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ADSORPTION OF REMAZOL BLACK 5 ON THE COCONUT SHELL ACTIVATED CARBON-EQUILIBRIUM AND KINETICS STUDIES

Shanmugananthan. S*
S. Suganthi**
*Department of Chemical Engineering, Annamalai University, Annamalainagar- 608002
**Department of Genetic and Plant Breeding, Annamalai University, Annamalainagar- 608002

ABSTRACT

The removal of Remazol Black 5 from the synthetic wastewater using coconut shell activated carbon was investigated in terms of initial pH, initial concentration, contact time and temperature. The optimum pH was found at the acidic range, pH 2. For equilibrium studies, two isotherm models were used in this study, which is Freundlich and Langmuir, for different temperatures and it is found that Freundlich fitted experimental data very well. In the kinetics study, pseudo-first order and pseudo-second-order were tested; the equation showed the best represent the experimental data. The change in entropy and enthalpy for adsorption of the dye were estimated -24.42j/mol K and -9.426kJ/mol respectively.

Key Words: Remazol Black 5, coconut shell-AC, Isotherms model and Kinetics

1. Introduction

There are more than 100,000 types of commercially dyes with over $7x10^5$ tonnes of dyes created yearly. Direct, reactive, acid, disperse, pre-metalized, vat and basic dyes account for about 85% of the total dyes used in the industry. The total dye consumption of the textile industries alone is in excess of 107 kg/year an estimated 90% of this total end-up on fabric (Hameed et al. 2007). Consequently, approximately 106 kg/year of dyes are discharged into the waste streams by textile industries. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands (BOD), suspended solids and content in the toxic compounds but also for colour. Moreover, the human eye can detect the concentration of 0.005 mg/L of dye in water and therefore, presence of dye exceeding this limit would not be permitted on the aesthetic grounds (Pierce, 1994) and also may be toxic to the aquatic environment.

The typical textile dye wastewater composition is quite complex. These waste streams contain dyeing process auxiliaries that may include xylenes, phenols, buffers, bleaches and scouring agents, water softeners, surfactants, enzymes, caustic compounds and acids. Considering both volumes discharged and effluent composition, the wastewater generated by the textile industry is rated as the most polluting among all the industrial sectors (Reid and Green, 1996). Dye usually has a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. Textile dyes are also designed to be resistant to fading by chemicals and light. They must also be resilient to both high temperatures and enzyme degradation resulting from the detergent washing. For these reasons, biodegradation of dyes is typically a slow process. Due to the characteristics of dyes, wastewater containing dyes must be properly treated before being discharged to the environment, because even when released in small concentrations, it will impart colour that will consequently reduce the aesthetical value to the receiving water. These dyes were also found to have a potential chronic health hazard to human beings and other adverse impacts such as toxicity to aquatic life.

There are several methods are available for colour removal from wastewater such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, adsorption and reverse osmosis (Chandra et al. 2006). Some of these techniques have been shown to be effective although they have limitation such as the excess amount of chemical usage, or accumulation of concentrated sludge with disposal problems, lack of effective colour reduction, and sensitivity to a variable wastewater input (Santhy and Selvapathy, 2005). Among them, the adsorption process is widely used and most promising removal technique that produce effluents containing very low levels of dissolved organic compounds, but this application is limited by the high cost of adsorbents. If an activated carbon with high adsorption capacity can be produced from the low cost or waste materials then, its use as adsorbent should be economical (Chandra et al., 2006). Recently, attentions have been focused on the development of low-cost adsorbent for the application concerning the treatment of wastewater. The carbon derived from agricultural wastes is gaining importance as it inexpensive and are perfectly suitable for the removal of organic and inorganic contaminants from wastewater. Some of the materials used with varying success include: myrobalan, rubber

