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ADSORPTION OF REMAZOL BRILLIANT BLUE ON AN ORANGE PEEL ADSORBENT

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Abstract - A novel orange peel adsorbent developed from an agricultural waste material was characterised and utilised for the removal of Remazol Brilliant Blue from an artificial textile-dye effluent. The adsorption thermodynamics of this dye-adsorbent pair was studied in a series of equilibrium experiments. The time to reach equilibrium was 15 h for the concentration range of 30 mg L^{-1} to 250 mg L^{-1}. The adsorption capacity decreased with increasing temperature, from 9.7 mg L^{-1} at 20 °C to 5.0 mg L^{-1} at 60 °C. Both the Langmuir and Freundlich isotherm models fitted the adsorption data quite reasonably. The thermodynamic analysis of dye adsorption onto the orange peel adsorbent indicated its endothermic and spontaneous nature. Thus, the application of orange peel adsorbent for the removal of dye from a synthetic textile effluent was successfully demonstrated.
Keywords: Orange peel; Adsorption; Dye; Kinetics; Thermodynamics; Wastewater.

INTRODUCTION

Wastewaters from the food colouring, paper, carpet, rubber, plastics, cosmetics and textile industries are polluted by dyes (Namasivayam *et al*., 1996; Crini, 2006; Azhar *et al*., 2005). The presence of very low concentrations of dyes in these effluents (less than 1 ppm for some dyes) is highly visible and undesirable (Crini, 2006; Nigan *et al*., 2000). Colour affects the nature of the water and inhibits the penetration of sunlight into the receiving water bodies, which has a deleterious effect on photosynthesis and thus aquatic life (Arami *et al*., 2005; Gómez *et al*., 2007). Some dyes are also carcinogenic and mutagenic (Namasivayam and Kavitha, 2002).

There are many chemical varieties of dyes, e.g., acidic, basic and dispersed, with structures such as azo-, diazo- and anthraquinone-based and metal-complex dyes. The highest rates of toxicity have been found amongst the basic and diazo direct dyes (Robinson *et al*., 2001).

The removal of dyestuffs from effluents is of great importance in many countries worldwide for both environmental and water reuse concerns (Choy *et al*., 1999). Due to the low biodegradability of dyes, conventional biological treatment processes are not very effective in treating dye wastewaters; therefore, they are usually treated by either physical or chemical processes (Azhar *et al*., 2005).

Activated carbon is the most widely used physicochemical treatment for the removal of dissolved organics from wastewater, effective even in dilute solution, but commercially available activated carbon is very expensive (Azhar *et al*., 2005; Namasivayam and Kavitha, 2002; Robinson *et al*., 2001). In order to decrease the treatment cost of dye removal, attempts have been made to find inexpensive and biodegradable alternative adsorbents

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(Namasivayam *et al*., 1996; Azhar *et al*., 2005; Namasivayam and Kavitha, 2002; Basava Rao and Ram Mohan Rao, 2006). In general, a sorbent can be assumed to be inexpensive if it requires little processing, is abundant in nature or is a by-product or waste material from another industry (Bailey *et al*., 1999).

Orange peel is an agro/industrial waste residue of the orange-juice and soft-drink industries all over the world (Namasivayam *et al*., 1996) and has been used to remove a number of dyes such as Direct Blue 86 (El Nemr *et al*., 2009), Direct N Blue-106 (Khaled *et al*., 2009[a]), Direct Yellow 12 (Khaled *et al*., 2009[b]), Direct Red 23 and Direct Red 80 (Arami *et al*., 2005), Acid Violet 17 (Sivaraj *et al*.; 2001) and methyl orange, methylene blue, Rhodamine B, Congo red, methyl violet and amido black 10B (Annadurai *et al*., 2002).

