



Trends in
**Applied Sciences
Research**

ISSN 1819-3579



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Utilization of Cocoa Pod Husk for the Removal of Remazol Black B Reactive Dye from Aqueous Solutions: Kinetic, Equilibrium and Thermodynamic Studies

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ABSTRACT

This study aims at investigating the adsorption of Remazol Black B reactive (RBBR) dye on cocoa pod husk based activated carbon (CPHAC) in batch process. The effects of initial dye concentration, contact time, temperature and pH were evaluated. At the lowest initial dye concentration (20 mg L⁻¹), the highest percentage RBBR dye removal by CPHAC was achieved (76.3%). Equilibrium was reached at 300 and 350 min, respectively. The equilibrium data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. It was found that Langmuir model fitted the adsorption most with maximum adsorption monolayer coverage of 22.12 mg g⁻¹. Two kinetic models were used to fit the kinetic data; pseudo-first-order and pseudo-second-order models. The pseudo second-order model provided the best correlation for the adsorption of RBBR dye on CPHAC. Thermodynamic parameters such as change in Gibb's free energy ΔG° , change in enthalpy ΔH° and change in entropy ΔS° were calculated. The adsorption process was found to be feasible, endothermic and spontaneous. Both the mean free energy of adsorption and the activation energy values obtained shows that the adsorption process follows a physisorption mechanism.

Key words: Adsorption, feasible, endothermic, spontaneous, activation energy

INTRODUCTION

Waste waters containing different dyes are often discharged in aqueous effluents from dyestuff manufacturing, dyeing and textile industries. The physical process of dye removal from effluents may be divided into two main categories: adsorption and membrane separation (Slokar and Le Marechal, 1998; Vandevivere *et al.*, 1998; Hao *et al.*, 2000). Adsorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent. In this regard, activated carbon has been extensively used for removal of color resulting from the different classes of dyes and is now the most widely used adsorbent for dyes. However, adsorption using activated carbon as adsorbent is very expensive, the cost of regenerating the spent

activated carbon is also high (Girods *et al.*, 2009). For this reason, there is growing interest in utilizing biomass wastes/alternatives to activated carbon as low-cost adsorbents (Gupta and Ali, 2002; Babel and Kurniawan, 2003; Izadyar and Rahimi, 2007; Moazed, 2008; Gokturk and Kaluc, 2008; Lori *et al.*, 2008; Ali and Muhammad, 2008; Atmani *et al.*, 2009; Demiral and Gunduzoglu, 2010; Nunes *et al.*, 2009; Sze and McKay, 2010).

Cocoa (*Theobroma cacao*) is a plant species from the family of Sterculiaceae. The evergreen tree growing crop, 6.0 to 8.0 m high in the tropical rainforest. In Mexico, cocoa bean is used as stimulant and foodstuff. From Mexico, it spread all over the world. Currently, Africa is the major producer of cocoa beans (53% of the total world production) followed by Latin America (31.3%) and Asia (8.8%). The five most important cocoa producing countries supply almost 75% of the total production (Ivory Coast, 26.0%; Brazil, 22.9%; Ghana, 12%; Malaysia, 6.5%; Nigeria, 6.2%). In Nigeria, more than 1.5 million tons of Cocoa Pod Husks (CPH) are wasted annually. Some of the CPH are used as organic fertilizer, soap making and animal feed production, whereas in Malaysia, an estimated amount of 217600 pods and 9500 million tons of bean shells are available (Hertrampf and Piedad-Pascual, 2003). Cocoa pod husks are produced after the removal of the cocoa bean from the fruit. Basically, each ton of dry cocoa beans is equivalent to about 10 tons of cocoa pod husks. Most of the husks are disposed as waste which in turn resulted in landfill problem. This is because the use of cocoa pod husks is limited to livestock feed due to theobromine content, a significant cause of disease called inoculums (Serra and Ventura, 1999). This cheap and abundant agricultural waste could be converted to activated carbon. Conversion of CPH to activated carbon has two advantages. First, the discarded agricultural waste is converted into useful and valuable adsorbent. Secondly, wastewater treatment problem caused by textile industries in Malaysia can be solved with the use of the adsorbent derived from CPH (Tan *et al.*, 2008).

This study is aimed at preparing and characterizing the activated carbon produced from cocoa pod husk, (CPHAC) investigating the adsorption of RBBR dye on CPHAC using batch process. Other factor studied includes; initial dye concentration, contact time, solution temperature, pH, adsorption isotherm, kinetics and thermodynamic parameters of the adsorption process.

MATERIALS AND METHODS

Preparation of CPHAC: CPH used for preparation of activated carbon was obtained from Cocoa Research and Development Centre, Cocoa Board Malaysia, Hilir Perak, Malaysia in 2010. CPH were firstly washed with water to remove dirt from it surface and subsequently dried at 105°C for 24 h to remove the moisture content. The dried CPH was ground into small pieces and sieved to the desired particle size of 1-2 mm and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization of the dried CPH was carried out at 500°C with heating rate of 10°C min⁻¹ under purified nitrogen flow through at a flow rate of 150 cm³ min⁻¹ for 1 h. In the second step, the char was activated under the same condition, but to a final temperature of 700°C for 2 h. Once the final temperature is reached, the nitrogen gas flow was switched to CO₂ (200 cm³ min⁻¹) to complete the activation process. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and hydrochloric acid (0.1 M) until the pH of the solution used for washing reached 6.5-7.0.

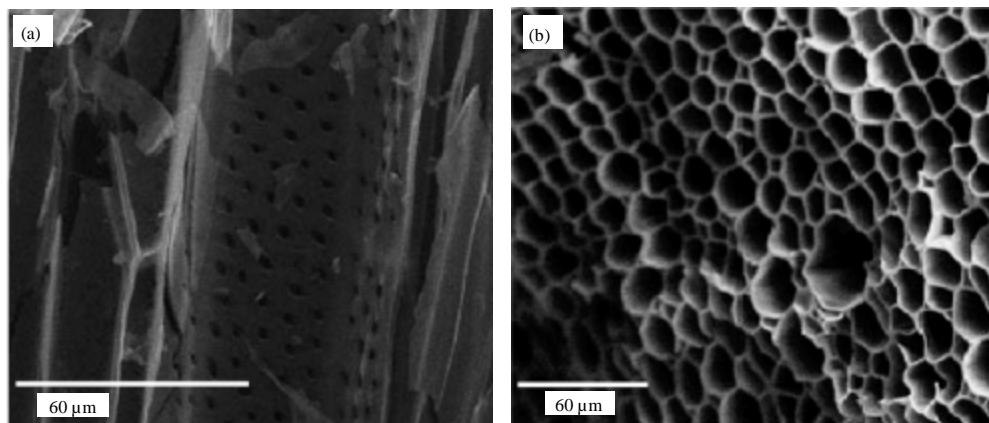


Fig. 1: SEM micrographs of (a) Char (magnification = 2000x) and (b) CPHAC (magnification = 2000x)

Characterization of adsorbents: The precursor and the prepared activated carbon were characterized using various techniques in order to study their physical and chemical properties.

