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# Adsorption of Rhodamine B from an aqueous solution onto NaOH-treated rice husk

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**ABSTRACT**

Batch adsorption of Rhodamine B (RhB) dye from wastewater onto NaOH-treated rice husk (TRH) was investigated at room temperature. Adsorption of RhB onto TRH was proved by using Fourier-transform infrared spectroscopy. The detail morphology of TRH was investigated by employing scanning electron microscopy. The effect of operational factors on the percentage removal of RhB from wastewater by using TRH and adsorption capacity was revealed. The percentage removal of RhB from wastewater was increased with mass of TRH, pH and contact time, whereas declined with temperature and initial concentration of RhB dye solution. Moreover, adsorption capacity was increased with contact time, pH and initial concentration RhB dye solution whereas declined with mass of TRH and temperature. Adsorption kinetics was investigated by employing several model including pseudo-first-order, pseudo-second-order, Elovich model, liquid-film diffusion model, modified Freundlich equation and Bangham equation but experimental data fitted well to pseudo-second-order kinetics ($R^2$ = 0.997). Experimental data was also explored by using several adsorption isotherms but fitted well to Langmuir adsorption isotherm ($R^2$ = 0.996). Moreover, the value of mean adsorption energy ($E$ = 1.03 kJ/mol) exhibited that adsorption of RhB onto TRH was physical adsorption process. Adsorption thermodynamics study exhibited that adsorption of RhB from wastewater onto TRH was exothermic and non-spontaneous process.

*Keywords:* Exothermic process; Rhodamine B; Langmuir isotherm; NaOH-treated rice husk; Pseudo-second-order model

## 1. Introduction

Dye stuff are organic compounds, and utilized in several industries including textile, ink, paint plastics, cosmetics, and varnishes that resulted environmental pollution because of their highly virulent compound [1,2]. The manufactured colorants are described as a main source of environmental pollution, based on both the volume of dye removed and the concord of the drainage. Resultantly, it is crucial to erase these compounds from the colored drainage before being dropped into the aqueous solution.

Rhodamine B (RhB) belongs to the class of cationic dyes. It is employed in larger number of industries. It is guessed that around 20% of the entire dye employed during the production mechanism last into the drainage [3]. Accordingly, a large quantity of this dye lasts in the environment by the removal of untreated drainage from such industries. Once imported into the environment, RhB results not only to a gorgeous impact but also for other environmental enterprises. It's highly toxicity, even at low concentrations, and its propensity to accumulate in the food chain called into question it's utilize.

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In fact, the existence of N-ethyl groups on either side of the xanthene rings provides the molecule toxic and carcinogenic characterization both for animals and humans [4]. It leads to redness, irritation to the skin, respiratory tract, eyes, and has also been culpable for thyroid and liver damage [5]. Therefore, it is essential to take to convenient transport measures to decrease or even elude any sad effect of RhB on human and animals.

A lot of methods such as physical, chemical, and biological were utilized for the removal of dyes from aqueous solution [6–8]. Among them, the removal of dyes by physical adsorption method is considered as an extraordinary method because of outstanding capability, easy to design and operations and economic feasibility [8–14]. Hence, it is crucial to use adsorbent with outstanding efficiency for the discharge of dyes from aqueous solution.

To date, several usually employed adsorbents that represented excellent efficiency were already studied [9,15]. Usually the commercial activated carbon is potent for the color discharge but the high price of it has blocked its large scale application. A lot of material including, hen feather [16], layered double hydroxides (LDHs) [17], synthesized metal- and halide-free variant of ordered mesoporous carbon (OMC) [18], metal–organic framework (MOF) [19], novel bio-nanocomposite (Alg-Cst/Kal) [20], ordered mesoporous carbon (OMC) [21], Kahwa tea (*Camellia sinensis*) carbon [22], ash of black turmeric rhizome [12], papaya peel carbon [23], *Curcuma caesia* based activated carbon [13], Ag doped $MnO_2$-CNT nanocomposite [24], chitosan-grafted-polyaniline-OMMT nanocomposite [25], ordered mesoporous carbon (OMC) [26], guar gum/activated carbon nanocomposite [27], iron based metal–organic framework [28], nano alumina [29], metal/halide-free variant of ordered mesoporous carbon [30], bimetallic carbon nanocomposite [31], swietenia mahagoni bark activated carbon (SMBAC) [32], chenopodium album ash [33], walnut husk [34], composites [35], biochars from crop residues [36], natural clinoptilolite [37], sesame hull [38], biomass of *Penicillium* YWO1 [39], natural zeolite [40], cross-linked succinyl chitosan [41], modified bentonite [42], eucalyptus barks [43] modified attapulgite [44], clay material [45–47], activated carbon [48], dehydrated beet pulp carbon [49], polyurethane foam [50], etc. were utilized as adsorbent for the removal of dyes from aqueous solution. Agriculture by-products had denoted its capability as a cheap adsorbent and they were mostly being modified chemically to increase adsorption efficiency of them toward the dyes [51]. Despite, there are some adsorbents which did not exhibited higher adsorption efficiency for the anionic dyes. It is associated to their anionic or hydrophobic surfaces. Hence, it is required to find a cheap and effective adsorbent for the discharge of dyes from aqueous solution.

