# Adsorption behavior of cationic dyes by rice husk

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## Abstract

The dye wastewater in textile industries is the major source of environmental pollution. It has a direct impact on the lives of humans and aquatic animals. Discharged dye wastewater contains mineral salts and dyes at high concentration. Low cost by–products from agricultural waste have been studied for wastewater treatment. In this work, rice husk was applied as an adsorbent for the cationic dyes (brilliant green and rhodamine B) removal in the batch adsorption process. The effect of contact time (1–360 min) and adsorbent dose (0.25–1.25 g) were evaluated at 30°C. The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR). The experimental data were analyzed using isotherm and kinetic models. The equilibrium adsorption data were fitted to the Langmuir isotherm and the maximum adsorption capacity was 8.93 mg/g for brilliant green and 5.12 mg/g for rhodamine B. The adsorption kinetic data were best described by the pseudo–second order model and intra-particle diffusion. The results revealed that the rice husk was an effective adsorbent for brilliant green and rhodamine B removal in aqueous solution.

**Keywords**: isotherm, kinetics, cationic dye, rice husk

## 1. Introduction

Dye effluent wastewater is a major problem in environmental pollution. Highly colored wastes are not only esthetically unpleasant, but also hinder light penetration and may disturb the ecosystem. Most of the synthetic dyes possess complex aromatic structures making them nonbiodegradable, stable against oxidation and photodegradation. Moreover, dyes and their metabolites are toxic to some organism [1]. Several methods have been used for the dye wastewater treatment, and the adsorption process provides an attractive treatment that has been successfully employed for color removal from wastewater. For the adsorption, activated carbon is an effective adsorbent but it is expensive due to its high costs of manufacturing.

Recently, many natural adsorbents have been used to reduce dye concentration from aqueous solutions [2–4]. Among the natural materials used as adsorbent, agricultural by–products are considered because of low–cost products. Agricultural waste products are complex materials containing cellulose and lignin which carry polar functional groups of alcohol, aldehyde, ketone, phenolic hydroxide, and ether. And, these groups can increase the affinity of the adsorbent material towards organic molecules [5].

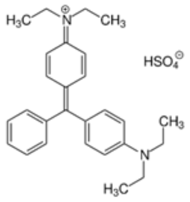
Rice husk is composed of lignin, cellulose and $SiO_2$, hence it can be considered as a natural organic-inorganic composite material [6]. The objective of this work was to study the adsorption efficiency of rice husk adsorbent for the cationic dyes, brilliant green and rhodamine B, from aqueous solutions. The adsorption isotherms and kinetic models were applied to analyze the adsorption data.

### Preparation of adsorbent

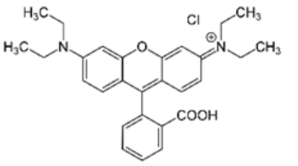
Rice husk was obtained in a rice mill from Khok Samrong District, Lopburi, Province, Thailand. The rice husk was washed with tap water and dried in a hot air oven. The dried adsorbent was powdered and sieved to particle size of 150–300 μm, then it was stored in a desiccator until used.

### Preparation of Adsorbate

Brilliant green (brilliant green : BG], C.I. 420140, molecular formula $C_{27}H_{34}N_2SO_4$, molecular weight = 482.65 g/mol) and rhodamine B (rhodamine B : RB, C.I. 83690, molecular formula $C_{28}H_{31}ClN_2O_3$, molecular weight = 479.02 g/mol) were used as adsorbates [7]. They are cationic dyes and products of Merck, Germany and Fluka, United Kingdom, respectively. All the reagents used in this study were analytical grade.



Brilliant green



Rhodamine B

### Characterization of adsorbent

Rice husk was characterized by Fourier transform infrared analysis (FTIR, Perkin Elmer, model two) in the range of 4000 to 500 $cm^{-1}$.