Nitrogen adsorption-desorption measurements: Nitrogen adsorption-desorption measurement was carried out to determine the surface area, total pore volume and mesopore volume of the samples by using Volumetric adsorption apparatus (Micromeritics Model ASAP 2020, US). The sample to be tested was degassed for 4 h under vacuum at 120°C prior to analysis. The sample was then cooled in liquid nitrogen. The analysis was carried out at 77 K by allowing known volume of nitrogen gas in and out of the sample and measuring the equilibrium pressure. The surface area, total pore volume and mesopore volume analysis were performed by a software (Micropore version 2.46). Mesopore volume was calculated by subtracting total volume, obtained at a relative pressure of 0.99 from the micropore volume, which was obtained from t-plot equation.

Surface morphology (SEM): Scanning electron microscopy (Model VPFESEM Supra 35VP) was used to study the surface morphology, surface textures and the development of porosity of char and activated carbon prepared. Results obtained are presented in Fig. 1a and b.

Proximate analysis (TGA): Thermo Gravimetric Analyzer (TGA) (Model Perkin Elmer TGA7, US) was used to analyze the moisture content, volatile matter, fixed carbon and ash contents in the precursor, char and the prepared activated carbon. Five gram of the sample was transferred into the platinum pan of the TGA analyzer. The furnace chamber was then raised and the sample was degassed for few min. Nitrogen gas was allowed to pass through the furnace to ensure an inert atmosphere and the sample was heated from ambient temperature to 110°C until a constant weight is obtained for the moisture content determination. The temperature was then increased to 850°C and held for 7 min. The temperature was then decreased to 800°C. The nitrogen gas was switch off while oxygen gas was allowed to burn the sample. Fixed carbon content was determined from the weight loss during the burning stage. Ash content and the remaining mass were determined at the end of the analysis.

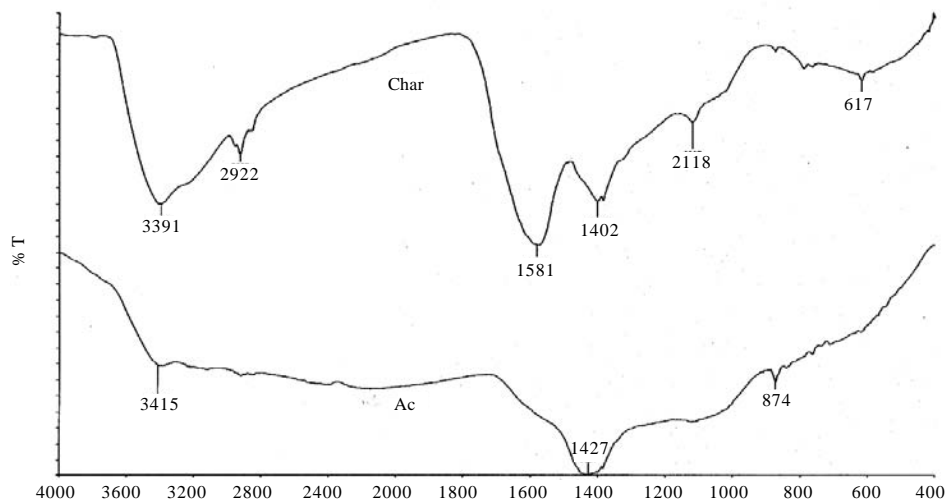


Fig. 2: FTIR spectrum of both char and CPHAC

Elemental analysis: Elemental analysis was performed to determine the elemental composition of organic matter of precursor, char and the prepared activated carbon using Perkin Elmer (Series II) elemental analyzer.

Fourier transform infrared (FTIR): Fourier transform infrared (FTIR) spectroscopic analysis was used to study the surface chemistry of the char and the prepared activated carbon using FTIR spectroscope (FTIR-2000, Perkin Elmer). The FTIR spectra (Fig. 2) give information about the characteristic functional groups on the surface of the char and the prepared activated carbon. The analysis was conducted by encapsulating the sample in potassium bromide pellets. The spectra were measured from 4000 to 400 cm^{-1} .

Remazol Brilliant Blue Reactive (RBBR) dye: RBBR dye supplied by Sigma-Aldrich (M) Sdn Bhd, Malaysia was used as adsorbate. De-ionized water was used to prepare all reagents and solutions.

Batch equilibrium studies: Batch equilibrium tests were carried out for adsorption of RBBR dye on the CPHAC prepared. The effects of initial dye concentration, contact time, temperature and solution pH on the adsorption uptake were investigated. Sample solutions were withdrawn at equilibrium to determine the residual concentration. The solutions were filtered prior to analysis in order to minimize interference of carbon fines with the analysis. For equilibrium studies, the experiment was carried out for 24 h to ensure that equilibrium was reached. The linear Beer-Lambert relationship between absorbance and concentration i.e., a calibration curve was established by plotting the graph of absorbance versus concentration of the dye solution. The concentration of RBBR dye solution before and after adsorption were determined using a double UV-vis spectrophotometer (UV-1800 Shimadzu, Japan) at a maximum wavelength of 597 nm. The amount of RBBR dye adsorbed at equilibrium, q_e (mg g^{-1}) was calculated using Eq. 1.

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

where, C_0 and C_e (mg L^{-1}) are the liquid-phase concentrations of RBBR dye at initial and at equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of CPHAC used.

Effect of initial RBBR dye concentration and contact time: In order to study the effect of initial concentration and contact time on the RBBR dye uptake, 100 mL of RBBR dye solution with initial concentration of 20-100 mg L^{-1} were prepared in a series of 250 mL Erlenmeyer flasks. An equal mass of 0.50 g of the CPHAC was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water bath shaker (Model Protech, Malaysia) at constant temperature (30°C), with rotation speed of 135 rpm, until equilibrium point was reached. In this case, the experiment was conducted without pH adjustment.

Effect of solution temperature: The effect of solution temperature on the RBBR dye adsorption process was examined by varying the adsorption temperature at 30, 45 and 60°C by adjusting the temperature controller of the water bath shaker, while other operating parameters such as volume of RBBR dye and rotation speed were kept constant. The concentration of RBBR dye was varied ranging from 20-100 mg L^{-1} .

Effect of solution pH: The effect of solution pH on the RBBR dye adsorption process was studied by varying the initial pH of the solution from 3 to 11. The pH was adjusted by adding 0.1 M hydrochloric acid or 0.1 M sodium hydroxide and was measured using pH meter (Model Delta 320, Mettler Toledo, China). The RBBR dye initial concentration was fixed at 100 mg L^{-1} with adsorbent dosage of 0.5 g/100 mL. The solution temperature was maintained at 30°C . The RBBR dye percent removal was calculated using Eq. 2.

$$\text{Removal(\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Batch kinetic studies: For the batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of RBBR dye were similarly measured. The RBBR dye uptake at any time, q_t (mg g^{-1}), was calculated using Eq. 3.

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where, C_t (mg L^{-1}) is the liquid-phase concentration of RBBR dye at any time, t (mins).

