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# Utilization of Agricultural Waste as Low-Cost Adsorbents in Dye Wastewater Treatment: Kinetic and Thermodynamic Study

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**Abstract.** In recent years, the treatment of dye wastewater has attracted more attention because of its harmful impact on the environment. Therefore, dye wastewater should be treated using effective treatment methods, such as adsorption, which is widely employed to remediate many dyes from wastewater. This work studied the use of Laurus Nobilis Leaves (LNL) and sawdust (SD) as low-cost natural adsorbents to remediate reactive blue (RB) dye from synthetic wastewater under the influence of their dosages (0.5-5.5 g) for each, pH (3-9), and contact time (10-190 min). The experimental design, analysis of results, and optimization were conducted using Response Surface Methodology (RSM) based on Box-Behnken method (BBM) and the Minitab-Statistical program. The BET and FT-IR tests have been used to characterize these adsorbents, which show that SD-adsorbent includes more pore volume and surface area than LNL-adsorbent. The adsorption isotherms study revealed that Langmuir isotherm was a more fitted model than Freundlich model. Adsorption kinetic shows that the current adsorption process obeys the pseudo-second order model ($R^2$=0.998) compared to the pseudo-first order model ($R^2$=0.973) and the intraparticle diffusion model ($R^2$=0.915). Thermodynamics study revealed that the present adsorption is endothermic, random irregularity at the solid-liquid, and a spontaneous nature. More than 60% of RB- dye removal efficiency was achieved at the optimal conditions, which were 5.5 g of SD-adsorbent, 0.8 g of LNL-adsorbent, pH 3, and 141 min of the contact time. The core results proved that the interaction effect of using multi-natural adsorbents was significant and cost-effective, providing considerable removal of dye from wastewater.

**Keywords.** Dye wastewater, Adsorption, Low-cost adsorbents, RSM-BBD, Thermodynamics parameters, Adsorption kinetics and isotherms.

## 1. Introduction

The rapid development of industries has raised the volume of effluent released into the soil and aquatic systems [1,2]. As an essential constituent, various contaminants have influenced water, such as toxic metals, dyes, pesticides, organic components, etc. [3,4]. Dyes are broadly employed in several fields, such as leather, paper, plastics, textile, rubber, etc. [1-3]. A huge amount of dyes are used in industries,

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and more than 700,000 tons of dyestuff are annually produced around the world. The discharge of synthetic dyes into the aquatic systems has caused a thoughtful crisis in the environment. The existence of a tiny small concentration of dyes in aquatic systems is undesirable [5-8].
In order to eliminate these dyes from the polluted water, numerous technologies are employed, such as chemical coagulation, adsorption, ion exchange, advanced oxidation process, filtration using different types of membrane, electrochemical techniques, etc. Adsorption technology is widely employed in wastewater treatment to minimize hazardous contaminants presented in industrial wastewater. Activated carbon (AC) is a preferred material for color elimination, but it is restricted in use because of its relatively high cost. Recently, natural low-cost adsorbents has taken more attention in wastewater treatment [9-11].
Natural dyes contain a restricted ranges of colors and are generated in low quantities. While synthetic types of dyes are advanced and have exchanged natural types of dyes regularly in several industries. Dyes can categorize belong to their chemical structure into indigoid, anthraquinone, azo, nitro, triarylmethane, and nitroso dyes. Sometimes, they are categorized based on their solubility in water, sulfur, azoic, vat, and dispersed dyes are insoluble. However direct, reactive, acid, and basic dyes are extremely highly soluble [4,8,12].
Furthermore, many industrial dyes are dangerous and mutagenic, teratogenic or carcinogenic for water organisms. These dyes cause diseases to human, such as liver, brain, dysfunctional kidney, and the nervous system [8, 20-22]. For these reasons, effective treatment technologies of dye wastewater is essential.
Several methods were utilized to remove dyes from wastewater to minimize their effect on the aquatic systems. Accordingly, all the physical, chemical, and biological methods are employed. [16,17]. Chemical dyes elimination technologies may be ineffective because of the interaction between the nature of the chemical performed and the pollutants present in the wastewater. These chemical methods are practical for decolorizing dye-water, but they are costly due to the large uses of reagents consumed and electrical power in addition to the formation of a toxic chemical resulting at the end of the elimination process [17].
The physical elimination methods of dyes are more extensive, involving adsorption and membrane filtration. Membrane filtration (MF) technique includes several processes, such as reverse osmosis microfiltration, nanofiltration, and ultrafiltration. But MF processes are suffered from some disadvantages, such as the short-life of the membrane and its high cost [18]. Base on the literature, adsorption technology is widely performed in wastewater treatment because it can eliminate pollutants and discolor dye-water resources. In recent years, low-cost adsorbents were produced from industrial wastes and agricultural by-products for dye elimination from wastewater [3,19].
This study aims to investigate the interaction effect of using two low-cost natural adsorbents, which are Laurus Nobilis Leaves (LNL) and sawdust (SD), for removing reactive blue (RB) dye from synthetic wastewater under the influence of selected operating variables. Response surface methodology based on Box-Behnken method (RSM-BBD) and Minitab program have been used to design experiments, analysis, and optimization.

