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## Batch Adsorption Studies on Rice Husk with Methyl Violet Dye

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### ABSTRACT

The potential of rice husks powder (RHP) for the removal of methyl violet 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 MV 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 1.66 mg/g for the adsorption of MV 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, adsorption, methyl violet, kinetics, methyl red dye, thermodynamics

### 1. INTRODUCTION

Water pollution has become a serious environmental problem around the world due to the addition of chemical, physical, or biological substances in certain concentrations, either naturally or of man-made origin [1, 2]. Many industrial sectors, such as the textile, paper, paint,

pharmaceutical, food, leather, cosmetics, tannery, printing, and plastics industries, use wide varieties of dye to colour their product [3]. There are more than 100,000 type of commercially available dyes, and more than 700,000 tons of dyes are produced annually [4]. Synthetic dyes are highly toxic causing negative effects on all life forms because they present sulfur, naphthol, vat dyes, nitrates, acetic acid, surfactants, enzymes chromium compounds and metals such as copper, arsenic, lead, cadmium, mercury, nickel, cobalt and certain auxiliary chemicals [5, 6].

Various methods of treatment have been exploited through the years by industries for removing colorants which include physicochemical, chemical, and biological methods, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, oxidation, and fungal decolourization [8]. However, because effluents contain different dyes of very complex structures, it is very difficult to treat using conventional methods [8]. Adsorption is one of the most effective processes of advanced wastewater treatment, which industries employ to reduce hazardous pollutants present in the effluents. This is a well-known and superior technique to other processes for removal of dyes from aqueous solution worldwide due to initial cost, operating conditions and simplicity of design [9]. Most of commercial dye removal systems for industrial wastewater make use of activated carbon as an adsorbent [10]. However, the production cost of activated carbon adsorbent is high because it requires a furnace and a burning process. The rate of combustion is directly proportional to carbon dioxide production, a significant greenhouse gas [11]. Recently, numerous approaches have been explored to determine a cheap and effective adsorbent derived from a variety of raw materials waste such as agro-waste.

## **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, dirt and other impurities. 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  $\mu\text{m}$  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**

Methyl violet (MV) dye was purchased from chemical laboratory and was chosen because of its known strong adsorption onto solids. Stock solution of MV 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. Equilibrium Studies**

Equilibrium Studies 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 MV dye removal was studied by shaking 100 ml of 50 mg/L of MV 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 MV 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 MV solution concentration respectively. After an optimum time 60 minutes for MV, 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 Studies

Isothermal studies were conducted by contacting the adsorbent (RHP) with solutions of different initial dye concentration of MV 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 MV 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:

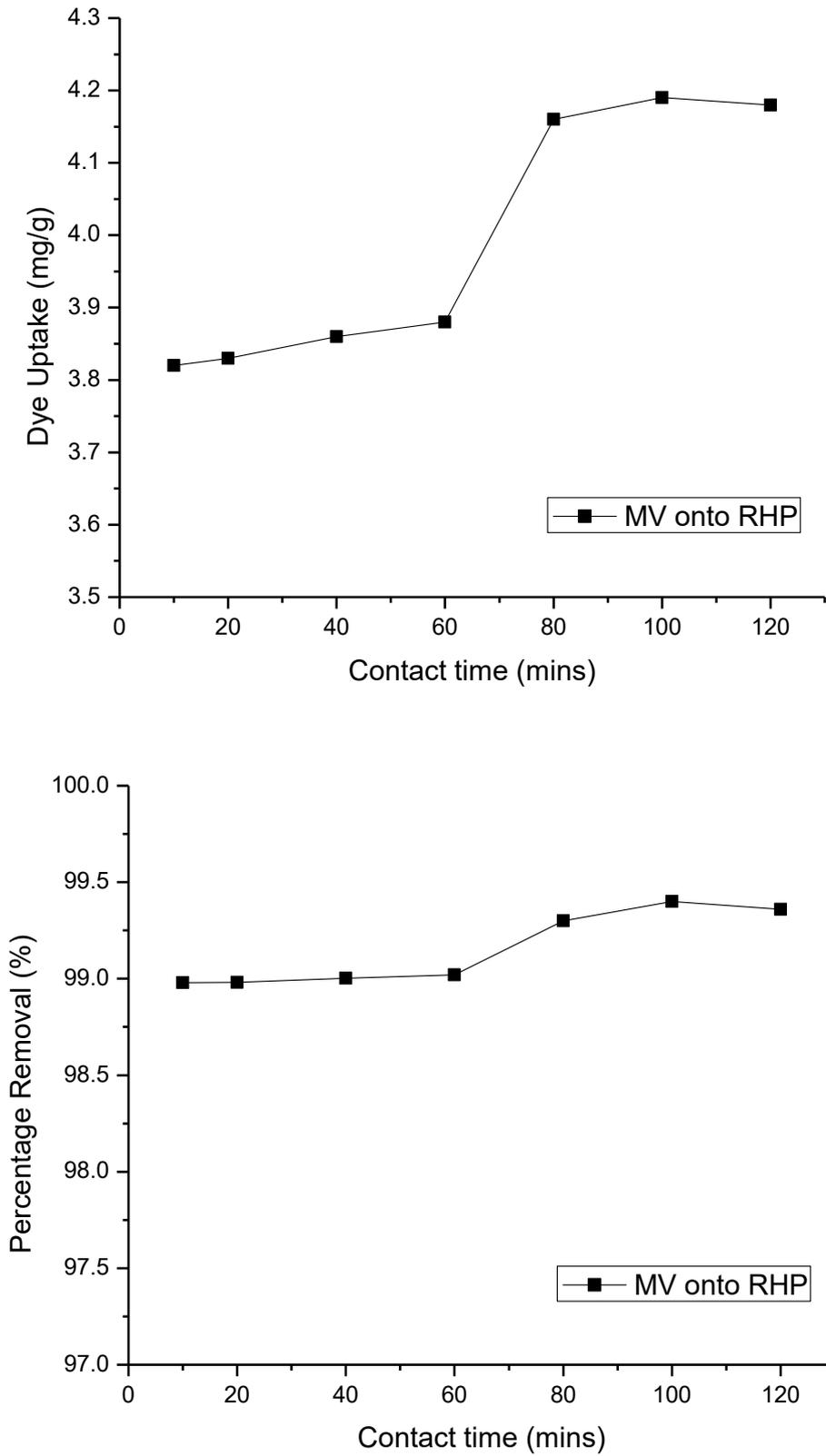
$$Removal = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (2)$$

