

The Effect of pH on the Removal of Anionic Dyes from Colored Textile Wastewater Using a Biosorbent

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ABSTRACT: The effect of pH on equilibrium and kinetics of dye adsorption onto canola hull as a biosorbent was studied. Reactive Red 198 (RR198), Reactive Blue 19 (RB19), Direct Red 79 (DR79), and Direct Red 80 (DR80) were used as model textile dyes. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and UV-vis spectroscopy were used. The presence of functional groups onto canola hull was investigated using FTIR spectroscopy. The pseudo first-order, pseudo second-order and intraparticle diffusion kinetics models were examined to evaluate the kinetics data. The Langmuir, Freundlich, and Tempkin adsorption isotherm models were applied to describe the equilibrium isotherms. The FTIR spectrum proved the presence of

functional groups such as hydroxyl and amino groups in canola hull surface. The results showed that the adsorption of RR198, RB19, DR79, and DR80 onto canola hull followed Tempkin isotherm. Adsorption kinetic of dyes followed pseudo second-order kinetics. Desorption tests showed maximum dye releasing of 88% for RR198, 86% for RB19, 91% for DR79, and 95% for DR80 at pH 12. Data showed that canola hull could be used as a novel natural material for the removal of anionic dyes from wastewater. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2996–3003, 2011

Key words: adsorption; dyes/pigments; electron microscopy; FTIR; UV-vis spectroscopy

INTRODUCTION

The presence of organic pollutants such as dyes, pesticides, etc., in the receiving surface and under ground waters is not safe, pleasant, and welcomed.^{1–4} Azo dyes, which contain one or more azo bonds (–N=N–), are among the most widely used synthetic dyes and usually become major pollutants in textile wastewater. It has been documented that some azo dyes are toxic and even mutagenic to living organisms in aquatic environment.^{5–7}

The discharge of untreated wastewater into natural streams has caused problems such as increasing the toxicity, eutrophication, reducing the light penetration, and derogatory effect on photosynthesis phenomenon. In addition, the stability of their molecular structures renders them resistant to biological or even chemical degradation.⁶ More recently, all governments are under severe pressure by their people, to stop this type of effluent to the public water-courses, unless to be treated properly.

Several physicochemical techniques have been tested to treat wastewater but only that of adsorption

is considered to be superior to other techniques. This is attributed to the low cost, easy availability, simplicity of design, high efficiency, ease of operation, biodegradable, and ability to treat dyes.^{8,9} As a result, many researchers have investigated the low cost and natural biodegradable materials to remove dyes from wastewater. Several natural adsorbents, such as soy meal hull,^{3,10} eucalyptus bark,¹¹ *Tamarindus indica* hull,¹² peat,¹³ bagasse pith,¹⁴ and orange peel,¹⁵ have been tried for this purpose. The dye adsorption capacity of some adsorbents are shown in Table I.^{16–21}

Dye removal using different biosorbents, such as soy meal hull, and *Tamarindus indica* hull, has already been established in our laboratory.^{3,10,12} A literature review showed that the removal of anionic dyes using canola hull was not done. The anionic dyes such as reactive and direct dyes are one of the most important and widely used dye groups in the textile dyeing industries. In this article, the effect of pH on equilibrium and kinetics of anionic dye adsorption onto canola hull as a novel biosorbent was studied. In addition, dye desorption from canola hull was investigated.

EXPERIMENTAL

Chemicals and materials

Canola hull was obtained from a local field in north of Iran. Reactive Red 198 (RR198), Reactive Blue 19 (RB19), Direct Red 79 (DR79), and Direct Red 80

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TABLE I
Dye Adsorption Capacity of Some Adsorbents

Adsorbent	Dyes	Adsorption capacities (mg/g)	References
Fly ash	Methylene blue	4.5	16
Banana peel	Amido black 10B	6.5	17
Carbonized coir pith	Congo red	6.7	18
Bituminous coal	Direct brown 1	2.0	19
Lignite coal	Direct brown 1	4.1	19
Charfines	Direct brown 1	6.4	19
Kaolinite	Metomega chrome orange	0.7	20
Wollastonite	Metomega chrome orange	0.7	20
Fly ash	Metomega chrome orange	0.7	20
Sepia pens	Reactive green 12	3.5	21
Canola hull	Reactive red 198	2.8	This work
Canola hull	Reactive blue 19	2.0	This work
Canola hull	Direct red 79	3.1	This work
Canola hull	Direct red 79	8.7	This work

(DR80) were used as model textile dyes. The description and chemical structure of dyes are shown in Table II and Figure 1, respectively.

Dyes were used without further purification. All other chemicals were of Analar grade and purchased from Merck (Germany).