seed coat, cashew nut sheath, palm seed coat, palm tree flower, pongam seed coat sawdust, rice husk (Malik, 2003), rice shells, peanut shells, cottonseed shell cornelian cherry, apricot stone, almond shell (Demirbas et al., 2004), oak wood waste, corn hulls, corn stover (Zhang et al., 2004) and cotton stalks. At present, India is among the leaders in coconut farming. The country is the 3rd largest coconut producing country in the world with an annual production of more than 21,500 million tonnes of nuts. the production of various coconut based products like coconut chips, coconut milk, coconut sugar, coconut water, tender coconut water, coconut honey, coconut jaggery, coconut milkshake, coconut snacks, virgin coconut oil, coconut natural cream, more nee cookies and other products. Beside the production of coconut oil, a large amount of solid waste is also output from the coconut oil industry. For example, 2.5 million tonnes of solid waste in the form of oil coconut shells are produced annually and it creates a huge disposal problem (Ma, 2002). Realizing the scale of this waste, several studies were initiated to utilize coconut shell as the raw material for activated carbon production. The coconut shell was chosen to be applied as a precursor material due to its granular structure, insolubility in water, chemical stability, high mechanical strength and its local availability at almost no cost and also help to reduce the waste (ministry of Agriculture 2014). Hussein et al. (1996) were focused on the preparation and characterization of coconut shell activated carbon. Since little is known on the adsorption of reactive dye on coconut shell activated carbon, the adsorptive properties of the carbon should be observed.

1.1 Equilibrium Modelling

Adsorption isotherms or known as equilibrium data are the fundamental requirements for the design of adsorption systems. The Langmuir, Freundlich and Redlich-Peterson isotherms are the most frequently in the literature describing the non-linear equilibrium. The Langmuir isotherm is a theoretical isotherm developed in 1916 (Coulson and Richardson, 1991). This model is based on the few assumptions; all sites are identical and generically equivalent, thermodynamically this implies that each site can hold one adsorbate molecule, adsorption cannot proceed beyond monolayer; the ability of a molecule to be adsorbed at a given site is independent of the occupation of neighboring sites, which mean, there will be no interactions between adjacent molecules on the surface and immobile adsorption, i.e., trans-migration of the

adsorbate in the plane of the surface is precluded. For adsorption of solute from a liquid, the Langmuir isotherm is expressed as Equation (1):

$$q_e = \frac{K_L C_e}{1 + \alpha_L C_e} \quad (1)$$

Where L K is the constant related to overall solute absorptivity (l/g); L αis the constant related to the energy of adsorption (l/mg). The plot of q_e versus C_e will show a characteristic 'plateau'. The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is 'favourable' or 'unfavourable (Waber and Chakravorti, 1974). Hall et al. (1966) proposed a dimensionless separation factor, RL, as an essential feature of the Langmuir Isotherm which is defined as:

$$R_L = \frac{1}{1 + \alpha_L C_{ref}} \quad (2)$$

Where, C_{ref} is the reference fluid-phase concentration of adsorbate (mg/l) and αL is the Langmuir constant. For a single adsorption system, Cref is usually the highest fluid-phase concentration encountered. Value of RL indicates the shape of the isotherm accordingly as shown in Table 1 below

Table-1
Type of isotherm according to the value of RL

Value of RL	Type of Isotherm
0 < RL < 1	Favourable
RL > 1	Unfavourable
RL = 1	Linear
RL = 0	Irreversible

Value of RL Type of Isotherm 0 < RL < 1 Favourable RL > 1 Unfavourable RL = 1 Linear RL = 0 Irreversible

The Freundlich isotherm is commonly used to describe adsorption characteristics for the heterogeneous surface. Derived empirically in 1912 (Metcalf and Eddy, 2003), Freundlich isotherm can be expressed as Equation 3:

$$q_e = K_F C_e^{1/n} \tag{3}$$

Where; F K is the constant related to overall adsorption capacity (mg/g); n /1 is the constant related to surface heterogeneity (dimensionless). Therefore, plotting qe versus Ce yields a non-regression line which permits the determination of 1/n and KF Value of 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

1.2 Kinetics Modelling

Adsorption is a time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the dyes in wastewater. In many cases, the kinetics of adsorption based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo-second-order. The first-order rate expression of Lagergren (Lagergren, 1898; Annadurai and Krishnan, 1997) is given as:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \tag{4}$$

Where qe and qt are the amount of dye adsorbed on adsorbent at equilibrium and time t, respectively (mg/g), and k1 is the rate constant of first-order adsorption (min-1). Integrating equation (7) for the boundary conditions t = 0 to t = t is the following:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

