature has two major effects on the adsorption process [9]. Increasing the temperature is known to increase the adsorption capability of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, increase in the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. A study of the temperature dependence of adsorption reactions gives valuable information about the enthalpy and entropy changes during adsorption. The removal of dyes on WS was studied at 308, 313, and 318 K to determine the adsorption isotherms and thermodinamic parameters. The adsorption ability of WS increase with increasing temperature for acid red 183. A similar observation was also reported by AL-Qodah [9] and Rao and Ashutosh [18]. The capacity of the adsorbent to adsorb dye molecules increases with the increase in operating temperature which is due to increase in diffusion coefficient at higher temperatures. However, the effect of temperature seems to be not very much pronounced. Adsorption for acid green 25 on WS increases with increasing temperature from 308 K to 313 K, while decreases at 318 K. The decreasing of adsorption with temperature at 318 K is mainly due to the weakening of adsorptive forces between the active sites of WS and acid green 25 ions. The extent of the decrease in adsorption of solute of definite concentration with increase in temperature depends on the nature of adsorbent–adsorbate system. This type of adsorption is likely to be classiffied as reversible adsorption [19].

3.4. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [20]. In order to study the influence of pH on the adsorption capacity of WS, the experiments were performed by using various initial solution pH values varying from 2 to 8, with other parameters being kept constant. Fig.1 shows the effect of pH on the removal of dyes by WS. The removal of dyes by WS decreased with increasing pH. As pH of the system increased, the number of negatively

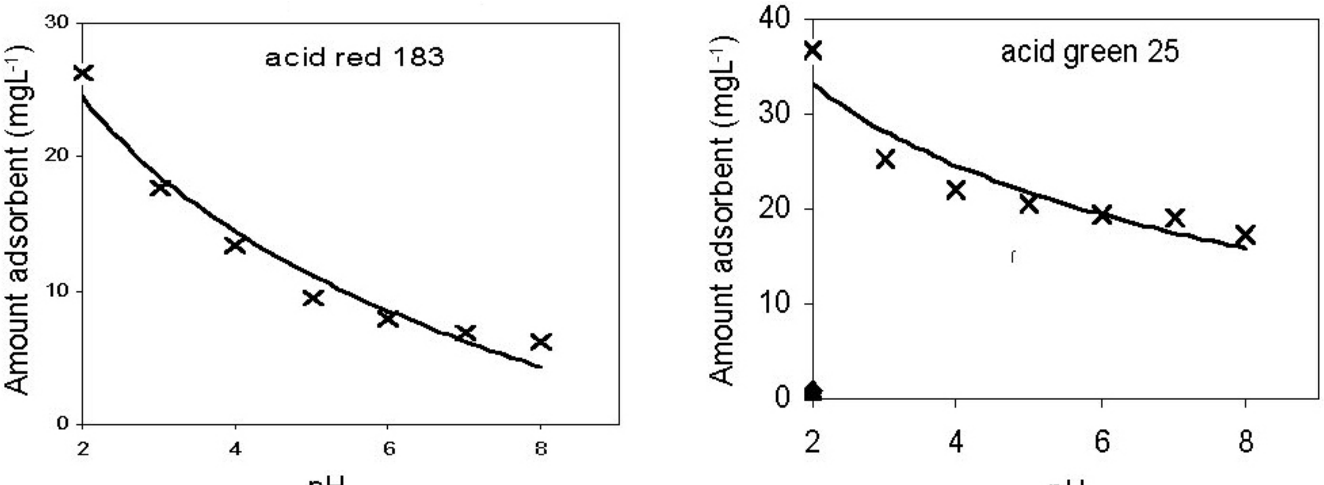

Fig. 1. Effect of pH on adsorption of dyes (T: 308 K, adsorbent: 1 g 0.05 L^{-1}, C_i: 27 mg L^{-1} and 38 mg L^{-1}, contact time: 45 min).