The pH measurements were made using a pH meter (Metrohm). UV-vis spectrophotometer CECIL 9200 was used to measure the dye removal. The maximum wavelength (λ_{\max}) of dyes for determination of residual dye concentration in solution was shown in Table II. The dye solutions were centrifuged using a Hettich EBA20 centrifuge.

To investigate the surface functional group of canola hull, Fourier transform infrared (FTIR; Perkin-Elmer Spectrophotometer Spectrum One) in the range 450–4000 cm^{-1} was studied. SEM images of raw canola hull and dye adsorbed canola hull were obtained using LEO 1455VP scanning electron microscope.

Adsorption procedure

The adsorption measurements were conducted by mixing canola hull (1 g/L for RR198 and RB19 and 2

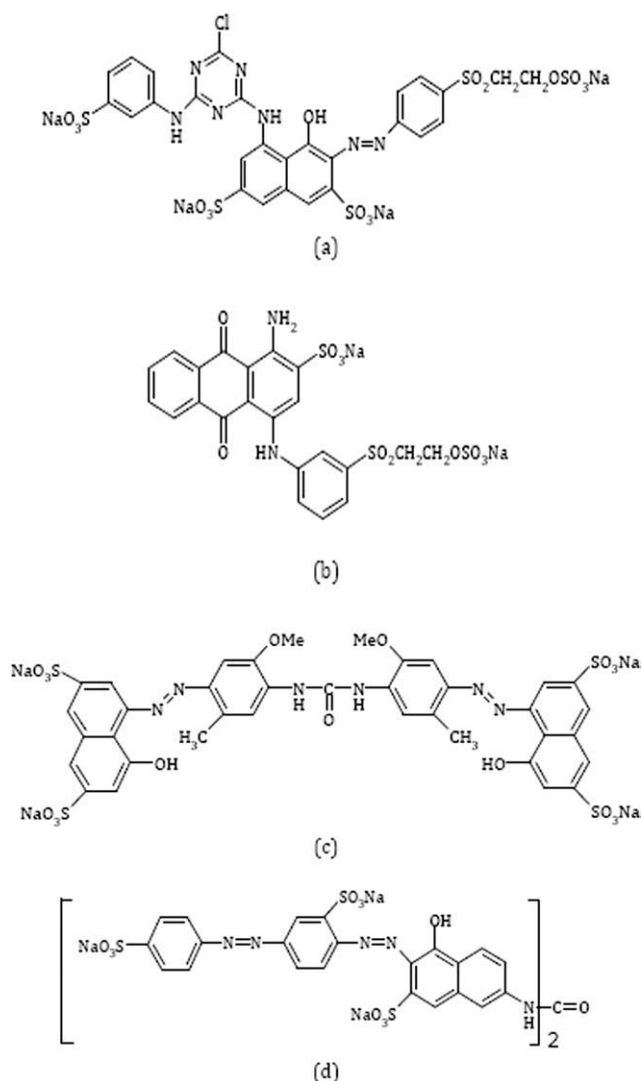


Figure 1 The chemical structure of dyes. (a) RR198, (b) RB19, (c) DR79, and (d) DR80.

g/L for DR79 and DR80) in jars (agitating speed of 200 rpm) containing 250 mL of a dye solution (50 mg/L). pH studies were conducted to determine the optimum pH at which maximum color removal could be achieved. The pH of the solutions was adjusted by adding a small amount of H_2SO_4 or NaOH. Experiments were carried out at different pH values (2.5–10) at 25°C for 1 h to attain the equilibrium conditions. The changes of absorbance were

TABLE II
The Characteristics of the Dyes

Dye	Dye formula	Molecular weight (g/mol)	Company	λ_{\max} (nm)
Reactive Red 198	$\text{C}_{27}\text{H}_{18}\text{N}_7\text{O}_{16}\text{S}_5\text{Na}_4\text{Cl}$	983.5	HOE	520
Reactive blue 19	$\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_{11}\text{S}_3\text{Na}_2$	626	HOE	594
Direct red 79	$\text{C}_{37}\text{H}_{28}\text{N}_6\text{O}_{17}\text{S}_4\text{Na}_4$	1048	CIBA	513
Direct red 80	$\text{C}_{45}\text{H}_{26}\text{N}_{10}\text{O}_{21}\text{S}_6\text{Na}_6$	1372	CIBA	540