RESULTS AND DISCUSSION

Characterization of CPHAC

Surface area and pore size characteristics: Table 1 reports the BET surface area, Langmuir surface area, pore volume and mesopore volume of the precursor, char and the CPHAC. The activated sample has a relatively high BET surface area of 502.7 $\text{m}^2 \text{g}^{-1}$ and possesses a high total pore volume of 0.504 $\text{cm}^3 \text{g}^{-1}$. The high BET surface area and total pore volume of the CPHAC were

Table 1: Properties of precursor char and CPHAC

Properties	Sample	
	Char	CPHAC
BET surface area ($\text{m}^2 \text{g}^{-1}$)	118.4	502.7
Langmuir surface area ($\text{m}^2 \text{g}^{-1}$)	132.1	584.3
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.091	0.504
Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	0.263	0.263

due to the CO_2 activation process. The CO_2 gas molecules diffuse into the char and activated samples thereby increasing the CO_2 -carbon reaction leading to the development of additional pores on the samples. CO_2 gasification was found to promote the formation of mesopores and enhance the surface area of activated carbon (Tseng *et al.*, 2006).

Surface morphology: Scanning Electron Microscopy (SEM) was used to characterize the surface morphology of the char and the activated carbon samples. Figure 1a and b show the SEM micrographs of both the char and activated sample, respectively. In Fig. 1a, the SEM micrograph shows that the char surface was rough and the pores were not properly developed, whereas in Fig. 1b, there are several pores formed on the activated carbon surface. The carbonization process created gradual porosity on the activated sample leading to the formation of additional pores on the sample thereby increasing the ability of inorganic material removal (Suzuki *et al.*, 2007). The well-developed pores resulted to large surface area and porous structure of the activated carbon (Hameed and Daud, 2008). These pores allowed a good surface for RBBR dye to be trapped and adsorbed into (Amin, 2008) thus, reflecting the potential use of CPH waste as a precursor for activated carbon preparation.

Proximate analysis: The volatile matter content in the precursor was very high but low in ash content. However, the volatile matter content in the CPHAC was sharply reduced when compared to that of the precursor. This is because organic substances present in the sample became unstable at elevated temperature; the heat breaks the molecular bond and linkage. As a result, these substances volatilizes off both as gas and liquid products. The fixed carbon content was satisfactory enough in CPHAC, having a value of 75.4% compared to the precursor which has only 19.3%, indicating that the precursor was suitable in activated carbon conversion. The ash content in CPHAC was considered high, due to silica and cellulose. For moisture content, it left only 2% in CPHAC compared to that of the precursor having 3.2%. The higher fixed carbon and low moisture contents made CPHAC a very good adsorbent in the adsorption of RBBR dye (Table 2).

Elemental analysis: In this case, the total amount of carbon present in the sample improved after pyrolysis when compared to the precursor. The heat supplied during the carbonization process initiates the thermal degradation process. Decomposition occurred since the volatile compounds could not maintain its stability at high temperatures, the volatiles matter are completely removed during carbonization leaving only the portion of stable carbon as residues. Hydrogen is a crucial element in organic molecule bonding and in all organic compounds. However, during pyrolysis process, the activation process does not make much difference in the amount of hydrogen present (Oh and Park, 2002) (Table 3).

Table 2: Proximate content of precursor, char and CPHAC

Proximate analysis (%)	Sample		
	Precursor	Char	CPHAC
Moisture	3.2	2.9	2.0
Volatile matter	75.3	28.7	16.7
Fixed carbon	19.3	63.6	75.4
Ash	2.2	4.8	5.9

Table 3: Elemental analysis of precursor, char and CPHAC

Elemental analysis (%)	Sample		
	Precursor	Char	CPHAC
Carbon	44.3	59.7	72.5
Hydrogen	6.5	5.5	5.3
Nitrogen	0.1	0.1	0.1
Others*	49.1	34.7	22.1

*Estimated by difference

Fourier transform infrared spectroscopy (FTIR): The FTIR spectra of both the char and CPHAC are shown in Fig. 2. OH stretching bonds were detected for both char and CPHAC at bandwidth around 3300-3500 cm^{-1} . Besides, there are other peaks detected on the char spectrum, which are at the bandwidth of 2922, 1402 and 1118 cm^{-1} assigned to C-H stretching related to alkanes and alkyl groups, CH_2 deformation in alkyl group and C-O-C stretch, respectively. Peaks at 1581 and 617 cm^{-1} on char spectrum indicated the presence of carboxylic acid and aliphatic C-H specie vibrations, respectively. On the other hand, the peaks appearing on CPHAC spectrum at 874 cm^{-1} reflects the existing C-H out of plane deformation groups. Some of the functional groups have disappeared in CPHAC, such as C-H stretch (2922 cm^{-1}), carboxylic acid (1581 cm^{-1}), C-O-C stretch (1118 cm^{-1}) and aliphatic C-H species vibration (617 cm^{-1}). These are as a result of high temperature in activation process that broke some intermolecular bonds.

Batch adsorption studies: Batch adsorption of RBBR dye on CPHAC was studied as a function of initial dye concentration, contact time, solution temperature and solution pH.

Effect of initial dye concentration and contact time on adsorption process: Figure 3 shows the effect of initial dye concentration and contact time on the adsorption of RBBR dye on CPHAC at 30°C. The plot showed that the adsorption of RBBR dye increases with increasing time. The properties of Remazol Black B Reactive Dye are shown in Table 4. The adsorption was fast at initial stage of the contact period; thereafter it became slow as it reaches equilibrium. This phenomenon was based on the fact that large numbers of vacant surface sites were available for adsorption during the initial stage (Tan *et al.*, 2008; Bello *et al.*, 2008; Bello *et al.*, 2010). After a lapse of time, the remaining vacant surface sites became difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases (Hameed and Ahmad, 2009). Equilibrium was reached within 300 min at (20 mg L^{-1} to 60 mg L^{-1}) and 350 min for (80 mg L^{-1} to 100 mg L^{-1}) initial concentrations.

The amount of dye adsorbed at equilibrium time reflected the maximum adsorption uptake of CPHAC. During the adsorption process, the dye molecules initially have to encounter the

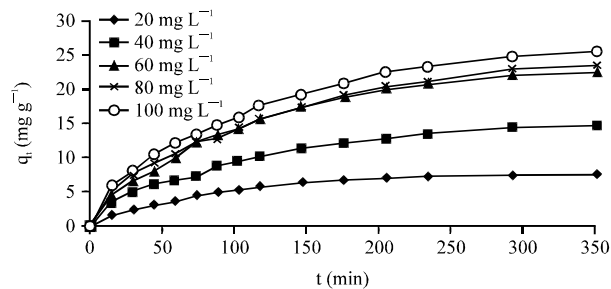


Fig. 3: Remazol Black B reactive dye adsorption uptake at different initial concentrations and contact time on CPHAC (T=30°C; 0.5 g of CPHAC; pH 7)

