

# Dye adsorption on unburned carbon: Kinetics and equilibrium

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## Abstract

Unburned carbon in fly ash is an important by-product from coal combustion. In this investigation, unburned carbon has been separated from fly ash and been employed as a low cost adsorbent for a basic dye adsorption (Rhodamine B) in aqueous solution. Adsorption isotherm and kinetics of adsorption have been investigated using batch experiments. It is found that dye adsorption capacity depends on initial concentration, pH of solution, and temperature. The adsorption isotherm can be described by Langmuir model and the adsorption capacity of Rhodamine B at 30, 40, and 50 °C can reach  $9.7 \times 10^{-5}$ ,  $1.14 \times 10^{-4}$ , and  $1.5 \times 10^{-4}$  mol g<sup>-1</sup>, respectively. The pseudo first- and second-order kinetic models have been employed to fit the dynamic adsorption. It is found that the dynamic adsorption follows the pseudo second-order model. Thermodynamic calculations indicate that the adsorption is endothermic reaction with  $\Delta H^\circ$  at 25 kJ mol<sup>-1</sup>.

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**Keywords:** Unburned carbon; Dye adsorption; Kinetics; Adsorption isotherm

## 1. Introduction

Dyes and pigments from several industrial branches can be emitted into water systems. The presence of dye in water is highly visible and affects water transparency, resulting in reduction of light penetration, and gas solubility in water. Moreover, several commonly used dyes have been reported to be carcinogenic and mutagenic for aquatic organisms. Removal of such compounds are difficult while many physical and chemical methods including adsorption, coagulation, precipitation, filtration, ozonation, and oxidation have been used for the treatment of dye-containing effluent [1]. The adsorption process provides an attractive alternative for the treatment of contaminated waters, especially, if the sorbent is inexpensive and does not require an additional pre-treatment step before its application [2].

Fly ash is a by-product of fuel combustion and its chemical compositions are influenced by the fuel source and the

combustion conditions. Unburned carbon is always present in fly ash at various contents. High content of the unburned carbon in fly ash limits the application of fly ash for cement production. Due to more stringent environmental regulations, especially, concerning NO<sub>x</sub> emissions, there is an alarming rise of unburned carbon in fly ash from coal combustion processes. Research on the physical properties of unburned carbon reveals that unburned carbon is a type of carbon powder composed of microsized particles, whose carbon content can be as high as 73–91%, and ash component approximately 5–19% [3]. The unburned carbon possesses adsorptive ability since it has gone through a devolatilisation process while in the combustor. However, the fate of unburned carbon is mainly disposal due to the present lack of routes for their effective use. In recent years, unburned carbon has been explored as low cost adsorbents replacing activated carbon for flue gas treatment [4,5]. However, no investigations have been conducted using unburned carbon for water treatment. Our previous investigation has shown that unburned carbon plays an important role for adsorption in fly ash [6]. In this paper, we report our investigation on adsorp-

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tion isotherm and kinetics of dye adsorption on unburned carbon.

## 2. Experimental

### 2.1. Adsorbent and dye material

Fly ash (FA) was obtained from a power station in Western Australia. The chemical compositions of the raw fly ash are SiO<sub>2</sub> (55%), Al<sub>2</sub>O<sub>3</sub> (29%), Fe<sub>2</sub>O<sub>3</sub> (8.8%), CaO (1.6%), MgO (1.0%), and 5% unburned carbon. To obtain the unburned carbon from fly ash, we used a physical sieving method to separate the raw fly ash to get a carbon-rich sample and then employed a water washing method to get higher concentrated unburned carbon sample (UC). Analysis of carbon content of the unburned carbon indicates that the carbon content is 85%. N<sub>2</sub> adsorption gave the specific surface area and pore volume as 224 m<sup>2</sup> g<sup>-1</sup> and 0.16 cm<sup>3</sup> g<sup>-1</sup>, respectively. SEM observation also shows that the unburned carbon has a well-developed porous structure [6].