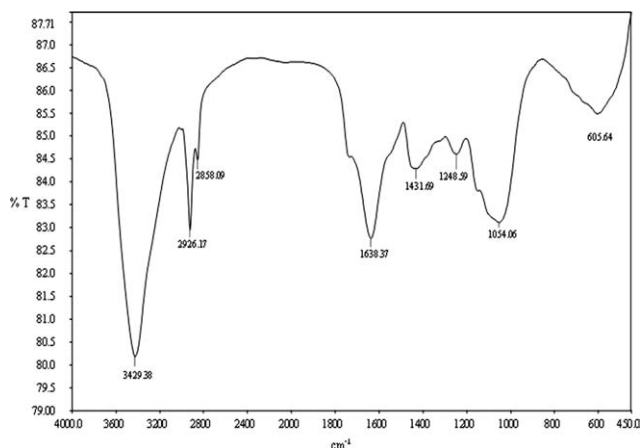


Figure 2 FTIR spectrum of canola hull.

determined at certain time intervals during the adsorption process. After experiments, the samples were centrifuged by Hettich EBA20 and then the dye concentration was determined. Dye removal was measured using CECIL 9200 spectrophotometer at maximum wavelength of dyes.

Desorption studies

The used canola hull for the adsorption of 50 mg/L of dye solution was separated from the solution and dried. Then, the adsorbent was agitated with 250 mL of distilled water at different pH values for the pre-determined equilibrium time of the desorption process. The desorbed dye was measured.

RESULTS AND DISCUSSION

Interaction between adsorbent and adsorbate

Figure 2 shows the FTIR spectrum of canola hull. The band positions are noticed at 3429.38, 2926.17, 2858.09, 1638.37, 1431.69, 1248.59, and 1054.06 cm^{-1} . The band at 3429.38 cm^{-1} is due to O—H and N—H stretching vibrations, whereas the bands at 2926.17 and 2858.09 cm^{-1} represent the CH_2 asymmetric and symmetric stretching vibrations, respectively. The bands at 1638.37 and 1431.69 cm^{-1} reflect the carbonyl group stretching (amide) and N—H bending, respectively. Bands at 1248.59 and 1054.06 cm^{-1} correspond to C—N and C—O stretching vibrations, respectively.²²

FTIR studies revealed that the surface of canola hull has various functional groups such as amino, hydroxyl, and carbonyl groups, which could also be affected by the pH of solution. Therefore, at various pH values, structure of dye molecules and functional groups of adsorbent surface could play very important roles in dye adsorption onto canola hull.

Figure 3 shows the effect of pH on dye removal. At pH 2.5, a significantly high electrostatic attraction exists between negatively charged anionic dyes and the positively charged surface of the adsorbent because of the ionization of functional groups of adsorbent. As the pH of the system increases, the number of negatively charged sites increased. A negatively charged site on the adsorbent does not favor the adsorption of anionic dyes because of the electrostatic repulsion.²³ Therefore, pH 2.5 was

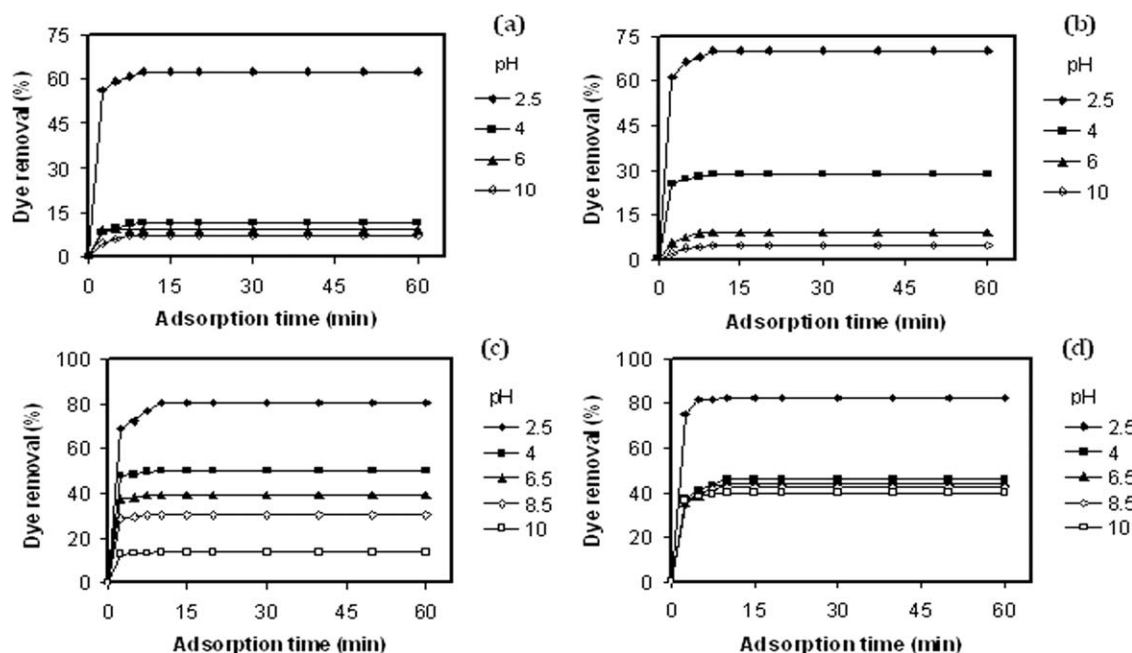


Figure 3 The effect of pH on dye removal using canola hull. (a) RR198, (b) RB19, (c) DR79, and (d) DR80.