## 2. Batch of adsorption

The batch adsorption experiments were conducted in 250-ml flasks containing 100 ml of dye concentration at 50 mg/L (without pH adjust). The factors of contact time (1–360 min) and adsorbent dose (0.25–1.25 g) were evaluated at 30°C. The flasks were then placed in a shaker with agitation speed of 200 rpm and temperature at 30°C. After adsorption at the appropriate time, the sample was filtered and residual dye concentration was measured using UV–visible spectrophotometer at the wavelength of 625 and 554 nm for BG and RB, respectively. The percentage (%) and the amount of adsorption, $q_t$ (mg/g) were calculated by equation (1) and (2):

$$\%\ \text{adsorption} = \frac{(C_o - C_e)\times 100}{C_o} \qquad (1)$$

$$q_t = \frac{(C_o - C_t)V}{W} \qquad (2)$$

where $C_o$ (mg/L) is initial dye concentration, $C_t$ (mg/L) is the concentration at any time, $q_t$ (mg/g) is the amount adsorbed at any time, V(L) is the volume of the solution and W(g) is the mass of adsorbent.

## 3. Adsorption Isotherm

The Langmuir isotherm in a linear form is represented as follows [5]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_m} \qquad (3)$$

where $C_e$ (mg/L) is the equilibrium concentration, $q_e$ (mg/g) is the amount adsorbed at equilibrium, $K_L$ is the Langmuir constant and $q_{max}$ (mg/g) is the maximum adsorption capacity.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor $(R_L)$ which is defined by:

$$R_L = \frac{1}{(1+K_L\,C_o)} \qquad (4)$$

The Freundlich isotherm in a linear form is represented as follows [5]:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (5)$$

where $K_F$ (L/g) is the adsorption capacity and 1/n is the adsorption intensity [2].

## 4. Adsorption Kinetics

The pseudo–first order kinetic model in a linear form is written as follows [5]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (6)$$

where $k_1$ ($\text{min}^{-1}$) is the rate constant of pseudo–first and $q_t$ (mg/g) is the amount adsorbed at any time (min).

The pseudo–second order kinetic in a linear form is written as follows [5]:

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

where $k_2$ ($\text{g.mg}^{-1}.\text{min}^{-1}$) is the rate constant of pseudo–second order kinetic adsorption.

The intraparticle diffusion model form is written as follows:

$$q_t = K_{id}(t)^{1/2} + C \qquad (8)$$

where $K_{id}$ is the intraparticle diffusion rate constant ($\text{mg/(g.min}^{1/2})$), and C gives the idea on the thickness of the boundary layer.

## 5. Free energy change

Free energy change ( $\Delta G^o$ ) can be expressed as follows [8]:

$$\Delta G^o = -RT \ln K \qquad (9)$$

where K (= $q_e$ / $C_e$ ) is the equilibrium constant, R is the gas constant and T is the absolute temperature.

## 6. Results and discussion

### 6.1 FTIR of adsorbent

The surface functional group of the rice husk before and after BG and RB adsorption was characterized by FTIR and the spectra were shown in Figure 1. The peaks in the region at 3200–3700 $\text{cm}^{-1}$ with a maximum at about 3350 $\text{cm}^{-1}$ were attributed to Si–OH [9]. The peak at around 2,920 $\text{cm}^{-1}$ represented the C–H asymmetric stretching in aliphatic methyl of $CH_2$ and $CH_3$ groups from cellulose, lignin, and hemicellulose [10]. The observed peak at around 1700$\text{cm}^{-1}$ was attributed to C=O stretching in carboxyl groups. Therefore, it indicated chemical interactions involving the cationic dyes and carboxyl groups on rice husk [11]. The peaks observed at 1,420–1,300 $\text{cm}^{-1}$ were attributed to C = C–H in plane bending indicating several bands in cellulose and xylose [12]. The strong peak at around 1030 $\text{cm}^{-1}$ reflected the siloxane (Si–O–Si) group [13]. However, after adsorption, the peaks belonging to Si–O and –OH vibrations were shifted and/or changed in their intensities, revealing the presence of strong electrostatic interaction and hydrogen bonds between dye molecules and these functional groups [14].

