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## Adsorption of Congo Red Dye Using Rice Husk

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### ABSTRACT

The potential of rice husks powder (RHP), for the removal of Congo red dye from aqueous solution was investigated. Batch adsorption studies were conducted and various parameters such as contact time, adsorbent dosage, initial dye concentration, pH and temperature were studied to observe their effects in the dye adsorption process. The optimum conditions for the adsorption of CR onto the adsorbent (RHP) was found to be: contact time (100 min) pH (10.0) and temperature (303 K) for an initial dye concentration of 50 mg/l and adsorbent dose of 1.0 g respectively. The experimental equilibrium adsorption data fitted best and well to the Freundlich Isotherm model for both dyes adsorption. The maximum adsorption capacity was found to be 33.88 mg/g for the adsorption of CR dye. The kinetic data conformed to the pseudo second order kinetic model. Thermodynamic quantities such as Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were evaluated and the negative values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  obtained indicate the spontaneous and exothermic nature of the adsorption process.

**Keywords:** Rice husks powder, Congo red, adsorption, kinetics, thermodynamics, Langmuir models, Freundlich model, Van't Hoff equation

### 1. INTRODUCTION

Several synthetic dyes are used in different industries such as Food, Cosmetics, Paint, Paper, Pharmaceutical, Textile Industries for different purposes. Among these industries, textile

industries are the largest consumers of dye and producers of dye effluent compared to other industries [1]. The effluents produced from textile industries are discharged into water bodies which cause environmental pollution due to high toxicity, high organic loading and aesthetic pollution related to colour [2], thereby causing lack of light penetration and inhibit effect of photosynthesis of aquatic organism [3, 4]. There has being different processes or methods used for removal of dyes from waste water such as biological (aerobic and anaerobic), precipitation, flocculation/ coagulation, filtration, oxidation, ion exchange, adsorption [5-7] etc., in which adsorption process has proven to be more cost effective, insensitive to toxic substances and efficient in dye removal from waste water [8]. Although, activated carbon is widely used as an effective adsorbent for dye removal from waste water due to its high adsorption capacity, but due to high cost of production and regeneration process which is a limitation to its application and efficiency lead to a constant search for other low cost adsorbents [9]. Numerous investigations have been carried out using byproducts of agricultural waste for removal of dyes from aqueous solutions [10]. In this study, rice husks powder was undertaken to analyze the possibility of using it as alternative and economic adsorbent for removal of Congo red (CR) from aqueous solutions.

## **2. MATERIALS AND METHODS**

### **2. 1. Preparation of adsorbent**

Agricultural waste (Rice husk) was obtained from local rice procedure in Abakiliki, Ebonyi State, Nigeria. The rice husk was screened and washed thoroughly with running water to remove sand and dirt After that, it was dried in an oven (at 50 °C) until moistures were removed. The dried samples were ground and sieved in a sieve shaker of particle size 300, 250 and 150 µm fine powder of rice husk powder (RHP) The fine powder adsorbent was stored in separate air tight container ready for further experiments.

### **2. 2. Preparation of adsorbate**

Congo red (CR) was chosen because of its known strong adsorption onto solids. Stock solution of CR dye were prepared by dissolving 1 g of dye in 1L distilled water respectively to give the concentration of 1000 mg/L. Experimental dyes solutions of desired concentrations were obtained by appropriate dilution of respective stock solution.

### **2. 3. Adsorption Experiment**

Adsorption experiments were carried out by batch adsorption techniques at room temperature with fixed adsorbent (RHP) dose of 1g into different 250 ml conical flasks containing 40 ml of different initial concentrations (25, 50, 75, 100 and 125 mg/L) of dye solution. The effect of pH on CR dye removal was studied by shaking 100 ml of 50 mg/L of CR dye solution concentration with 1 g adsorbent dose in conical flasks, adjusted by adding a few drops of diluted 0.1M NaOH or 0.1M HCl and measured by using a pH meter at pH of (2, 4, 6, 8, and 10). The effect of contact time and temperature were studied by shaking 100 ml 50 mg/L CR solutions concentration with 1 g. adsorbent in a 250 ml conical flask. After definite time intervals (10, 20, 40, 60, 80, 100, and 120 minutes) with temperature (30, 40, 50, 60, 70 °C). Adsorbent dose effect was studied using 50 mg/L CR solution concentration respectively. After an optimum time 60 minutes for CR, the samples were filtered using a Whatman No. 1

filter paper from the flask, the residual dye concentration of the supernatant solution was analyzed using a UV-Visible Spectrophotometer.

## 2. 4. Isotherm Experiment

Isothermal experiment were conducted by contacting the adsorbent (RHP) with solutions of different initial dye concentration of CR dye respectively ranging from 25 mg/L to 125 mg/L. The adsorbents dose was 1 g in 100 ml dye solutions. The series of such conical flasks were shaken on a rotary shaker at a constant speed of 100 RPM. Samples were withdrawn for spectrophotometric analysis at predetermined duration of contact time ranging from 10 to 120 minutes. The equilibrium dye concentration ( $C_e$ ) were then measured and the amount of dyes adsorbed per unit weight of the adsorbents at equilibrium ( $q_e$ ) were determined.

## 2. 5. Adsorption Kinetics

Adsorption Kinetics were carried out at known initial dye concentration of 50 mg/L for both CR dye. The adsorbent (RHP) dose was 1 g in 100 ml solutions. The temperature were maintained at room temperature (27 °C). Agitations of the samples were carried out at constant speed of 100 RPM on the rotary shaker and the samples were withdrawn at constant time of 10, 20, 40, 60, 80, 100 and 120 minutes. The agitated samples were filtered using Whatman No. 1 filter paper and the concentration in the supernatant solutions analyzed using UV-Visible Spectrophotometer.