Oranges are cultivated on a large scale in Brazil where they are of significant agronomic importance as the fruits are used both fresh and in the juice industry. Brazil is the largest orange-juice producer in the world so there is a need to find a use for the by-products of this industrial activity. In this work, orange peel was used as a low-cost adsorbent to remove the azo dye Remazol Brilliant Blue from aqueous solution. Kinetic and thermodynamic studies, the basic requirements for the design of adsorption systems, were conducted to evaluate its adsorption capacity.

MATERIALS AND METHODS

Chemicals and Materials

In order to obtain the orange peel adsorbent (OPA), fresh orange peel (orange exocarp and mesocarp), from Pêra sweet orange (*Citrus sinensis* (L.) Osbeck), was washed and cut into small pieces, dried in an oven at 60 °C for 24 h and crushed. The powdered orange peel was washed with hot water and dried in an oven at 60 °C for 12 h. After drying they were sieved and used as an adsorbent. The dye Remazol Brilliant Blue R, an anthraquinone dye, was obtained from Acros Organics. The chemical structure of this dye is shown in Fig. 1.

Characterisation of the Adsorbent

The surface of the orange peel adsorbent was imaged by a scanning electron microscope (SEM, Shimadzu SS 550). The chemical composition of the adsorbent was analysed by X-ray fluorescence (XRF) using a Philips Analytical fluorescence system (PW 2400/00). The X-ray diffraction (XRD) pattern of the material was recorded in the range 2θ=3 at 70°, in a Philips Analytical diffractometer (PW-1830) with a Cu anode. The diffractometer was operated at 40 mA and 40 KW and the spectrum was recorded at a scanning speed of 2°/min. FTIR (Fourier Transform Infrared Spectroscopy) of the adsorbent was performed in an Excalibur Bio-Rad interferometer FTS 3500 GX model over the range of 4,000 - 400 cm^{-1} (32 scans). The adsorbent was dried under vacuum and 2 mg of adsorbent was powdered and mixed with 300 mg of anhydrous KBr. The mixture was subjected to an 8-ton hydraulic press to obtain the pellets.

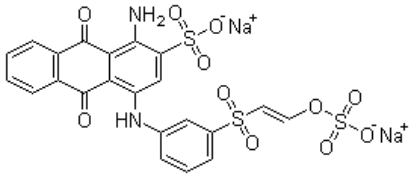

Figure 1: Chemical structure of Remazol Brilliant Blue R.

Adsorption Procedure

Batch adsorption experiments were carried out in a temperature-controlled orbital shaker (Tecnal TE-421) at a constant speed of 150 rpm. For all tests, 30 mL of dye solution were placed into a 125 mL conical flask with 300 mg of orange peel adsorbent. The equilibrium time of adsorption was determined by analysing adsorptive uptake of the dye solution (30 mg L^{-1}, 100 mg L^{-1} and 250 mg L^{-1}) at different time intervals and temperatures of 20 ± 0.2 °C and 60 ± 0.2 °C. To obtain the adsorption isotherms, dye solutions of different mass concentrations (20 mg L^{-1} to 350 mg L^{-1}) were agitated with the adsorbent until equilibrium was achieved (24 h) at temperatures of 20 °C, 30 °C, 40 °C, 50 °C and 60 °C. After the experiments, the samples were filtered through quantitative filter papers (J. Prolab® white ribbon filter) and the equilibrium solution dye concentration was determined using an Ultraviolet-Visible (UV-VIS) spectrophotometer at 590 nm. The amount of dye adsorbed onto the orange peel adsorbent at time t, q_t (mg g^{-1}), and at equilibrium, q_e (mg g^{-1}), were obtained by mass balance, according to Equations (1) and (2). All experiments were performed in triplicate.

$$q_t = \frac{V \cdot (C_o - C_t)}{W} \quad (1)$$

$$q_e = \frac{V \cdot (C_o - C_e)}{W} \quad (2)$$

where V (L) is the solution volume, C_o is the initial concentration of dye in mg L^{-1}, C_t (mg L^{-1}) is the liquid-phase concentration of dye at time t (min), C_e (mg L^{-1}) is the equilibrium concentration of dye and W (g) is the weight of the adsorbent.