## 2. Experimental work

### *2.1. Materials*

The Laurus Nobilis leaves (LNL) adsorbent was collected from a local market while the sawdust (SD) was obtained from a local carpentry factory. These materials have repeatedly cleaned with distilled water to remove impurities, dried in the oven for 24 h, crushed, sieved into a small size below 300 µm, and stored in well-closed containers. LNL and SD adsorbents were characterized using FT-IR and BET tests. The adjustment of solution pH was done by using 0.1 M HCl and 0.1 M NaOH. The dye selected for removal from synthetic was the reactive blue (RB) dye (chemical form: $C_{22}H_{16}N_2Na_2O_{11}S_3$, $\lambda_{max}$ = 585, Molar mass=626.5 g/mol). Fig. 1 presents the chemical structure.

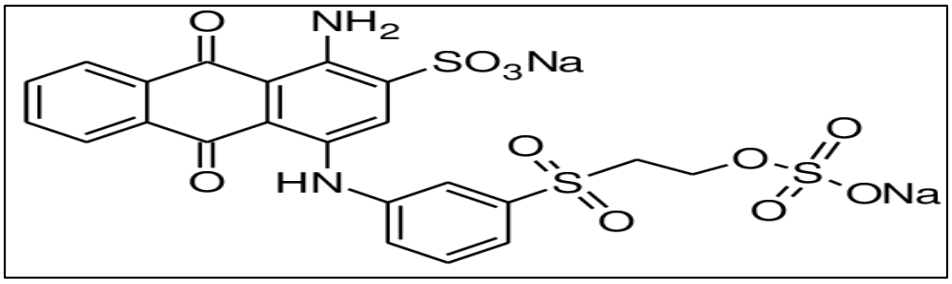



**Figure 1.** Chemical structure of (RB) dye.

A stock solution of 1000 mg/L of RB dye was prepared by dissolving one gram of this dye in one liter of distilled water where the concentration of RB in each experiment was fixed as 30 mg/L per 200 ml of the sample.

*2.2. Experimental Design*

The interactions among the studied operating variables and modeling of responses, response surface methodology based on Box–Behnken Design (RSM-BBD) and Minitab program were performed.

In this work, RSM-BBD optimized operational variables of SD-dosage ($X_1$: 0.5-5.5 gm), LNL-dosage ($X_2$: 0.5-5.5 gm), solution pH ($X_3$: 3-9), and contact time ($X_4$: 10-190 min) with a constant stirring speed of 150 rpm to enhance the removal efficiency of RB dye. Table 1 shows the real and coded values of the operational parameters and the experimental design matrix based on RSM-BBD is listed in Table 2, which consists of 27 actual conditions and the results obtained for the studied responses.

**Table 1.** Real and Coded variables of the operating variables.

| Variables | Units | Levels | | |
|---|---|---|---|---|
| | | -1 | 0 | +1 |
| $X_1$: SD-dosage (gm) | gm | 0.5 | 3 | 5.5 |
| $X_2$: LNL-dosage (gm) | gm | 0.5 | 3 | 5.5 |
| $X_3$: pH | - | 3 | 6 | 9 |
| $X_4$: contact time (min) | min | 10 | 100 | 190 |

**Table 2.** The studied variables and responses.

| Run | $X_1$: SD-dosage (gm) | $X_2$: LNL-dosage (gm) | $X_3$: pH (-) | $X_4$: contact time (min) | Final Color (ppm) | Color removal (%) | Final pH |
|---|---|---|---|---|---|---|---|
| 1 | 0.5 | 0.5 | 6 | 100 | 18.20 | 39.33 | 6.20 |
| 2 | 5.5 | 0.5 | 6 | 100 | 15.89 | 47.03 | 6.20 |
| 3 | 0.5 | 5.5 | 6 | 100 | 24.50 | 18.33 | 6.30 |
| 4 | 5.5 | 5.5 | 6 | 100 | 21.45 | 28.50 | 6.10 |
| 5 | 3.0 | 3.0 | 3 | 10 | 15.48 | 48.40 | 2.95 |
| 6 | 3.0 | 3.0 | 9 | 10 | 26.89 | 10.37 | 8.90 |
| 7 | 3.0 | 3.0 | 3 | 190 | 13.48 | 55.07 | 3.10 |
| 8 | 3.0 | 3.0 | 9 | 190 | 22.99 | 23.37 | 8.95 |
| 9 | 0.5 | 3.0 | 6 | 10 | 22.44 | 25.20 | 6.12 |
| 10 | 5.5 | 3.0 | 6 | 10 | 18.33 | 38.90 | 6.20 |
| 11 | 0.5 | 3.0 | 6 | 190 | 19.27 | 35.77 | 6.40 |
| 12 | 5.5 | 3.0 | 6 | 190 | 16.11 | 46.30 | 6.20 |
| 13 | 3.0 | 0.5 | 3 | 100 | 14.22 | 52.60 | 2.95 |
| 14 | 3.0 | 5.5 | 3 | 100 | 21.44 | 28.53 | 3.00 |
| 15 | 3.0 | 0.5 | 9 | 100 | 19.44 | 35.20 | 8.86 |
| 16 | 3.0 | 5.5 | 9 | 100 | 26.32 | 12.27 | 9.10 |
| 17 | 0.5 | 3.0 | 3 | 100 | 17.11 | 42.97 | 3.00 |
| 18 | 5.5 | 3.0 | 3 | 100 | 13.45 | 55.17 | 3.00 |