A basic dye, Rhodamine B (RB), was obtained from AJAX Chemical. Rhodamine B has moderate wash and light fastness properties on wool and has been used for dyeing silk, wool, jute, leather, and cotton. It is also a useful analytic reagent. The molecular formula is C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>Cl with molecular weight of 479.0 g mol<sup>-1</sup>. Fig. 1 shows its chemical structure. A stock solution with concentration at 10<sup>-4</sup> M was prepared and the solutions for adsorption tests were prepared from the stock solution to the desired concentrations (from 10<sup>-6</sup> to 10<sup>-5</sup> M).

### 2.2. Sorption test

Adsorption kinetics and isotherm experiments for unburned carbon were undertaken in a batch equilibrium technique. The adsorption of dye was performed by shaking 0.005–0.010 g of solids in a 200 ml of dye solution with varying concentrations at 100 rpm (Certomat R shaker from B. Braun) at different temperatures. The determination of dye concentration was done spectrophotometrically on a Spectronic 20 Genesis Spectrophotometer (USA) by measuring absorbance at λ<sub>max</sub> of 556 nm.

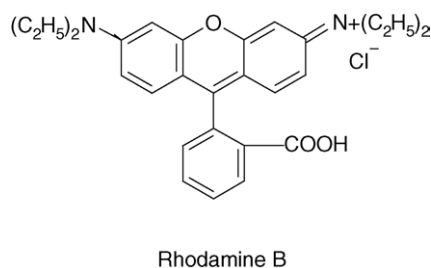


Fig. 1. Chemical structure of Rhodamine B.

The data obtained from the adsorption tests were then used to calculate the adsorption capacity,  $q_t$  (mol g<sup>-1</sup>), of the adsorbent by a mass–balance relationship, which represents the amount of adsorbed dye per amount of dry adsorbent,

$$q_t = \frac{C_0 - C_t}{W} V \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of dye in solution (mol dm<sup>-3</sup>) at time  $t=0$  and  $t$ , respectively,  $V$  the volume of the solution (dm<sup>3</sup>), and  $W$  is the weight of the dry adsorbent used (g).

## 3. Results and discussion

### 3.1. Dynamic adsorption and kinetics

Fig. 2 presents the dynamic adsorption of RB on unburned carbon at different initial concentrations. One can see that adsorption is fast before 20 h, and then it approaches to equilibrium. The time profile of dye adsorption is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the unburned carbon. The adsorption capacity generally increases with the increasing initial concentration and the adsorption equilibrium can reach as high as  $1.5 \times 10^{-4}$  mol g<sup>-1</sup>.

It is well-known that pH of solution influences the adsorption of dyes on adsorbent. Most of the dyes are ionic and upon dissociation release conferred dye ions into solution. The degree of adsorption of these ions onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. To study the influence of pH on the adsorption capacity, experiments were performed using various initial pH solutions. Fig. 3 shows the dynamic adsorption of Rhodamine B on unburned carbon at three different pH values. It is seen that the amount of adsorption increases as the pH is increasing. At low pH, the adsorption changes little while the adsorption

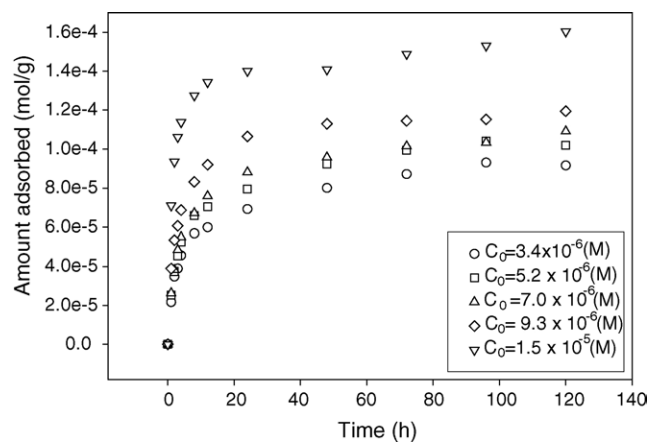


Fig. 2. RB adsorption on unburned carbon at different initial concentrations.