RESULTS AND DISCUSSION

Characterisation of the Adsorbent

The particle-size distribution of the adsorbent was determined as fractions in the ranges of > 1,180 µm (0.70%), 1,180-355 µm (80.46%), 355-180 µm (13.92%), 90-63 µm (0.47%) and <44 µm (0.48%).

The SEM images (Fig. 2) showed the highly heterogeneous porous structure of the orange peel particles. Arami *et al*. (2005) also observed the same characteristic in orange peel adsorbent.

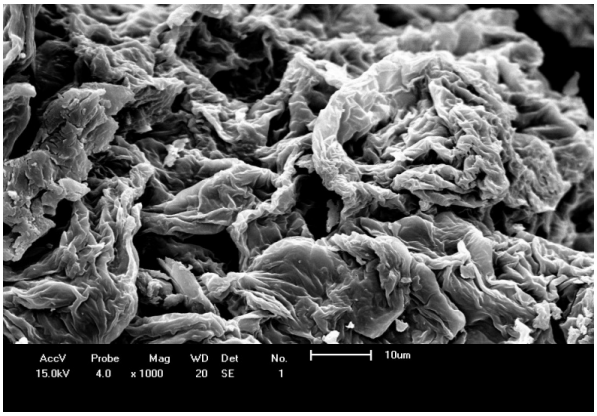

Figure 2: SEM image of orange peel adsorbent.

The chemical composition of the orange peel adsorbent as determined by X-ray fluorescence is shown in Table 1. The organic matter accounted for 97.83% of the chemical composition, which is expected for a vegetable tissue. Calcium content (1.42%) was higher than the other minerals.

The X-ray diffraction spectrum (Figure 3) did not exhibit well-defined peaks in any region, which indicated that no discrete mineral phase was detected. Thus, the orange peel has a completely amorphous structure, which is expected for organic materials. The database used for mineralogical interpretation in this analysis was JCPDS (Joint Committee on Powder Diffraction Standards) from the PHILIPS *X'Pert HighScore* software.

Table 1: Chemical composition of the OPA by X-ray fluorescence analysis.

Characteristic	Values
CaO	1.42%
K_2O	0.18%
SO_3	0.14%
MgO	0.12%
Fe_2O_3	0.11%
SiO_2	0.08%
P_2O_5	0.05%
BaO	0.02%
SrO	0.01%
Al_2O_3	0.01%
NiO	0.01%
WO_3	not detected
ZnO	not detected
Mn	not detected
Organic matter	97.83%

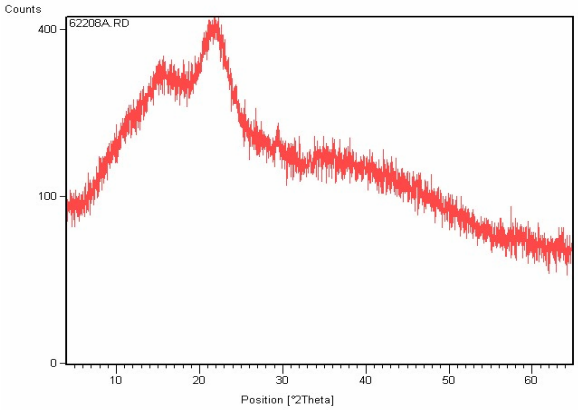

Figure 3: X-ray diffraction spectrum of orange peel adsorbent.

