Removal of Reactive Dye from Aqueous Solution by Activated Carbon

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(Received: 15 September 2011;

Accepted: 9 July 2012)

AJC-11823

This study investigates the potential use of activated carbon prepared from orange peel for the removal of remazol brilliant blue R (RBBR) dye from aqueous solution. The effects of different system variables, solution pH (from 4 to 10), solution temperature (from 25 to 55 °C), adsorbent dose (from 0.1 to 1 g) and contact time (from 15 to 75 min) were studied. The maximum dye removal was reached at 75 min. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. Sorption isotherms were analyzed by Langmuir, Freundlich, Redlich-Peterson, Tempkin and Dubinin-Radushkevich models at different temperatures of 25, 35, 45 and 55 °C. The maximum adsorption capacity obtained from Langmuir equation was 26.15 mg g⁻¹. Furthermore, adsorption kinetics of remazol brilliant blue R were studied and the rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation ($R^2 > 0.85$) with intraparticle diffusion as one of the rate determining steps. The results of this study showed that activated carbon developed from orange peel could be employed as effective and low-cost materials for the removal of dyes from aqueous solution.

Key Words: Remazol brilliant blue R, Orange peel, activated carbon, adsorption, sorption isotherm.

INTRODUCTION

Dyes are one of the most important hazardous species found in industrial effluents which needs to be treated, because its presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora^{1,2}, besides of being aesthetically objectionable for drinking and other purposes. Also, dyes can cause allergy, dermatitis, skin irritation and also provoke cancer and mutation in humans³.

Dyes are a kind of organic compound with a complex aromatic molecular structure that can bring bright and firm colour to other materials. However, the complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade⁴. The most efficient method for the removal of synthetic dyes from aqueous effluents is the adsorption procedure⁵. This process transfers the dye species from the water effluent to a solid phase thereby keeping the effluent volume to a minimum. Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment^{6,7}.

Activated carbon is the most employed adsorbent for toxic species removal from aqueous effluents because of well-developed pore structures and a high internal surface area that leads to its excellent adsorption properties. Besides these physical characteristics, the adsorption capacity is also dependent on the source of organic material employed for the production

of the activated carbon^{8,9}, as well as the experimental conditions employed in the activation processes¹⁰. Activated carbon can be prepared using a variety of chemical⁹ and physical¹¹ activation methods and in some cases using a combination of both types of methods¹².

The use of cheap and ecofriendly adsorbents have been studied as an alternative substitution of activated carbon for the removal dyes from wastewater. Orange peel principally consists of cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene and so on¹³. Orange peel was previously investigated to adsorb methyl orange, methylene blue¹⁴, direct red²³, direct red 80¹⁵, direct yellow 12¹⁶, direct N blue 106¹⁷, direct blue 86¹⁸ and malachite green¹⁹. The use of orange peel as adsorbent for the removal of remazol brilliant blue R (RBBR) from aqueous solution has not found in the literature, so far. In recent years, a considerable number of studies have focused on low cost alternative materials for the production of activated carbons from agricultural wastes such as, peach stone¹⁰, cherry stones²⁰, coconut shell^{21,22}, vine shoots²³, cassava pell, walnut shell, corn cob, pecan shell²⁴, peanut shell²⁵, banana peel²⁶ and rice husk²⁷.

In this study, orange peel was utilized as alternative adsorbent for the removal of remazol brilliant blue R from aqueous solution by sorption technique. Moreover, effects of

pH, temperature and sorbent dosage on sorption were investigated. On the other hand, the sorption isotherms were studied in detail.

EXPERIMENTAL

Preparation of orange peel: Orange peel was collected from a local fruit field in the south of Turkey. Orange peel was firstly washed and subsequently dried at 105 °C for 24 h to remove the moisture content. The dried orange peel were ground and sieved to the size of 0.5-1 mm. Carbonization step of the dried orange peel was carried out at 600 °C for 3 h. The activated carbon was stored in plastic containers for further use.

Preparation of the dye solution: Remazol brilliant blue R, a reactive dye was purchased from dye company (Istanbul, Turkey) and was used as received without further purification. A stock solution of 0.012 g L⁻¹ was prepared by dissolving the appropriate amount of remazol brilliant blue R in 1000 mL. Remazol brilliant blue R has a chemical formula of C₂₂H₁₆N₂O₁₁Na₂S₃ (Fig. 1) with molecular weight of 626.54 g/mol. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH.