| Run | $X_1$: SD-dosage (gm) | $X_2$: LNL-dosage (gm) | $X_3$: pH (-) | $X_4$: contact time (min) | Final Color (ppm) | Color removal (%) | Final pH |
|---|---|---|---|---|---|---|---|
| 19 | 0.5 | 3.0 | 9 | 100 | 20.47 | 31.77 | 8.95 |
| 20 | 5.5 | 3.0 | 9 | 100 | 19.30 | 35.67 | 9.00 |
| 21 | 3.0 | 0.5 | 6 | 10 | 19.40 | 35.33 | 6.20 |
| 22 | 3.0 | 5.5 | 6 | 10 | 23.60 | 21.33 | 6.20 |
| 23 | 3.0 | 0.5 | 6 | 190 | 16.44 | 45.20 | 6.30 |
| 24 | 3.0 | 5.5 | 6 | 190 | 21.15 | 29.50 | 6.40 |
| 25 | 3.0 | 3.0 | 6 | 100 | 18.45 | 38.50 | 6.00 |
| 26 | 3.0 | 3.0 | 6 | 100 | 18.11 | 39.63 | 6.00 |
| 27 | 3.0 | 3.0 | 6 | 100 | 18.33 | 38.90 | 6.00 |

## 3. Results and Discussions

### *3.1. Characterization of SD and LNL Adsorbents*

#### *3.1.1. FT-IR Analysis*

FT-IR measurements between 4000 and 600 $cm^{-1}$ were conducted to identify the functional groups found in the SD and LNL adsorbents (Fig. 2). As shown, the comprehensive band at 3445-2920 $cm^{-1}$ is recognized as (C-H), hydroxyl (O-H), and (N-H) stretching of amides and amines. The (C-N) bandsare and silicone compounds clear in the area 2363–2341 $cm^{-1}$. The (C=O), (C-O), the aromatic vibration (C-C) of lignin, and (-C-H) alkyl halide are presented at the peaks of 1731 to 1033$cm^{-1}$. The rest of peaks may refer to *v* and beta-rings.