The FTIR spectrum of the orange peel is shown in Figure 4, displaying a number of adsorption peaks indicating the complex nature of the material examined. The broad, intense absorption peaks around 3,434 cm^{-1} are indicative of the absorption of water molecules, resulting from the O-H stretching mode of hydroxyl groups characteristic of adsorbed water, while the bands at 2,924 cm^{-1} and 2,850 cm^{-1} were attributed to C-H interactions with the surface of the adsorbent (Al-Qodah and Shawabkah, 2009). The bands in the range of 3,200-3,650 cm^{-1} have been attributed to the hydrogen-bonded -OH group of alcohols and phenols (Yang and Lua, 2003). The peak around 1,635 cm^{-1} is due to the C=C stretching that can be attributed to the aromatic C-C bond, and

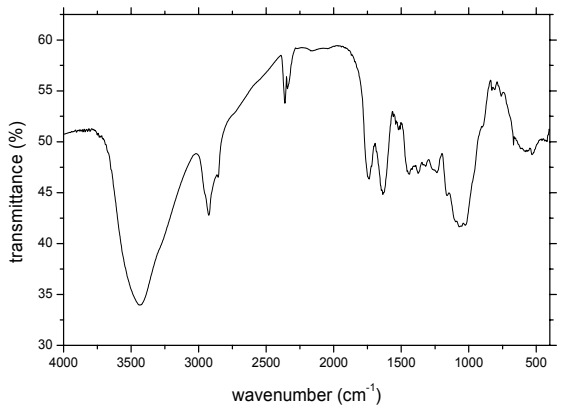

Figure 4: FTIR spectrum of orange peel adsorbent in KBr pellets.

the peak at 1,072 cm^{-1} can also be associated with either C-O symmetric or asymmetric stretching vibration (-C-O-C- ring) (Khaled *et al*., 2009[a]; Khaled *et al*., 2009[b]). The peaks at the region of 2,300-2,400 cm^{-1} indicated the carbon dioxide of normal air (Kalsi, 2004).

Equilibrium Time of Adsorption

The influence of contact time at 20 °C and 60 °C on the amount of dye adsorbed per unit mass of orange peel (q_t) is presented in Figures 5 and 6, respectively, showing the efficient adsorption of dye from wastewater. The uptake of dye by the adsorbent increased with initial dye concentration and decreased with temperature. The removal of dye was rapid in the initial stage of contact and gradually decreased with time until equilibrium was reached (Sivaraj *et al*., 2001). The time profiles of dye uptake were single, smooth and continuous curves leading to saturation, suggesting the possible monolayer coverage of dyes on the surface of the adsorbent (Malik, 2004). The contact time required to attain equilibrium was around 15 h for the three initial concentrations of dye studied.

Figures 5 and 6 show that the amount of dye adsorbed per unit mass of orange peel increased with increasing initial dye concentration. For a dilute concentration (30 mg L^{-1}) the amount of dye adsorbed per unit mass of orange peel was 2.2 mg g^{-1} (20 °C) and 1.7 mg g^{-1} (60 °C). In the case of the concentrated solution (250 mg L^{-1}) an increase to 8.7 mg g^{-1} (20 °C) and 4.7 mg g^{-1} (60 °C) was observed, meaning that the adsorption process was highly dependent on the initial dye concentration (Khaled *et al*., 2009[b]; Rao and Rao, 2006).

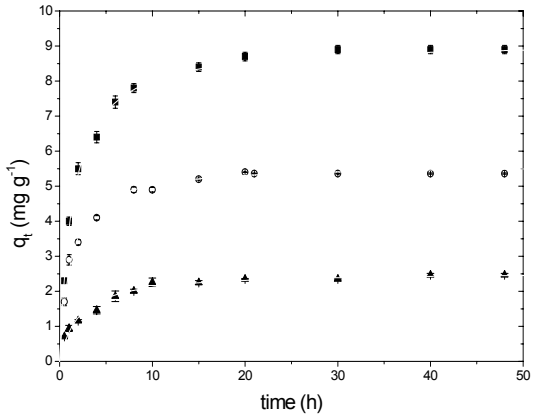

Figure 5: Effect of initial dye concentration and agitation time on adsorption by waste orange peel at 20 °C; (▲) 30 mg L^{-1}, (○) 100 mg L^{-1}, (■) 250 mg L^{-1}