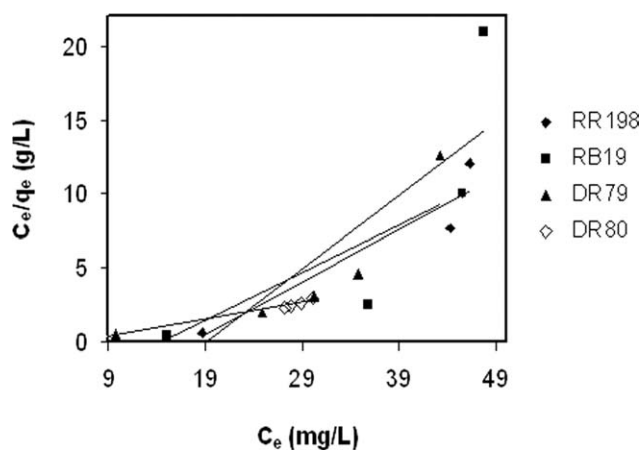


Figure 4 Linear plots of the Langmuir adsorption isotherms of dyes onto canola hull.

considered more effective pH, and it was used for further studies. A similar trend was observed for adsorption of anionic dyes onto other natural adsorbents surfaces.¹⁰

Adsorption isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. The distribution of dye molecule between the liquid phase and the biosorbent is a measure of the position of equilibrium in the adsorption process and can generally be expressed by one or more of a series of isotherm models. Adsorption isotherms are properties and equilibrium data, which described how pollutant interacts with adsorbent.²⁴ Isotherm data should accurately fit into different isotherm models to find the suitable model that can be used for design process.²⁵ Several isotherms such as Langmuir, Freundlich, and Tempkin were investigated.^{26–32}

The Langmuir isotherm has been widely used to describe single-solute systems. This isotherm assumes that intermolecular forces decrease rapidly with distance, and, consequently, it can predict monolayer coverage of the adsorbate on the outer surface of the adsorbent. Further assumption is that adsorption occurs at specific homogeneous sites

within the adsorbent, and there is no significant interaction among adsorbed species. Langmuir equation has been successfully applied to many adsorption processes.^{26–28}

The Langmuir equation can be written as follows:^{25–30}

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \quad (1)$$

where q_e , C_e , K_L , and Q_0 are the amount of dye adsorbed on the canola hull at equilibrium (mg/g), the equilibrium concentration of dye solution (mg/L), Langmuir constant (L/mg), and the maximum adsorption capacity (mg/g), respectively.

The linear form of Langmuir equation is:

$$C_e/q_e = 1/K_L Q_0 + C_e/Q_0 \quad (2)$$

Figure 4 shows the linear plots of the Langmuir adsorption isotherms of dyes using canola hull. The Q_0 , K_L , and correlation coefficients are given in Table III.

The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L , defined by

$$R_L = 1/(1 + K_L C_0) \quad (3)$$

where C_0 is the initial dye concentration (mg/L), and R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Table III).^{25–30}

Freundlich studied the sorption of a material onto animal charcoal and demonstrated that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations.^{26,31}

Freundlich isotherm can be expressed by:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the adsorption capacity at unit concentration and $1/n$ is the adsorption intensity. Equation (4) can be rearranged to a linear form:

TABLE III
Linearized Isotherm Coefficients for Dye Adsorption onto Canola Hull

Dye	Langmuir isotherm model				Freundlich isotherm model			Tempkin isotherm model		
	Q_0	K_L	R_L	R^2	K_F	$1/n$	R^2	A_T	B_T	R^2
RR198	2.7902	-0.0574	0.2584	0.9068	18310	-2.1726	0.9817	0.0189	-30.1030	1
RB19	2.0161	-0.0529	0.2743	0.6359	10349	-2.0352	0.8142	0.0183	-27.5950	1
DR79	3.0941	-0.0689	0.2114	0.7201	232	-0.9974	0.7671	0.0141	-10.5580	0.9546
DR80	8.7032	-0.1886	0.0959	0.9872	69	-0.5580	0.9897	0.0098	-8.4111	0.9974