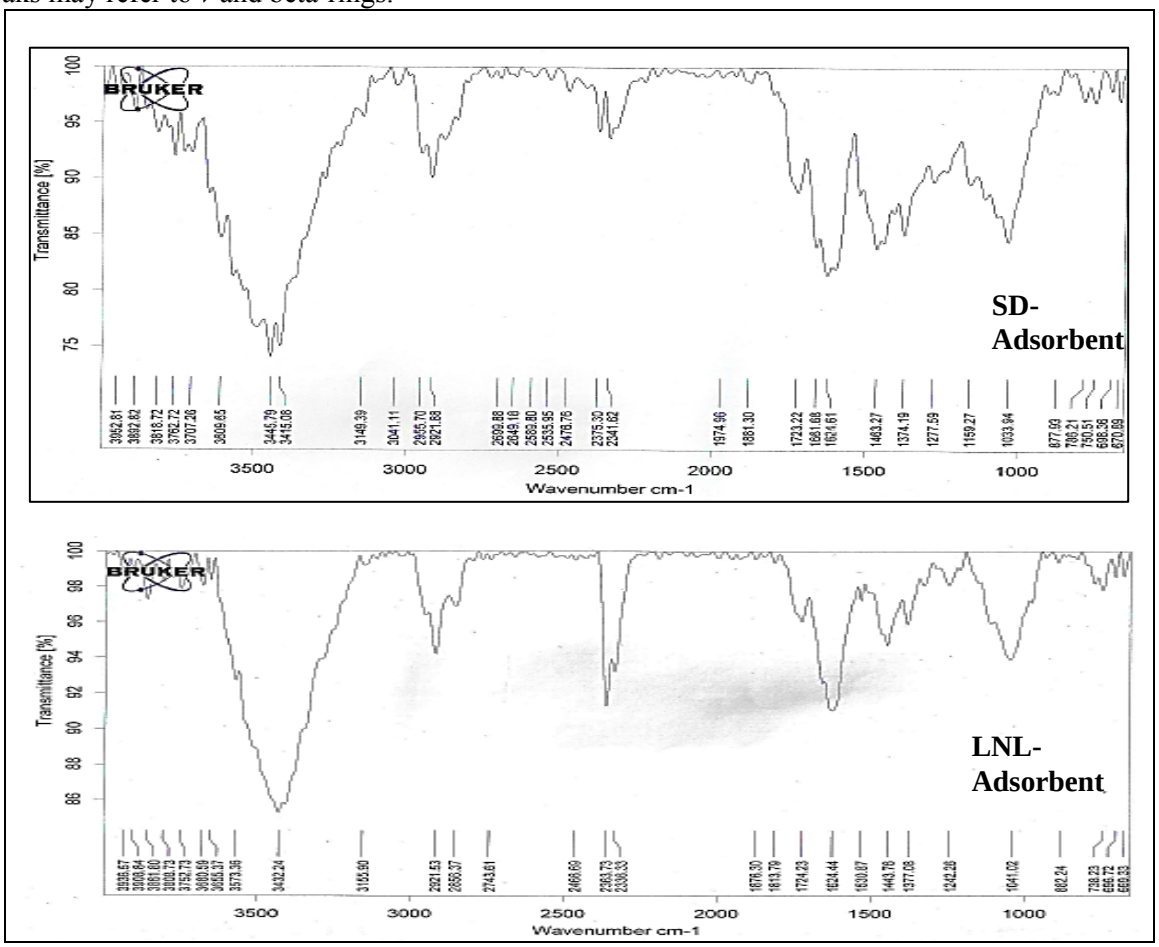



**Figure 2.** FT-IR analysis for SD and LNL adsorbents.

*3.1.2. BET Analysis*

The pore volume of SD and LNL adsorbents and their surface areas are very important subjects to evaluate in a porous material because they can significantly impact the properties of these adsorbents and their application processing abilities. Table 3 shows that SD-adsorbent includes more active area per one gram pore volume and surface area than LNL-adsorbent.

**Table 3.** Characterization of LNL and SD adsorbents by BET test.

| Items | LNL-Adsorbent | SD-Adsorbent |
|---|---|---|
| Pore volume ($cm^3/g$) | 0.1972 | 0.5582 |
| Specific surface area ($m^2/g$) | 0.8583 | 2.4296 |
| Mean pore size (nm) | 3.6661 | 4.1069 |

*3.2. Removal Efficiency of RB Dye*

Table 2 listed the final concentration and removal efficiencies of RB dye as well as the final value of solution pH. In Table 2, columns 2, 3, 4, and 5 refer to the actual values of the operational variables, SD-dosage, LNL-dosage, solution pH, and the contact time (min). The main effects of the operating variables on the dye removal is shown clearly in Fig. 3 while the interaction effects of these variables are presented in contour Fig. 4.

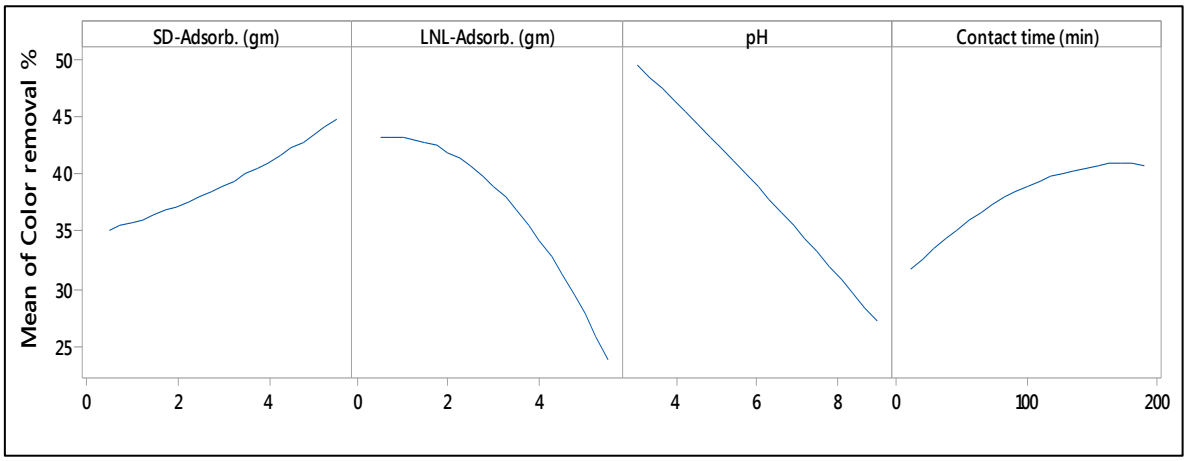



**Figure 3.** Main effects of the operation variables on 30 ppm RBD removal efficiency from synthetic wastewater.

Each panel of Fig. 3 reveals the effect of that variable on dye-removal% when other conditions are fixed at their mean values. Panel-01 indicates that dye removal efficiency increases with the increase of SD-dosage at 3 gm of LNL-dosage, pH 6, and 100 min of contact time. This means that the pores structure of SD-adsorbent is positively influencing the removal% response at near-moderate solution pH. While, removal% decreases as the dosage of LNL-adsorbent increases at mean values of other variables which are 3 gm of SD-adsorbent, pH 6, and 100 min of the contact time as explained in the second panel of Fig. 3. As observed, the highest removal of dye was attained at the acidic medium. So, from the finding observed first two panels of Fig. 3, the interaction between both adsorbents doses affects the elimination process where the SD-adsorbent was more effective when it increased and dominates the process. While the situation is different when the LNL-adsorbent has dominated the treatment process, except at a low amount. This means that the increment of LNL-adsorbent more than its optimal value will block the pores of SD-adsorbent and, consequently, minimize the RB- dye removal efficiency. Both cases occurred at near-moderate solution pH along the treatment time of 100 min.