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. Equilibrium Studies

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

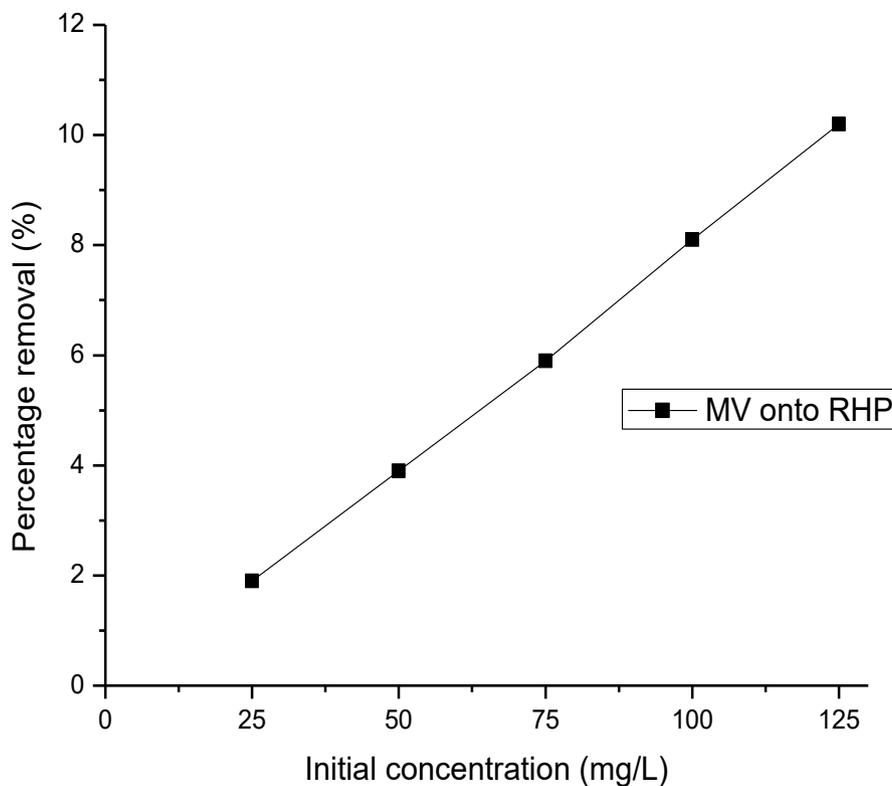


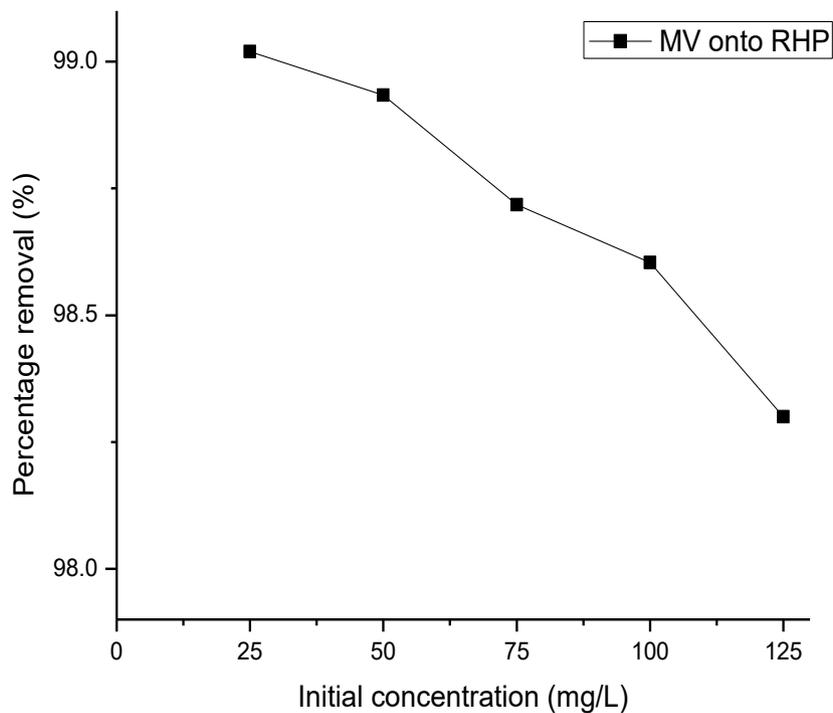
**Figure 1.** Effect of contact time on the adsorption capacity and percentage removal of MV onto RHP.

Figure 1 shows the adsorption capacity and percentage removal of MV dye. It was observed that the sorption of MV dye by RHP was rapid in the initial stages and becomes slow in the later stages until equilibrium time at 100 minutes for MV dye. This is as a result of 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 [12].