Table 2
Effect of adsorbent dosage on the adsorption of dyes with the different initial concentration (T = 308 K, contact time = 45 min)

Dye	Adsorbent dosage (g)	C_i: 30 mg L^{-1} q_{eq} (mg g^{-1})	% A	C_i: 42 mg L^{-1} q_{eq} (mg g^{-1})	% A	C_i: 52 mg L^{-1} q_{eq} (mg g^{-1})	% A	C_i: 62 mg L^{-1} q_{eq} (mg g^{-1})	% A
Acid red 183	1.0	12.1	40.3	15.1	36.0	18.6	35.8	22.2	35.8
	1.5	11.6	58.0	13.2	47.1	16.1	46.4	19.5	47.2
	2.0	9.6	64.0	11.4	54.3	14.2	54.6	17.1	55.2
	2.5	8.2	68.3	9.9	59.0	13.8	66.3	16.1	65.0
	3.0	7.5	75.0	9.3	66.4	13.2	76.2	15.2	73.5
	3.5	6.6	77.0	8.2	68.3	11.6	78.1	13.3	75.1
	4.0	6.3	84.0	7.3	69.5	10.3	79.2	12.0	77.4
Acid green 25	1.0	3.1	10.3	5.1	12.1	7.0	13.5	8.5	13.7
	1.5	2.9	14.3	3.9	13.8	6.9	20.0	7.3	17.7
	2.0	2.7	18.0	3.9	18.8	6.0	23.1	6.7	21.6
	2.5	2.5	20.8	3.6	21.7	5.8	26.9	6.2	25.0
	3.0	2.3	23.3	3.4	24.3	5.6	32.1	5.6	27.1
	3.5	2.1	24.5	3.4	28.3	5.2	34.8	5.3	30.0
	4.0	2.1	28.0	3.2	30.5	4.9	37.9	5.0	32.4

charged adsorbent sites increased, and the number of positively charged surface sites decreased, which did not favour the adsorption of negatively charged dye anions [13].

3.5. Effect of adsorbent dosage

Adsorbent dosage is an important parameter, since it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage (adsorbent prepared in different batches) was studied on dye removal keeping all other experimental conditions constant (Table 2). The results show that as the adsorbent concentration increases, percentage adsorption also increases, but the amount adsorbed per unit mass of the adsorbent decreases considerably. The decrease in unit adsorption with increase in the dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction [21].

3.6. Adsorption kinetics

The adsorption of dyes at a fixed concentration on WS was studied as a function of contact time in order to determine the equilibration time for maximum adsorption. The adsorption is very fast initially and reaches the equilibrium adsorption approximately at 30 min.

The equilibrium adsorption capacity of the adsorbent for dyes increased with a rise in initial dye concentration, as shown in Table 2. Dye removal is highly concentration dependent. The increase in loading capacity of the adsorbent with relation to dye ions concentration is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption. At 308 K, when the initial dye ions concentration was increased from 30 to 62 mg L^{-1}, the loading capacity of dried adsorbent increased from 12.1 to 22.2 mg of acid red 183 per gram of WS, 3.1 to 8.5 mg of acid green 25 per gram of WS , respectively (Table 2).

Adsorption is a physicochemical process that involves the mass transfer of solute (adsorbate) from the fluid phase to the adsorbent surface [14]. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process [4]. It is well known that the rate of the adsorption process is modified by several parameters such as the structural properties of the adsorbent (i.e. porosity, specific area, particle size, etc), the properties of the adsorbate (ionic radius, number of coordination, and speciation), the adsorbate concentration, chelates formation between adsorbate ions, the adsorbent, etc. [20].

The transient behaviour of the dye adsorption process was analyzed by using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion. The pseudo-first-order kinetic model has been widely used to predict dye adsorption kinetics. A linear form of the pseudo-first-order model was described by Lagergren [20] (Fig. 2).

$$\log (q_{eq}-q_t) = \log q_{eq} - k_{pf}\, t/2.303 \tag{2}$$

where q_t is the amount adsorbed at time t (mg g^{-1}), and k_{pf} is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). The values of log ($q_{eq}-q_t$) were calculated from the kinetic data. The calculated q_{eq}, k_{pf}, and the corresponding linear regression correlation coefficient