The plot of log (qe-qt) versus t will give a straight line and the value of k_1 can be obtained from the slope of the graph. The second-order kinetic model is expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{6}$$

Where, k_2 is the pseudo-second-order rate constant of adsorption (g mg-1min-1). The linearised integrated form of (9) is given as:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

The values of e q and 2 k can be determined from the slope and intercept and there is no need to know any parameters beforehand. The pseudo-second-order kinetics model has been successfully applied to several biosorption systems as reported by McKay and Ho, 1999 and Otero et al., 2003.

1.3 Thermodynamic Modelling

The thermodynamic parameters such as change in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) can be determined by using the following equations:

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (8)$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (9)$$

Where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and *Kc* (L/g) is the standard thermodynamic equilibrium constant defined by *qe/Ce*. By plotting a graph of *ln Kc* versus *1/T*the values ΔH° and ΔS° can be estimated from the slopes and intercepts.

2. Experimental Technique

2.1 Materials

Throughout the experiment, coconut shell -based activated carbon (CS-AC) in granular form is used as an adsorbent with the size of 8-15 mm, which is supplied by Techno Chem Industries India Ltd. While, the reactive dye, Remazol Black 5 (RB5) is employed as an adsorbate. Accurately weighed was 1.000 g (+ 0.0005g) dye was dissolved in 1L distilled water to prepare a stock solution of synthetic test dye effluent and diluted with distilled water whenever necessary. The properties of and activated carbon used in the experiment are as shown in Table 2

Figure 1: Chemical structure of RB-5

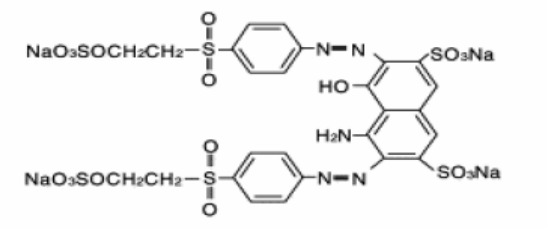


Table 2:
Product specification of coconut shell activated carbon (CS-AC)

Parameters	Typical value
Product	Coconut Shell Activated Carbon
Appearance	Black Granular & Irregular
Applications	Gas Application
Mesh Size	4 x 8 ASTM
CTC Adsorption	55-60 %
Over Size +	3.10%
Under Size -	2.60%
Bulk Density	0.499 gm /cc
Hardness	99.20%
Iodine no., mg/g	950-1150
Butane activity, %	20-30
CCl4 activity, %	55-70
Ball pan hardness,%	88- 96
Ash content,%	5 max
Apparent density,%	0.42-0.52
Moisture,%	5 max
pH	9-11
Particle size distribution,%	90
BET surface area, m2/g	1088

2.2 The Batch Adsorption Studies

The adsorption experiment was carried by adding a fixed amount of adsorbent (1.0 g) into 0.5 L of dye standard solution with the range of initial concentration within 50 to 500 mg/L (at optimum pH), which was put inside the 1L conical flask (Pyrex, England). The conical flask with activated carbon–dye mixture was then covered with aluminum foil to avoid evaporation of

dye solution before it is put into the incubator shaker (Cretomat Is) which operated at 150 rpm and with constant temperature 28ºC until it reaches equilibrium.

The amount of dye adsorbed which is also known as adsorption capacity, *qe*(mg/g) can be calculated from equation (10)

$$Q_e = \left(\frac{C_o - C_e}{m} \right) V \qquad (10)$$

Where *Co* is the initial concentration, *Ce* is the final concentration, *m* is the mass of adsorbent used and *V* is the volume of dye solution. Where $C_o$is the initial concentration, $C_e$is the final concentration, *m* is the mass of adsorbent used and *V* is the volume of dye solution.

2.3 Batch Experiment Study

The experiments were carried out at constant initial concentration, 200 mg/l at three different temperatures (30, 40 and 50ºC) and agitated at 150 rpm. The samples (1ml) were withdrawn before mixing the adsorbent and the dye bearing solution and at pre-determined time intervals; every 3 minutes for the first 30 minutes and at every 5 minutes for the next 30 minutes. For the next 120 minutes, sampling was in every 10 and 15 minutes. For the last 120 minutes, sampling was in every 60 minutes.