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

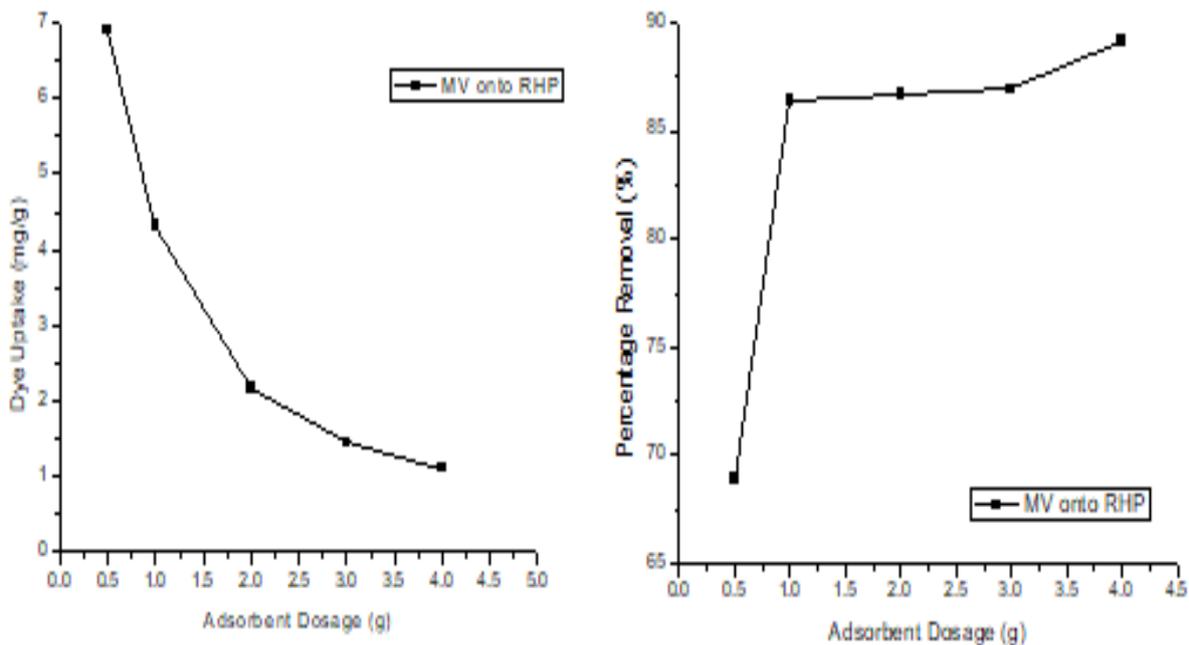
Figure 2 show the effect of initial concentration on the adsorption capacity and percentage removal of MV dye onto RHP. It was observed that the adsorption capacity increased from 1.36 mg/g to 10.52 mg/g while the percentage removal of MV decreased from 99.02 % to 98.30 % as the initial dye increased from 25 to 125 mg/L. 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 [13]. 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].