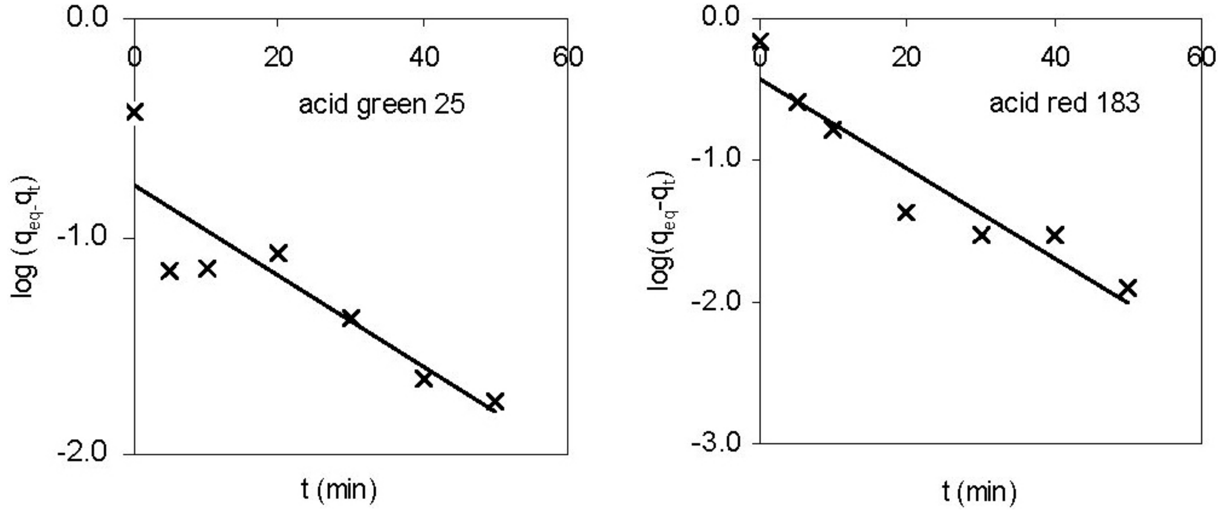

Fig. 2. Pseudo-first-order plots for dyes onto WS (*T:* 308 K, adsorbent: 4 g 0.05 L^{-1}, C_i: 40 mg L^{-1}).

Table 3
Adsorption kinetic parameters of dyes on WS (T: 308 K, adsorbent: 4 g 0.05 L^{-1}, C_i: 40 mg L^{-1})

		First-order kinetic model			Second-order kinetic model			Intraparticle diffusion	
Dyes	q_{eq}[a]	k_{pf} (min^{-1})	q_{eq} (mg g^{-1})[b]	R_1^2	k_{ps} (g/mol min)	q_{eq} (mg g^{-1})[b]	R_2^2	k_{id} (mg $g^{-1}\text{min}^{-1/2}$)	R_3^2
Acid red 183	0.331	0.182	0.718	0.997	1.362	0.354	0.999	0.150	0.970
Acid green 25	0.100	0.021	0.372	0.998	1.779	0.111	0.998	0.057	0.990

[a] Calculated; [b] Experimental.

R_1^2 values are shown in Table 3. A good agreement was not observed between experimental and calculated q_{eq} values (Table 3). This shows inapplicability of the pseudo-first-order model in predicting the kinetics of the dyes adsorption onto WS particles. The kinetic data were further analyzed by using Ho's pseudo-second-order kinetics, represented by [15]:

$$t/q_t = 1/k_{ps}\, q_{eq}^2 + t/q_{eq} \qquad (3)$$

where k_{ps} is the rate constant of second-order adsorption (g mol^{-1} min^{-1}). If the second-order kinetics is applicable, then the plot of t/q_t vs t should show a linear relationship (Fig. 3). The calculated q_{eq}, k_{ps}, and the corresponding linear regression correlation coefficient R_2^2 values are summarized in Table 3. The linear plots of t/q_t vs t show good agreement between experimental and calculated q_{eq} values (Table 3). The correlation coefficients for the second-order kinetics model (R_2^2) are greater than 0.99, indicating the applicability of this kinetics equation and the second-order nature of the adsorption process of dyes onto WS.

The rate constant for intraparticle diffusion (k_{id}) is given as:

$$q_t = k_{id}\, t^{1/2} \qquad (4)$$

where q_t is the amount adsorbed (mg g^{-1}) at time t (min). The plots of q_t vs $t^{½}$ for different adsorbents are shown in Fig. 4. Both plots have a similar general trend in initial curved part, followed by a linear one and then a plateau. The initial curved part may be attributed to the bulk diffusion, the linear one to the intraparticle diffusion and plateau to the equilibrium.