Our previous research represented the utilization of different type of adsorbents including bioadsorbents [8,10] and polymeric ion exchange membranes (both commercial and synthesized) [52–54] for the removal of dyes from aqueous solution at room temperature. We also studied adsorption of heavy metal ions onto rice husk from aqueous solution [55,56]. This article reported the usage of NaOH-treated rice husk (TRH) for adsorption of Rhodamine B from aquous solution to extend our research. To the best of our knowledge, adsorption of RhB onto TRH has not been reported yet. Moreover, it is cheap adsorbent for dye removal from aqueous solution compared to adsorbent reported in literature [28]. Adsorption of RhB onto TRH was demonstrated by using Fourier-transform infrared (FTIR) spectroscopy. The morphology of TRH was evaluated by scanning electron microscopy in detail. The effect of operational factors such as contact time, mass of TRH, initial concentration of RhB in aqueous solution, pH and temperature on the percentage removal of RhB and adsorption capacity was explored. Moreover, adsorption isotherm, kinetic and thermodynamic studies were also conducted for RhB adsorption onto TRH.

## 2. Experimental

### 2.1. Adsorbent

Husk of basmati rice was kindly provided by the rice mill, Punjab, Pakistan. It was thoroughly washed to extract the dust particle with distilled water and oven dried at 80°C till consistent weight was obtained. Methods including neutron activation analysis and atomic adsorption spectrometry were utilized for chemical analysis of husk for their trace metal contents and received results were reported [56,57]. It was noted that the quantity of metals such as Na, K, Pb and Fe were present in μg per g of sample. Silica contents were found to be 18.27 (0.62%) of TRH [57,58]. The standard methods were used to study the small amount of elements in TRH.

### 2.2. Modification of rice husk

Rice husk was modified with 1.0 M NaOH solution. Firstly, 50 g of rice husk was soaked into NaOH solution into a 1.0 L beaker. It was stirred vigorously for 24 h. Then it was washed with distilled water until neutral pH was gained. Lastly, it was dried at 80°C in oven till constant weight and stored in airtight container and named as TRH.

### 2.3. Adsorbate

Rhodamine B dye was utilized as adsorbate in this work. It was kindly supplied by Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was utilized throughout this research. All the chemicals were utilized as received. Its structure is represented in Fig. 1.

### 2.4. Batch adsorption of RhB onto TRH

Batch adsorption of RhB from wastewater onto TRH was carried as described [10,53,59–61] (See Section S1 for detail in supporting information).

### 2.5. Instrumentation

The FTIR spectrometer (Vector 22, Bruker) containing resolution of 2 $cm^{-1}$ and total spectral range of 4,000–400 $cm^{-1}$ was utilized to reveal TRH before and after adsorption of RhB from wastewater by employing attenuated total reflectance (ATR). Field-emission scanning electron microscope

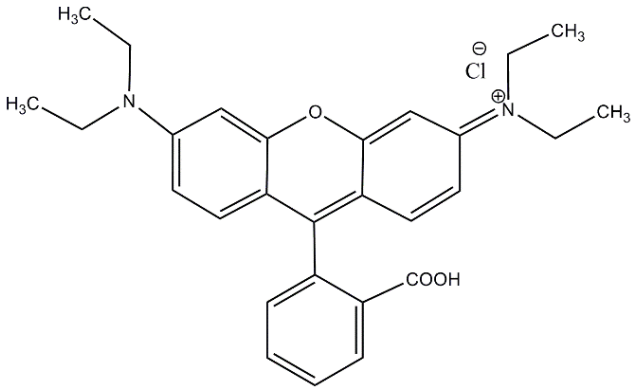


Fig. 1. Chemical structure of Rhodamine B dye.

(FE-SEM, Sirion200, FEI Company, USA) was employed to study morphology of rice husk before and after treatment with NaOH.

### 2.6. Adsorption isotherms

Several adsorption isotherms including Langmuir, Freundlich, Temkin and Dubinin–Radushkevich were used to explore experimental data for adsorption of RhB onto TRH (See Section S2 for detail in supporting material).

### 2.7. Adsorption kinetics

Many kinetic models such as pseudo-first-order, pseudo-second-order, Elovich model, liquid-film diffusion model, modified Freundlich equation and Bangham equation were used to study adsorption kinetics for RhB adsorption onto TRH (See Section S3 for detail in supporting information).

### 2.8. Adsorption thermodynamic

To explore adsorption thermodynamics, we determined the change in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) as described [27,29,38] (See Section S4 for detail in supporting information).

## 3. Results and discussion

### 3.1. Fourier-transform infrared spectroscopy

FTIR spectroscopy was employed to represent successful adsorption of RhB from wastewater onto TRH. The bands at 1,217.0; 1,365.4; 1,737.8 and 1,027.4 $cm^{-1}$ were due to carboxyl group on TRH in the range of reported bands at 1,208–1,230; 1,367–1,371; 1,740 and 1,029 $cm^{-1}$ for carboxyl group [58,62,63]. The band at 3,400–3,200 $cm^{-1}$ was because of the surface O–H stretching, whereas aliphatic C–H stretching had a broad peak at 2,921–2,851 $cm^{-1}$. The bands at 1,737.8; 1,435.6 and 1,365.4 $cm^{-1}$ were associated to C=O stretching, OH bending of the adsorbed $H_2O$ and aliphatic C–H bending, respectively [64]. Extraordinary, the peak at 1,074.0 $cm^{-1}$ coincided to anti-symmetric stretching vibration of Si–O, whereas at 476.2 $cm^{-1}$ exhibited the bending vibration of Si–O–Si bond [62,65,66]. During treatment of rice husk with NaOH, the lack of band related to non-conjugated carbonyl functional groups in the TRH spectra showed hydrolyses of carbonyl groups.

The small changes in the peak of TRH were noted after adsorption of RhB from wastewater. The decline into intensities of peak after adsorption of RhB was noted. It proved adsorption of RhB from wastewater onto TRH.