Table 4: Properties of remazol black b reactive dye

Dye name	Remazol black B
Molecular formula	C ₂₆ H ₂₁ O ₁₉ N ₅ S ₆ Na ₄
Molecular weight (g mol ⁻¹)	991.8
CAS no.	17095-24-8
λ max.(nm)	597
Chemical structure	$\text{Na}^+\text{O}_3\text{S} + \text{SO}_2\text{CH}_2\text{CH}_2\text{O}_2\text{S} - \text{C}_6\text{H}_4 - \text{N}=\text{N} - \text{C}_6\text{H}_2(\text{OH})(\text{NH}_2) - \text{N}=\text{N} - \text{C}_6\text{H}_4 - \text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$ NaO_3S SO_3Na

boundary layer effect before diffusing from the boundary layer film onto the adsorbent surface. Finally, the dye molecules have to diffuse into the porous structure of the adsorbent (Senthilkumaar *et al.*, 2005). This theory explains the fact that due to the presence of large amount of dye molecules it takes a relatively longer contact time to attain equilibrium at higher initial concentrations. The plot shows that there was an increase in the adsorption capacity at higher initial concentration of RBBR dye. This phenomenon was due to the fact that the initial dye concentration provides an important driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases (Ozlem *et al.*, 2009). The equilibrium adsorption capacity (q_e) for RBBR dye adsorption increased from 6.1-25.3 mg g⁻¹ for the concentration increase from 20-100 mg L⁻¹ at 30°C. As the initial dye concentration increased, the mass transfer driving force becomes larger and this resulted in higher RBBR dye removal. The percentage of RBBR dye removal decreased from 76.3 to 38.3%. Thus, the percentage of RBBR dye removal was higher at low concentration due to the availability of unoccupied binding sites on the CPHAC. At higher concentration, the binding sites on CPHAC were almost completely occupied, thus leading to a decrease in the percent of RBBR dye removal. Ozlem *et al.* (2009) showed that the percentage of RBBR dye adsorption on cotton stalk and cotton hull decreased from 54.9 to 10.8% and 79.6 to 16.7%, respectively with increasing concentration from 25-300 mg L⁻¹. The percentage of RBBR dye removal was strongly affected by its initial concentration as shown in Table 5.

Effect of solution temperature: Figure 4 shows the amount of RBBR dye adsorbed at equilibrium, q_e (mg g⁻¹) on CPHAC as a function of the solution temperature at different initial concentrations (20 to 100 mg L⁻¹). RBBR dye adsorption uptake was found to increase with

Table 5: Percentage removal of Remazol Black B Reactive Dye on CPHAC at 30°C

Sample	Removal (%)				
	20	40	60	80	100
CPHAC	76.32	60.18	54.34	42.84	38.29

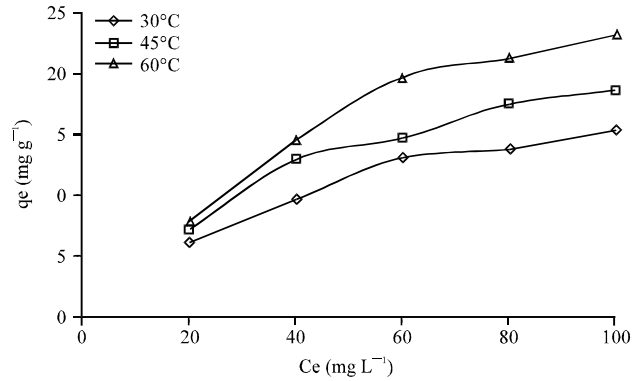


Fig. 4: Adsorption isotherm of Remazol Black B Reactive Dye on CPHAC at different temperatures

increasing solution temperature from 30 to 60°C at all concentrations, indicating the endothermic nature of the adsorption process. Increasing the temperature was known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent, creating new adsorption sites hence increasing the rate of intraparticle diffusion of adsorbate molecules into the pores of the CPHAC at higher temperatures. The amount of RBBR dye removed at equilibrium increased from 6.1 to 14.9 mg g⁻¹ and 7.0 to 23.1 mg g⁻¹, respectively as temperature increases from 30 to 60°C (Fig. 4).

Effect of solution pH: The pH of the solution was varied from pH 3 to 11. Initial concentration was set at 100 mg L⁻¹ at 30°C. Plots of the equilibrium adsorption capacity (q_e) against pH of the solution for RBBR dye adsorption was shown in Fig. 5. From the plot, the influence of pH on the adsorption capacity was considered negligible. RBBR dye adsorption was hardly affected by the pH variation. Similar trend was reported by Vijayaraghavan *et al.* (2009) in a study on the treatment of complex remazol dye effluent using sawdust-and coal-based activated carbons. The decolorization of Remazol dyes was reported to be unaffected by the solution pH.

Adsorption kinetics: Adsorption kinetics was investigated for better understanding of the dynamics of adsorption of RBBR dye onto CPHAC and to obtain predictive models that allow estimations of the amount adsorbed with respect to time.

The pseudo first order kinetic model: The pseudo first-order equation generally expressed by Lagergren and Svenska (1898) where, q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg g⁻¹). k₁ is the rate constant for pseudo-first order adsorption (min⁻¹). A plot of ln (q_e-q_t) against t at various concentrations and temperatures resulted

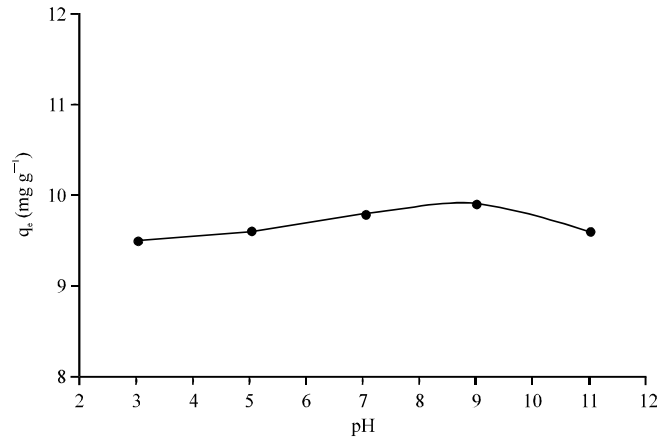


Fig. 5: Effect of solution pH on the adsorption of Remazol Black B Dye onto CPHAC ($C_o = 100 \text{ mg L}^{-1}$; 0.5 g CPHAC ; $T = 30^\circ\text{C}$)

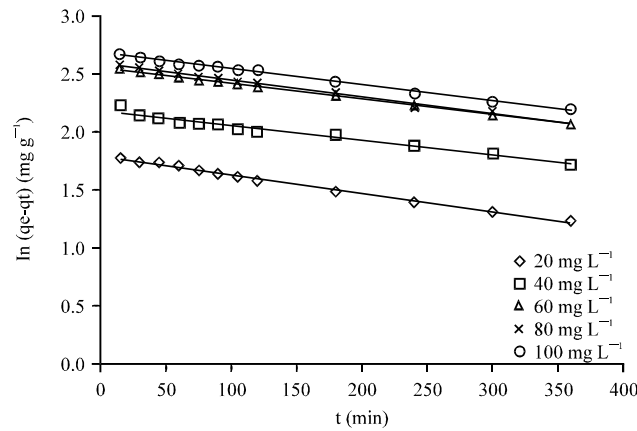


Fig. 6: Pseudo-first order kinetic plot of the adsorption of Remazol Black B Reactive Dye onto CPHAC at 30°C

in graphs with negative slopes. k_1 and q_e are calculated from the slopes and intercepts, respectively (Fig. 6). Although, the correlation coefficients were high but comparison of the $q_{e, \text{calc.}}$ to the $q_{e, \text{exp.}}$, the values do not agree. Results are presented in Table 6a. Therefore, the adsorption of RBBR dye onto CPHAC does not follow the pseudo-first order kinetics.