Fig. 1. Chemical structure of remazol brilliant blue R

Sorption studies were conducted in 100 mL conical flasks at solution pH 6. Orange peel (1 g L⁻¹) was thoroughly mixed individually with 20 mL of remazol brilliant blue R solution (12 mg L⁻¹) and the suspensions were shaken at different temperatures (25, 35, 45 and 55 °C). Samples of 5 mL were collected from the duplicate flasks at required time intervals *viz.* 15, 30, 45, 60 and 75 min and were centrifuged for 5 min. The clear solutions were analyzed for residual remazol brilliant blue R concentration in the solution.

Adsorption isotherm: Batch sorption experiments were done by shaking with 20 mL aqueous solution of remazol brilliant blue R of known concentration in 100 mL-Erlenmeyer flasks placed in a temperature controlled shaking water bath at different pHs (between 4 and 10), temperatures (between 25 and 55 °C) and sorbent doses (between 0.1 and 1.0 g) at a constant shaking rate of 200 rpm. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and centrifuged for 5 min at 5000 rpm. After centrifuged, supernatants were analyzed for the determination of the final concentration of remazol brilliant blue R by using an UV-VIS spectrophotometer (Shimadzu UV-1601) set at a wavelength of 595 nm, maximum absorbance. All the

experiments are duplicated and only the mean values are reported.

Adsorption of remazol brilliant blue R from aqueous solution was studied using 1 g L⁻¹ of orange peel and remazol brilliant blue R concentration 12 mg L⁻¹ at pH 6.0. The amount of dye adsorbed at equilibrium onto carbon, $q_{e(exp)}$, was calculated by the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where, q_e is the amount of dye adsorbed (mg/g). C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/L), respectively. V is the volume of the solution (l) and W is the weight of the sorbent used (g).

RESULTS AND DISCUSSION

Effect of pH on dye removal: The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Fig. 2 shows the variations in the removal of dye from wastewater at various system pH. From the figure, it is evident that the maximum removal of remazol brilliant blue R colour is observed at pH 6. Similar trend of pH effect was observed for the adsorption of direct red 28 and acid violet on activated carbon prepared from coir pith^{28,29}, as well as for the adsorption of direct blue 2B and direct green B on activated carbon prepared from Mahogany sawdust³⁰. That may be attributed to the hydrophobic nature of the developed carbon, which led to absorb hydrogen ions (H⁺) onto the surface of the carbon when immersed in water and make it positively charged. As the orange peel surface is positively charged at low pH value, a significantly strong electrostatic attraction appears between the positively charged carbon surface and dye molecule leading to maximum adsorption of remazol brilliant blue R. On the other hand, increase of the pH value (basic condition) led to increase of the number of negatively charged sites and the number of positively charged sites decreases.

Fig. 2. Effect of solution pH on adsorption of remazol brilliant blue R (12 mg L⁻¹) onto orange peel (1 g L⁻¹) at 25 °C, agitation speed 200 rpm for the minimum contact time required to reach the equilibrium (75 min)

Effect of temperature on dye removal: The effect of temperature on dye removal by sorbent was studied in temperature range of 25 and 55 °C for remazol brilliant blue R concentration of 20 mg/L at pH 6 and obtained results are shown in Fig. 3. As can be seen from the figure, the adsorption capacity decreases with the increasing temperature. It is also possible that a very high temperature could favour the desorption process, in case of exothermic adsorption. Taking these factors into account and in agreement with the observed results, a temperature of 35 °C was used in subsequent adsorption procedures.

Fig. 3. Effect of temperature on adsorption of remazol brilliant blue R (12 mg L⁻¹) onto orange peel (1 g L⁻¹) at different temperatures (from 25 to 55 °C), agitation speed 200 rpm for the minimum contact time required to reach the equilibrium (75 min)

Effect of contact time on dye removal: The relation between removal of remazol brilliant blue R and reaction time were studied to observe the rate of dye removal. The results of percentage removal of remazol brilliant blue R at pH 6 with increasing of contact time using orange peel are presented in Fig. 4. The maximum dye removal by orange peel was determined to occur nearly at 75 min under all conditions. After this time, no change in the removal of dye observed. Therefore, this time was assumed as an equilibrium time which indicates a saturation time. The maximum amounts of removal of dye at equilibrium time are termed as an equilibrium sorption capacity.