This indicates that the transport of dyes from solution through the particle solution interface into the pores of the particles as well as the adsorption on the available surface of adsorbents are both responsible for the uptake of dye. The intraparticle rate constants calculated from Fig. 4 are 0.150 and 0.057 mg g^{-1} $\text{min}^{-1/2}$ for acid red 183 and acid green 25, respectively (Table 3).

3.7. Adsorption isotherm models

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [9]. The equilibrium adsorption of dyes was

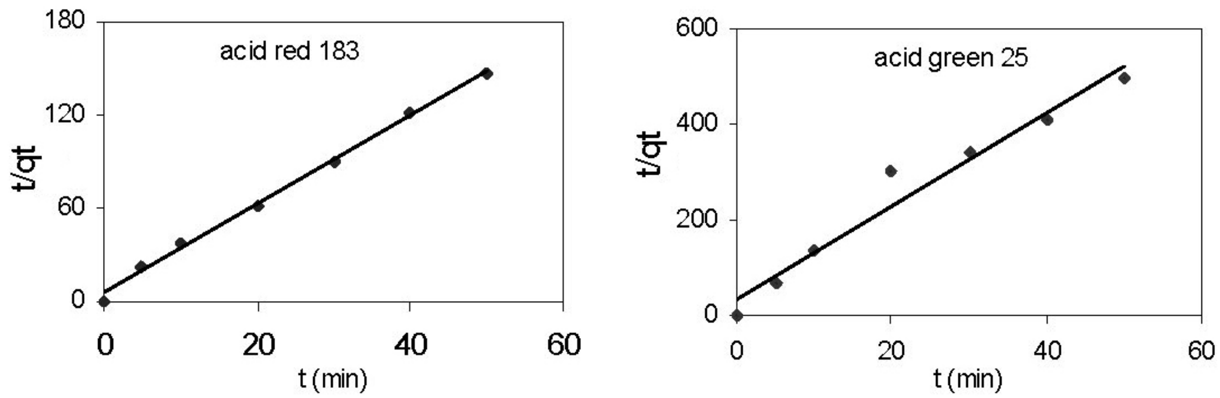

Fig. 3. Pseudo-second-order plots for dyes onto WS (T: 308 K, adsorbent: 4 g 0.05 L^{-1}, C_i: 40 mg L^{-1}).

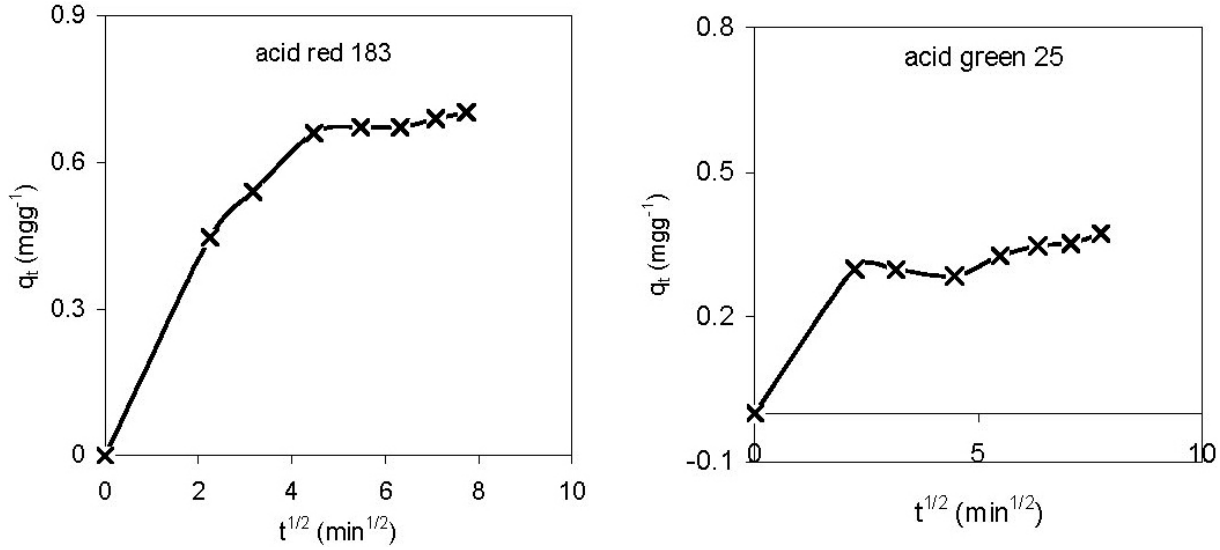

Fig. 4. Intraparticle diffusion plots of dyes on WS (T: 308 K, adsorbent: 4 g 0.05 L^{-1}, C_i: 40 mg L^{-1}).

studied as a function of concentration. Several isotherm models are available. In this study, the Langmuir and Freundlich adsorption isotherms were employed [5, 22].