The amount of adsorbate adsorbed at equilibrium condition  $q_e$  (mg/g) was calculated using the following equation:

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

The dye removal percentage can be calculated as follows:

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

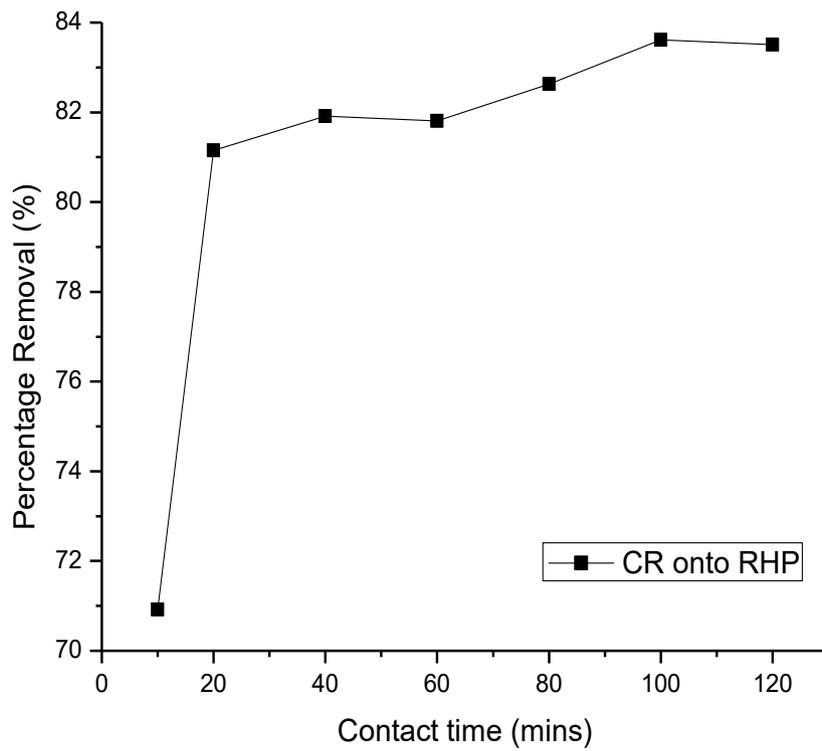
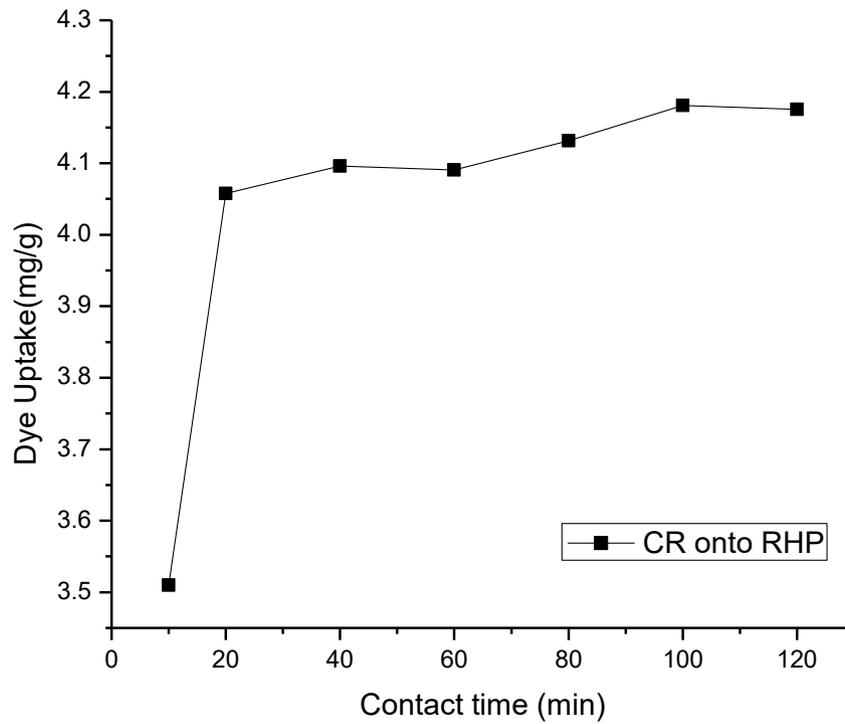
where,  $C_o$  and  $C_e$  are the initial and equilibrium adsorbate concentrations (mg/ L), respectively,  $V$  is the volume of solution (L) and  $W$  is the mass of adsorbent (g).