### 6.2 Effect of contact time

The amount of dyes adsorbed onto the rice husk was examined as a function of contact time at initial concentration of 50 mg/L, 1.25 g of adsorbent, and temperature at 30°C. The results were shown in Figure 2. The rate of adsorption was rapid in the beginning, but it gradually reduced with time until the system reached equilibrium. The data showed that the adsorption capacity increased with the increase of contact time (3.00–3.99 mg/g for BG and 0.94–2.27 mg/g for RB), and became constant at the equilibrium time. This is due to an aggregation of dye molecules with the increase in contact time, and dye molecules cannot diffuse deeper into the rice husk structure at the higher energy sites [11]. The adsorption reached equilibrium at 120 min for BG and 180 min for RB. As seen in Figure 2, the time of dye removal is single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of the dye on the rice husk surface [15 and 16]. It was also found

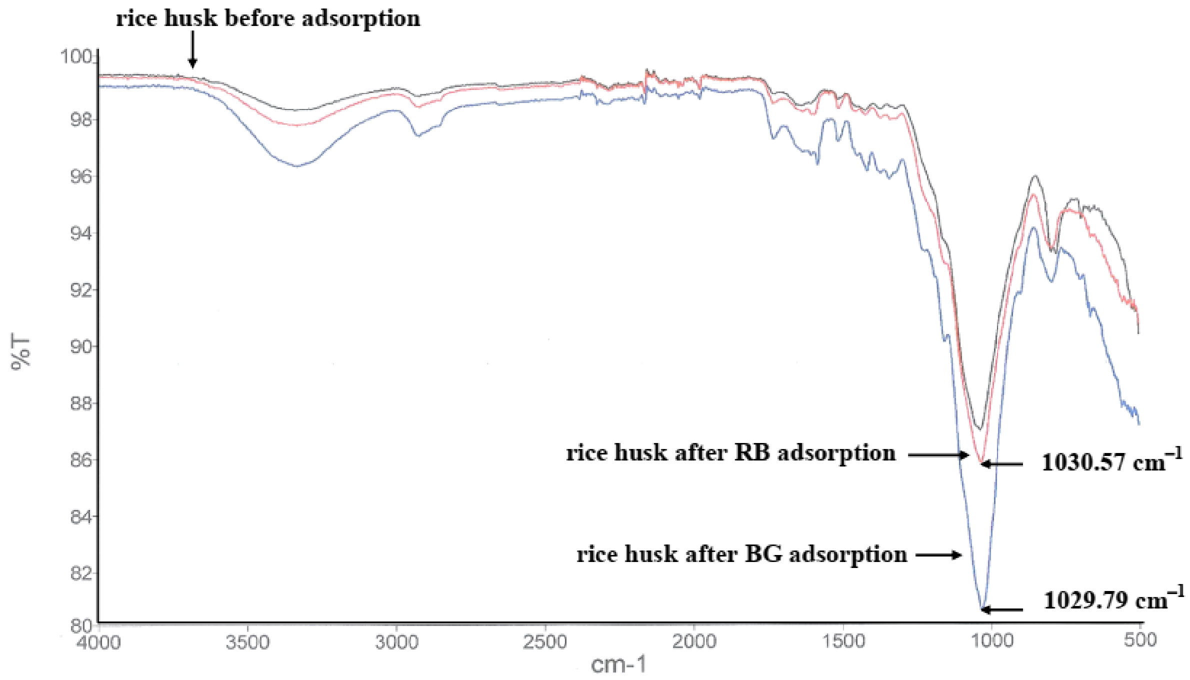


**Figure 1** FTIR spectra of rice husk before and after adsorption

that the adsorption capacity of BG was higher than that of RB at any contact time. This was due to RB formed zwitterion and became dimer, therefore it got difficult to enter into the pore of adsorbent [17].