### 3.2. Morphology

Morphological features of untreated and NaOH-treated rice husk (TRH) were investigated by employing scanning electron microscopy (SEM). Results showed that morphology of untreated rice husk was rough. On the other hand, morphology of NaOH treated rice husk (TRH) was found to be smooth. It also exhibited pores on it which are significant for adsorption of RhB from wastewater onto TRH.

### 3.3. Effect of operating parameters on percentage discharge of RhB and adsorption capacity

The influence of operating parameters including contact time, mass of TRH, initial concentration RhB dye aqueous solution, pH and temperature on adsorption of RhB from wastewater onto TRH was studied in detail. Fig. 2 represents the effect of contact time, mass of TRH and initial concentration of RhB dye aqueous solution onto the percentage discharge of RhB and adsorption capacity. It was observed that the percentage discharge of RhB from wastewater and adsorption capacity were enhanced with contact time (Fig. 2a). Table 1 provides an interesting comparison of TRH adsorption performance for RhB with other adsorbents reported in the literature. With contact time, the percentage discharge of RhB was enhanced from 55% to 83% whereas adsorption capacity from 1.10 to 1.66 mg/g. As noted from Fig. 2a, the increase in the value of adsorption capacity and the percentage discharge of RhB by TRH from wastewater was rapid initially because of presense of a lot of empy sites onto adsorbent surface. With the passage of time, it slowed down and got saturation within 48 h. From here, it was noted that equilibrium was occurred whitin 48 h and this optimum time was utlized for future investigations.

Fig. 2b denotes the effect of mass of TRH on the percenage discharge of RhB from wastewater by utilizing TRH and adsorption capacity at room temperature. Results showd that the percentage discharge of RhB was increased from 44% to 76% becuase of existence of large number of active sites with enhancing amount of TRH from 0.03 to 0.20 g. On the other hand, adsorption capacity was declined from 5.86 to 1.52 mg/g with enhancing the amount of TRH from 0.03 to 0.20 g. The decline in adsorption capacity with enhancing mass of TRH at room temperature was because of limited concentration of RhB in wastewater [53].

The effect of initial concentration of RhB dye aqueous solution on the percentage discharge of RhB from wastewater by employing TRH and adsorption capacity is represented in Fig. 2c. Results represented that the percentage discharge of RhB from wastewater was declined from 76% to 52% with increasing initial concentration of RhB dye

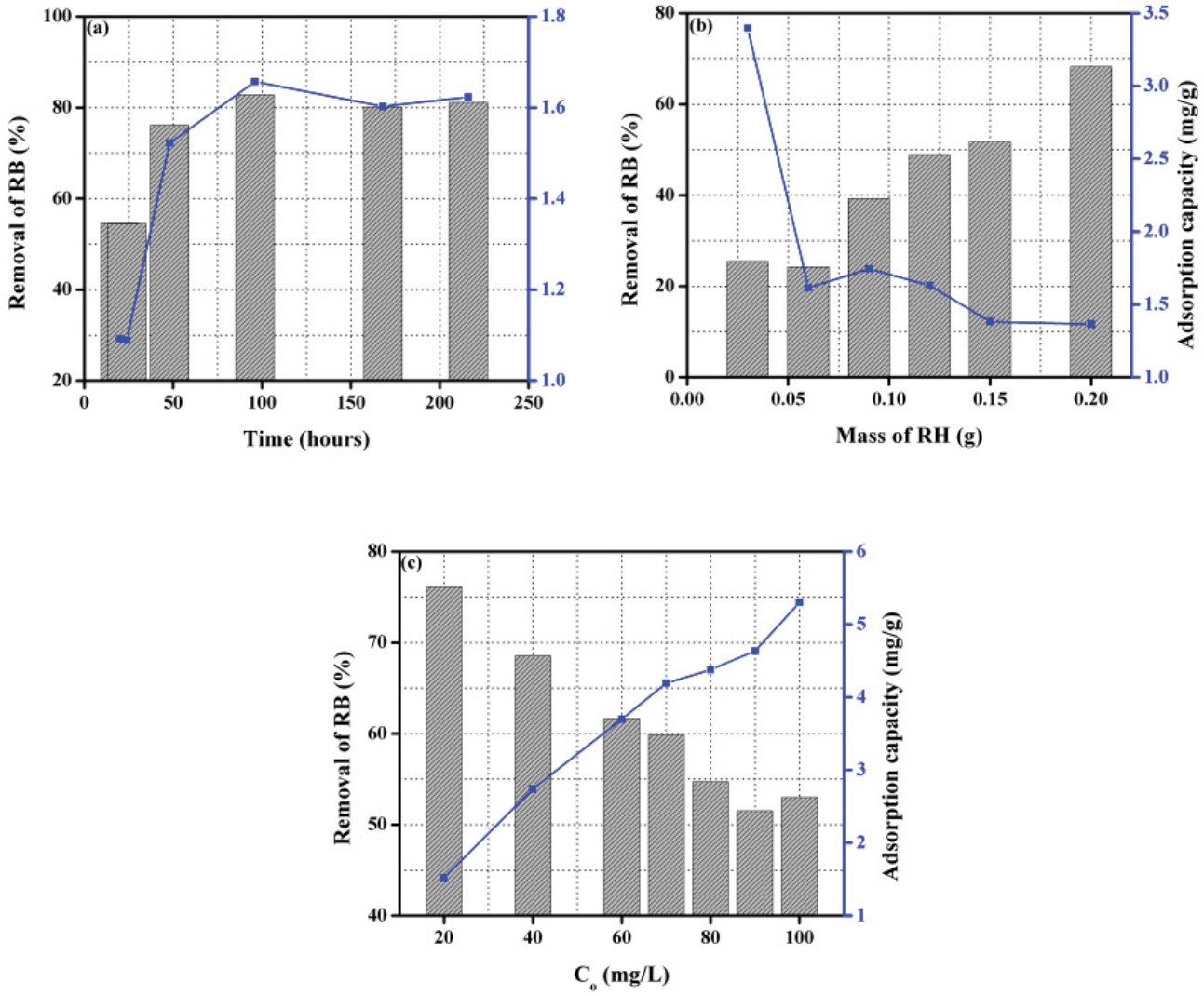


Fig. 2. (a) Effect of contact time, (b) effect of mass of TRH, and (c) effect of initial concentration of RhB dye solution onto the percentage removal of RhB from aqueous solution and adsorption capacity.