## 3. RESULTS AND DISCUSSION

### 3. 1. Adsorption Experiment

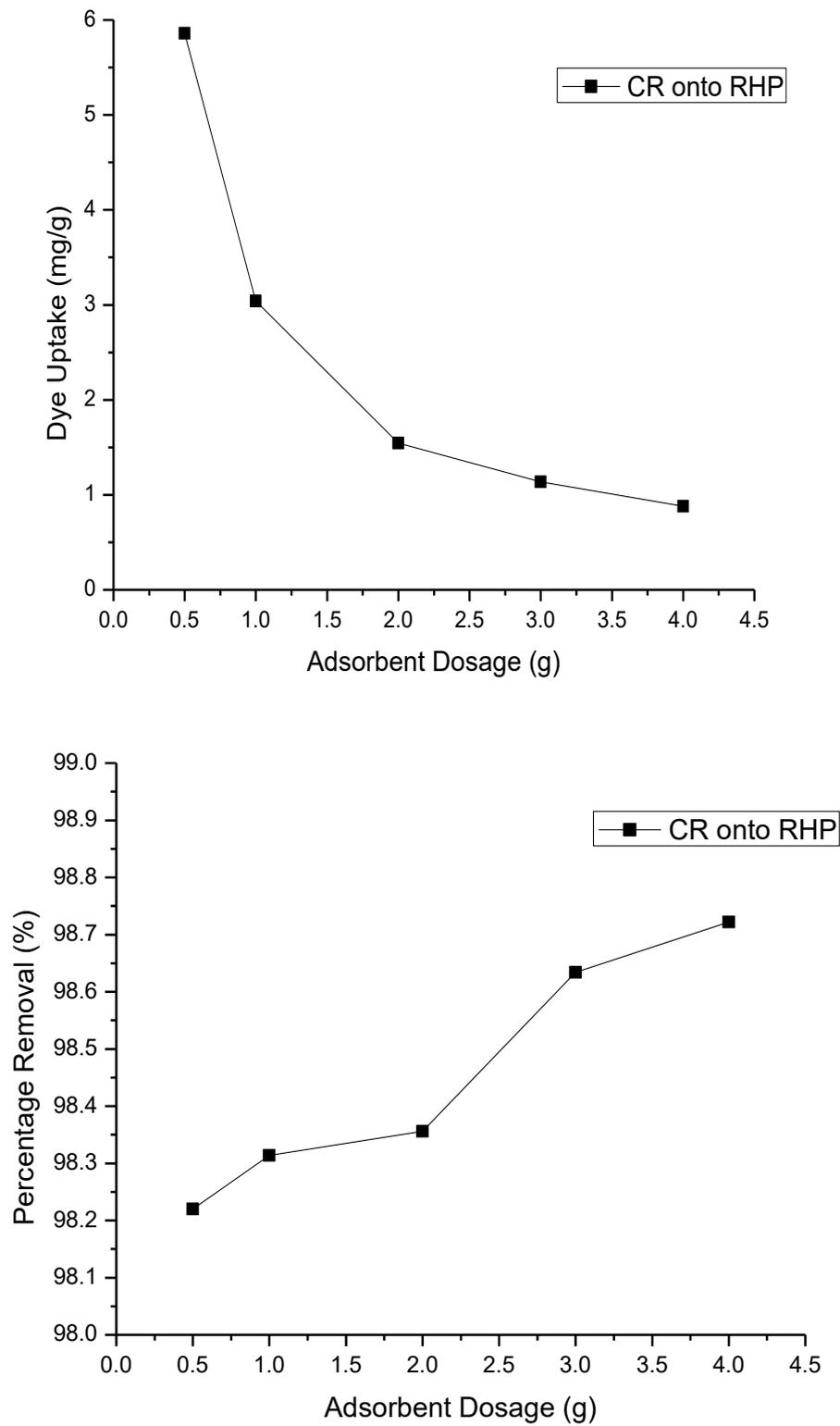
#### 3. 1. 1. Effect of contact time

Figure 1 shows the adsorption capacity and percentage removal of CR dye. It was observed that the sorption of CR dye by RHP was rapid in the initial stages and becomes slow in the later stages until equilibrium time at 100 minutes for CR dye. It can be inferred from the rapid sorption at the initial stages that there was abundance of active sites on the external surface of RHP which resulted in the rapid dye removal. The slower rate in the later stages as due to the dyes being diffused into the interior of the adsorbent [11].



**Figure 1.** Effect of contact time on the adsorption capacity and percentage removal of CR onto RHP

### 3. 1. 2. Effect of initial concentration



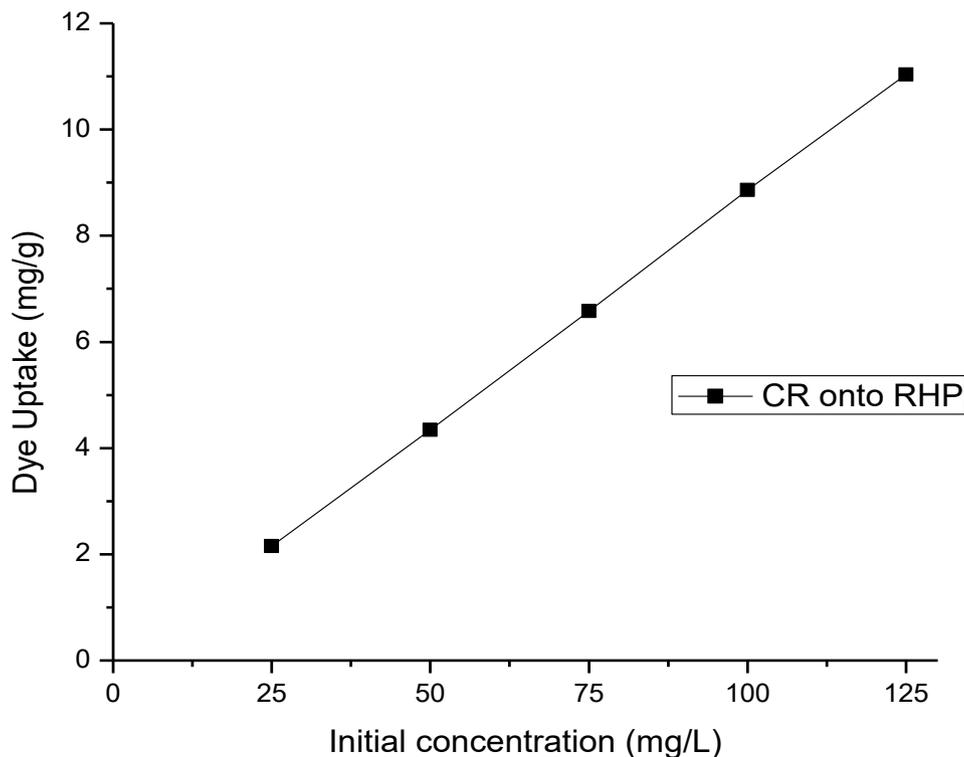
**Figure 2.** Effect of initial concentration on the adsorption capacity and percentage removal of CR onto RHP.