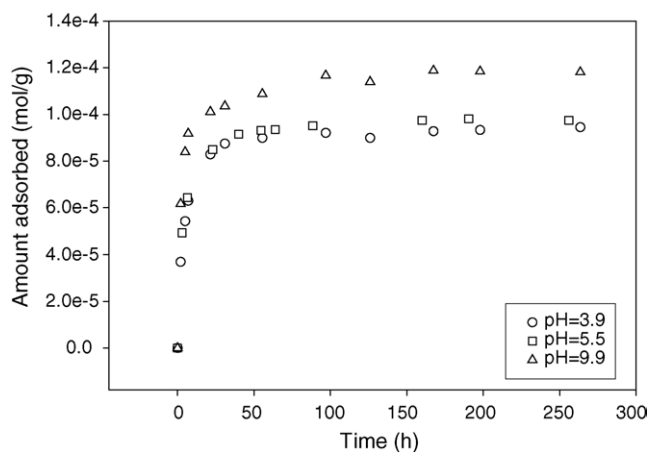


Fig. 3. Effect of pH on RB adsorption on unburned carbon.

shows large difference at high pH. Lower adsorption of RB at acidic pH is probably due to the presence of excess  $H^+$  ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye, RB and the surface of the carbon is lowered, which may result in an increase in the rate of adsorption.

The adsorption experiments were also conducted at various temperatures and the amount of adsorption variation with time is shown in Fig. 4. It is seen that temperature significantly influences the adsorption capacity. High temperature results in high adsorption, suggesting the endothermic property. The adsorption at  $50^\circ C$  can reach  $1.5 \times 10^{-4} \text{ mol g}^{-1}$ .

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. Successful application of the adsorption demands innovation of cheap, easily available and abundant adsorbents of known kinetic parameters, and sorption characteristics. Adsorption kinetics can be

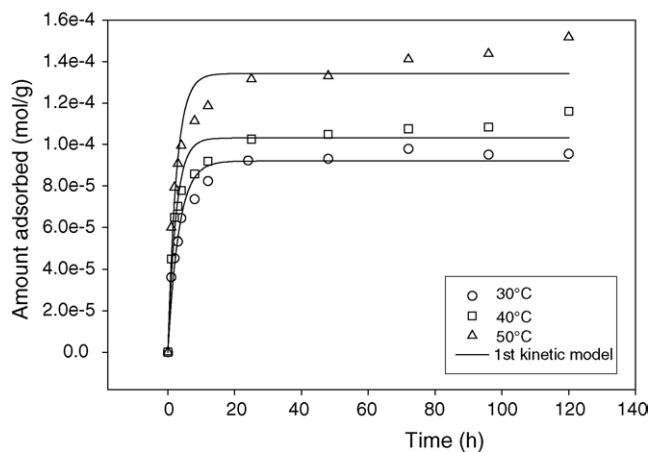
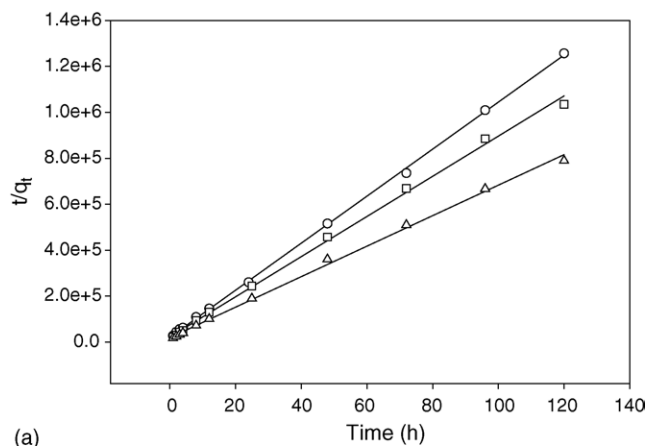
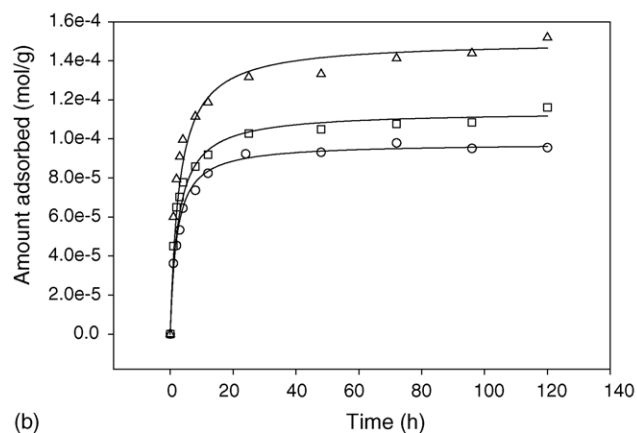