The pseudo second order kinetic model: The pseudo second order equation expressed by Ho and McKay (1999) was used. Plots of t/q_t versus t gave linear graphs from which q_e and k_2 were estimated from the slopes and intercepts of the plot (Fig. 7) for temperatures $30\text{-}60^\circ\text{C}$. The correlation coefficients were as high as 0.99 and there were good agreement between $q_{e, \text{cal.}}$ and $q_{e, \text{exp.}}$ data obtained. The results are presented in Table 6. The good agreement shows that the pseudo-second order kinetic equation fits the adsorption data well. Hence, the adsorption of RBBR dye onto CPHAC follows the pseudo-second order kinetics (Table 6b).

Adsorption isotherms: The adsorption isotherm indicates how the adsorbed molecules distribute themselves between the liquid phase and the solid phase until the adsorption process reaches an

Table 6a: Pseudo-first-order and pseudo-second-order kinetic model parameters for Remazol Black B Reactive Dye adsorption on CPHAC at 30°C

C ₀ (mg L ⁻¹)	q _e exp (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		q _e cal (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _e cal (mg g ⁻¹)	k ₂ (min ⁻¹)	R ²
20	6.11	7.56	0.0016	0.99	6.36	0.0012	0.99
40	9.63	14.10	0.0015	0.96	9.85	0.0005	0.99
60	13.04	17.82	0.0014	0.97	13.51	0.0004	0.99
80	13.71	24.11	0.0014	0.95	14.06	0.0003	0.99
100	15.32	29.98	0.0012	0.96	16.42	0.0002	0.99

Table 6b: Intraparticle diffusion model and Elovich kinetic models parameters for Remazol Black B Reactive Dye adsorption on CPHAC at 30°C

Initial Conc. C ₀ mg L ⁻¹	Intraparticle diffusion model			Elovich model		
	k _{diff} (mg g ⁻¹ min ^{1/2})	C	R ²	a (mg g ⁻¹ min)	b (g mg ⁻¹)	R ²
20	0.17	1.26	0.97	0.04	1.24	0.94
40	0.21	1.01	0.98	0.07	0.96	0.95
60	0.33	0.80	0.97	0.09	0.64	0.92
80	0.35	0.59	0.98	0.09	0.65	0.89
100	0.37	0.15	0.96	0.11	0.57	0.89

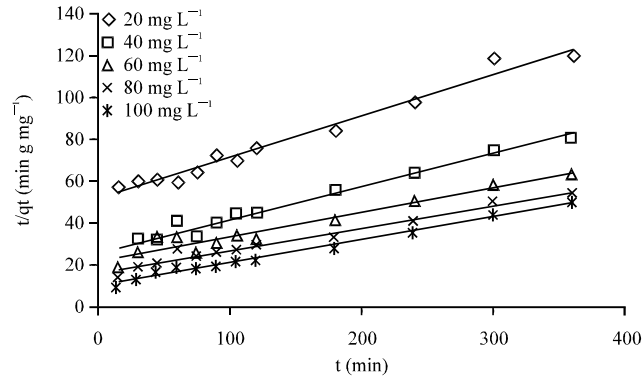


Fig. 7: Pseudo-second order kinetic plot of the adsorption of Remazol Black B Reactive Dye onto CPHAC at 30°C

equilibrium state. This is basically important in describing how solutes interact with adsorbents and is critical in optimizing the use of the adsorbent (Buckley, 1991; Carliell, 1993). The analysis of equilibrium adsorption isotherm data were then carried out by fitting them to different isotherm models so as to find a suitable model to describe the experimental data. The adsorption isotherm studies were carried out using the following models.

Langmuir isotherm model: Langmuir isotherm assumes monolayer adsorption into a surface containing a finite number of adsorption sites which are uniform for adsorption with no trans-migration of adsorbate in the plane of surface (Langmuir, 1916). The linearized form of Langmuir adsorption model is expressed as:

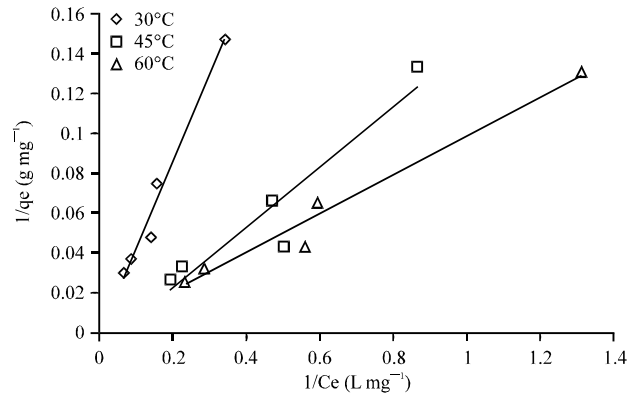


Fig. 8: Langmuir isotherm plot for Remazol Black B Reactive Dye adsorption onto CPHAC at different temperatures

Table 7a: Langmuir isotherm model parameters and correlation coefficients for adsorption of Remazol Black B reactive dye at different temperatures

Temp (°C)	q ₀ (mg g ⁻¹)	K _L	R ²	R _L
30	17.61	0.0929	0.99	0.01
45	19.80	0.2014	0.99	0.03
60	22.12	0.5722	0.98	0.08

Table 7b: Comparison of maximum monolayer adsorption of some dyes unto various adsorbents

Dyes	Adsorbents	q ₀ (mg g ⁻¹)	Reference
RBBR	CPHAC	22.12	This Work
Congo red	Activated red mud	7.08	(Tor and Cengeloglu, 2006)
Congo red	Coir pith AC	6.70	(Namasivayam and Kavitha, 2002)
Methylene blue	Apricot stones- AC	4.11	(Aygun <i>et al.</i> , 2003)
Methylene blue	Walnut shell- AC	3.53	(Mall <i>et al.</i> , 2005)
Methylene blue	Almond shell- AC	1.33	(Aygun <i>et al.</i> , 2003)

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \quad (4)$$

where, C_e is the dye concentration in the solution at equilibrium (mg L⁻¹), q_e is the dye concentration on the adsorbent at equilibrium (mg g⁻¹), q₀ is the monolayer adsorption capacity of CPHAC (mg g⁻¹) and b is the Langmuir biosorption constant (L mg⁻¹). A plot of C_e/q_e versus C_e gave a straight line with a slope 1/q₀ and an intercept of 1/q₀b (Fig. 8). The R² value of Langmuir isotherm (Table 7a and c) when compared with Freundlich isotherm indicates that the adsorption of the RBBR dye onto CPHAC fits the Langmuir isotherm. Values of q₀ are calculated and reported in Table 7a. The value of q₀ obtained was compared with those from other adsorbents; the values are reported in Table 7b. The q₀ values obtained from this study showed that CPHAC is a good adsorbent for the removal of RBBR dye from aqueous solutions.