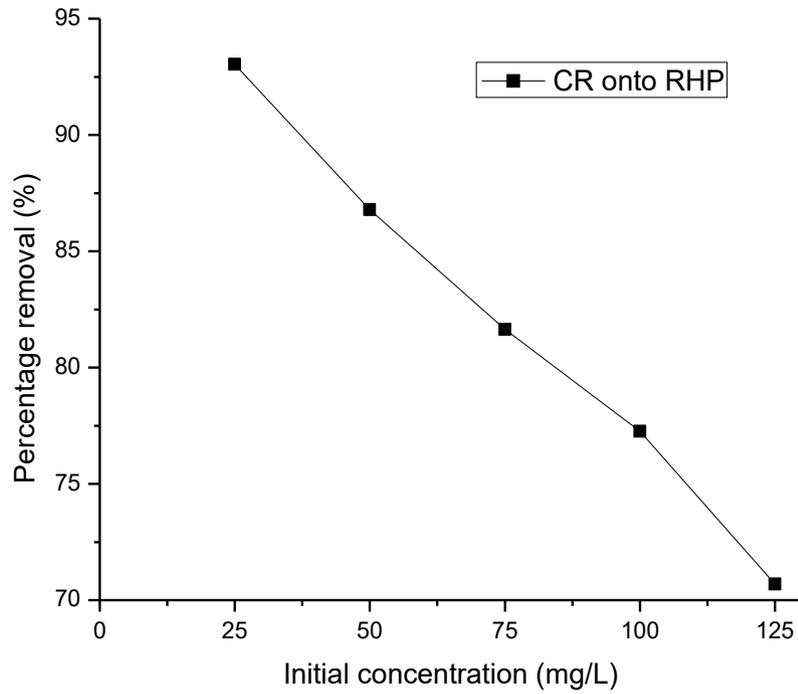
Figure 2 show the influence of adsorbent dose on the percentage removal and adsorption capacity of CR dye. The percentage removal of CR dye increased from 98.22 % to 98.72 %. The adsorption capacity of CR decreased from 5.86 mg/g to 0.88 mg/g. it was observed that as the adsorbent dosage increased, the amount of dye adsorbed decreased while the percentage removal of the dye increased.

This decrease in adsorption capacity with increase in adsorbent dosage mainly attributed to non-saturation of the adsorption sites during the adsorption process [12]. The increase in adsorption removal of the dye with increase in adsorption dose maybe because of availability of more adsorption sites which increase with increase in adsorption dose [13].

### 3. 1. 3. Effect of adsorbent dosage

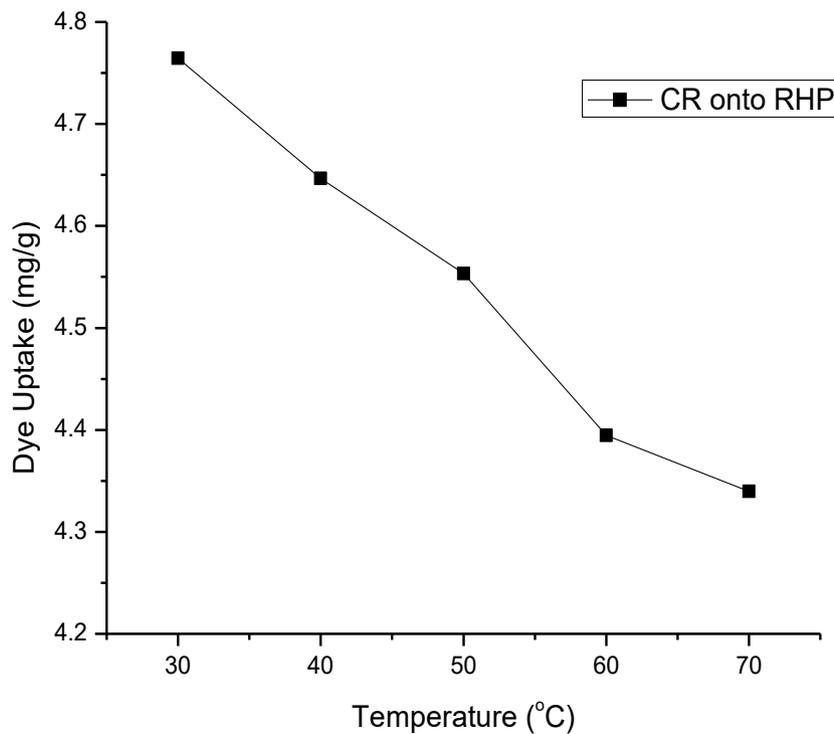
Figure 3 shows the effect of initial concentration on the adsorption capacity and percentage removal of CR dye onto RHP. It was observed that the adsorption capacity increased from 2.15 mg/g to 11.03 mg/g while the percentage removal of CR decreased from 93.04 % to 70.68 % as the initial dye increased from 25 to 125 mg/L. The increase in adsorption capacity with increasing initial concentration is due to high driving force which overcomes the mass transfer resistance at higher initial dye concentration [14]. The decrease in percentage removal with increasing in dye concentration is because for a given mass of adsorbent, the amount of dye it can adsorb is fixed. Thus, the higher the concentration of the dye, the smaller the percentage it can remove [15].