aqueous solution at room temperature. It was because of saturation of the active sites of the TRH by enhancing the initial concentration of RhB into aqueous solution [52,53]. Contrary, adsorption capacity was increased with increasing the initial concentration of RhB from 20 to 100 mg/L. Adsorption capacity was found to be enhanced from 1.52 to 5.30 mg/g due to higher concentration of RhB dye in the aqueous solution which increased the migration of dye molecules from the solution to the surface of TRH. It results to enhance the interaction between dye molecules (RhB) and TRH surface. Hence, adsorption capacity enhanced with increasing initial concentration of RhB dye aqueous solution.

Fig. 3a indicates the influcence of temperature on the percentage discharge of RhB from wastewater by TRH and adsorption capacity at room temperature. It was noted that both the percentage discharge of RhB from wastewater and adsorption capacity were decreased with rise in temperature from 298 to 333 K. As shown in Fig. 3a, the percentage

Table 1
Comparison of adsorption performance of TRH for RhB with other reported adsorbents

| Adsorbent | Removal (%) | References |
|---|---|---|
| TRH | 83.0 | This work |
| Fly ash based inorganic polymer | 62.45 | [1] |
| CMK-8 carbon replica | ~100 | [69] |
| Mesoporous silica (KIT-6) | 65.0 | [69] |
| Co-FeOOH/g-$C_3N_4$ composite | 91.5 | [70] |
| Activated biochar | 54.0 | [71] |
| P-CZIF-86 | 99.90 | [72] |
| MgO-FCM-NP | 99.0 | [73] |
| A-rGO/cobalt oxide nanoparticles composite | 95 | [74] |
| *Raphia hookeri* fruit epicarp | 89.0 | [75] |

discharge of RhB was declined from 76% to 53% whereas adsorption capacity from 1.52 to 1.33 mg/g with rise in temperature. From here, it was concluded that adsorption of RhB onto TRH from wastewater was exothermic process.

The pH of dye solution has significant effect on its adsorption onto adsorbent surface. The variation in the pH of the solution can change the surface charge of the adsorbent and the degree of ionization of the dye [67,68]. The effect of pH on the percentage removal of RhB by TRH from wastewater and adsorption capacity was studied by changing the pH values from 2 to 11 and the attained results are represented in Fig. 3b. It was noted that the values of both percentage removal of RhB and adsorption capacity were enhanced with increasing pH of medium. As we know RhB is cationic dye. It was dissociated into positively charged form into aqueous solution. At pH 2, the lower adsorption of RhB was associated to the electrostatic repulsion between cationic dye and positively charged adsorbent while the enhancement in adsorption of RhB onto TRH with increase in pH was due to electrostatic force of repulsion between cation dye and negatively charged adsorbent [67]. The percentage removal of RhB and adsorption capacity was reached to maximum at pH 2 (neutral) (Fig. 3b) which was used to conduct further work.

### 3.4. Adsorption isotherms

Langmuir adsorption isotherm for adsorption of RhB onto TRH from wastewater is represented in Fig. 4a. The determined values of its endowments ($Q_m$, $K_L$, and $R_L$) are given in Table 2. The correlation coefficient value for it was close to unity ($R^2$ = 0.996). It exhibited that experimental data for adsorption of RhB obeyed Langmuir isotherm. The value of $R_L$ (0.13–0.43) indicated that adsorption of RhB onto TRH was favorable process. Freundlich adsorption isotherm for adsorption of RhB from wastewater onto TRH is depicted in Fig. 4b and the measured values of its parameter ($n$ and $k_F$) are given in Table 2. The correlation coefficient value ($R^2$ = 0.980) denoted that experiment data for adsorption of RhB obeyed Freundlich adsorption isotherm. As shown in Table 2, the value of Freundlich constant "$n$" was found to be 1.95 representing that adsorption of RhB onto TRH from wastewater was good because the value of "$n$" ranges from 2–10 representing good adsorption, 1–2 moderate adsorption and less than one shows poor adsorption [55,58]. Fig. 4c depicts Temkin isotherm for adsorption of RhB onto TRH from wastewater. The determined values of it endowments ($b_T$ and $A_T$) are given Table 2. The correlation coefficient value ($R^2$ = 0.991) represented that experimental data obeyed Temkin isotherm. For adsorption of RhB from wastewater onto TRH, Dubinin–Radushkevich adsorption isotherm is shown in Fig. 4d and the values its parameters ($C_m$ and β) are given in Table 2. For it, the determined value of mean adsorption energy was 1.03 kJ/mol exhibiting that adsorption of RhB onto TRH was physical adsorption process [8,10]. The value of $E$ greater than 8 kJ/mol means chemical ion exchange adsorption process whereas values of $E$ below 8 kJ/mol were the characteristic of physical adsorption process [52].