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

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

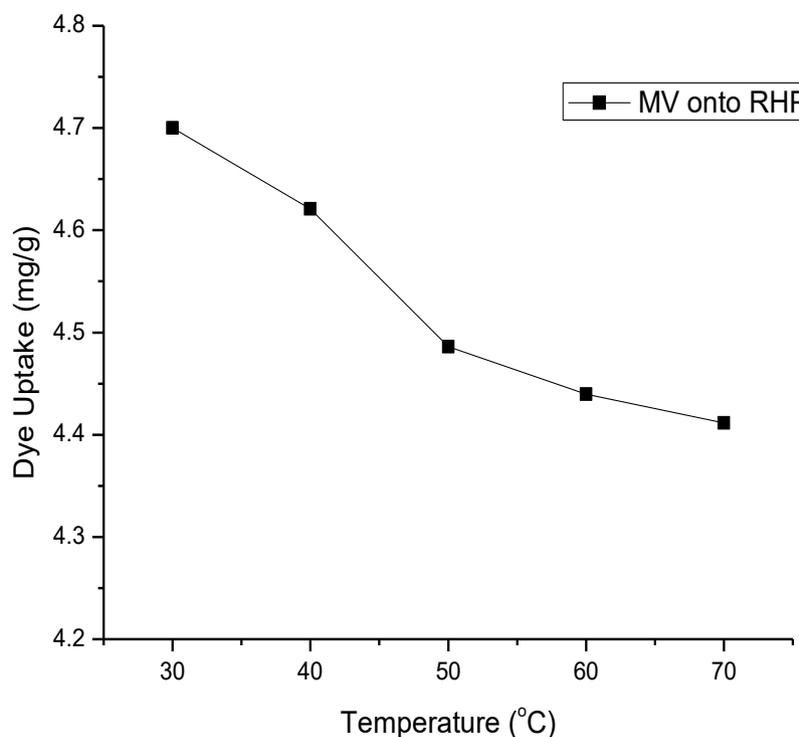


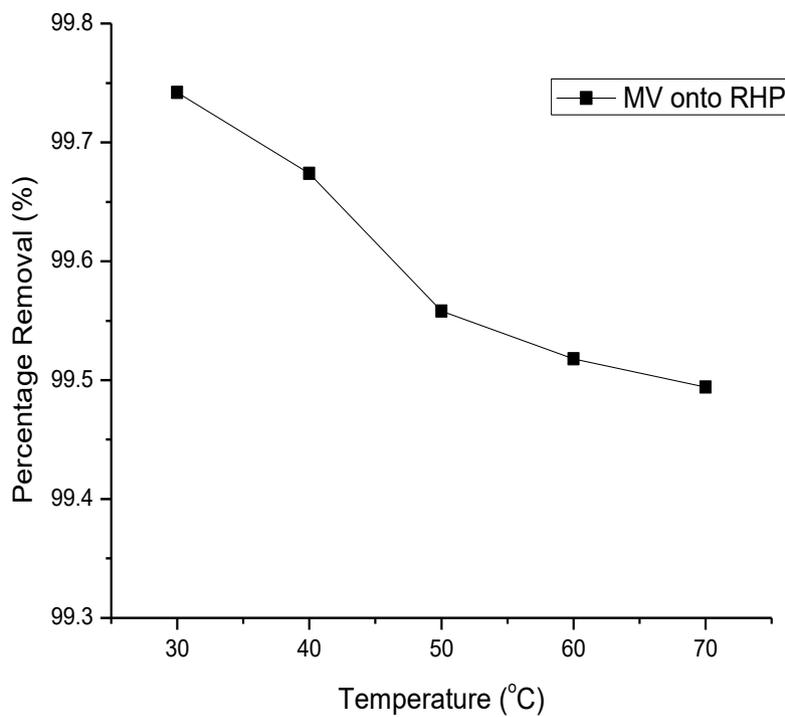
**Figure 3.** Effect of adsorption dosage on the adsorption capacity and percentage removal of MV onto RHP

Figure 3 show the influence of adsorbent dose on the percentage removal and adsorption capacity of MV dye. The percentage removal of MV dye increased from 68.93 % to 89.09 %. The adsorption capacity of MV decreased from 6.89 mg/g to 0.11 mg/g. it was inferred that as the adsorbent dosage increased, the amount of dye adsorbed decreased while the percentage removal of the dye increased. The increase in percentage removal of the dye with increase in adsorption dose maybe because of availability of more adsorption sites which increase with increase in adsorption dose [15]. This decrease in adsorption capacity with increase in adsorbent dosage mainly attributed to non-saturation of the adsorption sites during the adsorption process [16].