Fig. 4. Effect of temperature on RB adsorption on unburned carbon and fitting of pseudo first-order kinetic model.



(a)



(b)

Fig. 5. Plots of pseudo second-order kinetics of RB on unburned carbon: (a) linear and (b) experimental form.

modelled by several models, the pseudo first-order Lagergren equation and pseudo second-order rate equation given below as Eqs. (2) and (3), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad (3)$$

where  $k_1$  is the rate constant of pseudo first-order adsorption ( $\text{h}^{-1}$ ),  $k_2$  ( $\text{g mol}^{-1} \text{h}$ ) the rate constant of pseudo second-order adsorption,  $q_e$  and  $q_t$  are amount of dye adsorbed on adsorbent ( $\text{mol g}^{-1}$ ) at equilibrium and at time  $t$ , respectively.

For the pseudo first-order kinetic model, Eq. (2) can be transformed to Eq. (4), which can be used to predict the adsorption equilibrium.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

Figs. 4 and 5 presents the curves for fitting experimental data at different temperatures using the pseudo first-order and pseudo second-order kinetic models. As shown that the first model seems not good in modelling the kinetics and the regression coefficients are less than the ones obtained from

Table 1  
Parameters of kinetic models on unburned carbon

$T$ (°C)	Pseudo first-order model			Pseudo second-order model		
	$k_1$ (h <sup>-1</sup> )	$q_e$ (mol g <sup>-1</sup> )	$R^2$	$k_2$ (g mol <sup>-1</sup> h)	$q_e$ (mol g <sup>-1</sup> )	$R^2$
30	0.30	$9.21 \times 10^{-5}$	0.963	4994.9	$9.77 \times 10^{-5}$	0.999
40	0.42	$1.03 \times 10^{-4}$	0.942	3468.6	$1.14 \times 10^{-4}$	0.998
50	0.40	$1.34 \times 10^{-4}$	0.937	2329.0	$1.50 \times 10^{-4}$	0.998

the second-order kinetics (Table 1). From the results, it is also seen that the equilibrium adsorption from the pseudo second-order model are much close to the experimental data, suggesting the better application of the second-order kinetics.

The pseudo second-order rate constant of dye adsorption is expressed as a function of temperature by the Arrhenius-type relationship

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (5)$$

where  $E_a$  is the Arrhenius activation energy of sorption, representing the minimum energy that reactants must have for the reaction to proceed,  $A$  the Arrhenius factor,  $R$  the gas constant and is equal to  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $T$  is the solution temperature. When  $\ln k_2$  is plotted versus  $1/T$ , a straight line with slope  $-E_a/R$  is obtained and shown in Fig. 6. The activation energy is obtained as  $-31 \text{ kJ mol}^{-1}$ . This suggests that the adsorption is not a chemically activated process but a physical diffusion process. Ho and Chiang [7] investigated the adsorption of an acid dye onto the mixture of activated clay and activated carbon and found that the kinetics of acid dye adsorption followed the pseudo second-order rate expression and the activation energy was  $-11.7 \text{ kJ mol}^{-1}$ .