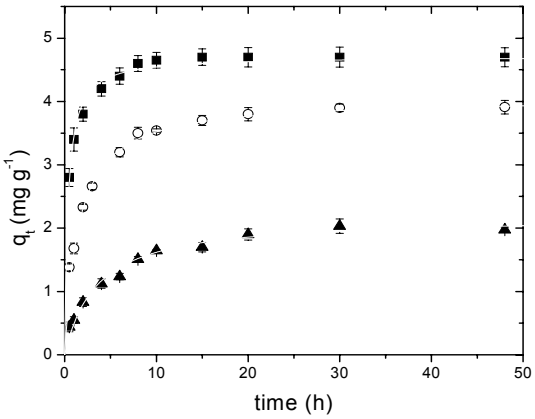

Figure 6: Effect of initial dye concentration and agitation time on adsorption by waste orange peel at 60 °C; (▲) 30 mg L^{-1}, (○) 100 mg L^{-1}, (■) 250 mg L^{-1}

Adsorption Isotherm Studies

The equilibrium measurements were focused on the determination of the adsorption isotherms. Figure 7 shows the relationship between the amounts of adsorbed dye per unit mass of the orange peel adsorbent (q_e) and the equilibrium solution dye concentration (C_e) for the temperature range of 20-60 °C.

It was found that the adsorption capacity decreased as the temperature was increased from 20 °C to 60 °C (Figure 7). According to Rao and Rao (2006) the reason for the fall in the adsorption capacity at elevated temperatures may be that at higher temperatures a part of the dye leaves the solid phase and re-enters the liquid phase.