To confirm the favorability of the process, the dimensionless equilibrium parameter (R_L) defined by Eq. 5 was used:

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

Table 7c: Freundlich, Temkin and Dubinin-Radushkevich isotherm model parameters and correlation coefficients for adsorption of Remazol Black B Reactive Dye onto CPHAC at different temperatures

Isotherms									
		Freundlich		Temkin			Dubinin-Radushkevich		
Temp (°C)	1/n	K_f ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$)	R^2	A_T (L mg^{-1})	b_T (L mg^{-1})	R^2	q_0 (mg g^{-1})	E (J mol^{-1})	R^2
30	0.36	3.56	0.98	1.10	3.60	0.98	13.21	408.25	0.85
45	0.28	6.25	0.95	4.36	3.38	0.97	16.17	790.57	0.91
60	0.23	9.69	0.91	24.00	3.18	0.92	19.08	2236.07	0.88

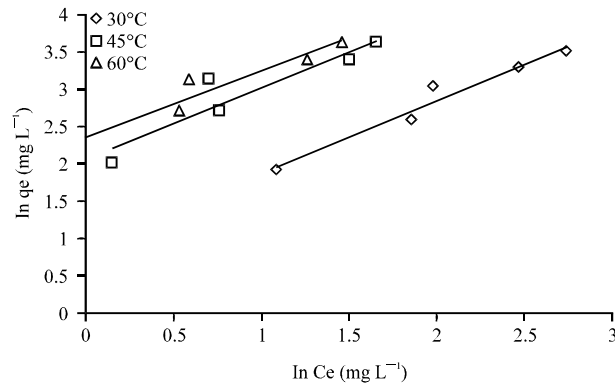


Fig. 9: Freundlich isotherm plot for Remazol Black B Reactive Dye adsorption onto CPHAC at different temperatures

where, C_0 is the highest initial dye concentration in solution, is used to confirm the favorability of the adsorption process, that is ($0 < R_L < 1$) favorable, $R_L = 1$ linear, $R_L = 0$ irreversible or $R_L > 1$ unfavorable (Langmuir, 1916). The values of R_L reported in Table 7a obtained at various temperatures were less than one, indicating that the adsorption of RBBR dye onto CPHAC is favorable.

Freundlich isotherm model: This assumes heterogeneous surface energies, in which the energy term in Langmuir varies as a function of the surface coverage. The linearized form of Freundlich model is represented by Freundlich (1906) where, q_e is the amount of RBBR dye adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}); k_f and n are constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium, respectively. Plots of $\log q_e$ versus $\log C_e$ gave linear graphs (Fig. 9) with lower values of R^2 compared to Langmuir model indicating that the adsorption data does not fits the Freundlich isotherm model. The parameters are reported in Table 7c.

The values of k_f and n from the graph are reported in Table 7c, it shows the heterogeneity of the material as well the possibility of multilayer adsorption of RBBR dye through the percolation process and the values of $1/n$ less than one indicates that the adsorption is favorable.

Temkin isotherm model: In order to consider the effect of the adsorbate interaction on the adsorbent, Temkin isotherm model was tested on the experimental data (Temkin and Pyzhev,

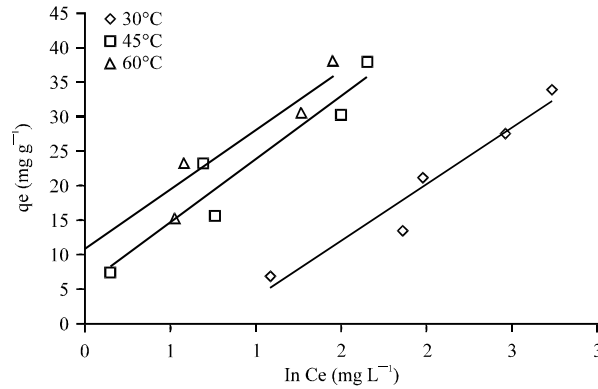


Fig. 10: Temkin isotherm plot for Remazol Black B Reactive Dye adsorption onto CPHAC at different temperatures

1940). where, A_T and b_T are constants, R is the gas constant and T is the temperature. A plot of q_e versus $\ln C_e$ gave a straight-line graph (Fig. 10) where, b_T and A_T values were calculated and presented in Table 7c. A_T increases as the temperature increases thereby inferring that the adsorbate interaction with adsorbent increased with increasing temperature hence, higher rate of sorption was observed as energy increases.

Dubinin-Radushkevich isotherm model, (D-R model): The D-R model (Dubinin and Radushkevich, 1947) which does not, assumes a homogeneous surface or a constant biosorption potential as the Langmuir model, is used to estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption. It was also used to test the experimental data. It is written as

$$q_e = q_0 e^{-\beta \epsilon^2} \tag{6}$$

where, β is the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from an infinite distance in the solution (mol^2/J^2), q_0 is the maximum adsorption capacity and ϵ is the Polanyi potential (J/mol) that can be written as:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{7}$$

A plot of $\ln q_e$ versus ϵ^2 gave a linear plot (Fig. 11) where, β and q_0 are obtained from the slopes and intercepts, respectively. The values are presented in Table 7c. Similarly, the β value obtained was then used to estimate the mean free energy of adsorption (E). The results are presented in Table 7c.

$$E = \frac{1}{\sqrt{2}\beta} \tag{8}$$

The values of E were found to be between the ranges 0.408-2.236 kJ mol^{-1} over the range of temperatures used in this study. Since $E < 8 \text{ kJ mol}^{-1}$, it suggests that the adsorption mechanism is physical in nature (Helfferich, 1962; Arivoli and Thenkuzhali, 2008; Dang *et al.*, 2009).