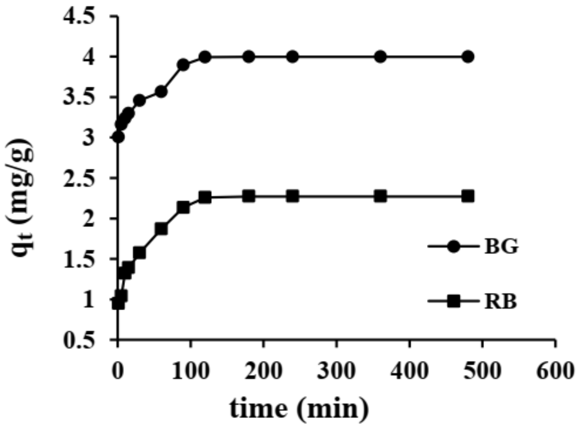
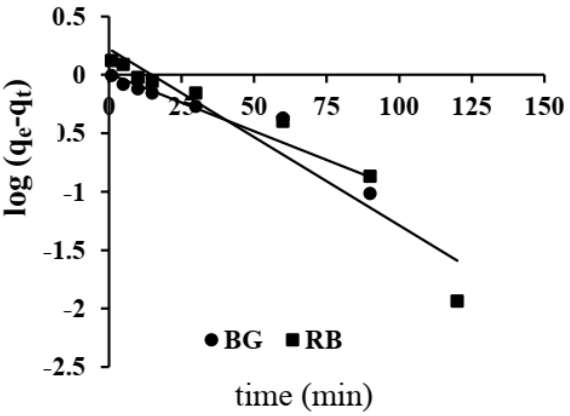


**Figure 2** Effect of contact time

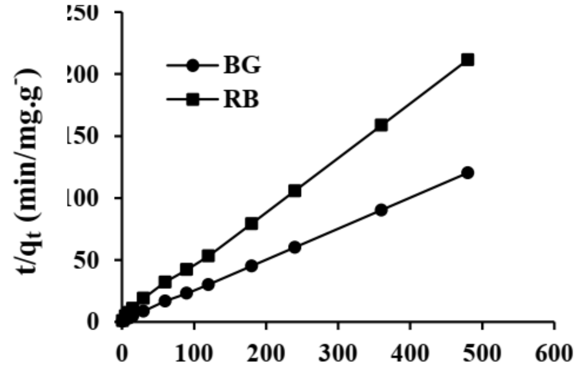
### 6.3 Kinetic of adsorption

For the adsorption of dye from wastewater, the rate at which sorption takes place is important for designing batch sorption systems [18]. The pseudo–first order and pseudo–second order models have been used to test for the experimental data at different contact time.

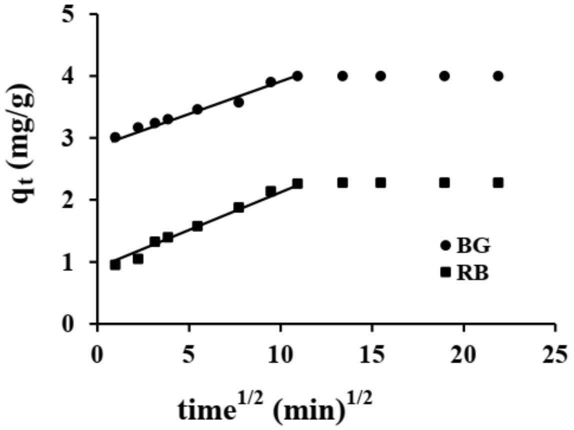
The kinetic adsorption experiment data of BG and RB onto rice husk were analyzed by linear pseudo–first order, pseudo–second order kinetic and intraparticle diffusion as shown in Figure 3(a, b and c) and Table 1.