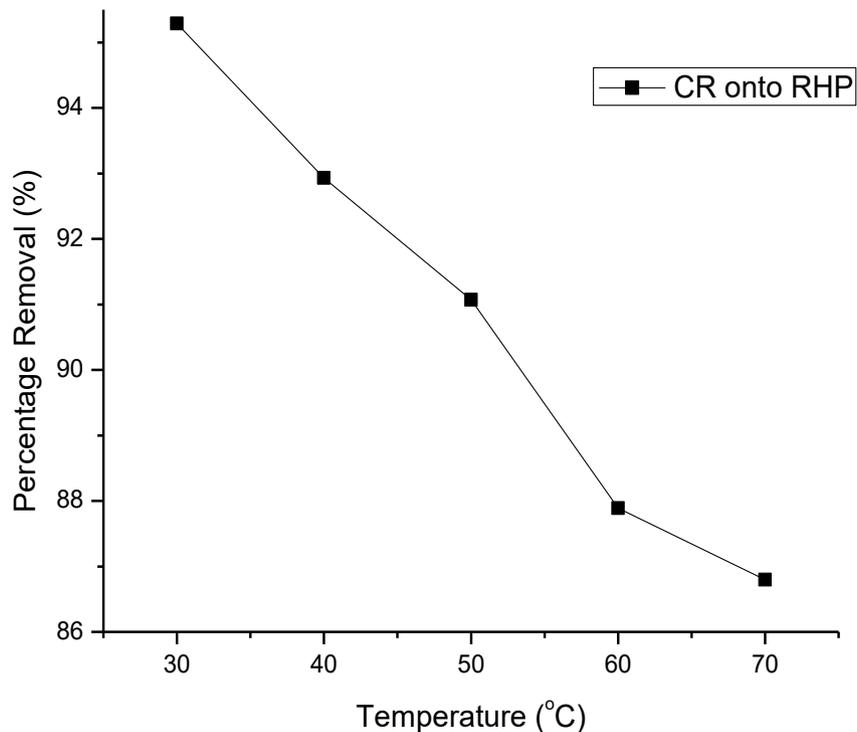




**Figure 3.** Effect of adsorption dosage on the adsorption capacity and percentage removal of CR onto RHP

### 3. 1. 4. Effect of temperature





**Figure 4.** Effect of temperature on the adsorption capacity and percentage removal of CR onto RHP

Figure 4 shows the effect of percentage removal and adsorption capacity of CR onto RHP. The percentage removal and adsorption capacity decreased from 95.2% to 86.79% and 4.76 mg/g to 4.34 mg/g for CR onto RHP.

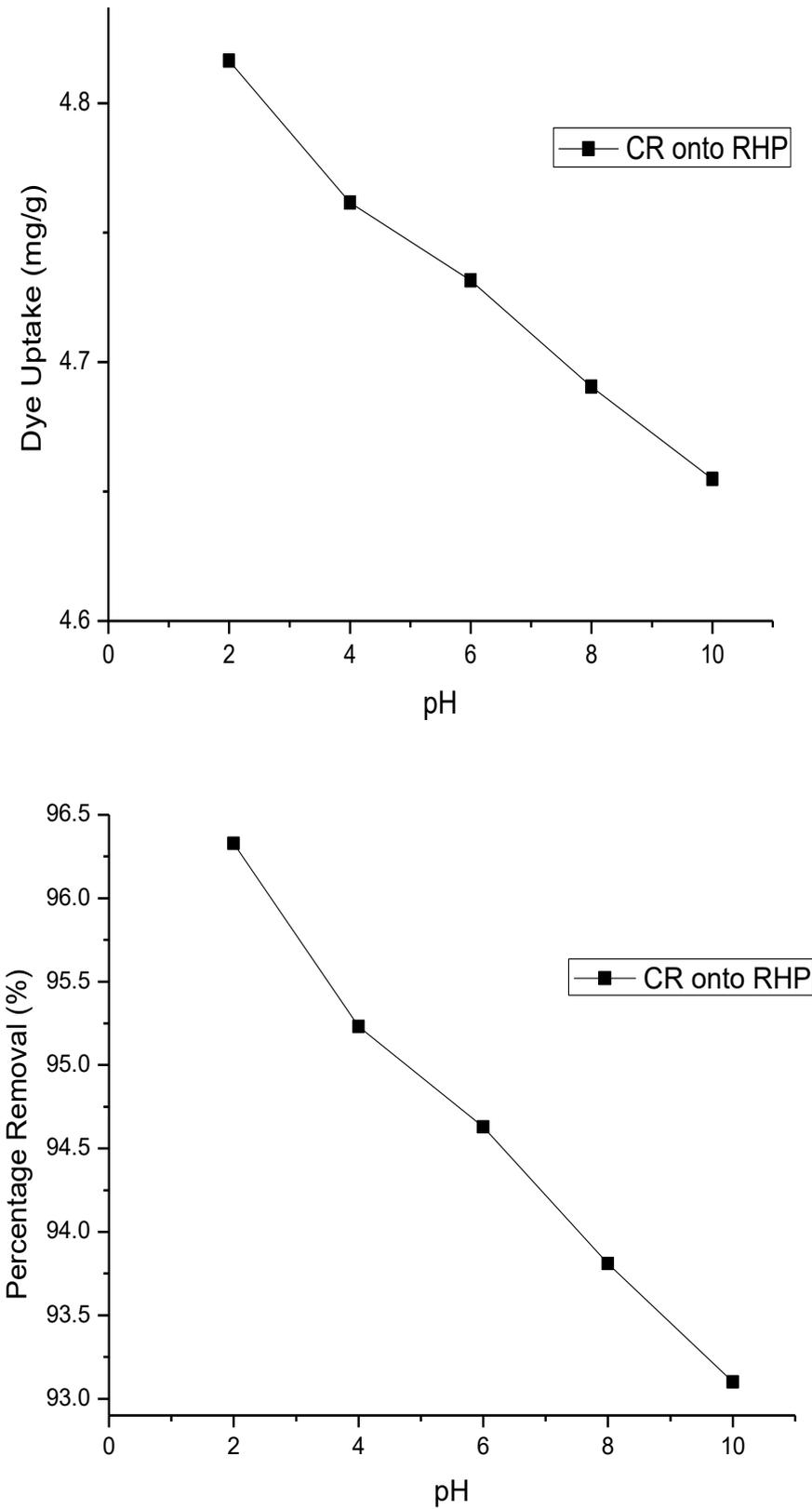
This decrease in adsorption capacity and efficiency with increase in temperature can attributed mainly to the fact that as the temperature increases, the physical bonding between the dye (adsorbate) and the active sites of the adsorbent weakened. In addition, the dye solubility also increased which caused the interaction between the solute and solvent to be stronger than that between solute and adsorbent.

Therefore, the solute became more difficult to adsorb [16].

### 3. 1. 5. Effect of pH

Figure 5 shows the effect of pH on the adsorption capacity and percentage removal of CR onto RHP, which decreased from 4.82 to 4.65 mg/g and from 96.35 to 93.0 % respectively as pH, increased from 2 to 10. The decrease in percentage removal and adsorption capacity with increase in pH can attributed to the fact that at high pH values of the solution, the presence of excess hydroxyl ion in the solution competes with the anionic groups of the CR dye for the adsorption sites on the adsorbent surface.