Equilibrium, Kinetics and Thermodynamic Studies: Adsorption of Remazol Black 5 on the Coconut Shell Activated Carbon (CS-AC)

2.4 Analysis of Dye

All the samples were analyzed using UV spectrophotometer (Genesys 10uv) at the maximum wavelength (λ_{max}) of 597 nm.

3. Results and Discussion

3.1 Effect of Initial pH

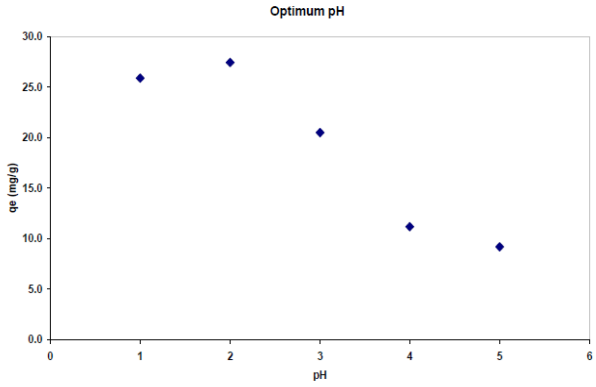
The pH value of dye solutions plays an important role in the whole adsorption process and particularly in adsorption capacities. In this study, the effect of pH can be explained by

considering the surface charge on the adsorbent. The effect of initial pH on adsorption capacity was studied in the range of 1.0 – 5.0 at 50 mg/l initial dye concentration. From the study, the adsorption of the dye is highly pH dependent, which can be shown in Figure 2.

The removal of the dye by CS-AC was found to be in the acidic range, which is pH 2, with maximum uptake at 27.44 mg/g, and then, the uptake was declined significantly. Solution pH influences both the carbon surface dye binding sites and the dye chemistry in the water. At lower pH values, the carbon will have a net positive charge. Higher uptakes obtained at lower pH may be due to the electrostatic attractions between negatively charged functional groups located on the reactive dye and positively charged adsorbent surface. Hydrogen ion also acts as a bridging ligand between the adsorbent wall and the dye molecule (Aksu and Tezer, 2004). The reduction in adsorption capacity of dye on adsorbent with increasing pH can be attributed to change in surface characteristics and charge

As the pH of the system increases, the number of hydroxide ion increases and will compete with anionic ion of the dye on the adsorption site in the alkaline condition and could reduce the adsorption capacity since the number of positively charged sites decreases. Moreover, there are also more exchangeable anions on the outer surface of the adsorbent. A negatively charged surface site on the adsorbent does not favour the adsorption of dye ions due to electrostatic repulsion and abundance ofOH^- ion.

Figure 2: Effect of initial pH (pH 1-5) on adsorption capacity of (CS-AC) activated carbon (wt = 0.1 g, C_o = 50 mg/l and agitated for 24 hours)



3.2 Equilibrium Modelling

The experimental data were fitted with selected adsorption isotherm. Figures 3 to 6 show the isotherm models plot for adsorption of Remazol Black 5 (RB 5) onto the activated carbon. All the values of parameters and correlation coefficient of each model obtained are tabulated in Table 3. From the correlation coefficient (R^2) values of all isotherm equations, it is found that the Freundlich isotherm an empirical for heterogeneous surface fitted very well the experimental data. However, the Langmuir model did not fit the experimental data very well. The maximum uptake of the dye was 98.6 mg/g, it is showed that coconut shell based granular activated carbon has a potential to be a good adsorbent that can be employed in wastewater treatment due to its rather high adsorption capacity and availability.