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

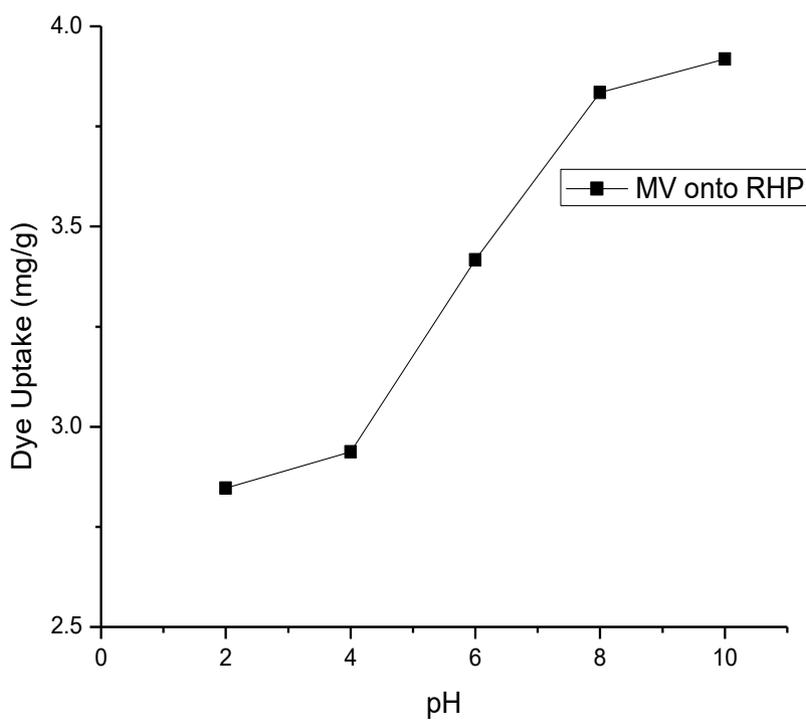
Figure 4 shows the effect of percentage removal and adsorption capacity of MV onto RHP. The percentage removal and adsorption capacity decreased from 99.74 % to 99.49 % and 4.70 mg/g to 4.41 mg/g for MV onto RHP. This decrease in adsorption capacity and efficiency with increase in temperature can attributed mainly to the fact that as the temperature increases, the physical bonding between the dye (adsorbate) and the active sites of the adsorbate 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 [17]. Therefore, the solute became more difficult to adsorb.