While at low pH, the negative charges ( $\text{OH}^-$ ) in the solution decreases and the adsorbent surface is more positively charged, thus enhancing attraction of more amounts of the anions of the CR dye [17].



**Figure 5.** Effect of pH on the adsorption capacity and percentage removal of CR onto RHP

### 3. 2. Adsorption isotherms

Two isotherm models have been tested in the research, namely Langmuir and Freundlich models. The linear form of Langmuir equation is given as [18]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \quad (3)$$

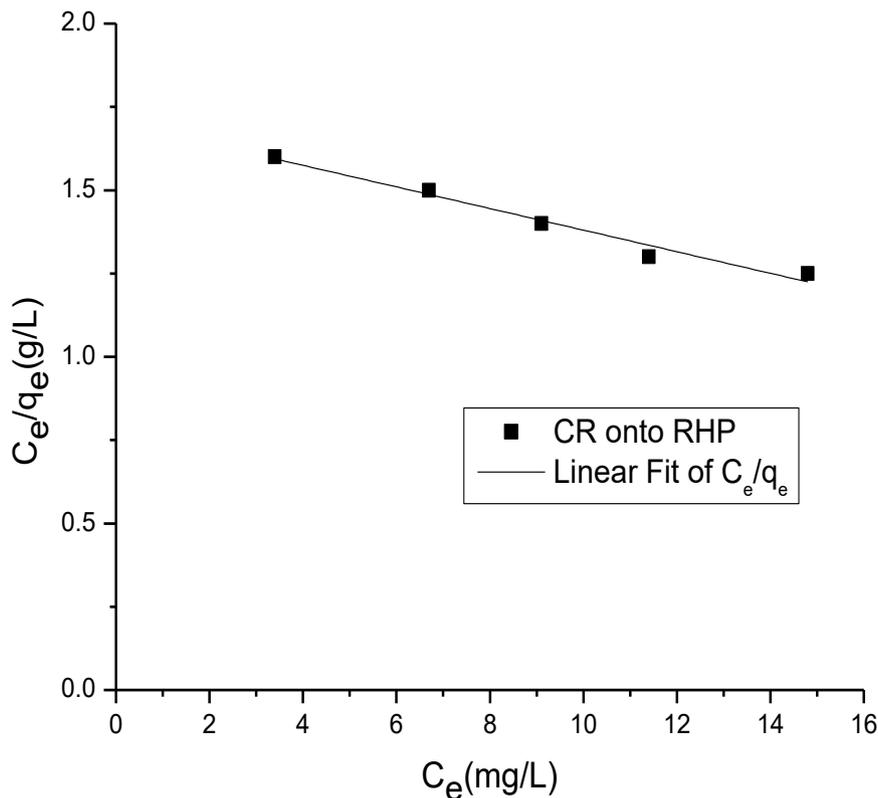
where  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $q_m$  (mg/g), the amount of dye adsorbed where saturation is attained,  $C_e$  is the equilibrium dye concentration (mg/l) and  $K_l$  is the Langmuir constant related to the binding strength of the dye onto the adsorbent.

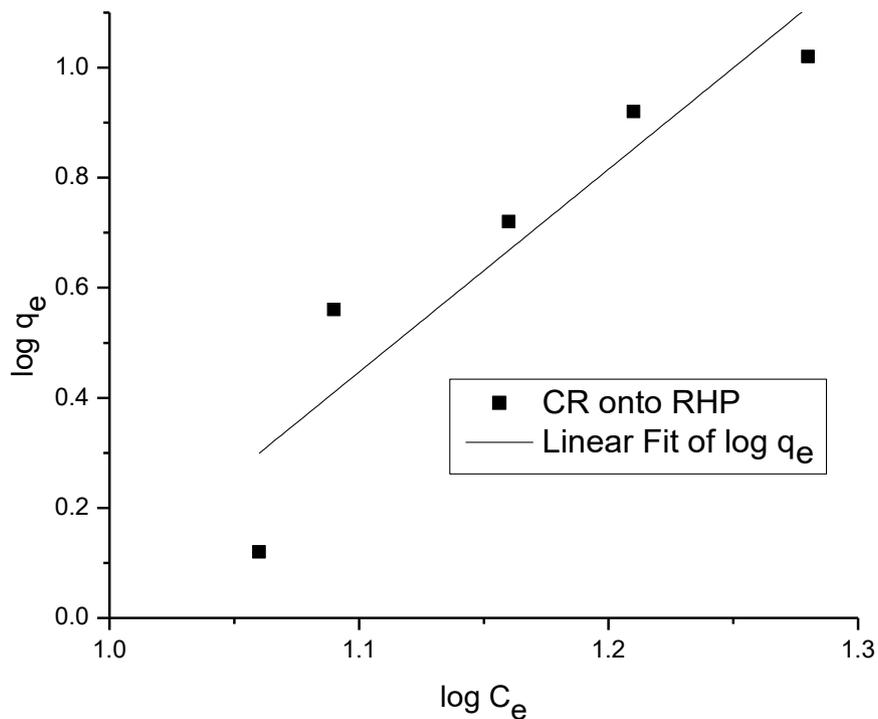
The linear form of Freundlich equation is expressed as [19]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

where  $K_f$  and  $n$  are the Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively.

Figure 6 show the Langmuir and Freundlich model for the adsorption of CR onto RHP. The isotherm parameter and  $R^2$  values are summarized in Table 1. It is evident from the plots and values of correlation coefficient ( $R^2$ ) that the Langmuir plot was inadequate in describing the adsorption processes.





**Figure 6.** Langmuir and Freundlich plot for adsorption of MV onto RHP

**Table 1.** Isotherm parameters and correlation coefficient.

<b>Langmuir</b>			
RHP with MV	$E_{\max}$ (mg/g) 33.88	$K_l$ 0.017	$R^2$ 0.7880
<b>Freundlich</b>			
RHP with MV	$K_F$ (mg/g) L/mg) <sup>1/n</sup> 0.501	$n$ 0.8610	$R^2$ 0.9963

The experimental data fitted well with the Freundlich isotherm model, hence, this evidence the adequacy of Freundlich isotherm to describe the adsorption of CR onto RHP and such adsorptions mainly occurred on heterogeneous surface of the RHP powder.