a. pseudo–first order kinetic



b. pseudo–second order kinetic



c. intraparticle diffusion

**Figure 3** Kinetics of adsorption

**Table 1.** Kinetics of adsorption

| Kinetic model | Cationic dye<br>BG | <br>RB |
|---|---|---|
| $q_e$ (exp) (mg/g) | 3.99 | 2.77 |
| Pseudo–first order | | |
| $q_e$ (cal) (mg/g) | 1.01 | 1.66 |
| $k_1$ (min$^{-1}$) | 0.02 | 0.03 |
| $R^2$ | 0.904 | 0.911 |
| Pseudo–second order | | |
| $q_e$ (cal) (mg/g) | 4.02 | 2.31 |
| $k_2$ (g.mg$^{-1}$.min$^{-1}$) | 0.08 | 0.05 |
| $R^2$ | 0.999 | 0.999 |
| Intraparticle diffusion | | |
| $K_{id}$ | 0.096 | 0.139 |
| C (mg/g) | 2.921 | 0.809 |
| $R^2$ | 0.971 | 0.988 |

As seen in Table 1, the kinetic data were fitted better with pseudo–second order than pseudo–first order. The kinetic of dye adsorption could be explained by pseudo–second order model for the adsorbates. The equilibrium adsorption capacity calculated from pseudo–second order ($q_e$, cal) was 4.02 and 2.31 mg/g for BG and RB, respectively. Therefore, the adsorption of BG and RB onto rice husk may be chemisorption.

For the intraparticle diffusion plot shown in Figure 3 (c), the plots were represented that the adsorption process followed two steps. The multi-linearity relation suggested that the intraparticle diffusion model was dominant in the adsorption. However, the $q_t$ in the first portion did not pass through the origin which indicated that the intraparticle diffusion was not the only rate limiting step. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of adsorption [19]. Therefore, the adsorption of dyes on rice husk was a multistep process involving adsorption on the external surface and diffusion into the interior [20].

### 6.4 Effect of adsorbent dose

Effect of adsorbent dose (0.25–1.25 g) of adsorption was investigated at equilibrium time and initial concentration at 50 mg/L, and the results were shown in Figure 4.

As seen in Figure 4, the percentage of dye adsorption increased with increasing of adsorbent dose from 0.25 to 1.25 g. The percentage of dye adsorption was 43.96 to 99.91% for GB and 15.38 to 55.94% for RB. The higher adsorption at higher dose may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents [1].

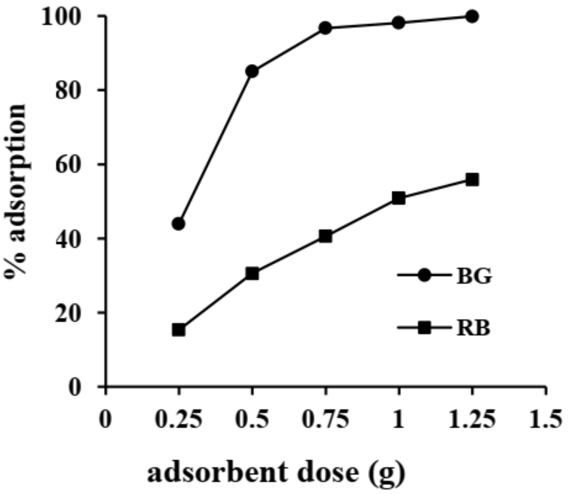
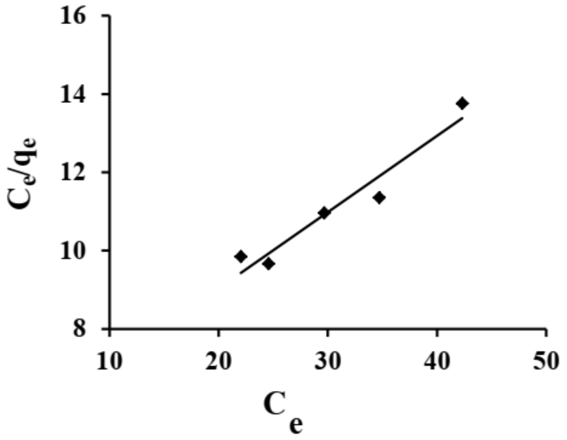