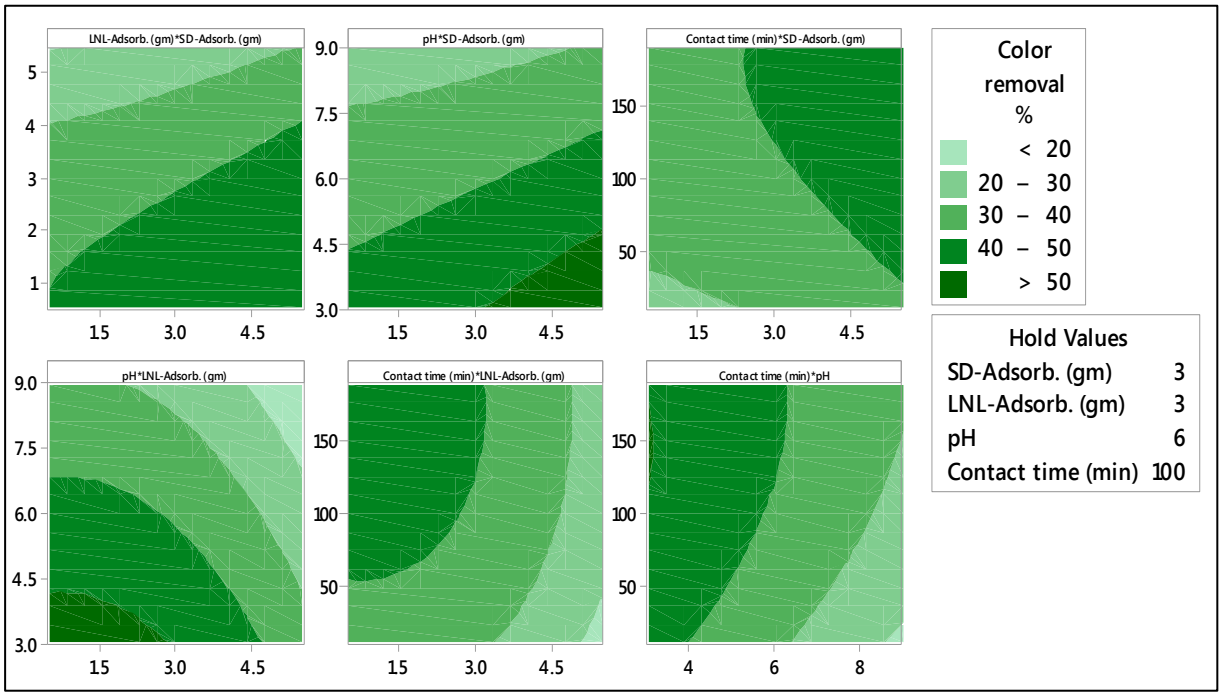



**Figure 4.** The contour plot for 30 ppm RBD removal efficiency from synthetic wastewater.

As revealed in Fig. 4, the highest removal efficiency of RB dye was attained at restricted conditions of each pair of the operating variables with the mean vales of others. The following observations explain the highest removal efficiency of dye was obtained at:

- The lowest amount of LNL-adsorbent for all values of SD-adsorbent indicates that the pores structure of SD-adsorbent is more effective to adsorb pollutants from wastewater with the condition of the low amount of LNL-adsorbent to prevent the blockage of SD-pores.
- The acidic medium and the highest amount of SD-adsorbent are due to the nature of the anionic dye, which is adsorbed efficiently to the adsorbent in the acidic solution.
- The highest contact time permits the SD-adsorbent to eliminate more concentration of dye, especially at a larger amount of this adsorbate.
- The acidic medium of wastewater is preferred to eliminate anionic RB dye in the case of the low amount of LNL-adsorbent in addition to the mean value of the other adsorbent (3 gm of SD).
- The low value of LNL-adsorbent could be more effective in removing RB dye, but needs more contact time.
- The highest ranges of contact time with the acidic medium of samples are preferred to remove RB dye from wastewater when 3 gm of each adsorbent is performed.

The effect of employing two types of adsorbents at the same time on dye removal efficiency from synthetic wastewater is shown clearly in Fig. 5. As shown in Fig. 5, the highest removal efficiency is obtained when the amount of SD-adsorbent increases and the amount of the LNL-adsorbent decreases. This observation indicates that the excessive weight of LNL-adsorbent will impact the adsorption process, which means it affects the ability of the SD-adsorbent to eliminate pollutants when SD-pores are closed by the other adsorbent [20,21].