### 3.5. Adsorption kinetics study

Kinetics study for adsorption of RhB from wastewater onto TRH was conducted by using several model including pseudo-first-order, pseudo-second-order, Elovich model, liquid-film diffusion model, modified Freundlich equation and Bangham equation. The graphical representation of pseudo-first-order model for adsorption of RhB onto TRH is denoted in Fig. 5a. The value of adsorption capacity ($q_e$) was calculated from intercept of the plot of $\log(q_e - q_t)$ vs. time and is given in Table 3. From here, it was seen that there was a largre difference between the values of experimental adsorption capacity (1.52 mg/g) and calculated adsorption capacity (0.728 mg/g). The correlation cofficient ($R^2$) value for pseudo-first-order model was 0.916. It showed that pseudo-first-order model is not able explain the rate process. The plot of $t/q_t$ vs. time for pseudo-second-order model is denoted in Fig. 5b. The correlation coefficient value ($R^2$ = 0.997) was close to unity. The measured value of adsorption capacity ($q_e$) is given in Table

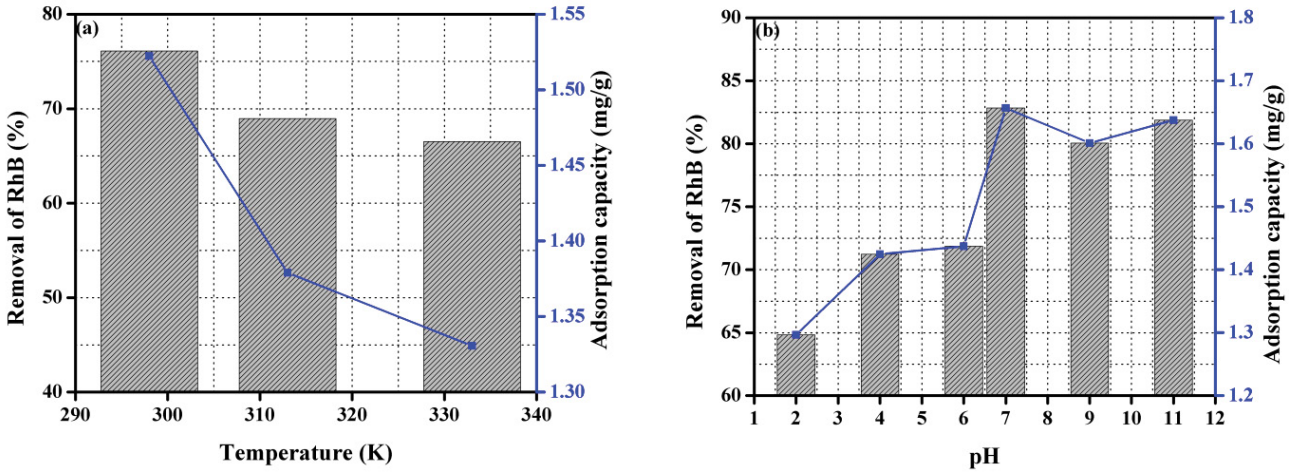


Fig. 3. (a) Effect of temperature and (b) effect of pH onto the percentage removal of RhB from aqueous solution by TRH and adsorption capacity.

Table 2
Measured parameters of adsorption isotherm for adsorption of RhB onto TRH

| Adsorption isotherms | Measured parameters | |
|---|---|---|
| Langmuir isotherm | $Q_m$ | 6.28 |
| | $K_L$ | 0.065 |
| | $R^2$ | 0.996 |
| | $R_L$ | 0.13–0.43 |
| Freundlich isotherm | $n$ | 1.95 |
| | $k_F$ | 0.715 |
| | $R^2$ | 0.98 |
| Temkin isotherm | $A_T$ | 0.28 |
| | $b_T$ | 1715 |
| | $R^2$ | 0.991 |
| Dubinin–Radushkevich isotherm | $q_e$ | 4.12 |
| | β | 0.47 |
| | $R^2$ | 0.874 |
| | $E$ | 1.03 |

$Q_m$ (mg/g); $K_L$ (L/mol); $k_F$ ((mg/g)(L/mg)$^{1/n}$); $C_m$ (mol/g); β (mol$^2$/J$^2$); $E$ (kJ/mol).

3 which was in good agreement with the experimental adsorption capacity (1.70 mg/g). It showed that experimental data for adsorptin of RhB onto TRH fitted well to pseudo-second-order model. For adsorption of RhB onto TRH, the plot of Elovich model is shown in Fig. 5c and the determined values of α and β from intercept and slope respectively are given in Table 3. For it, the correlation cofficient value ($R^2$ = 0.753) was lower than pseudo-second-order model. Hence it was not good to explain experimental data. Fig. 5d represents the plot of liquid-film diffusion model and the measured value of $K_{fd}$ is given in Table 3. The correlation coefficient value ($R^2$ = 0.716) for it was lower than pseudo-second-order model. Therefore, it was also not good to explain adsorption of RhB onto TRH. Fig. 5e denotes the plot of modified Freundlich equation and the calculated values of its parameters are given in Table 3. The lower value of correlation coefficient ($R^2$ = 0.743) represented that it is not convenient to explain experimental results for adsorption of RhB onto TRH. Further, the plot of Bangham equation is shown in Fig. 5f and the calculated values of its endowments are given in Table 3. For it, the double logarithmic plot did not give linear curves denoting that the diffusion of adsorbate (RhB) into pores of the adsorbent (TRH) is not the only rate controling step [52,58]. It may be that