Effect of adsorbent mass on remazol brilliant blue R adsorption: The adsorption of remazol brilliant blue R on orange peel was studied by changing the quantity of adsorbent (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 g/50 mL) in the test solution while keeping the constant remazol brilliant blue R concentration (12 mg L⁻¹) at different temperatures (from 25 to 55 °C) and pH (6.0) constant at contact times for 75 min (Fig. 5). The adsorption increased from 75 to 97 %, as the orange peel dose increased from 0.1 to 1.0 g/20 mL at equilibrium time (75 min) at 35 °C. Maximum remazol brilliant

blue R removal was achieved within 75 min after, which remazol brilliant blue R concentration in the reaction solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to increased orange peel surface area and availability of more adsorption sites, while the unit adsorbed of remazol brilliant blue R decreased with increase in orange peel dose.

Fig. 4. Effect of contact time on the removal of remazol brilliant blue R (12 mg L⁻¹) using orange peel (1 g L⁻¹) at pH 6.0. ○: 25 °C, ◇: 35 °C, ●: 45 °C, ◆: 55 °C

Fig. 5. Effect of adsorbent concentration on remazol brilliant blue R removals (remazol brilliant blue R concentration: 112 mg L⁻¹, pH 6.0, agitation speed: 200 rpm, temperatures: 25-55 °C). Key as in Fig. 4

Isotherm data analysis: The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the

adsorption isotherm. The adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental sorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the sorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich (D-R) isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir isotherm: The theoretical Langmuir isotherm³¹ is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface³². Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The Langmuir nonlinear equation is commonly expressed as followed:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

In eqn. (2), C_e and q_e are as defined before in eqn. (1), Q_m is a constant reflect a complete monolayer (mg g^{-1}); K_a is adsorption equilibrium constant (l mg^{-1}) that is related to the apparent energy of sorption. The Langmuir isotherm eqn. (2) can be linearized into the following form³³.

Langmuir-1

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \quad (3)$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$.

The results obtained from the Langmuir model for the removal of remazol brilliant blue R onto orange peel are shown in Table-1. The correlation coefficients reported in Table-1 showed strong positive evidence on the adsorption of remazol brilliant blue R onto orange peel follows the Langmuir isotherm. The applicability of the four linear forms of Langmuir model to orange peel was proved by the high correlation coefficients $R^2 > 0.99$. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Q_m obtained from the Langmuir is 26.1511 mg g^{-1} at 25 °C. The orange peel was previously used to remove different dyes from aqueous solution¹⁴⁻¹⁹ and the maximum capacity of dyes removal was reported in Table-2.

Freundlich isotherm: The Freundlich isotherm model³⁴ is the earliest known equation describing the adsorption process. The empirical equation can be used for non-ideal sorption that involves heterogeneous sorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in

TABLE-1
COMPARISON OF THE COEFFICIENTS ISOTHERM
PARAMETERS FOR REMAZOL BRILLIANT BLUE R
ADSORPTION ONTO ORANGE PEEL

Isotherm model	Temperatures (°C)			
	25	35	45	55
Langmuir				
Q_m (mg g^{-1})	26.1511	6.1253	13.4636	17.2033
K_a (l mg^{-1})	0.1767	2.0787	0.4876	0.2210
R^2	0.9868	0.9998	0.9967	0.9843
Freundlich				
$1/n$	0.898	0.6189	0.5119	0.6636
K_F (mg l^{-1})	3.8291	4.5961	4.4708	3.2627
R^2	0.9996	0.9890	0.9966	0.9998
Redlich-Peterson				
A (l g^{-1})	0.2013	12.6311	17.1350	37.2856
B (l g^{-1}) ^g	0.0577	2.0611	2.8405	10.4493
g	0.5796	0.9866	0.6058	0.3606
R^2	0.9913	0.9999	1.000	1.000
Tempkin				
α (l g^{-1})	6.8095	20.0941	3.9091	2.1512
β (mg l^{-1})	2.2916	1.3639	3.2399	3.7113
b	1081.6980	1878.4069	816.4138	735.1168
R^2	0.9592	0.9944	0.9954	0.9917
Dubinin-Radushkevich				
Q_m (mg g^{-1})	1.7892	4.4013	9.2051	8.6882
K	0.0993	0.0386	0.2176	0.3317
E (kJ mol^{-1})	2.2439	3.5991	1.5159	1.2278
R^2	0.9536	0.9948	0.9409	0.9446