### 3. 3. Adsorption kinetics

#### 3. 3. 1. Pseudo first order kinetic model

The linear form of the pseudo first order kinetic mode is represented by [20, 21]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (5)$$

where  $q_e$  and  $q_t$  are the values of amount of the dye adsorbed per mass on the adsorbent at equilibrium and at various time  $t$ , respectively,  $K_1$  is the Pseudo first order adsorption rate constant ( $\text{min}^{-1}$ ). The values of  $K_1$  and calculated  $q_e$  can be determined from the slope and intercept respectively, of the linear plot of  $\ln(q_e - q_t)$  versus  $t$ .

### 3. 3. 2. Pseudo second order kinetic model

The pseudo second order kinetic model is expressed by [22, 23]

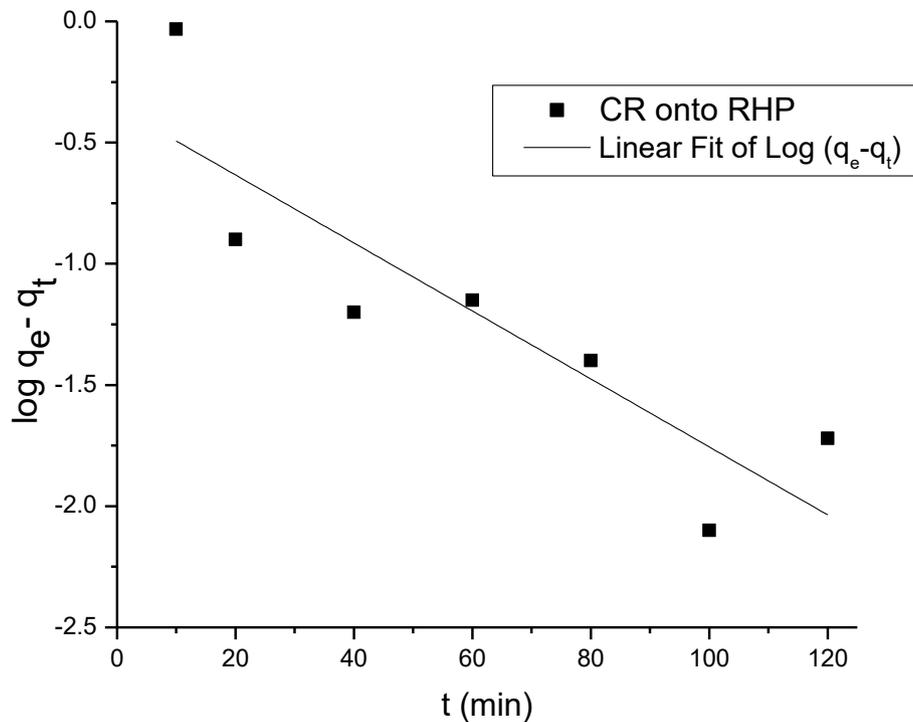
$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

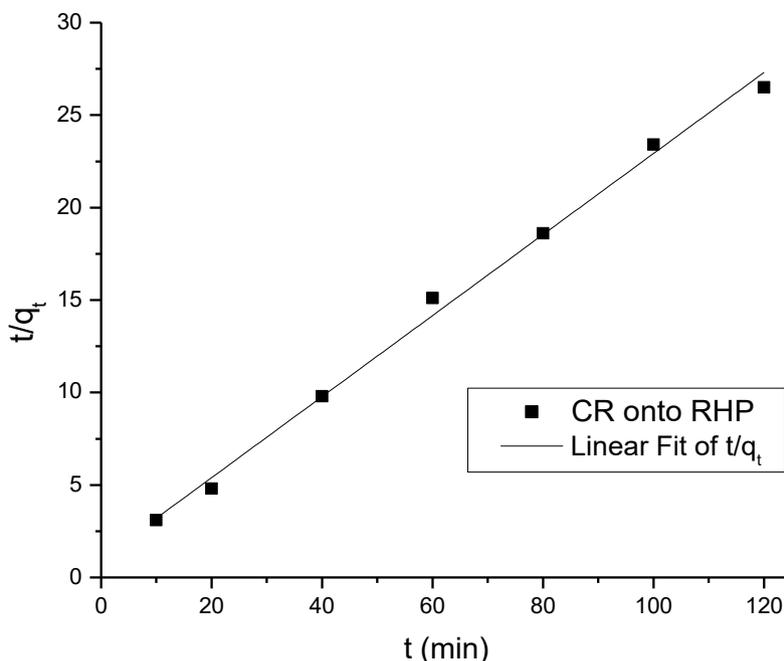
where  $K_2$  is the pseudo second order adsorption rate constant ( $\text{g/mg}\cdot\text{min}$ ) and  $q_e$  is the amount of dye adsorbed ( $\text{mg/g}$ ) on the adsorbent at equilibrium.

The initial adsorption rate,  $h$  ( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ ) is expressed as:

$$h = K_2 q_e^2 \quad (7)$$

The plot of  $t/q_t$  versus  $t$  gives a linear relationship which allow computation of  $K_2$ ,  $h$  and calculated  $q_e$ . Among these models, the criterion for their applicability is based on judgement on the respective correlation coefficient ( $R^2$ ) and agreement between experimental and calculated value of  $q_e$ .