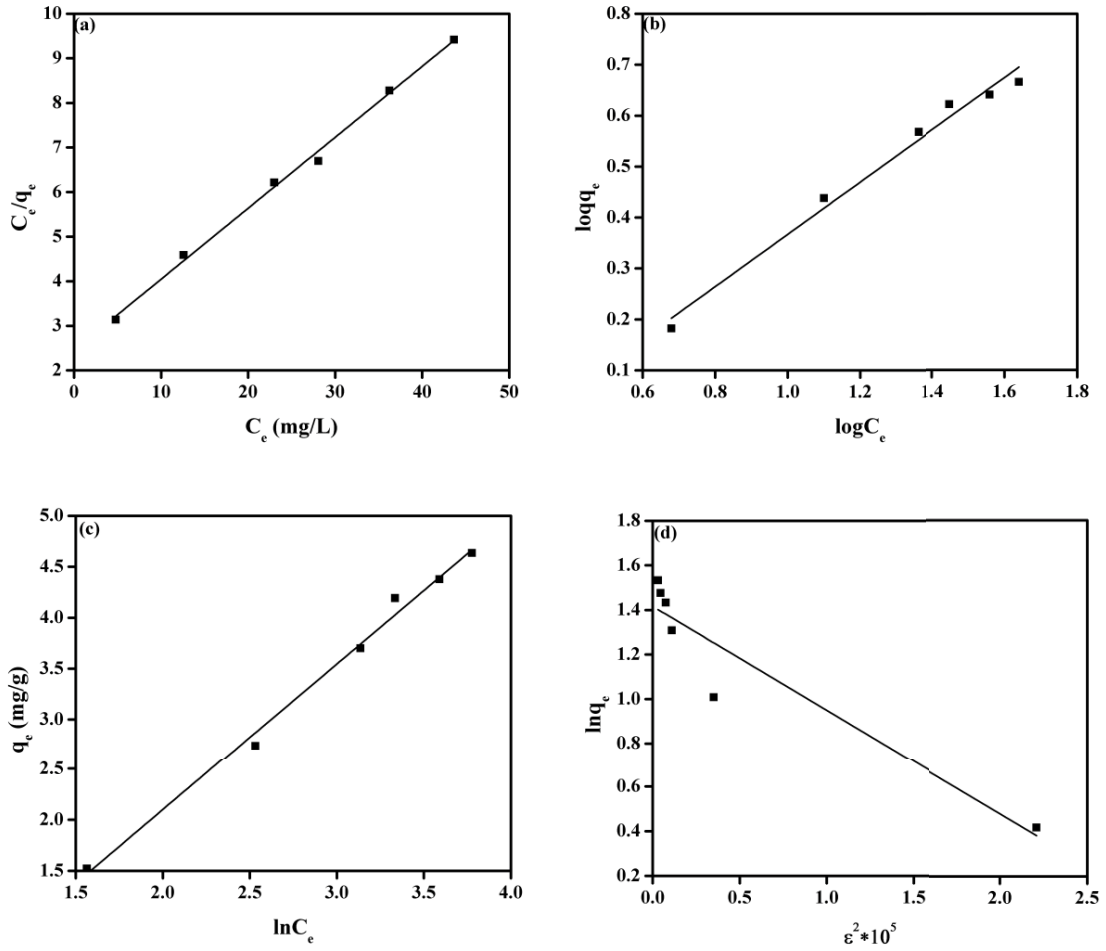


Fig. 4. (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm, and (d) Dubinin–Radushkevich isotherm for adsorption of RhB from aqueous solution onto TRH.