The linearized equation of Langmuir can be represented as follows:

$$C_{eq}/q_{eq} = 1/bQ_m + C_{eq}/Q_m \qquad (5)$$

where q_{eq} (mg g^{-1}) is the amount of dye adsorbed per unit mass of adsorbent particles at equilibrium, C_{eq} (mg L^{-1}) is the equilibrium liquid phase concentration of dye, and b is the equilibrium constant. The Langmuir constant is related to the affinity of binding sites (L mg^{-1}) or (L mol^{-1}), and Q_m represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance.
b and Q_m are calculated from the slope and intercept of the straight lines of plot of C_{eq}/q_{eq} vs C_{eq} (Fig. 5).

The Freundlich isotherm is given in logarithmic form as

$$\log q_{eq} = \log k_F + 1/n \log C_{eq} \qquad (6)$$

where k_F is roughly an indicator of the adsorption capacity and $(1/n)$ of the adsorption intensity. k_F and $(1/n)$ can be determined from the linear plot of $\log q_{eq}$ vs $\log C_{eq}$ (Fig. 6).

Adsorption isotherms (Figs. 5 and 6) were obtained in terms of Eqs. (5) and (6) by using experimental adsorption results in these equations. Values b, Q_m, k_F, and n are summarised in Table 4. 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 the Table 4 and Fig. 5, the Langmuir isotherm fits well with the experimental data (R^2 = 0.94–0.98), whereas the low correlation coefficients (R^2 = 0.90–0.94) show poor agreement of the Freundlich isotherm with the experi-

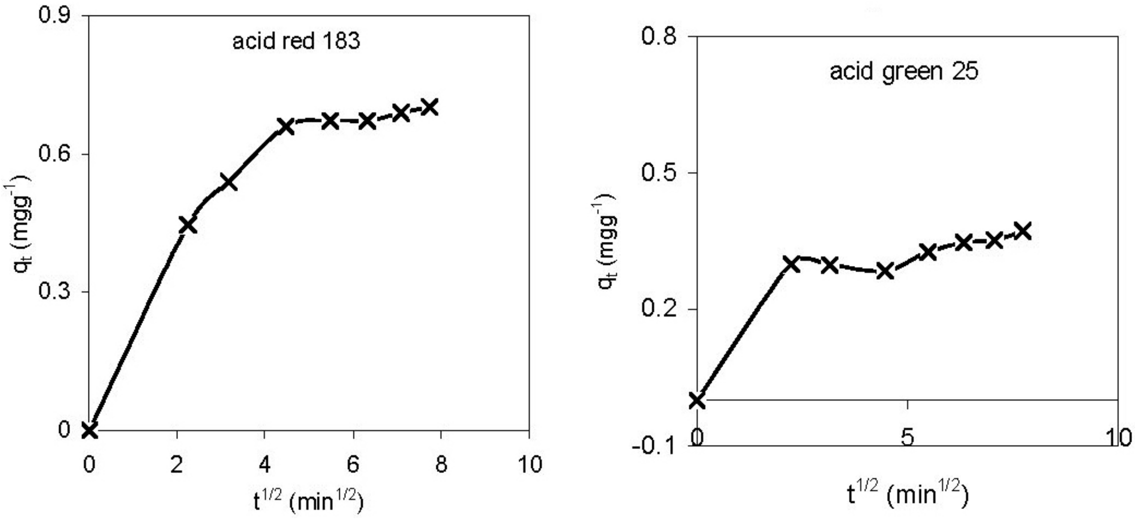

Fig. 5. Langmuir adsorption isotherm at different temperatures (adsorbent: 1 g 0.05 L^{-1}, contact time: 45 min).