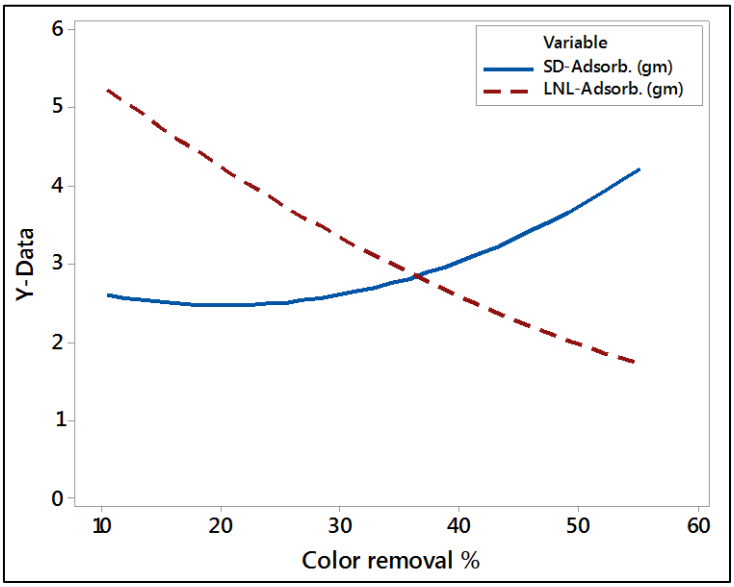



**Figure 5.** The interaction effect of adsorbents on the RB-dye removal efficiency.

*3.3. Adsorption Kinetic Study*

The investigation of adsorption kinetics still takes considerable attention due to its importance in the estimation and application of different types adsorbents. The common kinetic models are the pseudo-first order (Eq. 1), pseudo-second order (Eq. 2), and intraparticle diffusion (Eq. 3).

$$\mathrm{Ln}\,(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where $q_e$ refers to equilibrium amount of adsorption, $q_t$ (mg/g) is the amount of adsorption at time $t$ (min), and $k_1$ (1/min) is the rate constant of the pseudo-first order model. The parameters, $q_e$ and $k_1$ can be estimated the plot ln $(q_e - q_t)$ versus $t$.

$$t/q_t = 1/(k_2\, q_e^{\,2}) + t/q_e \tag{2}$$

where $k_2$ (g/mg min) is the rate constant of the pseudo-second order model where the parameters of $q_e$ and $k_2$ are obtained from the plot of $(1/qt)$ versus $(1/t)$.

$$q_t = K_{id}\, t^{1/2} + c \tag{3}$$

where $K_{id}$ (mg/g·min$^{1/2}$) is the intraparticle diffusion rate constant and $c$ is a constant of the thickness of the boundary layer.

Figure 6 explains the results of the kinetic study of the current adsorption, which reveals that the pseudo-second model was more fitted ($R^2$=0.998) compared to the First-Order Model ($R^2$=0.973) and the intraparticle diffusion model ($R^2$=0.915).

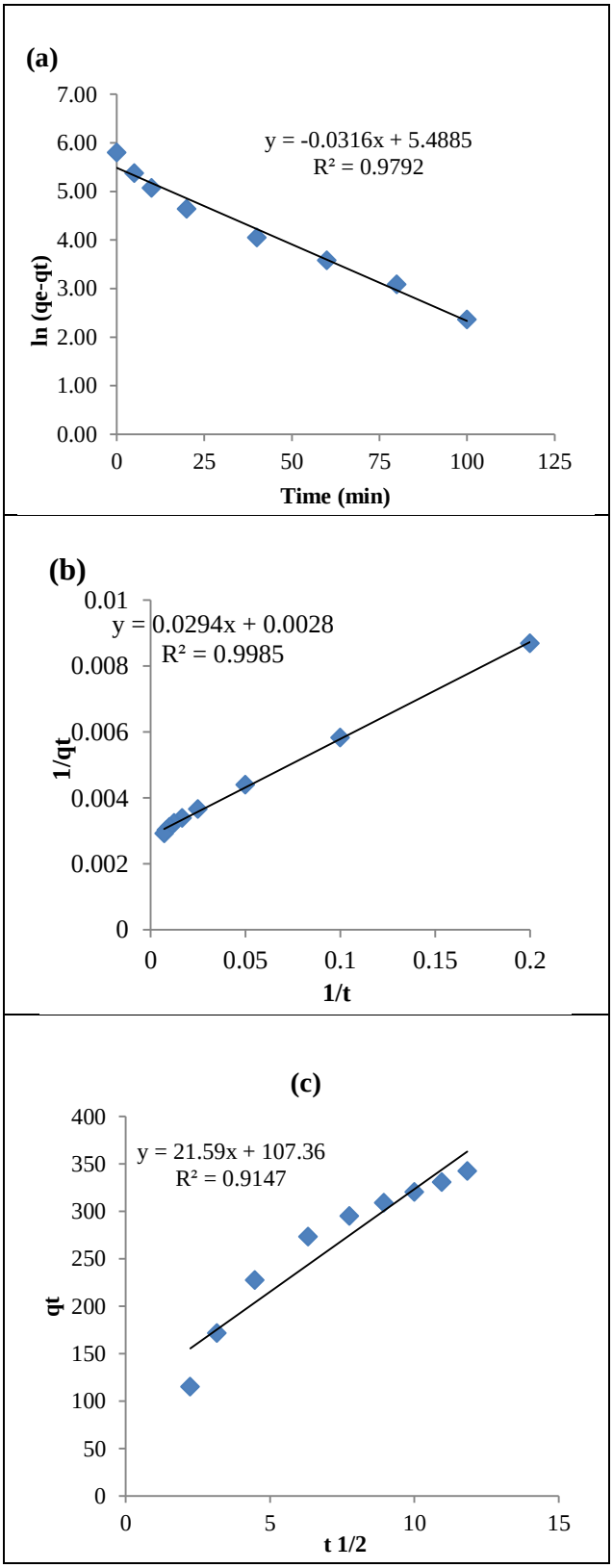



**Figure 6.** Results of kinetic study: (a) pseudo-first model, (b) pseudo-second model, and (c) intraparticle diffusion.