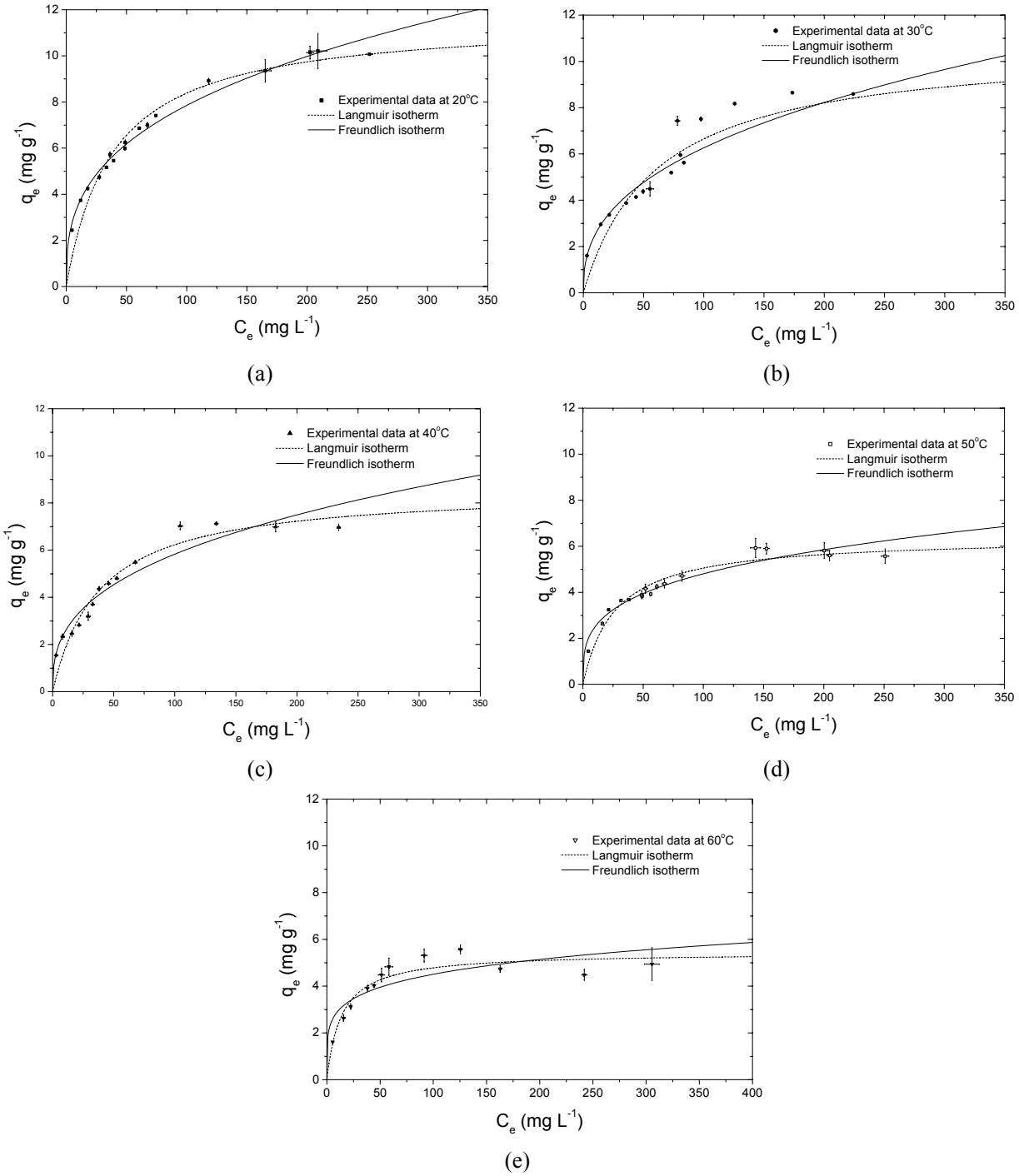

Figure 7: Isotherms for adsorption of Remazol Brilliant Blue R on orange peel adsorbent. Experimental conditions: contact time 24 h; agitation 150 rpm; temperature (a) 20 °C, (b) 30 °C, (c) 40 °C, (d) 50 °C and (e) 60 °C.

Isotherm data should be accurately fit to a suitable isotherm model to find adsorption parameters that can be used in a design process (Khaled *et al*., 2009[a]). There are several isotherm equations available for analysing experimental sorption equilibrium data in single-solute systems. The most widely used are the Langmuir and Freundlich models.

The non-linear Langmuir and Freundlich isotherms are represented by Equations (5) and (6), respectively:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, C_e (mg L^{-1}) is the equilibrium liquid-phase dye concentration, K_L (L mg^{-1}) is the Langmuir constant related to the apparent energy of adsorption, K_F ((mg g^{-1}) (L $mg^{-1})^{1/n}$) is the Freundlich constant related to the distribution coefficient, q_{max} is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg g^{-1}) and n is a measure of the deviation from linearity of an adsorption.

The essential characteristics of a Langmuir isotherm can also be expressed in terms of a dimensionless constant-separation factor, R_L, given by Equation (7).

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

where C_o is the initial dye concentration (mg L^{-1}). The R_L value indicates the shape of the isotherm and hence the type of adsorption: irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) (Magdya and Daifullah, 1998).

The isotherm parameters and the coefficients of determination (R^2) (Table 2) were obtained by non-linear least square regression analysis at a 95% confidence interval using StatSoft® STATISTICA software (version 7.0). The chi-square (χ^2) and standard deviation (SD) (Table 2) were obtained to determine the validity of the models and to reproduce experimental data.

The maximum adsorption capacity of the adsorbent for the dye (i.e., the q_{max} value in the Langmuir equation) decreased from 11.62 mg g^{-1} to 5.44 mg g^{-1} with the increase in temperature from 20 °C to 60 °C. Otherwise, the Langmuir constant (K_L) increased with increasing temperature, indicating that the adsorption process was endothermic. The K_L value decreased from 20 °C to 30 °C, which may be explained by greater values of χ^2 and SD in comparison to the data fitting at the others temperatures.