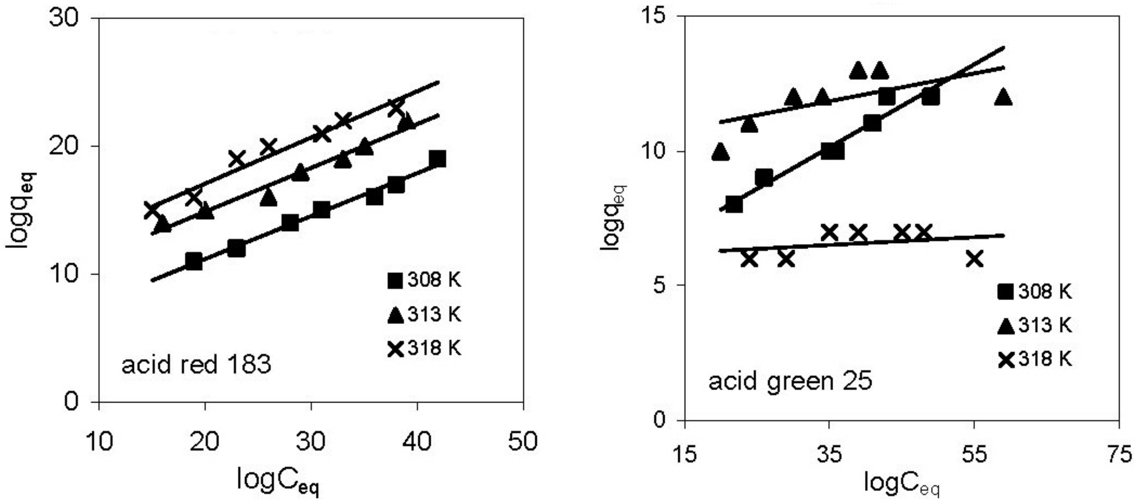

Fig. 6. Freundlich adsorption isotherm at different temperatures (adsorbent: 1 g 0.05 L^{-1}, contact time: 45 min).

Table 4
Langmuir and Freundlich isotherm constants for adsorption of dyes on WS

Dye	T (K)	Q_m (mg g^{-1})	Langmuir constants			Freundlich constants		
			b (L mg^{-1})	b (L mol^{-1})	R^2	k_F	n	R^2
Acid red 183	308	45	0.02	9358	0.94	0.7	0.10	0.91
	313	37	0.03	20120	0.95	0.8	0.30	0.90
	318	37	0.03	20354	0.98	1.4	2.20	0.94
Acid green 25	308	21	0.03	17433	0.94	0.4	2.90	0.93
	313	14	0.21	132612	0.97	0.5	0.01	0.94
	318	7.0	1.41	87611	0.91	0.8	0.07	0.90

mental data. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the WS, since the Langmuir equation assumes that the surface is homogenous [23].

As it can be seen in Table 4, the maximum adsorption capacities for acid red 183 and acid green 25 on WS at 308, 313, and 318 K were found to be 45, 37, and 37; 21, 14, and 7 mg g^{-1}, respectively. Also, the maximum adsorption

Table 5
Previously reported adsorption capacities of various adsorbents for dyes

Adsorbent	Adsorbate	Q_m (mg g^{-1})	Reference
Spent brewery grain	Acid dye	30.47	14
Speiolite	Acid dye	8.32	23
Activated carbon	Basic dye	309.20	11
Industrial waste products	Acid dye	221.20	4
Silica fumes	Acid and direct dye	7.70–50.00	7
Banana pith	Acid and direct dye	4.42	1
Modified bentonite	Direct and reactive dye	19.49–42.02	16
Shale oil ash	Reactive dye	6.92	9
Shells of bittim (*Pistacia khinjuk* Stocks)	Acid dye	33–16	17
Waste metal hydroxide sludge	Reactive dye	275±45	24
Chitosan	Reactive dye	130	25
Yellow passion fruit	Methylene blue	44.70	26
Walnut shells	Acid dye	7.00–45.00	This study

Table 6
Values of thermodynamic parameters for the adsorption of dyes on WS

T (K)	Acid red 183			Acid green 25		
	$-\Delta G^0$ (cal mol^{-1})	ΔH^0 (cal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})	$-\Delta G^0$ (cal mol^{-1})	ΔH^0 (cal mol^{-1})	ΔS^0 (cal mol^{-1} K^{-1})
308	5596			5977		
313	6163	15,202	68	7336	32,982	130
318	6269			8646		

capacities of WS for acid red 183 and acid green 25 increase and follows the order acid red 183 > acid green 25.