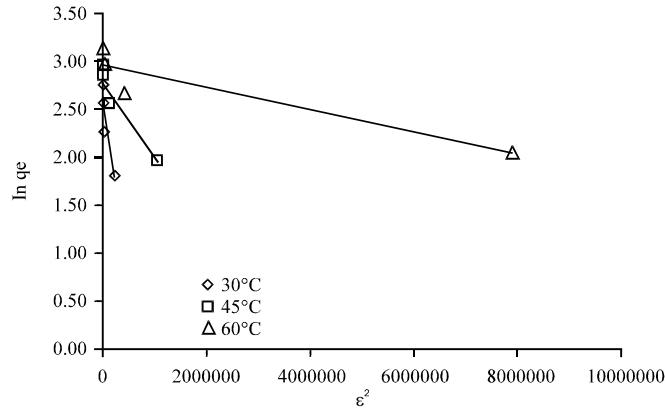


Fig. 11: Dubinin-Radushkevich isotherm plot for Remazol Black B Reactive Dye adsorption onto CPHAC at different temperatures

Thermodynamic studies: There are three thermodynamic parameters that must be considered to characterize the adsorption process; they are: the enthalpy (ΔH°), Gibb's free energy (ΔG°) and entropy (ΔS°) due to transfer of one mole of solute from the solution onto solid-liquid interface. The values of ΔH° and ΔS° can be obtained from the following equation:

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

where, R (8.314 J/mol/K) is the universal gas constant, T (°C) is the absolute solution temperature and K_L (L mg⁻¹) is the Langmuir isotherm constant i.e., b. The values of ΔH° and ΔS° can be calculated, respectively from the slope and intercept of the Van't Hoff plot of $\ln K_L$ versus $1/T$ (Fig. 12). ΔG° can then be calculated using the relation below:

$$\Delta G^\circ = -RT \ln K_L \quad (10)$$

In order to evaluate the activation energy of adsorption representing the minimum energy that reactants must have for the reaction to proceed, Arrhenius equation was applied. It is expressed as:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (11)$$

where, k_2 (g mg⁻¹ min) is the rate constant obtained from the pseudo second-order kinetic model, E_a (kJ mol⁻¹) is the Arrhenius activation energy of adsorption and A is the Arrhenius factor. When $\ln k_2$ was plotted against $1/T$, a straight line with slope of $-E_a/R$ was obtained (Fig. 13).

The calculated values of ΔH° , ΔS° and ΔG° for adsorption of RBBR dye on CPHAC are reported in Table 8. The important thermodynamic function ΔH° is very useful whenever a differential change occurs in the system. The positive ΔH° value obtained indicates that the adsorption process was endothermic in nature. Endothermic adsorption process could be due to the increased rate of

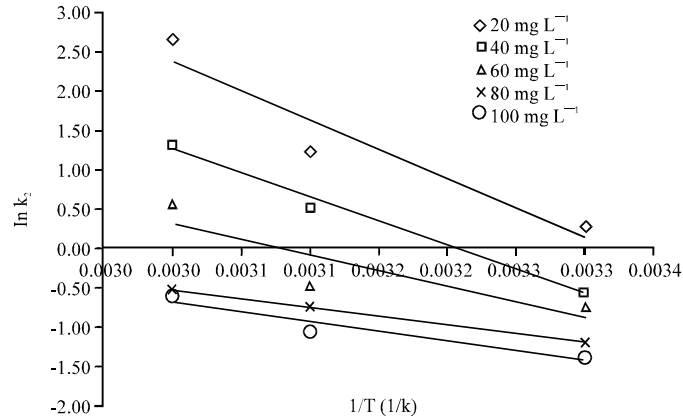


Fig. 12: Plots of $\ln k_2$ versus $1/T$ for adsorption of Remazol Black B Reactive Dye onto CPHAC at different temperatures

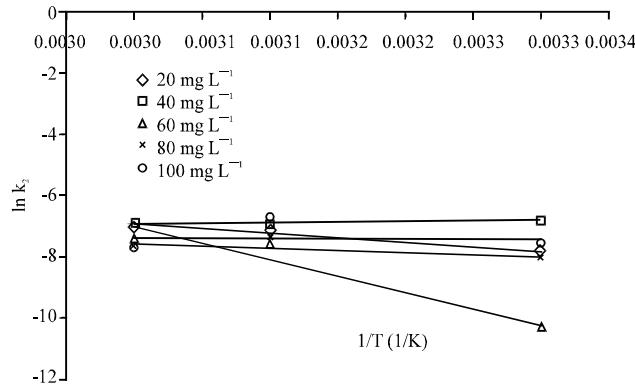


Fig. 13: Plots of $\ln k_2$ versus $1/T$ for adsorption of Remazol Black B Reactive Dye onto CPHAC at different temperatures

Table 8: Thermodynamic parameters for the adsorption of Remazol Black b Reactive Dye onto CPHAC at different temperatures

Concentration (mg L^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}$)	ΔG° (J mol^{-1})		
			30°C	45°C	60°C
20.00	61.77	204.87	-303.70	-3376.80	-6449.91
40.00	49.57	159.03	-1386.95	-998.50	-3383.96
60.00	32.80	101.01	-2195.34	-680.24	-834.86
80.00	20.76	56.57	-3022.20	-2262.54	-1502.88
100.00	18.37	50.64	-3617.94	-2769.37	-1920.79

diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbents as a result of increase in temperature (Wang and Zhu, 2007). The positive value of standard entropy change, ΔS° , shows increased randomness at the solid/solution interface occurring in the adsorption process reflecting the affinity of the adsorbent toward the RBBR dye molecules. The overall free energy change, ΔG° for RBBR dye adsorption was negative showing that the adsorption process is spontaneous. Besides, E_a value obtained was 34.6 kJ mol^{-1} , a value lower than

40 kJ mol⁻¹, indicating that the rate-limiting step in the Remazol Black B Dye adsorption process is physically controlled. This fact further confirmed that the adsorption of RBBR dye onto CPHAC is physisorption in nature.

CONCLUSIONS

The present investigation showed that CPHAC is an effective adsorbent for removal of RBBR dye from aqueous solution. Adsorption of RBBR dye was found to increase with increase in contact time, RBBR dye initial concentration and solution temperature. The Langmuir isotherm model and the pseudo-second order kinetic model were found to fit the adsorption data well. The effect of pH on the adsorption process was negligible. The intraparticle diffusion model was found to be more favorable compared to Elovich model in the adsorption process. In addition to this, the positive values of ΔH° indicated that the adsorption process was endothermic in nature. E_a value of 34.6 kJmol⁻¹ was obtained, showing that the rate-limiting step in the RBBR dye adsorption process is physically controlled.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support received in the form of research grants (PJ/KIMIA 814003 and PJ/AWAM 814021) from Universiti Sains Malaysia that resulted in this article. The one year Post Doctoral Fellowship jointly awarded by USM-TWAS to Dr. Olugbenga Solomon BELLO (FR Number: 3240223483 in Year 2009) of the Department of P/A Chemistry Ladoke Akintola University of Technology, P.M.B 4000, Ogbomoso, Oyo State, Nigeria and the 12 month study leave granted him by his host institution to honor this fellowship are equally acknowledged.

REFERENCES

- Ali, H. and S.K. Muhammad, 2008. Biosorption of crystal violet from water on leaf biomass of *Calotropis procera*. *J. Environ. Sci. Technol.*, 1: 143-150.
- Amin, N.K., 2008. Removal of acid blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics. *J. Hazard. Mater.*, 165: 52-62.
- Arivoli, S. and M. Thenkuzhali, 2008. Kinetic, mechanistic, thermodynamic and equilibrium studies on the adsorption of rhodamine B by acid activated low cost carbon. *Elect. J. Chem.*, 5: 187-200.
- Atmani, F., A. Bensmaili and N.Y. Mezenner, 2009. Synthetic textile effluent removal by skin almonds waste. *J. Environ. Sci. Technol.*, 2: 153-169.
- Aygun., A., S. Yenisooy-Karakas and I. Duman, 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. *Micropor. Mesopor. Mater.*, 66: 189-195.
- Babel, S. and T.A. Kurniawan, 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazar. Mat.*, 97: 219-243.
- Bello, O.S., A.I. Adeogun, C.J. Ajaelu and E.O. Fehintola, 2008. Adsorption of methylene blue onto activated carbon derived from periwinkle shells: Kinetics and equilibrium studies. *Chem. Ecol.*, 24: 285-295.
- Bello, O.S., M.A. Oladipo, M.A. Hameed and A.O. Popoola, 2010. Kinetic and Equilibrium studies of methylene blue removal from aqueous solution by adsorption on treated sawdust. *Maced. J. Chem. Chem. Eng.*, 29: 77-85.