TABLE-2
REPORTED MAXIMUM DYES ADSORPTION
OBTAINED FOR ORANGE PEEL

Dye name	Maximum adsorption (mg g^{-1})	Reference
Methyl orange	20.5	[14]
Methylene blue	18.6	[14]
Direct red 23	10.72	[15]
Direct red 80	21.05	[15]
Direct yellow 12	75.76	[16]
Direct N blue 106	107.53	[17]
Direct blue 86	33.78	[18]
Malachite green	483.63	[19]

the enthalpy of sorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

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

where, K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is indicating the adsorption intensity of dye onto the sorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption. (eqn. 4) can be linearized in the logarithmic form (eqn. 5) and the Freundlich constants can be determined:

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

The applicability of the Freundlich sorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of the remazol

brilliant blue R onto orange peel is presented in Table-1. The correlation coefficients (> 0.98) showed that the Freundlich model is comparable to the Langmuir model. The $1/n$ is lower than 1.0, indicating that remazol brilliant blue R is favourably adsorbed by orange peel.

Redlich-Peterson isotherm: The Redlich-Peterson isotherm³⁵ contains three constants, A, B and g and involves the features of both the Langmuir and the Freundlich isotherm models. It can be described by the following non-linear equation (6):

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (6)$$

where, g must fluctuated between 0 and 1 and it can characterize the isotherm as if $g=1$, the Langmuir will be the preferable isotherm, while if $g=0$, the Freundlich will be the preferable isotherm.

Tempkin isotherm: Tempkin adsorption isotherm model was used to evaluate the adsorption potentials of the orange peel for remazol brilliant blue R. The derivation of the Tempkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has commonly been applied in the following form³⁶:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (7)$$

The Tempkin isotherm eqn. (7) can be simplified to the following equation:

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad (8)$$

where $\beta = (RT)/b$, T is the absolute temperature in Kelvin and R is the universal gas constant, $8.314 \text{ J (mol K)}^{-1}$. The constant b is related to the heat of adsorption³⁷. The adsorption data were analyzed according to the linear form of the Tempkin isotherm eqn. 8. Examination of the data shows that the Tempkin isotherm fitted well the remazol brilliant blue R adsorption data for orange peel. The linear isotherm constants and coefficients of determination are presented in Table-1. The heat of adsorption of remazol brilliant blue R onto orange peel was found to decrease from 1.081 to $0.735 \text{ kJ mol}^{-1}$ with increasing temperature from 25 to 55°C . The correlation coefficients R^2 obtained from Tempkin model were comparable to that obtained for Langmuir and Freundlich equations, which explain the applicability of Tempkin model to the adsorption of remazol brilliant blue R onto orange peel.

Dubinin-Radushkevich (D-R) isotherm: The D-R model was also applied to estimate the porosity apparent free energy and the characteristics of adsorption^{38,39}. The D-R isotherm does not assume a homogeneous surface or constant sorption potential. The D-R model has commonly been applied in the following eqn. 9 and its linear form can be shown in eqn. 10:

$$q_e = Q_m \exp(-K \epsilon^2) \quad (9)$$

$$\ln q_e = \ln Q_m - K \epsilon^2 \quad (10)$$

where K is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ϵ the Polanyi potential, calculated from eqn. (11).

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (11)$$

The slope of the plot of $\ln q_e$ versus ϵ^2 gives K [$\text{mol}^2 (\text{kJ}^2)^{-1}$] and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation⁴⁰:

$$E = \frac{1}{\sqrt{2K}} \quad (12)$$

The calculated value of D-R parameters is given in Table-1. The saturation adsorption capacity Q_m obtained using D-R isotherm model for adsorption of remazol brilliant blue R onto orange peel is 4.4013 mg g^{-1} for 1.0 g L^{-1} sorbent dose at 35°C , which is close to that obtained (6.1253 mg g^{-1}) from Langmuir isotherm model (Table-1).

Kinetic models applied to the adsorption of remazol brilliant blue R onto orange peel: Several steps can be used to examine the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of remazol brilliant blue R onto orange peel. The kinetics of remazol brilliant blue R adsorption onto orange peel is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of remazol brilliant blue R adsorption onto orange peel were analyzed using pseudo-first order⁴¹, pseudo-second-order⁴², Elovich⁴³ and intraparticle diffusion⁴⁴ kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of remazol brilliant blue R adsorption onto orange peel.