The thermodynamic parameters such as change in standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) were determined by using the following equations [8] and are given in Table 2,

$$K_C = \frac{C_A}{C_S} \quad (6)$$

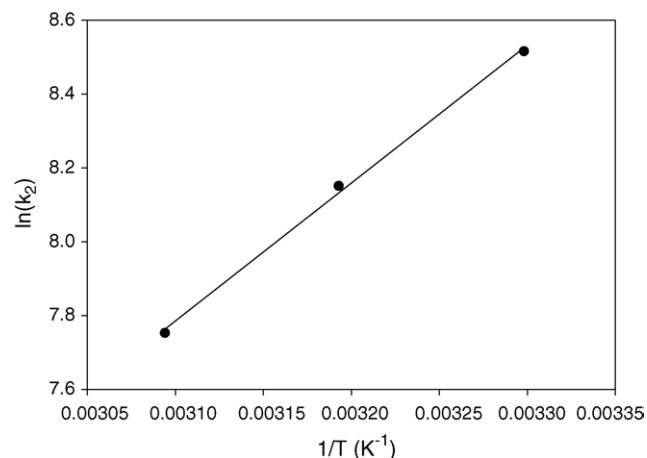


Fig. 6. Arrhenius plot of the pseudo second-order kinetics.

Table 2  
Parameters of kinetic models on unburned carbon

$T$ (°C)	$K_C$	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J K mol <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )
30	9.97	-5.8			
40	12.80	-6.6	25.2	102.1	-31.0
50	18.57	-7.8			

$$\Delta G^0 = -RT \ln K_C \quad (7)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where  $K_C$  is the distribution coefficient for the adsorption,  $C_A$  the amount of dye (mol) adsorbed on the adsorbent per dm<sup>3</sup> of the solution at equilibrium, and  $C_S$  is the equilibrium concentration (mol dm<sup>-3</sup>) of the dye in the solution.  $T$  is the solution temperature (K) and  $R$  is the gas constant.  $\Delta H^0$  and  $\Delta S^0$  were calculated from the slope and intercept of van't Hoff plots of  $\ln K_C$  versus  $1/T$  (see Fig. 7). The results of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  are listed in Table 2. It is seen that the adsorption process is spontaneous with the negative values of  $\Delta G^0$ . The standard enthalpy change ( $\Delta H^0$ ) for the adsorption on unburned carbon is positive indicating that the process is endothermic in nature. The adsorption of dyes on adsorbents involves several processes, diffusion, and surface reaction. The kinetic calculation has suggested that the process is not a surface chemical reaction but a diffusion process, as diffusion is an endothermic process. The positive value of  $\Delta S^0$  shows

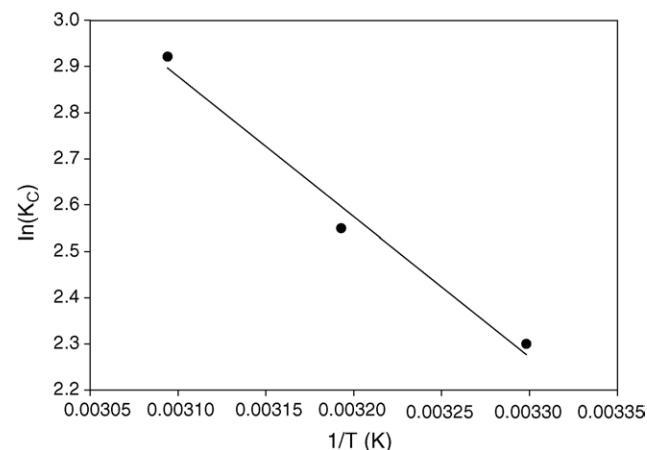


Fig. 7. Plot of  $\ln K_C$  vs.  $1/T$  for estimation of thermodynamic parameters.

Table 3  
Parameters of kinetic models on unburned carbon

$T$ (°C)	Langmuir isotherm				Freundlich isotherm		
	$K_L$ (dm <sup>3</sup> mol <sup>-1</sup> )	$q_{\max}$ (mol g <sup>-1</sup> )	$R^2$	$R_L$	$1/n$	$K_F \cdot \{\text{mol g}^{-1} (\text{L mol}^{-1})^{1/n}\}$	$R^2$
30	$2.82 \times 10^6$	$9.68 \times 10^{-5}$	0.898	0.020	0.0416	$1.49 \times 10^{-4}$	0.880
40	$4.03 \times 10^6$	$1.14 \times 10^{-4}$	0.904	0.014	0.0471	$1.89 \times 10^{-4}$	0.892
50	$1.57 \times 10^6$	$1.49 \times 10^{-4}$	0.955	0.035	0.140	$6.97 \times 10^{-4}$	0.933

increased disorder at the solid–solution interface during the adsorption of dye. The adsorption increases randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent, and an affinity of the adsorbent toward RB [1,9].