The R_L values of 0.0259-0.0730 calculated at different temperatures lie between 0 and 1.0, indicating a favourable adsorption.

The values of n (from the Freundlich equation) between 2.9 - 5.3 represent good adsorption of the dye on orange peel adsorbent (Agrawal and Sahu, 2006).

Adsorption Thermodynamics

The thermodynamic equilibrium constants (K_c) of the dye adsorption onto the studied adsorbent were calculated from the intercept of the plots of $\ln(q_e/C_e)$ versus q_e by extrapolating to $q_e = 0$ (Khan and Singh, 1987, Lyubchik *et al*., 2000, Niwas *et al.*, 2000, Chen *et al.*, 2009). The K_c values increased with increasing temperature (Table 3). This K_c value was further used to calculate the thermodynamic parameters.

Table 2: Langmuir and Freundlich constants for adsorption of dye on orange peel adsorbent.

Conditions	Langmuir isotherm						Freundlich isotherm				
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	χ^2	SD	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	n	R^2	χ^2	SD
20°C	11.62	0.0259	0.099	0.9790	0.0655	0.4849	1.600	2.895	0.9919	0.0131	0.3013
30°C	10.70	0.0164	0.15	0.9573	0.1181	0.6396	1.024	2.543	0.9612	0.0527	0.6104
40°C	8.61	0.0262	0.098	0.9699	0.0858	0.4742	1.097	2.757	0.9602	0.0576	0.5436
50°C	6.39	0.0377	0.070	0.9680	0.0295	0.3099	1.299	3.522	0.9657	0.0292	0.3207
60°C	5.44	0.0730	0.037	0.9394	0.0340	0.3992	1.879	5.261	0.8189	0.1327	0.6682

Table 3: Thermodynamic parameters for the adsorption of dye on orange peel adsorbent.

Thermodynamic constant	Temperature (K)			
	303.15	313.15	323.15	333.15
K_c	340.8	485.9	696.0	744.0
ΔG^o (kJ mol^{-1})	-14.70	-16.11	-17.59	-18.32
ΔH^o (kJ mol^{-1})	22.82			
ΔS^o (J mol^{-1} K^{-1})	124.2			

The thermodynamic parameters of the adsorption, i.e., the standard Gibbs free energy ΔGº, enthalpy ΔHº and entropy ΔSº, were calculated according to Equations (8) and (9).

$$\Delta G^o = -RT \ln K_c \quad (8)$$

The slope and the intercept of the plots of $\ln K_c$ versus 1/T were used to determine the ΔHº and ΔSº values (Figure 8).

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (9)$$

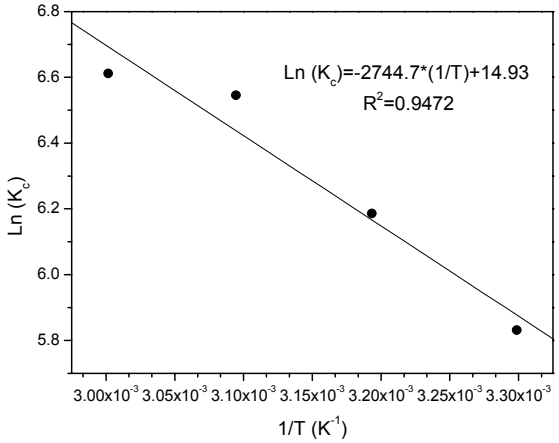

Figure 8: Van't Hoff plot of adsorption equilibrium constant Kc.