**Figure 4**. Effect of adsorbent dose

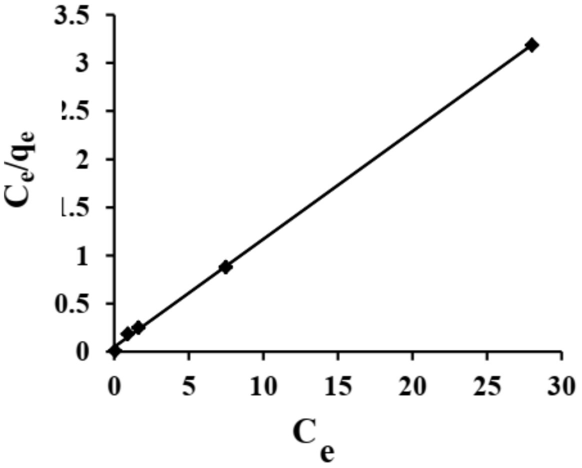
For the study of effect adsorbent dose at constant dye concentration (50 mg/L), the equilibrium data of BG and RB adsorption on rice husk were analyzed using the Langmuir and Freundlich isotherms, and the linear plots of Langmuir were shown in Figure 5 (a and b). The parameters of isotherms were calculated as seen in Table 2.

For the linear coefficient ($R^2$) as shown in Table 2, the results showed better fitting by the Langmuir isotherm ($R^2$ = 0.999, 0.935 for BG and RB, respectively) than Freundlich isotherm ($R^2$ = 0.912, 0.901 for BG and RB, respectively). The maximum monolayer adsorption capacity ($q_{max}$) for BG and RB adsorption were 8.93 and 5.12 mg/g, respectively. The adsorption data obeyed the Langmuir model, revealed the uniform adsorption and strong dye–adsorbent interactions over the surfaces of the adsorbent [12].

For the $R_L$, the value of $0 < R_L < 1$ indicated that the adsorption was favorable.



a. Langmuir isotherm of BG by rice husk



b. Langmuir isotherm of RB by rice husk

**Figure 5.** Langmuir isotherm of BG and RB adsorption on rice husk

**Table 2.** Langmuir and Freundlich isotherm parameters

| **isotherm model** | **cationic dye** | |
|---|---|---|
| | **BG** | **RB** |
| Langmuir isotherm | | |
| $q_{max}$ (mg/g) | 8.93 | 5.12 |
| $K_L$ (L/g) | 2.22 | 0.99 |
| $R_L$ | 0.008 | 0.019 |
| $R^2$ | 0.999 | 0.935 |
| Freundlich isotherm | | |
| $K_F$ (L/mg) | 5.81 | 1.91 |
| 1/n | 0.13 | 0.48 |
| $R^2$ | 0.912 | 0.901 |

### 6.5 Free energy of adsorption

The Gibbs free energy change of adsorption was determined at 30°C, and its value determined from Equation (9) was estimated to be −11.17 and 5.66 kJ/mol for BG and RB, respectively. Therefore, the adsorption of BG was spontaneous, but the adsorption of RB was non–spontaneous at 30°C. Generally, the Gibbs free energy changes for physical and chemical adsorption are usually in the range of 0.0 to 20 kJ/mol and 80 to 400 kJ/mol, respectively [21]. Therefore, the adsorption of BG and RB dyes on rice husk could be considered as physical adsorption.

## 7. Conclusion

In this study, rice husk has been used for its potential application as an adsorbent for the cationic dyes (BG and RB) adsorption. The equilibrium time of adsorption was 120 min for BG and 180 min for RB. The equilibrium adsorption data were better fitted to the Langmuir isotherm model. The maximum monolayer adsorption capacity was 8.93 mg/g for BG and 5.12 mg/g for RB. The adsorption process was found to followed pseudo–second order kinetics and intraparticle diffusion. Also, the surface adsorption and intraparticle diffusion were concurrently operating during the adsorption.

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