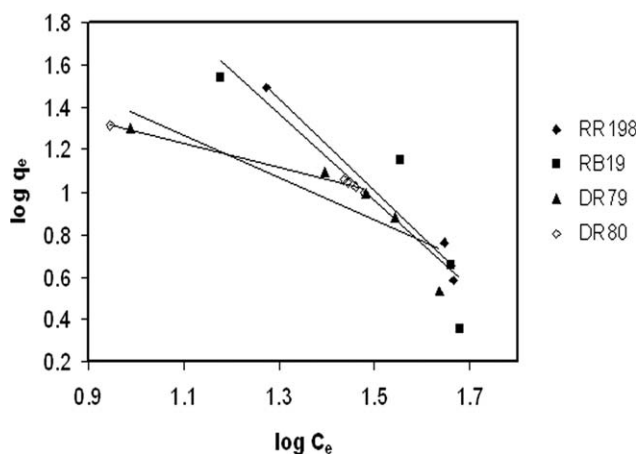


Figure 5 Linear plots of the Freundlich adsorption isotherms of dyes onto canola hull.

$$\log q_e = \log K_F + (1/n) \log C_e \quad (5)$$

The equilibrium isotherm for the adsorption of dyes on canola hull was determined with 250 mL of dye solution (50 mg/L). The systems were agitated for 1 h (200 rpm) in a constant temperature. Figure 5 shows the linear plots of the Freundlich adsorption isotherms of dyes using canola hull. The K_F , $1/n$, and correlation coefficients are given in Table III.

Tempkin isotherm assumes that the heat of adsorption of all the molecules on the adsorbent surface layer decreases linearly with coverage due to adsorbate–adsorbate interactions. Therefore, the adsorption potentials of the adsorbent for adsorbates can be evaluated using Tempkin adsorption isotherm model, which assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has generally been applied in the following form eq. (6):³²

$$q_e = (RT/b) \ln(A_T C_e) \quad (6)$$

Equation (6) can be written to the following eq. (7):

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (7)$$

where $B_T = (RT)/b$ and A_T (L/g) are the Tempkin constants and can be determined by a plot of q_e versus $\ln C_e$. Also, T is the absolute temperature in Kelvin, and R is the universal gas constant, 8.314 J/mol K. The constant b is related to the heat of adsorption. The linear plots of the Tempkin isotherm eq. (7) for the adsorption data are shown in Figure 6. The A_T , B_T , and correlation coefficients are given in Table III.

The results (Table III and Figs. 4–6) showed that the adsorption of RR198, RB19, DR79, and DR80

onto canola hull obeys Tempkin isotherm. This means that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

Adsorption kinetics

Adsorption kinetics must be taken into account because they explain how fast the chemical reaction occurs and provides information on the factors affecting the reaction rate.¹⁸ The kinetic models are used to examine the controlling mechanism of adsorption process such as adsorption surface, chemical reaction, and/or diffusion mechanisms. Three kinetic models have been widely used in the literature for adsorption processes:^{33–38} (i) pseudo first-order kinetic model, (ii) pseudo second-order kinetic model, and (iii) intraparticle diffusion model.

The pseudo first-order model suggests that adsorption is preceded by diffusion through a boundary.³³ A linear form of pseudo first-order model described by Lagergren as follows:

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303 \quad (8)$$

where q_t and k_1 are the amount of dye adsorbed at time t (mg/g) and the equilibrium rate constant of pseudo first-order adsorption (min^{-1}), respectively.

The applicability of pseudo first-order adsorption kinetics of dyes onto canola hull was studied. The values of k_1 , calculated q_e [$(q_e)_{\text{Cal.}}$], and correlation coefficients (R^2) for pseudo first-order adsorption kinetics were calculated and shown in Table IV.

The pseudo second-order equation is based on the sorption capacity of the solid phase.³⁴ A linear form of pseudo second-order model as follows:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (9)$$

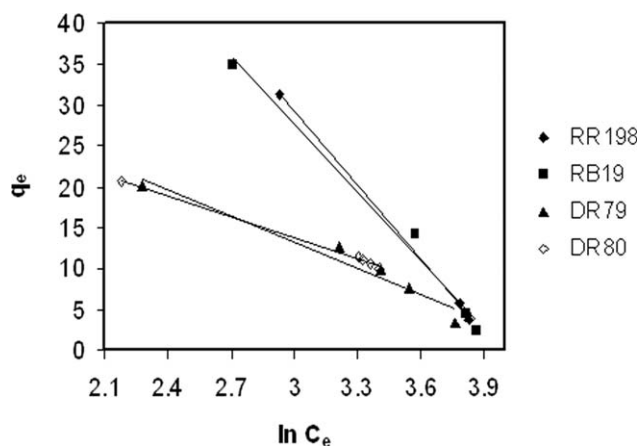


Figure 6 Linear plots of the Tempkin adsorption isotherms of dyes onto canola hull.