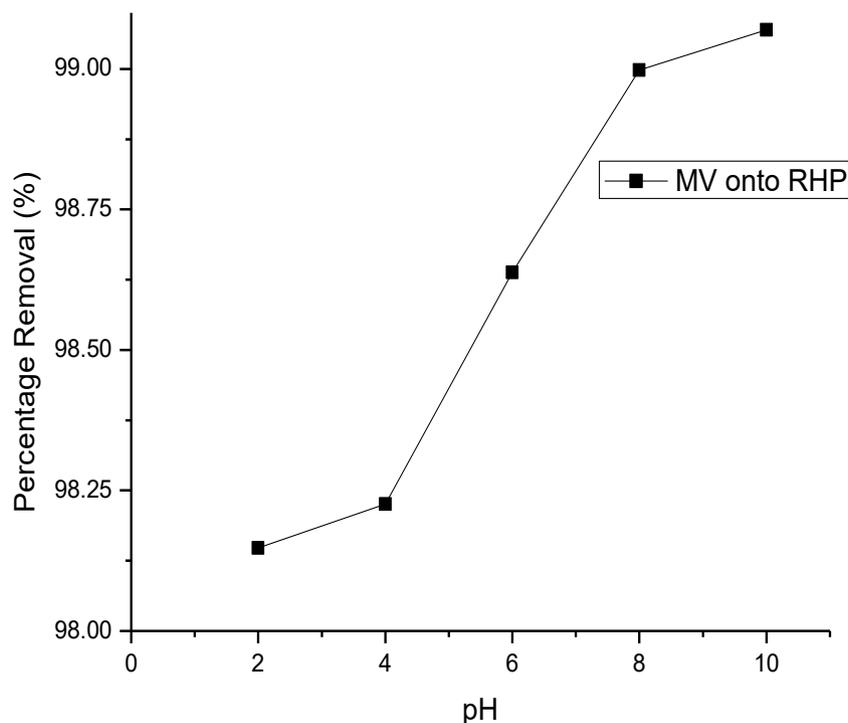




**Figure 4.** Effect of temperature on the adsorption capacity and percentage removal of MV onto RHP

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





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

Figure 5 shows the effect of pH on the adsorption capacity and percentage removal of MV onto RHP which increased from 2.85 mg/g to 3.91 mg/g and from 98.14 % to 99.07 % respectively as pH increased from 2 to 10. Optimum sorption was obtained at pH of 10. The increase in percentage removal and adsorption capacity with increase in pH can attributed to the fact that at low pH values of the solution, the presence of excess hydrogen ion in the solution competes with the cationic groups of the MV dye for the adsorption sites on the adsorbent surface [18]. While at high pH values, the positive charges ( $H^+$ ) at the solution interphase decreases and the adsorbent surface is more negatively charged, thus enhancing attraction of more amounts of the anions of the MV dye [19].

### 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 [20]:

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

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:

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

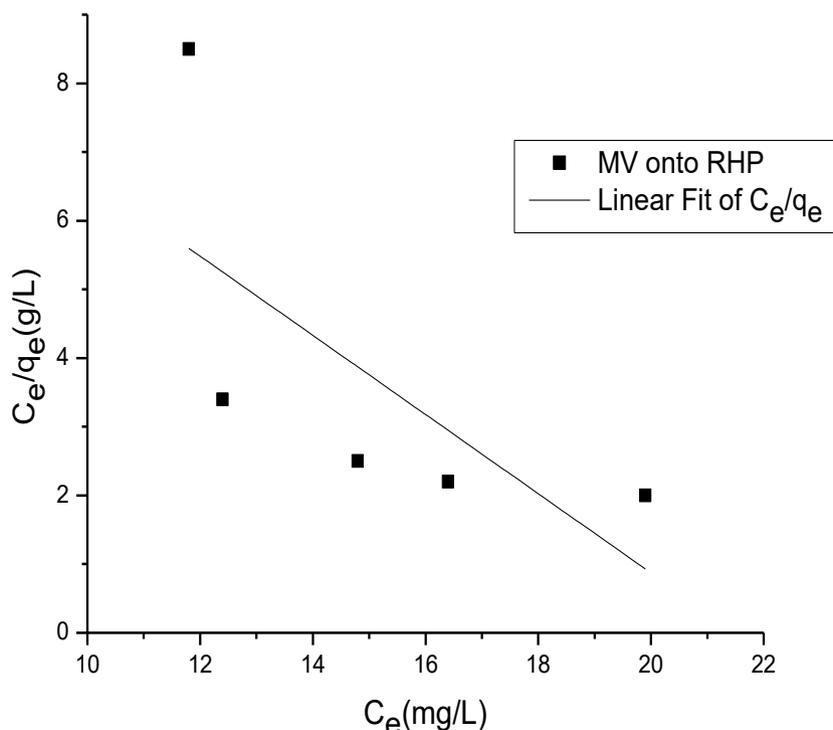
where  $K_f$  and  $n$  are the Freundlich constants that represent adsorption capacity and intensity (strength) of adsorption respectively.

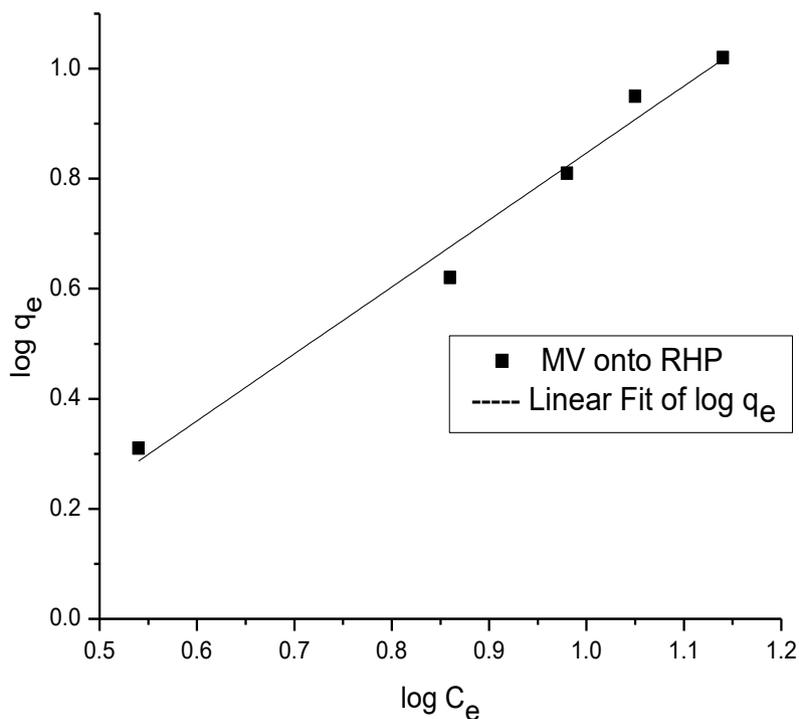
Figure 6 show the Langmuir and Freundlich model for the adsorption of MV onto RHP. The isotherm parameter and  $R^2$  values are summarized in Table 1.