The performing of the pseudo second-order kinetic indicates that the chemical interaction between the molecules of RB dye with the SD-adsorbent and LNL-adsorbent surfaces contained electron transfers.

To achieve the equilibrium concentration, the first part involved quick chemisorption of the dye molecules on the SD adsorbent, followed by the slow part of physisorption [22].

*3.4. Isotherm Models of Adsorption*

The isotherm models of adsorption are crucial tools for explaining the mechanism of interaction among the molecules of any adsorbate and the selected adsorbent at constant temperature [7, 14]. Therefore, they play an significant role in understanding the adsorption method. Several isotherm models are performed for investigating this subject, but Langmuir model and Freundlich model (Eqs. 4 and 6) are the most commonly conducted to depict the adsorption isotherms.

$$q_e = (q_m.K_L.C_e) / (1+K_L.C_e) \quad (4)$$

The parameter ($R_L$) is an important indicator used to inform the status of the adsorption process whither irreversible case ($R_L = 0$), favorable case ($0 < R_L < 1$), linear case ($R_L = 1$), or unfavorable case ($R_L > 1$). It can be estimated from Eq. 5 as follows:

$$R_L = 1/(1+K_L.C_0) \quad (5)$$

where $C_e$ is the concentration of dye in solution in (mg/L) at equilibrium, $q_m$ is the maximum capacity of adsorption in (mg/g), $K_L$ is the isotherm constant in (L/mg) and $C_0$ is initial concentration of dye in (mg/L).

$$q_e = K_F C_e^{1/n} \quad (6)$$

where $K_F$ is the capacity of the SD or LNL adsorbents, and $n$ is the intensity constant of adsorption.

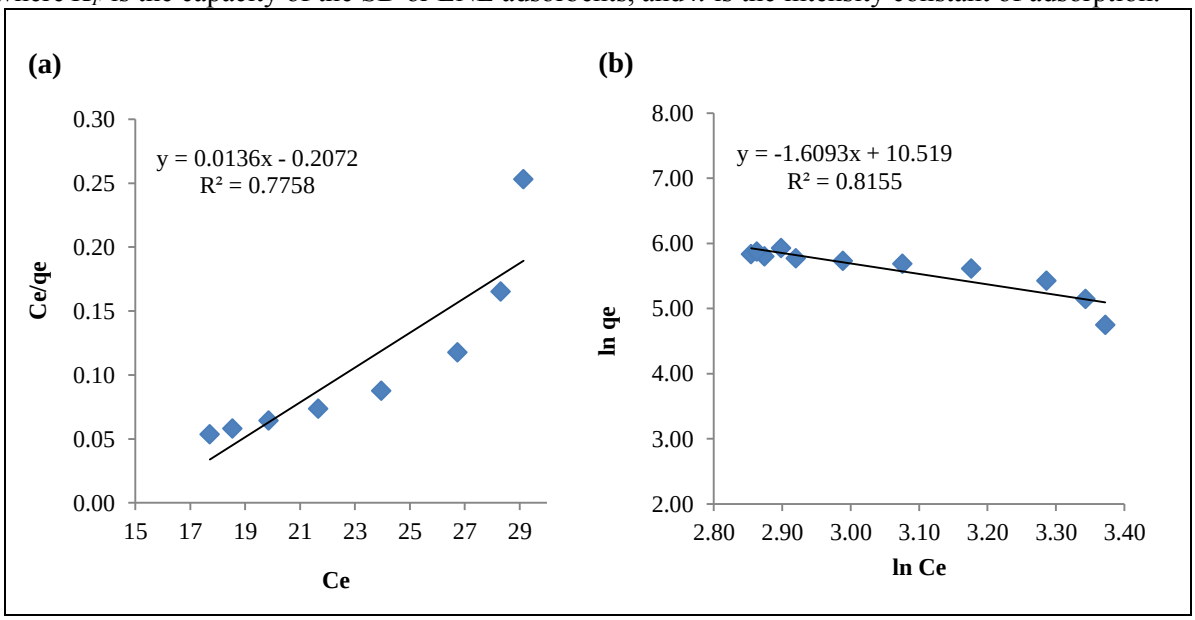



**Figure 7.** Results of adsorption isotherm models study: (a) Langmuir model (b) Freundlich model.

As observed in Fig. 7, Freundlich model was more fitted than Langmuir model, which means that the adsorbent process that occurred in the present system is not limited to the monolayer formation as the Langmuir isotherm model proposed. Moreover, it reflects that the surface of adsorption is heterogeneous and possess un-equal available sites with different values of the energy of adsorption. Tables 4 and 5 summarized the core findings of kinetic study and adsorption isotherm models.