Pseudo-first-order equation: The adsorption kinetic data were described by the Lagergren pseudo-first-order model⁴¹, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expresses as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (13)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). Integrating eqn. (13) for the boundary conditions $t = 0 \rightarrow t$ and $q_t = 0 \rightarrow q_t$ gives.

$$\ln \left(\frac{q_e}{q_e - q_t} \right) = k_1 t \quad (14)$$

Equation (14) can be rearranged to obtain the following linear form:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (15)$$

In order to obtain the rate constants, the values of $\ln(q_e - q_t)$ were linearly correlated with t by plot of $\ln(q_e - q_t)$ versus t to give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively (Fig. 6). The variation in rate should be propor-

TABLE-3
COMPARISON OF THE FIRST- AND SECOND-ORDER ADSORPTION RATE CONSTANTS AND CALCULATED AND EXPERIMENTAL q_e VALUES AT DIFFERENT TEMPERATURES; k_1 (min^{-1}), k_2 ($\text{g} (\text{mg min})^{-1}$), q_e (mg g^{-1}), h ($\text{mg} (\text{g min})^{-1}$)

Parameter	First-order kinetic model				Second-order kinetic model		
Temp. ($^{\circ}\text{C}$)	q_e (exp.)	k_1	R^2	k_2	q_e (calcd.)	h	R^2
25	13.0354	0.0354	0.7841	0.0023	15.7423	0.5699	0.8095
35	5.5794	0.0230	0.9012	9.0370×10^{-3}	12.8760	1.4983	0.9862
45	11.9453	0.0128	0.7312	1.9631×10^{-4}	22.8696	0.1027	0.0078
55	10.7213	0.0119	0.6685	5.3765×10^{-4}	14.0172	0.1056	0.0550

tional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Fig. 5 shows that the pseudo-first-order equation fits well for the first 30 min and thereafter the data deviate from theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots and the correlation coefficient R^2 are relatively low for most adsorption data (Table-3). This shows that the adsorption of remazol brilliant blue R onto orange peel cannot be applied and the reaction mechanism is not a first-order reaction.

Fig. 6. Pseudo-first-order kinetics for remazol brilliant blue R adsorption onto orange peel. Conditions: adsorbent dose 1 g L^{-1} , pH 6.0, remazol brilliant blue R concentration: 12 mg L^{-1} at different temperatures (from 25 to 55°C). Key as in Fig. 4

Pseudo-second-order equation: The adsorption kinetic may be described by the pseudo-second-order model⁴². The differential equation is generally given as follows.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (16)$$

where, k_2 [$\text{g}(\text{mg min})^{-1}$] is the second-order rate constant of adsorption. Integrating eqn. (16) for the boundary conditions $q_t = 0 - q_t$ at $t = 0 - t$ is simplified as can be rearranged and linearized to obtain:

$$\left(\frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (17)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = k_2 q_e^2 \quad (18)$$

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t (Fig. 7). The linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at different initial remazol brilliant blue R and adsorbent concentrations (Table-3). The correlation coefficient for the second-order kinetic model is 0.9862, which led to believe that the pseudo-second-order kinetic model provided good correlation for the sorption of remazol brilliant blue R onto orange peel.

Fig. 7. Plot of the pseudo-second-order model at different temperatures (from 25 to 55°C), OP 1 g L^{-1} , pH 6.0, RBBR (12 mg L^{-1}). Key as in Fig. 4

The values of initial sorption (h) that represents the rate of initial sorption, is practically increased from 0.5699 to $1.4983 \text{ mg} (\text{g min})^{-1}$ with an increase in temperature from 25 to 35°C onto 1.0 g L^{-1} orange peel dose (Table-3). It was observed that the pseudo-second-order rate constant (k_2) increased from 0.0023 to 9.0370×10^{-3} with an increase in temperature from 25 to 35°C for 1 g L^{-1} orange peel dose.

TABLE-4
PARAMETERS OBTAINED FROM ELOVICH KINETICS MODEL AND INTRAPARTICLE DIFFUSION MODEL DIFFERENT TEMPERATURES. A_E (g mg^{-1}), B_E (mg(g min)^{-1}), K_{dif} ($\text{mg g}^{-1}\text{min}^{-1/2}$) AND C (mg g^{-1})

Temperature ($^{\circ}\text{C}$)	Elovich			Intraparticle diffusion		
	A_E	B_E	R^2	K_{dif}	C	R^2
25	0.3032	1.3341	0.6871	1.1538	1.6139	0.7957
35	0.5427	13.3351	0.8286	0.6267	6.3322	0.8582
45	0.3628	0.2878	0.5068	0.9854	-2.5221	0.6403
55	0.4354	0.2692	0.4854	0.8250	-1.8614	0.7907

Elovich equation: The Elovich equation is another rate equation based on the adsorption capacity generally expressed as following⁴³:

$$\frac{dq_t}{dt} = B_E \exp(-A_E q_t) \quad (19)$$

where, B_E is the initial adsorption rate [mg(g min)^{-1}] and A_E is the de-sorption constant (g mg^{-1}) during any experiment.