It is evident from the plots and values of correlation coefficient ( $R^2$ ) that the Langmuir plot was inadequate in describing the adsorption processes. The experimental data fitted well with the Freundlich isotherm model, hence, this evidence the adequacy of Freundlich isotherm to describe the adsorption of MV onto RHP and such adsorptions mainly occurred on heterogeneous surface of the RHP powder.

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

<b>Langmuir</b>			
RHP with MV	$E_{\max}$ (mg/g) 1.656	$K_1$ 0.049	$R^2$ 0.38278
<b>Freundlich</b>			
RHP with MV	$K_F$ (mg/g) L/mg) <sup>1/n</sup> 0.005	$n$ 0.2930	$R^2$ 0.7990





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

### 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:

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

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:

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

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.

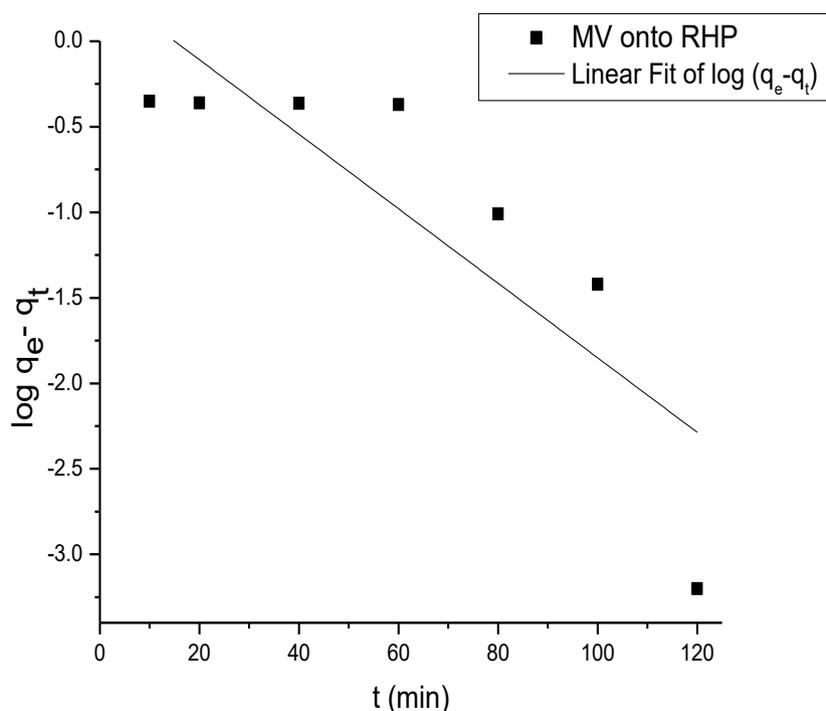
The initial adsorption rate,  $h$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) is expressed as:

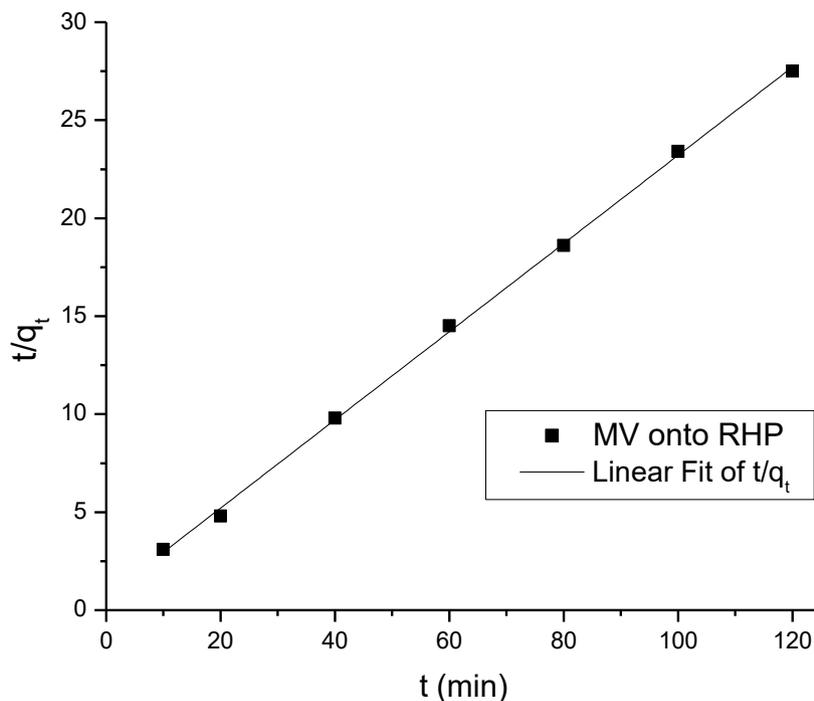
$$h = K_2 q_e^2 \tag{7}$$

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 show the pseudo first order and pseudo second order kinetics for the adsorption of MV 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. Therefore, pseudo first order model was inadequate in representing the adsorption of MV onto RHP.

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

1 <sup>st</sup> Order				
RHP with MV	$K_1$ 0.041	$q_e$ 1.3730	$R^2$ 0.38656	
2 <sup>nd</sup> Order				
RHP with MV	$K_2$ 0.060	$q_e$ 4.3740	$h$ 1.152	$R^2$ 0.9963





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

The pseudo second order rate constant  $K_2$  and  $q_e$  determined from the model are presented in Table 2. It was observed that there was good agreement between the calculated  $q_e$  values and the experimental  $q_e$  values from the adsorption of MV by RHP. In addition, higher linear plots with high values of correlation coefficient were also observed from Figure 7b for the adsorption of MV 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.

### 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:

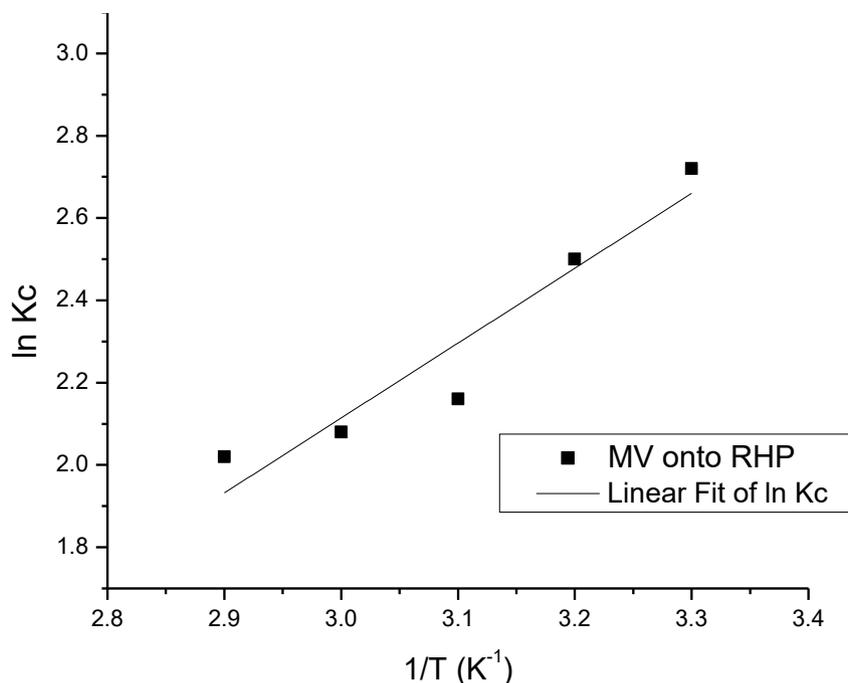
$$\ln K_{ads} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

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

**Table 3.** Thermodynamic parameters

RHP with MV	$\Delta H = -15.8370$
	$\Delta S = -29.9680$



**Figure 8.** Van't Hoff plot for the adsorption of MV onto RHP

#### 4. CONCLUSIONS

The potential of Rice husk peels (RHP) powder as an effective adsorbent for the removal of MV dye from aqueous medium has been identified. The adsorption of MV onto RHP powder

was found to be influenced by constant time, adsorbent dose, initial concentration, temperature and initial pH of the solution. The optimum adsorption of MV dye was found at pH 10 respectively. Maximum adsorption capacity was found 1.66 mg/g at 50 mg/L, initial MV 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 MV dye, after which there was no increase in dye adsorption. The kinetic studies revealed that the adsorption of MV dye onto RHP followed the pseudo second order kinetic model. The 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 MV dye onto RHP powder. The study showed that RHP powder can be effectively used as an inexpensive and efficient adsorbent without any pre-treatment or modification for the removal of methyl violet dye from aqueous solution and effluents.

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