Table 3
The values of parameters and correlation coefficient for each isotherm model

Temperature (°C)	Langmuir Isotherm				*Freundlich Isotherm*		
	a_L	K_L	R_L	R^2	K_F	*1/n*	R^2
30	0.13	7.65	0.015	0.47	28.62	0.12	0.99
40	0.11	10.53	0.017	0.75	31.58	0.2	0.97
50	1.13	99.75	0.002	0.6	44.89	0.14	0.96

3.3 Kinetics Modelling

The first order rate constant (k_1) and equilibrium uptake (qe,calc) value were determined from the nonlinear form of the pseudo-first-order kinetic model at all temperatures used in this study. The values of rate $k_1$and R^2 are presented in Table 4. The first order rate constants exhibited a notable decrease with increasing temperature. The correlation coefficients obtained at every temperature are more than 0.96.

Table 4
The comparison of the first-order and second-order rate constant and correlation coefficients at different temperature

Temperature (K)	Pseudo-first order kinetic model		Pseudo-second order kinetic model	
	k_1	R^2	k_2	R^2
303.15	0.017	0.96	0.0009	0.97
313.15	0.016	0.98	0.0007	0.96
323.15	0.012	0.97	0.0006	0.92

Using the equation (7), *t/q* was plotted against *t*, and second-order rate constant and equilibrium uptake value were determined from the slope and intercept (the figure not shown). The values of second-order rate constant and equilibrium uptake were also presented in Table 4. As shown in the table, the rate constant for the second-order kinetic model decreased as the temperature increases. The correlation coefficients obtained at various temperatures used were more than 0.92.

Both adsorption constant rate were affected by the increasing of temperature. These suggest that each of the sorption processes can be described using the first-order kinetic model with fairly high correlation coefficients.

3.4 Thermodynamics Studies

In order to determine thermodynamic parameters, experiments were carried out at three different temperatures (30 – 50 C). Using the equation 10, the values of entropy change S and enthalpy change H can be calculated from the intercept and slope of the plot of *ln Kc* vs. *1/T* as shown in Figure. All the parameters obtained from the plotted graph are tabulated in Table 5.

Equilibrium, Kinetics and Thermodynamic Studies: Adsorption of Remazol Black 5 on the Coconut Shell Activated Carbon (CS-AC)

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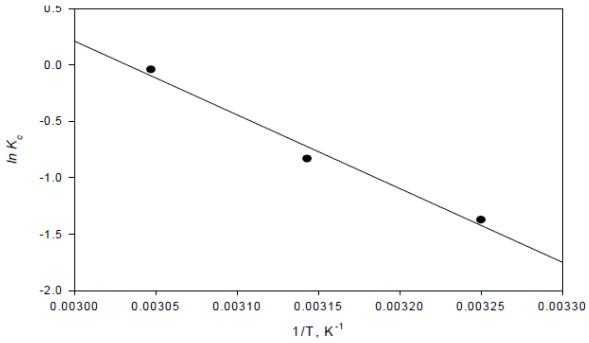
Table 5
Thermodynamic parameters of RB 5

Temperature (K)	Thermodynamic parameters		
	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)
303.15	-1.77		
313.15	-1.53	-24.42	-9.246
323.15	-1.29		

Figure 3
The plot of *ln Kc* vs. *1/T* for estimation of thermodynamic parameters



The negative G value obtained from equation 11 confirmed that the feasibility of the adsorption process and the spontaneous nature of the adsorption. A negative value of H indicates the exothermic nature of the process. This is also confirming the possibility of physical adsorption as with the increase in temperature f the system (Singh and Pant, 2004). Moreover, the negative value of S corresponds to a decrease in the degree of freedom of the adsorbed species.

4. Conclusion

The results of this study indicate that CS-AC can be successfully used for the adsorption of RB 5 from aqueous solutions. Freundlich isotherm well fitted with the equilibrium data for adsorption of RB5 dye, and the maximum adsorption capacity was determined to be 58.8, 96.7 and 98.6 mg/g at 30, 40, and 50 ◦C, respectively. The *R*L values showed that palm ash was favourable for the adsorption of RB 5 dye. Two simplified kinetic models, pseudo-first order, and pseudo-second-order were tested to investigate the adsorption mechanism. The pseudo first-order kinetic model fits very well with the dynamical adsorption behaviour of RB5 dye. The

negative values of ΔG° and ΔH° obtained indicated that the AG25 dye adsorption process is spontaneous and an endothermic.

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