The free energy of the process at all temperatures was negative and changed with the rise in temperature (Table 3). This indicates that the adsorption process was spontaneous and thermodynamically favourable. The more negative values of ΔGº imply a greater driving force for the adsorption process. As the temperature increased, the ΔGº value increased, indicating a higher driving force resulting in a greater adsorption affinity at higher temperatures (Aman *et al*., 2008). The value of ΔHº was positive, indicating that the adsorption process was endothermic in nature. The positive value of ΔSº suggested increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent toward dye (Srivastava *et al.*, 2006). Though the adsorption of dyes is currently described as an exothermic phenomenon (Jain *et al*., 2003; Iqbal and Ashiq, 2007), endothermic adsorption was also reported in the literature: acid orange 7 dye in aqueous solutions using spent brewery grains (Silva *et al*., 2004), methylene blue adsorption using wheat shells (Bulut and Aydin, 2006) and malachite green and basic red using activated carbon and activated slag (Gupta *et al*., 1997; Gupta *et al*., 2003). Iqbal and Ashiq (2007) reported ΔSº negative values for the adsorption of the following dyes from aqueous solutions on activated carbon: alizarine red-S, methyl blue, methylene blue, eriochrome black-T, malachite green, phenol red and methyl violet, indicating that the randomness at the solid-solution interface decreased during adsorption. However in case of dye bromophenol blue, the entropy increased like in the present work and the same phenomenon was reported by Gupta *et al*. (1997), Gupta *et al*. (2003), Silva *et al*. (2004), Bulut and Aydin (2006) for others dyes. These differences may be attributed to the physical and chemical characteristics of the dyes and adsorbents, which play an important role in adsorption.

CONCLUSIONS

The results presented here show that orange peel is a promising and cheap adsorbent for the removal of the dye Remazol Brilliant Blue R. The OPA particle size distribution showed that 80.46% of the particles are in the range of 1,180-355 μm. SEM micrographs of the adsorbent showed a highly heterogeneous surface and the X-ray diffraction spectrum revealed a completely amorphous structure. The experimental data indicated that the adsorption capacity was dependent on operating variables such as contact time, temperature and initial dye concentration. The contact time required to attain equilibrium was around 15 h for the three initial concentrations of dye studied (30 mg L^{-1}, 100 mg L^{-1} e 250 mg L^{-1}). The adsorption obeyed both Langmuir and Freundlich isotherms. Regarding adsorption thermodynamics, negative values of ΔGº indicated that the adsorption processes was favourable and, as the temperature increased, the ΔGº value increased, indicating a higher driving force resulting in a greater adsorption affinity at higher temperatures. A positive value of ΔHº suggested an endothermic process and a positive value of ΔS° indicated that the solid/liquid interface was less ordered after adsorption.

NOMENCLATURE

ΔGº	Standard Gibbs free energy of adsorption	kJ mol^{-1}
ΔHº	Standard Enthalpy of adsorption	kJ mol^{-1}

ΔS^o	Standard Entropy of adsorption	J mol^{-1} K^{-1}
C_e	Equilibrium liquid-phase dye concentration	mg L^{-1}
C_o	Initial dye concentration	mg L^{-1}
C_t	Liquid-phase concentration of dye at time t (min)	mg L^{-1}
FTIR	Fourier transform infrared spectroscopy	
JCPDS	Joint Committee on Powder Diffraction Standards	
K_c	Thermodynamic equilibrium constant	
K_F	Freundlich constant	(mg g^{-1}) (L mg^{-1})$^{1/n}$
K_L	Langmuir constant	L mg^{-1}
n	Freundlich constant	
OPA	Orange peel adsorbent	
q_e	Amount of dye adsorbed at equilibrium	mg g^{-1}
q_{max}	Maximum adsorption capacity	mg g^{-1}
q_t	Amount of dye adsorbed at time t	mg g^{-1}
R^2	Coefficient of determination	
R_L	Dimensionless constant-separation factor	
SD	Standard deviation	
SEM	Scanning electron microscope	
t	Time	min
V	Solution volume	L
W	Weight of the adsorbent	g
XRD	X-ray diffraction	
XRF	X-ray fluorescence	
χ^2	Chi-square	

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