**Figure 7.** Pseudo first order and Pseudo second order plot for the adsorption of CR onto RHP.

Figure 7 show the pseudo first order and pseudo second order kinetics for the adsorption of CR by RHP. The pseudo first order rate constant  $K_1$  and  $q_e$  determined from the model are presented in Table 2. It was observed from Figure 7a depicts the relationship between the dye solution diffusivity,  $\ln (q_e - q_t)$  against time (t) is non-linear and the calculated  $q_e$  values did not agree with the experimental  $q_e$  since the calculated  $q_e$  values were neither equal nor reasonably close to the experimental  $q_e$  values [24, 25]. Therefore, pseudo first order model was inadequate in representing the adsorption of CR onto RHP. The pseudo second order rate constant  $K_2$  and  $q_e$  determined from the model are presented in Table 2.

**Table 2.** Kinetics parameters and correlation coefficient

1 <sup>st</sup> Order				
RHP with MV	$K_1$ 0.032	$q_e$ 0.4870	$R^2$ 0.8050	
2 <sup>nd</sup> Order				
RHP with MV	$K_2$ 0.132	$q_e$ 4.2320	h 2.724	$R^2$ 0.9998

It was observed from Figure 7b, that there was good agreement between the calculated  $q_e$  values and the experimental  $q_e$  values from the adsorption of CR by RHP. In addition, higher linear plots with high values of correlation coefficient were also observed from Figure 9 for the

adsorption of CR by RHP. It is also evident that Pseudo second order is the best fit kinetic model in describing the adsorption processes. This indicates that the pseudo second order model fits well with the adsorption processed and is therefore very adequate in describing and representing the kinetics of the adsorptions [25, 26].

### 3. 4. Adsorption thermodynamics

The thermodynamic parameters such as change in Gibb’s free energy ( $\Delta G^\circ$ ), change in enthalpy ( $\Delta S^\circ$ ) for the adsorption have been determined using the following equations.

The Gibb’s free energy,  $\Delta G$  equation is expressed as follows:

$$\Delta G = -RT\ln K_{ads} \quad (8)$$

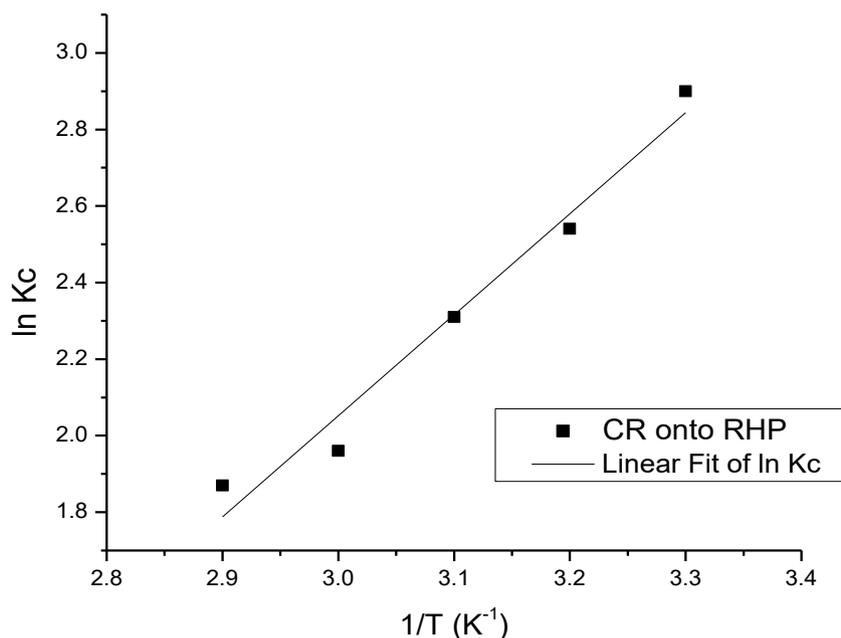
The equilibrium constants ( $K_{ads}$ ) were calculated according to the following equation:

$$K_{ads} = \frac{\text{Dye concentration on the solid (adsorbent) at equilibrium } (q_e^m)}{\text{Dye concentration in solution at equilibrium } (C_e)} \quad (9)$$

The Van’t Hoff equation is expressed as follows:

$$\ln K_{ads} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where R is gas constant, T is absolute temperature in kelvin,  $\Delta S^\circ$  and  $\Delta H^\circ$  are entropy and enthalpy respectively. The plot of  $\ln K_{ads}$  versus  $1/T$  gives a linear relationship, which allows the computation of  $\Delta H$  and  $\Delta S$  values from the slope and intercept respectively.



**Figure 8.** Van’t Hoff plot for the adsorption of CR onto RHP

Figure 8 shows the linear Van't Hoff equation plots for the adsorption of CR onto RHP as indicated in Table 3. The negative  $\Delta G^\circ$  values obtained at all temperatures indicate the feasibility and spontaneous nature of CR dye adsorption onto RHP and the negative for  $\Delta H^\circ$  the adsorption of CR dye reveal decreased randomness at the solid/solute interfaces and suggests the adsorption of CR dye onto RHP were enthalpy driven [27].

**Table 3.** Thermodynamic parameters.

RHP with MV	$\Delta H = - 23.6260$
	$\Delta S = - 53.6700$

#### 4. CONCLUSIONS

The potential of Rice husk peels (RHP) powder as an effective adsorbent for the removal of CR dye from aqueous medium was found to be influenced by constant time, adsorbent dose, initial concentration, temperature and initial pH of the solution. The optimum adsorption of CR dye was found at pH 10. Maximum adsorption capacity was found 33.88 mg/g at 50 mg/L, initial CR dye concentration respectively. Temperature had strong influence on the adsorption processes and the maximum removal was observed at 303 K. The equilibrium was attained at 100 min for the adsorption of CR dye, after which there was no increase in dye adsorption. The adsorption study on equilibrium sorption revealed that Freundlich isotherm model gave best fit to the experimental data. The calculated thermodynamic parameters indicated a spontaneous and exothermic nature of the adsorption of CR dye onto RHP powder. The kinetic studies revealed that the adsorption of CR dye onto RHP followed the pseudo second order kinetic model. The study showed that RHP powder is an effectively adsorbent, which is inexpensive and efficient without any pre-treatment or modification for the removal of Congo red dye from aqueous solution and effluents.

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