k_F is a Freundlich constant that shows adsorption capacity of adsorbent, and n is a constant which shows the extent of relationship between adsorbate and adsorbent [3]. The value k_F of WS for acid red 183 and acid green 25 at 308, 313, and 318 K increased and follows the order 0.7, 0.8 and 1.4; 0.4 ,0.5, and 0.8, respectively. k_F values of acid red 183 are greater than acid green 25 for WS. It has generally been reported that the values of n in the range 1–10 represent good adsorption [3]. In the present work, the exponent for acid red 183 at 318 K and acid green 25 at 308 K was $1 < n < 10$, indicating favourable adsorption. However, the other n values in Table 4 were $1 > n$, indicating unfavourable adsorption.

The removal of dyes (mg g^{-1}) on WS decreases with increase in adsorbent dosage, while increases with initial dye concentration (Table 2).When the results obtained from this study were compared works to the previously reported (Table 5) on adsorption capacities of various low-cost adsorbent in aqueous solution for acid red 183 and acid green 25, it could be stated that our findings are good.

3.8. Estimation of thermodynamic parameters

The free energy of adsorption (ΔG^0) can be related with the equilibrium constant K (L mol^{-1}) corresponding to the reciprocal of the Langmuir constant, b, by the following equation [14]:

$$G^0 = -RT \ln b \quad (7)$$

where R is the gas universal constant (1.987 cal mol^{-1} K^{-1}) and T is the absolute temperature. Also enthalpy (ΔH^0) and entropy (ΔS^0) changes can be estimated by the following equation:

$$\ln b = \Delta S^0/R - \Delta H^0\, T/R \quad (8)$$

Thus, a plot of ln$b$ vs $1/T$ should be a straight line. ΔH^0 and ΔS^0 values were obtained from the slope and intercept of this plot, respectively. ΔG^0, ΔH^0, and ΔS^0 were obtained from Eqs. (7) and (8) and are given in Table 6.

The estimated values of ΔG^0 for the adsorption acid red 183 and acid green 25 on WS were −5596, −6163, and −6269; −5977, −7336, and −8646 cal mol^{-1}, respectively at 308, 313, and 318 K, which are rather low, indicating that a spontaneous physiosorption process has occurred [14]. The enthalpy changes (ΔH^0) and entropy (ΔS^0) of adsorption for acid red 183 and acid green 25 were 15,202 cal mol^{-1} and 68 cal mol^{-1} K^{-1}, 32982 cal mol^{-1} and 130 cal mol^{-1} K^{-1}, respectively. The positive value for ΔH^0 confirms that the adsorption of dyes on WS is an endothermic process. Though the adsorption of dyes is currently described as an exothermic phenomenon [4, 23], endothermic adsorption of acid orange 7 to spent brewery grains has also been reported [14]. The positive value of entropy reflects the affinity of the adsorbent for acid red 183 and acid green 25 dyes.

4.Conclusions

Based upon the experimental and theoretical results in this investigation, the following conclusions can be drawn:

- WS is a potential adsorbent for acid red 183 and acid green 25 dyes from aqueous solutions.
- The adsorption of dyes to WS is dependent on its contact time, temperature, pH, adsorbent doses and initial dye concentration.
- The inital rate of adsorption of dyes with WS was high, and then it declined with time until it reached equilibrium.
- The removal of dyes (mg g^{-1}) on WS decreases with an increase in adsorbent dosage and initial dye concentration.
- The maximum adsorption capacities for acid red 183 and acid green 25 on WS at 308, 313, and 318 K were found to be 45, 37, and 37; 21, 14, and 7 mg g^{-1}, respectively.
- The data obtained from the adsorption isotherm at different temperatures were used to calculate thermodynamic quantities such as ΔG^0, ΔH^0, and ΔS^0. The results indicate that acid red 183 and acid green 25 adsorption on WS is spontaneous and physical in nature.
- Technologies for the removal of dyes are generally expensive. WS, being a cheap and easily available material, could be an alternative for more costly adsorbents used for removal of dyes from aqueous systems for environmental cleaning purposes.

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References

[1] C. Namasivayam, D. Prabha and M. Kumutha, Removal of direct red and acid brillant blue by adsorption on to banana pith. Bioresour. Technol., 64 (1998) 77–79.