TABLE IV
Kinetics Constants for Dye Adsorption onto Canola Hull

Dye	pH	$(q_e)_{Exp}$	Pseudo first-order			Pseudo second-order			Intraparticle diffusion		
			$(q_e)_{Cal.}$	k_1	R^2	$(q_e)_{Cal.}$	k_2	R^2	k_p	I	R^2
RR198	2.5	31.2844	19.6381	0.4788	0.9082	31.4465	0.1908	1	0.4188	28.9590	0.5150
	4	5.7673	6.4774	0.5083	0.9303	5.8343	0.3522	1	0.2078	4.6212	0.4654
	6	4.5283	2.8787	0.1812	0.6000	4.5208	3.2839	1	0.0189	4.6371	0.3244
RB19	10	3.8139	2.8688	0.1872	0.7212	3.8730	0.3978	1	0.1769	2.8449	0.4233
	2.5	34.9635	23.0091	0.4666	0.9202	35.0877	0.1504	1	0.5415	31.9630	0.4989
	4	14.2351	8.7841	0.4530	0.8904	14.2857	0.3859	1	0.2053	13.0930	0.5197
DR79	6	4.5454	4.8685	0.3966	0.9827	4.6254	0.2938	1	0.2239	2.2108	0.4706
	10	2.2790	2.5539	0.3577	0.9880	2.3386	0.3950	1	0.1433	1.4910	0.4576
	2.5	20.1413	13.6993	0.3899	0.9000	20.2840	0.1665	1	0.4280	17.7470	0.5591
DR80	4	12.5662	6.4269	0.5456	0.8579	12.5945	0.9006	1	0.0729	12.1240	0.5013
	6.5	9.8719	5.1952	0.5622	0.8759	9.8912	1.2025	1	0.0570	9.5269	0.4837
	8.5	7.6413	4.4249	0.5596	0.9043	7.6570	1.3120	1	0.0532	7.3197	0.4688
	10	3.4231	2.0216	0.4613	0.8775	3.4364	1.7828	1	0.0357	3.2063	0.5054
DR80	2.5	20.5972	13.2434	0.7045	0.9071	20.6186	0.6190	1	0.1484	19.7180	0.2875
	4	11.4000	8.1189	0.3775	0.9191	11.4942	0.2557	1	0.2289	10.0070	0.5129
	6.5	11.1111	8.9372	0.3846	0.9514	11.2233	0.2146	1	0.2699	9.4727	0.4951
	8.5	10.6230	7.9013	0.4456	0.9407	10.6838	0.3518	1	0.1781	9.5483	0.4835
DR80	10	9.9683	5.7385	0.4981	0.8841	10.0000	0.7633	1	0.0870	9.4413	0.4845

where k_2 is the equilibrium rate constant of pseudo second-order (g/mg min).

Figure 7 shows the pseudo second-order adsorption kinetics of dyes onto canola hull. The values of k_2 , calculated q_e , and correlation coefficients for pseudo second-order adsorption kinetics were calculated and shown in Table IV.

The adsorption process required a multistep involving the transport of solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process and is, therefore, rate-determining step. The

intraparticle diffusion model is explored using the following equation:^{32,36}

$$q_t = k_p t^{1/2} + I \quad (10)$$

where I is the intercept and k_p (mg/g min^{1/2}) is the intraparticle diffusion rate constant.

The plot of q_t against $t^{1/2}$ may present a multilinearity correlation, which indicates that two or more steps occur during adsorption process. The values of k_p , I , and correlation coefficients for intraparticle diffusion model were calculated and shown in Table IV.