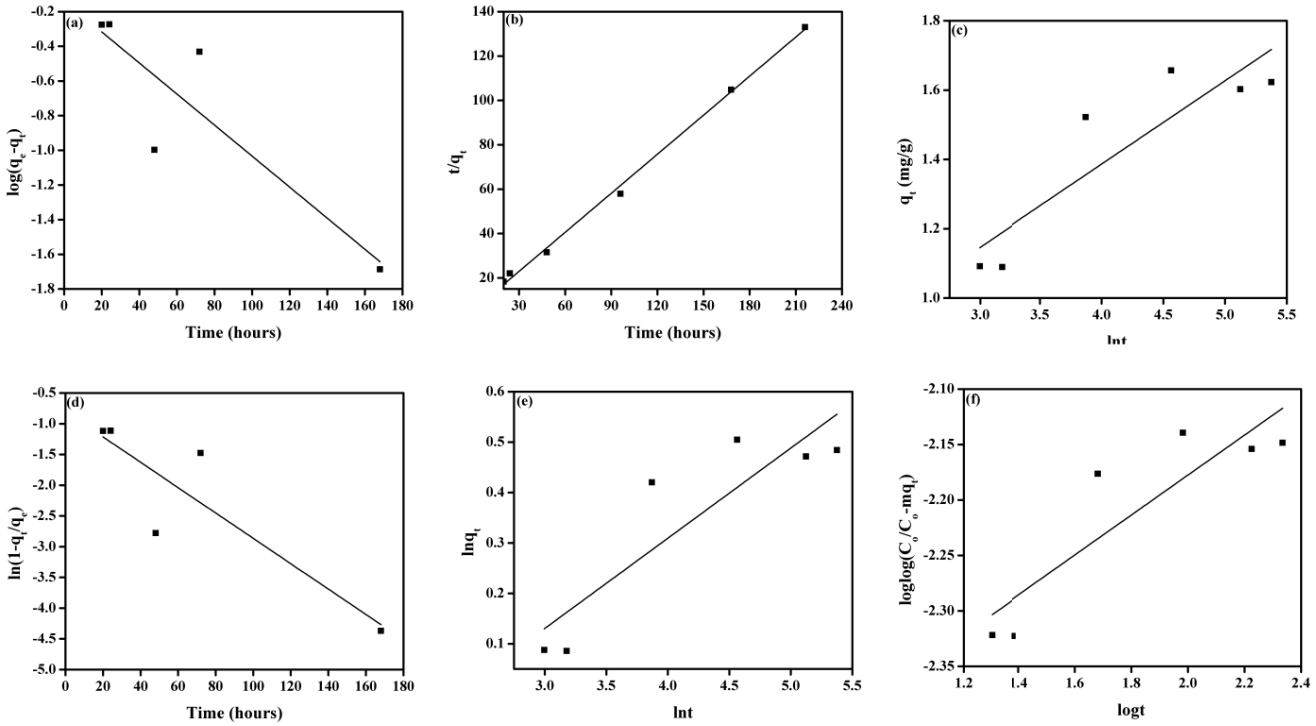


Fig. 5. (a) Pseudo-first-order model, (b) Pseudo-second-order model, (c) Elovich model, (d) liquid-film diffusion model, (e) modified Freundlich equation, and (f) Bangham equation for adsorption of RhB from aqueous solution onto TRH.

Table 3
Calculated values of kinetic parameters for adsorption of RhB onto TRH

| Kinetic models | Measured parameters | |
|---|---|---|
| Pseudo-first-order model | $q_{e,\exp}$ | 1.52 |
| | $q_{e,\mathrm{cal}}$ | 0.728 |
| | $k_1$ | 0.0089 |
| | $R^2$ | 0.916 |
| Pseudo-second-order model | $q_e$ | 1.70 |
| | $k_2$ | 0.065 |
| | $R^2$ | 0.997 |
| Elovich model | α | 1.41 |
| | β | 4.16 |
| | $R^2$ | 0.753 |
| Liquid-film diffusion model | $K_{\mathrm{fd}}$ | 0.021 |
| | $C_{\mathrm{fd}}$ | –0.81 |
| | $R^2$ | 0.716 |
| Modified Freundlich equation | $m$ | 5.59 |
| | $k$ | 0.033 |
| | $R^2$ | 0.743 |
| Bangham equation | $k_o$ | 0.67 |
| | α | 0.18 |
| | $R^2$ | 0.743 |

$q_e$: (mg/g); $k_1$: ($\mathrm{min}^{-1}$); $k_2$: (g/mg min); α: (mg/g min); β: (g/mg); $K_{\mathrm{fd}}$: ($\mathrm{min}^{-1}$); $k$: (L/g min); $k_o$: (mL/g/L).

both film and pore diffusion were crucial to different extent for adsorpion of RhB onto TRH from wastewater.

### 3.6. Adsorption thermodynamics

Adsorption thermodynamics for RhB adsorption onto TRH was evaluated in detail by calculating the change in Gibbs free enegry (Δ$G$°), enthalpy (Δ$H$°) and entropy (Δ$S$°). The measured values of thermodynamic endowments (Δ$G$°, Δ$H$°, Δ$S$°) are given in Table 4. At all the temperature investigated, the values of Gibbs free energy was positive and found to be increased with enhancement in temperature from 298 to 333 K. It was associated to the intraction between adsorbent and adsorbate, with unbalanced competition imputed to heterogeneity of adsorbent (TRH) surface and system attained energy from external source at elevated temperatures [54,59]. Moreover, the positive value of Gibbs energy showed that adsorption of RhB was non-spontaneous process. The attained value of enthalpy (Δ$H$°) was nagative for adsorption of RhB onto TRH. It represented that adsorption of RhB was an exothermic process. Likewise, the negative value of entropy denoted the decline in randomnes at the adsorbate–adsorbent (TRH) interface during adsoption process.

## 4. Conclusions

In this article, adsorption of RhB from wastewater onto TRH was investiagted at ambient temperature. Adsorption of RhB onto TRH was proved by using FTIR spectroscopy.

Table 4
Determined thermodynamic parameters for adsorption of RhB onto TRH

| Temperature (K) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol) | $\Delta G$ (kJ/mol) |
|---|---|---|---|
| 298 | | | 8.27 |
| 313 | –11.01 | –27.71 | 8.68 |
| 333 | | | 9.24 |

The percentage removal of RhB was increased with contact time, pH and mass of TRH whereas decline with initial concentration of RhB solution and temperature. On the other hand, adsorption capacity was increased with contact time, pH and initial concentration of RhB solution whereas decreased with mass of TRH and temperature. Adsorption kinetic study showed that adsorption of RhB onto TRH followed pseudo-second-order kinetics. Adsorption isotherm study exhibited that adsorption of RhB onto TRH fitted well to Langmuir isotherm. Adsorption thermodynamic evaluation demostrated that adsorption of RhB onto TRH was an exothermic and non-spontaneous process. From this it was concluded that TRH could be utilized as adsorbent for adsorption of RhB at room temperature.