- Buckley, C.A., 1991. Membrane technology for the treatment of dyehouse effluent. *Water Sci. Technol.*, 25: 203-209.
- Carliell, C.M., 1993. Biological degradation of azo dyes in an anaerobic system. M.Sc. Dissertation, University of Natal, Durban.
- Dang, V.B.H., H.D. Doan, T. Dang-Vu and A. Lohi, 2009. Equilibrium and kinetics of biosorption of Cd(II) and Cu(II) ions by wheat straw. *Bioresour. Technol.*, 100: 211-219.
- Demiral, H. and G. Gunduzoglu, 2010. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresour. Technol.*, 101: 1675-1680.
- Dubinin, M.M. and L.V. Radushkevich, 1947. Equation of the characteristic curve of activated charcoal. *Proc. Acad. Sci. Phys. Chem. Sect.*, 55: 331-333.
- Freundlich, H.M.F., 1906. Over the adsorption in solution. *J. Phys. Chem.*, 57: 385-470.
- Girods, P., A. Dufour, V. Fierro, Y. Rogaume, C. Rogaume, A. Zoulalian and A. Celzard, 2009. Activated carbons prepared from wood particleboard wastes: Characterisation and phenol adsorption capacities. *J. Hazard. Mater.*, 166: 491-501.
- Gokturk, S. and S. Kaluc, 2008. Removal of selected organic compounds in aqueous solutions by activated carbon. *J. Environ. Sci. Technol.*, 1: 111-123.
- Gupta, V.K. and I. Ali, 2002. Adsorbents for Water Treatment: Low-Cost Alternatives to Carbon. In: *Encyclopedia of Surface and Colloid Science*, Hubbard, A.T. (Ed.). Marcel Dekker, New York, pp: 136-166.
- Hameed, B.H. and A.A. Ahmad, 2009. Batch adsorption of methylene blue from aqueous solution by garlic peel and agricultural waste biomass. *J. Hazard. Mater.*, 164: 870-875.
- Hameed, B.H. and F.B.M. Daud, 2008. Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat. *Chem. Eng. J.*, 139: 48-55.
- Hao, O.J., H. Kim and P.C. Chiang, 2000. Decolorization of wastewater. *Crit. Rev. Environ. Sci. Technol.*, 30: 449-505.
- Helfferich, F., 1962. *Ion-Exchange*. McGraw-Hill Book, New York.
- Hertrampf, J.W. and F. Piedad-Pascual, 2003. *Handbook on Ingredient for Aquaculture Feeds*. Springer, USA.
- Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. *Process Biochem.*, 34: 451-465.
- Izadyar, S. and M. Rahimi, 2007. Use of beech wood sawdust for adsorption of textile dyes. *Pak. J. Biol. Sci.*, 10: 287-293.
- Lagergren, S. and B.K. Svenska, 1898. On the theory of so-called adsorption of stoffe. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24: 1-13.
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, 38: 2221-2295.
- Lori, J.A., A.O. Lawal and E.J. Ekanem, 2008. Adsorption characteristics of active carbons from pyrolysis of bagasse, sorghum and millet straws in ortho phosphoric acid. *J. Environ. Sci. Technol.*, 1: 124-134.
- Mall, I.D., V.C. Srivastava, N.K. Agarwal and I.M. Mishra, 2005. Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses. *Chemosphere*, 61: 492-501.
- Moazed, H., 2008. Ammonium ion removal from wastewater by a natural resin. *J. Environ. Sci. Technol.*, 1: 11-18.

- Nunes, A.A., A.S. Franca and L.S. Oliveira, 2009. Activated carbons from waste biomass: An alternative use for biodiesel production solid residues. *Bioresour. Technol.*, 100: 1786-1792.
- Oh, G.H. and C.R. Park, 2002. Preparation and characteristics of rice-straws-based porous carbons with high adsorption capacity. *Fuels*, 81: 327-336.
- Ozlem, T., H. Tanaci and Z. Aksu, 2009. Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. *J. Hazard. Mater.*, 163: 187-198.
- Senthilkumaar, S., P.R. Varadarajan, K. Porkodi and C.V. Subbhuraam, 2005. Adsorption of methylene blue onto jute fiber carbon: Kinetics and equilibrium studies. *J. Coll. Inter. Sci.*, 284: 78-82.
- Serra, J.B. and F.C. Ventura, 1999. Protein quality assessment in cocoa pod husk. *Food Res. Int.*, 32: 201-208.
- Slokar, Y.M. and A.M. Le Marechal, 1998. Methods of decoloration of textile Waste waters. *Dyes Pigments*, 37: 335-356.
- Suzuki, R.M., A.D. Andrade, J.C. Sousa and M.C. Rollemberg, 2007. Preparation and characterization of activated carbon from rice bran. *Bioresour. Technol.*, 98: 1985-1991.
- Sze, M.F.F. and G. McKay, 2010. An adsorption diffusion model for removal of para chlorophenol by activated carbon derived from bituminous coal. *Environ. Pollut.*, 158: 1669-1674.
- Tan, I.A.W., A.L. Ahmad and B.H. Hameed, 2008. Adsorption of basic dye on high-surface- area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *J. Hazard. Mater.*, 154: 337-346.
- Temkin, M.J. and V. Pyzhev, 1940. Recent modifications to Langmuir isotherms. *Acta Physiochim. USSR*, 12: 217-222.
- Tor, A. and Y. Cengeloglu, 2006. Removal of Congo red from aqueous solution by adsorption onto acid activated red mud. *J. Hazard Mater.*, 138: 409-415.
- Tseng, R.L., S.K. Tseng and F.C. Wu, 2006. Preparation of high surface area carbons from corncob with koh etching plus CO₂ gasification for the adsorption of dyes and phenols from water. *Coll. Surfaces A: Physicochem. Eng. Aspects*, 279: 69-78.
- Vandevivere, P.C., R. Bianchi and W. Verstraete, 1998. Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies. *J. Chem. Technol. Biotechnol.*, 72: 289-302.
- Vijayaraghavan, K., S.W. Won and Y.S. Yun, 2009. Treatment of complex Remazol dye effluent using sawdust- and coal-based activated carbons. *J. Hazard. Mater.*, 167: 790-796.
- Wang, S. and Z. Zhu, 2007. Effects of acidic treatment of activated carbons on dye adsorption. *Dyes Pigments*, 75: 306-314.