### 3.2. Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Several isotherms equations are available and the two important isotherms are selected in this study, the Langmuir and Freundlich isotherms.

The well-known expression of the Langmuir model is:

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (9)$$

where  $q_e$  is the equilibrium dye concentration on adsorbent (mol g<sup>-1</sup>),  $C_e$  the equilibrium dye concentration in solution (mol dm<sup>-3</sup>),  $q_{\max}$  the monolayer capacity of the adsorbent (mol g<sup>-1</sup>), and  $K_L$  is the Langmuir adsorption constant (dm<sup>3</sup> mol<sup>-1</sup>) which relates to the adsorption energy. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal sorption activation energy.

On the other hand, the Freundlich equation is:

$$q_e = K_F C_e^{1/n} \quad (10)$$

where  $q_e$  is the equilibrium dye concentration on adsorbent (mol g<sup>-1</sup>),  $C_e$  the equilibrium dye concentration in solution (mol dm<sup>-3</sup>), and  $K_F$  (dm<sup>3</sup> g<sup>-1</sup>) and  $n$  are the Freundlich constants characteristic of the system, indicators of adsorption capacity and adsorption intensity, respectively. The Freundlich equation is employed to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayers.

Fig. 8 shows the adsorption isotherms of RB on unburned carbon at different temperatures and the fitted curves using the two equilibrium isotherms. The parameters for two isotherms obtained from experimental data are presented in Table 3. As seen that the adsorption equilibrium obtained from Langmuir isotherm is quite close to the experimental data and the regression coefficients are better than those obtained from Freundlich isotherm, suggesting the nonapplicability of Freundlich model to this system.

From the Langmuir parameter,  $K_L$  at different temperatures, we can also estimate the thermodynamic parameter, enthalpy, using the van't Hoff Eq. (11). The enthalpy ( $\Delta H^0$ )