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## Supporting information

### S1. Batch adsorption of Rhodamine B onto NaOH-treated rice husk

Initially, we synthesized aqueous solution of Rhodamine B (RhB) by dissolving a calculated quantity of it into distilled water at room temperature. The calculated quantity of NaOH-treated rice husk (TRH) was shaked into 20 mL of RhB aqueous solution at agitation speed of 180 rmp. The optimized contact time was determined by shaking the measured amount of TRH into 20 mL of RhB aqueous solution with initial concentration of 20 mg/L for different time intervals such as 20, 24, 48, 72, 96, 168 and 216 h. To find out optimized amount of TRH, we employed 0.03, 0.06, 0.09, 0.12, 0.15 and 0.20 g of TRH into 20 mL of RhB aqueous solution with initial concentration of 20 mg/L of RhB for 48 h at room temperature. The effect of pH on adsorption of RhB was evaluated by shaking measured mass of TRH (0.20 g) into measured volume of RhB aqueous solution (20 mL), with concentration of RhB aqueous solution (20 mg/L) by changing pH values of RhB aqueous solution from 2 to 11 for 48 h at room temperature. Adsorption isotherm was revealed by shaking the measured mass of TRH (0.20 g) into 20 mL of RhB aqueous solution with initial concentration of 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L for 48 h at room temperature. To investigate adsorption thermodynamics, we shaked the measured quantity of TRH (0.20 g) into 20 mL of RhB aqueous solution with initial concentration of 20 mg/L at 298, 313, 323 and 333 K for 48 h at speed 180 rmp. The RhB concentration of was calculated by determining the absorbance of the supernatant at wavelength ($\lambda_{max}$ = 556 nm for RhB) by utilizing UV/VIS spectrophotometer (UV-2550, SHIMADZU). The concentration of RhB was determined by utilizing calibration curve. The percentage removal of RhB from wastewater by TRH and adsorption capacity was calculated by using below equations:

$$\text{Removal} = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

$$q_t = \frac{C_o - C_t}{W} \times V \tag{2}$$

where $C_o$ (mg/L) and $C_t$ (mg/L) represent concentration of RhB at initial state and at time $t$ respectively. Similarly $V$ (mL) denotes volume of dye aqueous solution and $W$ (g) shows the amount of TRH.

### S2. Adsorption isotherms

*S2.1. Langmuir isotherm*

It is based on the maximum adsorption corresponds to the saturated monolayer of liquid molecules on the solid surface. It is given as follows [S1].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \tag{3}$$

where $Q_m$ (mg/g) is Langmuir monolayers adsorption capacity, $C_e$ is supernatant concentration at equilibrium state of the system (mg/L), $K_L$ is Langmuir constant (L/mg) (mg/g), and $q_e$ is the amount of dye adsorbed at equilibrium state of system (mg/g). The essential characteristics of Langmuir isotherm can be represented in term of dimensionless constant separation factor $R_L$ that is given by [S2].

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

The value of $R_L$ denoted the shape of the isotherm to be either unfavorable ($R_L$ > 1), linear ($R_L$ = 1), favorable (0 < $R_L$ > 0), or irreversible ($R_L$ = 0) [S3].

*S2.2. Freundlich isotherm*

It is an empirical relationship employed to discuss the heterogeneous system. It is represented as [S4].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

where $K_f$ and $n_F$ are Freundlich constant.

*S2.3. Tempkin isotherm*

It is shown as [S5]:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{6}$$

where $B_T = RT/b_T$, $T$ is absolute temperature (K) and $R$ is gas constant (8.31 J/mol K). The constant $b_T$ is related to the heat of adsorption and $A_T$ is equilibrium binding constant coinciding to the maximum binding energy.

*S2.4. Dubinin–Radushkevich isotherm*

The Dubinin–Radushkevich model is shown as [S5]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{7}$$

where β (mol²/KJ) is constant related to the adsorption energy and ε is the Polanyi potential can be determined by using below relationship:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{8}$$

where $R$ is gas constant (8.31 kJ/mol) and $T$ is absolute temperature (K). The mean free energy $E$ (kJ/mol) can be calculated by below equation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{9}$$

**S3. Adsorption kinetics**

*S3.1. Pseudo-first-order model*

Its linear form is represented as [S6–S9]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1 t}{2.303} \tag{10}$$

where $K_1$ (min), $q_e$ (mg/g) and $q_t$ (mg/g) shows rate constant of pseudo-first-order model, concentration of RhB adsorbed at equilibrium and time $t$ respectively.

*S3.2. Pseudo-second-order model*

Its linear form is expressed as [S9,S10]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where $K_2$ (g/mg min) is the rate constant of pseudo-second-order model.

*S3.3. Elovich model*

The Elovich model is shown as [S11,S12]:

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln t \tag{12}$$

where α (mg/g.min) and β (g/mg) are constant. The α denotes the initial adsorption rate and β the extent of surface coverage and activation energy for chemisorption.

*S3.4. Liquid-film diffusion model*

It is shown as [S13]:

$$\ln\left(1-F\right) = -K_{\text{fd}} t \tag{13}$$

where $K_{\text{fd}}$ is liquid-film diffusion rate constant, and $F = q_t/q$.

*S3.5. Modified Freundlich equation*

It was originally developed by Kuo and Lotse [S10,S14]:

$$q_t = kC_o t^{1/m} \tag{14}$$

where $k$, $C_o$, $t$ and $m$ are adsorption rate constant (L/g min), initial concentration of dye (mg/L), contact time (min) and the Kuo–Lotse constant respectively. Its linear form is represented as:

$$\ln q_t = \ln\left(kC_o\right) + \frac{1}{m}\ln t \tag{15}$$

*S3.6. Bangham equation*

It is shown as [S9,S12]:

$$\log\log\left(\frac{C_o}{C_o - q_t m}\right) = \log\left(\frac{k_o m}{2.303V}\right) + \alpha\log t \tag{16}$$

where $m$ is mass of the TRH (adsorbent) employed (g/L), $V$ is volume of RhB dye solution (mL), α (<1) and $k_o$ (mL/(g/L)) are constants.

**S4. Adsorption thermodynamics**

Adsorption thermodynamics was explored by determining the parameters including change in Gibb's free energy (Δ$G$°), enthalpy (Δ$H$°) and entropy (Δ$S$°) by using below relationship:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{17}$$

$$K_c = \frac{C_a}{C_e} \tag{18}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19)$$

where $K_c$, $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ are equilibrium constant, change in Gibb's free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively.

## S5. References


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