It is simplified by assuming $A_E B_E t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ eqn. 19, becomes:

$$q_t = \frac{1}{A_E} \ln(B_E A_E) + \frac{1}{A_E} \ln(t) \quad (20)$$

If remazol brilliant blue R adsorption by orange peel fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/A_E)$ and an intercept of $(1/A_E) \ln(B_E A_E)$ (Fig. 8). Thus, the constants can be obtained from the slope and the intercept of the straight line (Table-4). The initial adsorption rate B_E increase from 1.3341 to 13.3351 with increasing temperature from 25 to 35 $^{\circ}\text{C}$. Similar pattern is mentioned above for the initial adsorption rate, h , obtained from pseudo-second-order model. The desorption constant, A_E change from 0.3032 to 0.4354 in the range of temperature between 25 and 55 $^{\circ}\text{C}$ for 12 mg L^{-1} of remazol brilliant blue R concentration at pH 6.0 and the obtained results are shown in Table-4.

Fig. 8. Elovich model plot for the adsorption of remazol brilliant blue R (12 mg L^{-1}) onto orange peel (1 g L^{-1}) at different temperatures (from 25 to 55 $^{\circ}\text{C}$). Key as in Fig. 4

Intraparticle diffusion model: The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor⁴⁴. Since the remazol brilliant blue R are probably transported from its aqueous solution to the orange peel by intraparticle diffusion, so the intraparticle diffusion is another kinetic model should be used to study the rate of remazol brilliant blue R adsorption onto orange peel. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model, which is commonly expressed by the following equation:

$$q_t = K_{\text{dif}} t^{1/2} + C \quad (21)$$

where C (mg g^{-1}) is the intercept and K_{dif} is the intraparticle diffusion rate constant (in $\text{mg g}^{-1}\text{min}^{-1/2}$). The values of q_t were found to be linearly correlated with values of $t^{1/2}$ (Fig. 9) and the rate constant K_{dif} directly evaluated from the slope of the regression line (Table-4). The values of intercept C (Table-4) provide information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase. The constant C was found to increase from 1.6139 to 6.3322 with increasing temperature from 25 to 35 $^{\circ}\text{C}$, which indicating the increase of the thickness of the boundary layer and decrease of the chance of the external mass transfer and hence increase of the chance of internal mass transfer. On the other hand, the constant C was found to decrease with the increasing temperature from 35 to 55 $^{\circ}\text{C}$, which reflect decrease of the thickness of the boundary layer and hence increase of the chance of the external mass transfer. The R^2 values given in Table-4 are close to unity indicating the application of this model. This may confirm that the rate-limiting step is the intraparticle diffusion process. The intraparticle diffusion rate constant, K_{dif} , were in the range of $1.1538\text{--}0.6267 \text{ mg g}^{-1}\text{min}^{-1/2}$ and it decrease with increase of temperature. The linearity of the plots demonstrated that intraparticle diffusion played a significant role in the uptake of the adsorbate by sorbent.

Conclusion

The results of this investigation show that activated carbon developed from orange peel has a suitable adsorption capacity for the removal of remazol brilliant blue R from aqueous solutions. The equilibrium adsorption is practically achieved in 75 min. The experimental results were analyzed by using Langmuir, Freundlich, Redlich-Peterson, Tempkin and Dubinin-Radushkevich isotherm models. The kinetic study of remazol brilliant blue R on orange peel was performed based on pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion equations. The data indicate that the

Fig. 9. Intraparticle diffusion model plot for the adsorption of remazol brilliant blue R onto orange peel (1 g L^{-1}) at different temperatures (from 25 to 55 °C). Key as in Fig. 4

adsorption kinetics follow the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps. The present study concludes that the orange peel could be employed as low-cost adsorbents as alternative to commercial activated carbon for the removal of colour and dyes from water and wastewater, in general and for the removal of remazol brilliant blue R in particular.

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