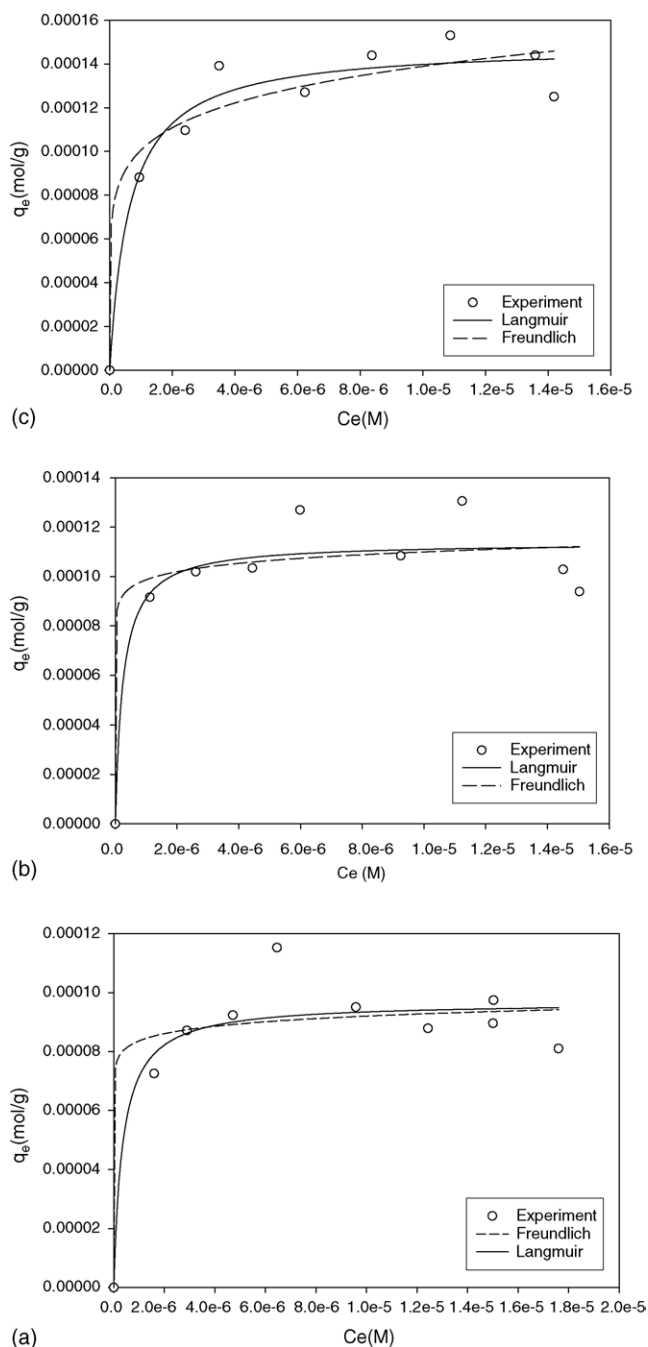


Fig. 8. RB adsorption isotherms on unburned carbon at different temperatures: (a) 30 °C; (b) 40 °C; (c) 50 °C.



Table 4  
Comparison of adsorption capacity for various adsorbents

Dye	Adsorbent	Capacity (mol g <sup>-1</sup> )	References
Methylene blue	Activated carbon from coconut shell	$0.52 \times 10^{-4}$	[9]
Methyl orange	Activated carbon from coconut shell	$0.29 \times 10^{-4}$	[9]
Methylene blue	Fly ash	$0.14 \times 10^{-4}$	[2]
Methylene blue	Red mud	$0.078 \times 10^{-4}$	[2]
Malachite green	Activated carbon from fertiliser waste	$1.25 \times 10^{-4}$	[11]
Malachite green	Blast furnace slag	$1.05 \times 10^{-4}$	[11]
RB	Iron humate	$0.44 \times 10^{-4}$	[12]
RB	rice husk-based porous carbons	$7 \times 10^{-4}$	[13]
RB	Bagasse fly ash	$(1.18-1.43) \times 10^{-4}$	[14]
RB	Activated carbon from pistachio shells	$(1.6-1.9) \times 10^{-4}$	[15]
RB	Carbon from fertiliser waste	$(1.7-1.9) \times 10^{-4}$	[16]
RB	Unburn carbon	$(0.97-1.5) \times 10^{-4}$	This work

at 30–50 °C is obtained as 23.8 kJ mol<sup>-1</sup>, which is close to the value obtained from the kinetic studies:

$$\Delta H^0 = -R \left( \frac{T_2 T_1}{T_2 - T_1} \right) \ln \frac{K_{L2}}{K_{L1}} \quad (11)$$

For Langmuir isotherm, a method has been adapted to calculate the dimensionless separation factor ( $R_L$ ) [10], which splendidly determines the favourability and the shape of the isotherm of the adsorption process by applying the equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (12)$$

where  $K_L$  signifies the Langmuir constant and  $C_0$  is the initial concentration. The value of  $R_L$  indicates the type of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). The calculated values of separation factor for the adsorbent at different temperatures are presented in Table 3. It is clear from the table that all the values of  $R_L$  are less than unity, confirming thereby the favourable adsorption process.

Several investigations have been conducted using various wastes for dye adsorption. Table 4 presents a comparison of the adsorption capacity of the results. It is seen that unburned carbon in this report shows the comparable adsorption capacity to other activated carbons, revealing that unburned carbon can be employed as a promising adsorbent for dye adsorption.

#### 4. Conclusion

Equilibrium and kinetic studies were conducted for dye adsorption on unburned carbon separated from fly ash in aqueous solution. The adsorption of Rhodamine B was found to be dependent on solution pH, adsorption temperature, and concentration. A comparison of the kinetic models and the overall adsorption capacity was best described by the pseudo

second-order kinetic model. Equilibrium data agree well with Langmuir's isotherm model.

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