[2] W. Chu, Dye removal from textile dye wastewater using recycled alum sludge. Water Res., 35(13) (2001) 3147–3152.

[3] M.M. Nassar and Y.H. Magdy, Removal of different basic dyes from aqueous solution by adsorption on palm-fruit bunch particles. Chem. Eng. J., 66 (1997) 223–226.

[4] A.K. Jain, V.K. Gupta, A. Bhatnagar and Suhas, Utilization of industrial waste products as adsorbents for the removal of dyes. J. Haz. Mater., B101 (2003) 31–42.

[5] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40 (1918) 1361–1403.

[6] K.S. Low and C.K. Lee, Quaternized rice husk as sorbent for reactive dyes. Bioresour. Technol., 61 (1997) 121–125.

[7] S.V. Mohan, V.V.S. Mamatha and J. Karthikeyan, Removal of color from acid and direct dyes by adsorption onto silica fumes. Fresenius Envir. Bull., 7 (1998) 51–58.

[8] B.H. Tan, T.T. Teng and A.K.M. Omar, Removal of dyes and industrial dye wastes by magnesium chloride. Water Res., 34(2) (2000) 597–604.

[9] Z. Al-Qodah, Adsorption of dyes using shale oil ash. Water Res., 34(17) (2000) 4295–4303.

[10] R. Liu and H. Tang, Oxidative decolorization of direct light red F3B dye at natural manganese minaral surface. Water Res., 34(16) (2000) 4029–4035.

[11] V. Meshko, L. Markovska, M. Mincheva and A.E. Rodrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite. Water Res., 35(14) (2001) 3357–3366.

[12] U.M. Sawada, Adsorption behavior of direct dye on cotton in non-aqueous media. Dyes Pigments, 58 (2003) 37–40.

[13] V.K. Garg, R. Gupta, A.B. Yadav and R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust. Bioresour. Technol., 89 (2003) 121–124.

[14] S.P. Silva, S. Sousa, J. Rodrigues, H. Antunes, J.J. Porter, I. Gonçalves and S.F. Dias, Adsorption of acid orange 7 dye in aqueous solutions by spent brewery grains. Sep. Purif. Technol., 40(3) (2004) 309–315.

[15] Y. Bulut and H. Aydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination, 194 (2006) 259–267.

[16] A.H. Aydin, E. Şahin and G. Akçay, The removal of dyes from water by modified bentonite. Fresenius Envir. Bull., 13(126) (2004) 1530–1535.

[17] H. Aydin and G. Baysal, Adsorption of acid dyes in aqueous solutions by shells of bittim (*Pistacia khinjuk* Stocks). Desalination, 196 (2006) 248–259.

[18] K.C.L.N. Rao and K.K. Ashutosh, Colour removal from a dyestuff industry effluent using activated carbon. Ind. J. Chem. Technol., 1 (1994) 13–19.

[19] R.S. Juang, F.C. Wu and R.L. Tseng, The ability of activated clay for the adsorption of dyes from aqueous solutions. Envir. Technol., 18 (1997) 525–531.

[20] S. Lagergren, Zur Theorie der Sogenannten Adsorption Gelöster Stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar, 24 (1898) 1–39.

[21] C. Raji and T.S. Anirudhan, Kinetics of Pb(II) adsorption by polyacrylamide grafted sawdust. Ind. J. Chem. Technol., 4 (1997) 157–162.

[22] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–471.

[23] M. Alkan, Ö Demirbaş, S. Çelikçapa and M. Doğan, Sorption of acid red 57 from aqueous solution onto sepiolite. J. Haz. Mater., B116 (2004) 135–145.

[24] C.R. Santos Sílvia, J.P. Vilar Vítor and A.R. Boaventura Rui, Waste metal hydroxide sludge as adsorbent for a reactive dye. J. Haz. Mater., 153(3) (2008) 999–1008.

[25] G. Annadurai L.Y. Ling and J.F. Lee, Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis. J. Haz. Mater., 152(1) (2008) 337–346.

[26] F.A. Pavan, E.C. Lima, S.L.P. Dias and A.C. Mazzocato, Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. J. Haz. Mater., 150(3) (2008) 703–712.

[27] R. Jain and S. Sikarwar, Removal of hazardous dye congored from waste material. J. Haz. Mater., 152(3) (2008) 942–948.