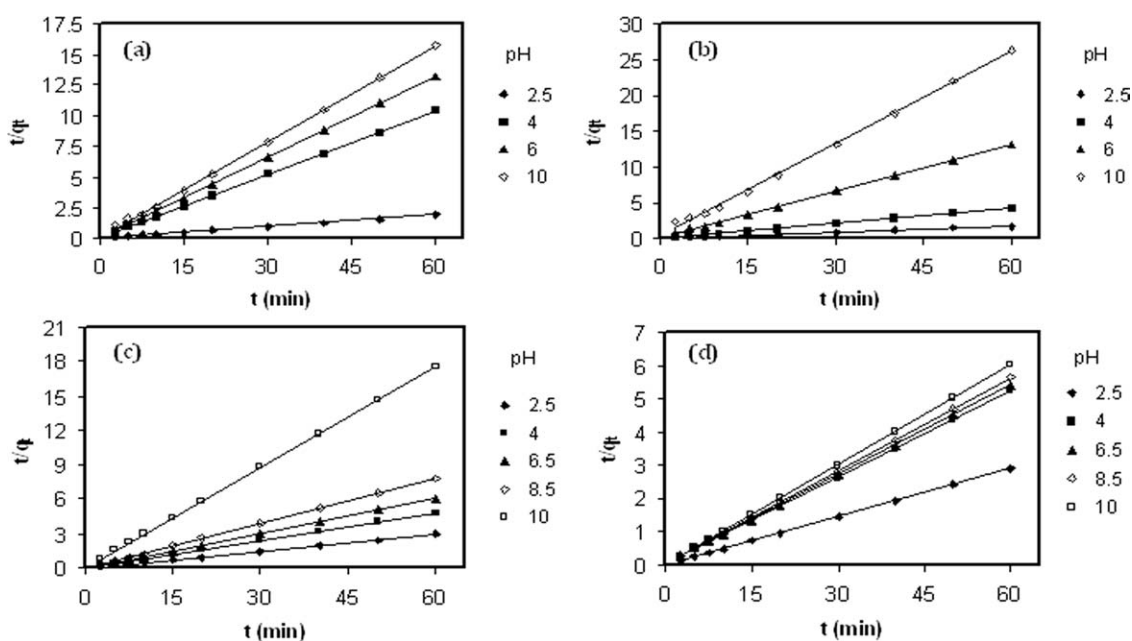


Figure 7 Pseudo second-order kinetics of dye adsorption onto canola hull. (a) RR198, (b) RB19, (c) DR79, and (d) DR80.

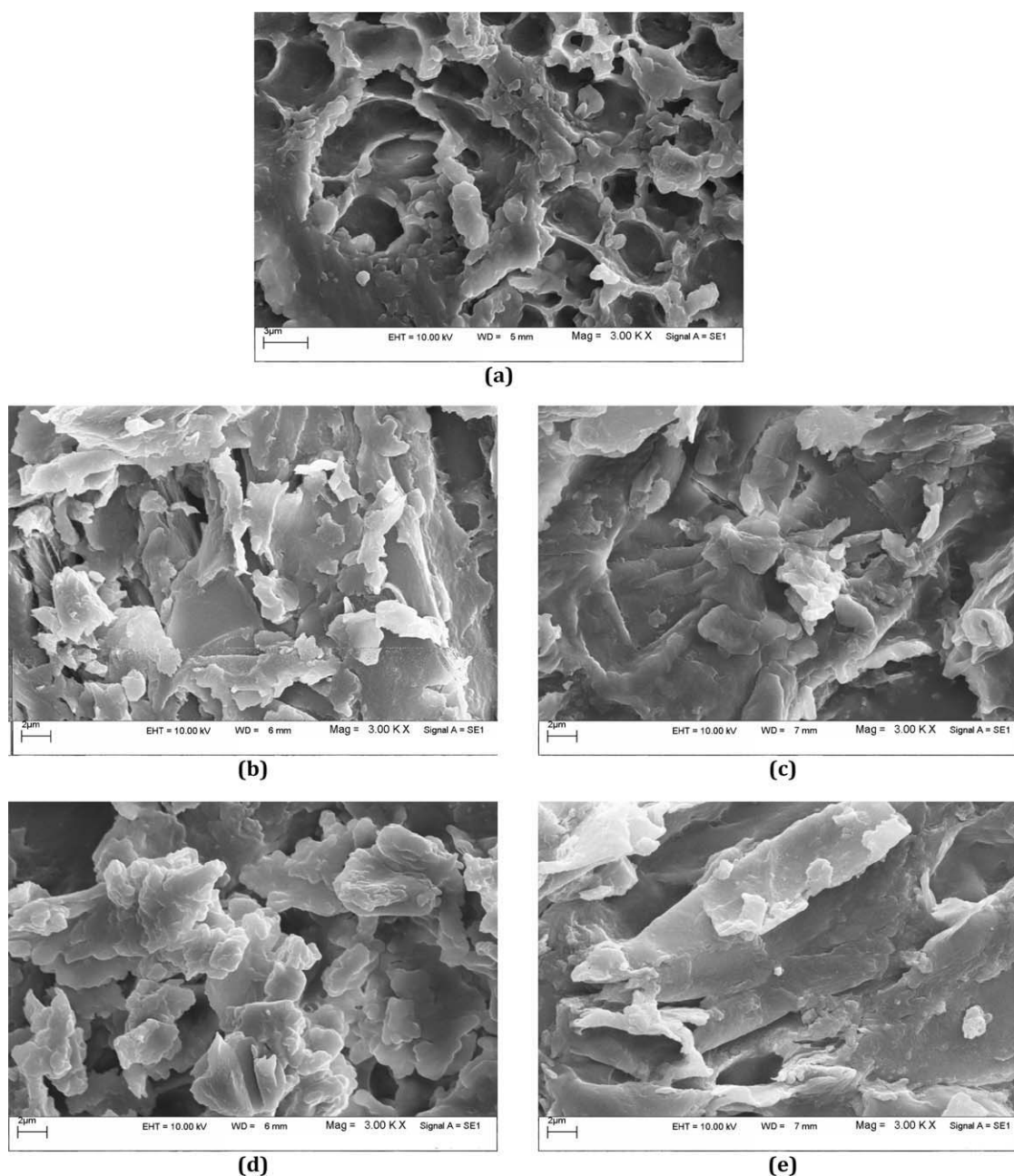


Figure 8 SEM images of raw and dye-adsorbed canola hulls after 60 min dye adsorption process. (a) Raw canola hull, (b) RR198, (c) RB19, (d) DR79, and (e) DR80.

The values I provide information about the thickness of the boundary layer because the resistance to the external mass transfer increases as the intercept increases. Correlation coefficient (R^2) values given in Table IV ranged between 0.2875 and 0.5197, confirming that the rate-limiting step is not actually the intraparticle diffusion. The nonlinearity of the plots demonstrated that intraparticle diffusion did not play a significant role in the uptake of the dye by sorbent. It has been reported that if the intraparticle diffusion is the sole rate-limiting step,³² it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin, which is not the case in this study. It may be concluded that surface adsorption

and intraparticle diffusion were concurrently operating during the dye–canola hull interactions.

The results showed that the adsorption kinetic of dyes followed the pseudo second-order kinetic. The straight lines with extremely high correlation coefficients for pseudo second-order were obtained. In addition, the calculated q_e values also agree with the experimental q_e [$(q_e)_{Exp.}$] in the case of pseudo second-order kinetic model.

SEM studies

SEM has been a primary tool for characterizing the surface morphology and fundamental physical

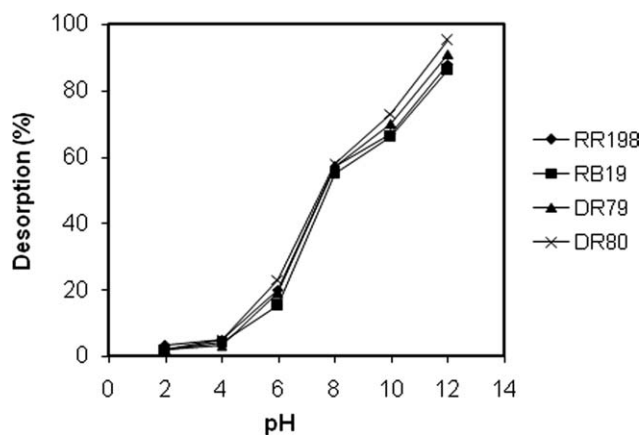


Figure 9 The effect of pH on desorption of dyes from canola hull.

properties of the adsorbent surface. It is useful for determining the particle shape, porosity, and appropriate size distribution of the adsorbent. SEM images of raw canola hull and dye-adsorbed canola hull are shown in Figure 8. From Figure 8, it is clear that canola hull has considerable numbers of pores, where there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM pictures of canola hull samples show very distinguished dark spots, which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent.

Desorption studies

The regeneration of the adsorbent may make the treatment process economical. Desorption studies help to elucidate the recovery of the adsorbate and adsorbent. Desorption tests showed maximum dye releasing of 88% for RR198, 86% for RB19, 91% for DR79, and 95% for DR80 at pH 12 (Fig. 9). As the pH of the system increases, the number of positively charged sites decreases, which favors desorption of dyes.

CONCLUSION

The results showed that canola hull has a suitable adsorption capacity toward Reactive Red 198 (RR198), Reactive Blue 19 (RB19), Direct Red 79 (DR79), and Direct Red 80 (DR80) as model anionic textile dyes. The FTIR spectrum proved the presence of functional groups such as hydroxyl and amino groups in canola hull surface. Isotherm and kinetic of dye adsorption onto canola hull at different pH values followed Tempkin isotherm and pseudo second-order kinetic model, respectively. The SEM images of canola hull samples show effective adsorption of dye molecules in the cavities and pores of this adsorbent. Results indicate that canola

hull could be used as a novel natural material for the removal of anionic textile dyes from wastewater.

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