**Table 4.** Adsorption kinetics and isotherms.

| | |
|---|---|
| Pseudo-first order | $q_e$ (mg/g) per 200 mL: 241.89<br>$K_1$ ($min^{-1}$): 0.0316<br>$R^2$: 0.979 |
| Pseudo-second order | $q_e$ (mg/g) per 200 mL: 357.14<br>$K_2$ (g $mg^{-1}$ $min^{-1)}$: 0.0048<br>$R^2$: 0.998 |
| Intraparticle diffusion | $K_{id}$: 21.59 (mg. $g^{-1}$ $min^{-1/2}$)<br>c (mg/g) per 200 mL: 107.36<br>$R^2$: 0.915 |

**Table 5.** Adsorption isotherms.

| | |
|---|---|
| Langmuir isotherm model | $q_{max}$: 73.53<br>b: 0.07<br>$R_L$: 0.201<br>$R^2$: 0.776 |
| Freundlich isotherm model | $K_F$: 37012.1<br>n: 0.622 (Chemical adsorption)<br>$R^2$: 0.816 |

For the adsorption of dye on the surface of the present adsorbents, the ($R_L$) factor was equivalent to 0.201, indicating good adsorption.

Table 6 shows the ANOVA-test results for RB-dye removal% where the value of $p < 0.05$ indicates that, the obtained model is significant at 95% of the probability level. However, the mathematical model of the studied response is listed in Eq. 7 with ($R^2 = 0.911$ and adjusted $R^2 = 0.801$).

**Table 6.** ANOVA-test results for RB-dye removal efficiency.

| Source | Sum of Squares | DF | Mean Square | F-value | P-value | |
|---|---|---|---|---|---|---|
| Model | 3425.08 | 14 | 244.65 | 8.77 | <0.0001 | Highly-significant |
| $X_1$: SD-Adsorb. (gm) | 282.27 | 1 | 282.27 | 10.12 | 0.008 | Highly-significant |
| $X_2$: LNL-Adsorb. (gm) | 1125.78 | 1 | 1125.78 | 40.37 | <0.0001 | Highly-significant |
| $X_3$: pH | 1498.34 | 1 | 1498.34 | 53.73 | <0.0001 | Highly-significant |
| $X_4$: Contact time (min) | 258.36 | 1 | 258.36 | 9.26 | 0.010 | Significant |
| $X_1^2$ | 5.60 | 1 | 5.60 | 0.20 | 0.662 | |
| $X_2^2$ | 158.36 | 1 | 158.36 | 5.68 | 0.035 | Significant |
| $X_3^2$ | 2.39 | 1 | 2.39 | 0.09 | 0.775 | |
| $X_4^2$ | 40.35 | 1 | 40.35 | 1.45 | 0.252 | |
| $X_1$ $X_2$ | 1.53 | 1 | 1.53 | 0.05 | 0.819 | |
| $X_1$ $X_3$ | 17.22 | 1 | 17.22 | 0.62 | 0.447 | |
| $X_1$ $X_4$ | 2.51 | 1 | 2.51 | 0.09 | 0.769 | |
| $X_2$ $X_3$ | 0.32 | 1 | 0.32 | 0.01 | 0.916 | |
| $X_2$ $X_4$ | 0.72 | 1 | 0.72 | 0.03 | 0.875 | |
| $X_3$ $X_4$ | 10.02 | 1 | 10.02 | 0.36 | 0.560 | |
| Residual | 334.62 | 12 | 27.89 | | | |
| Lack of Fit | 333.97 | 10 | 33.40 | 101.73 | 0.010 | |
| Pure Error | 0.66 | 2 | 0.33 | | | |
| Total | 3759.71 | 26 | | | | |

$$Y_{RBD\text{-}Removal\,\%} = 48.0 + 2.67\,X_1 + 1.02\,X_2 - 2.70\,X_3 + 0.101\,X_4 + 0.164\,X_1^2 - 0.872\,X_2^2 - 0.074\,X_3^2 - 0.0003\,X_4^2 + 0.099\,X_1\,X_2 - 0.277\,X_1\,X_3 - 0.004\,X_1X_4 + 0.038\,X_2\,X_3 - 0.002\,X_2X_4 + 0.006\,X_3\,X_4 \quad (7)$$

*3.5. Study of Thermodynamic*

The heat of adsorption (ΔH), free Gibbs energy (ΔG), and the entropy (ΔS) thermodynamic parameters of the adsorption process have been estimated to assess the current system using the following equations:

$$\Delta G^o = -\,R\,T\,\ln K_d \quad (8)$$

$$K_d = q_e / C_e \quad (9)$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad (10)$$

where ($K_d$) is the equilibrium constant.

The plot of ln $K_d$ versus 1/T is useful to estimate ΔH (J/mol) and ΔS (J/mol.K) then, consequently, the value of ΔG° (J/mol).

The obtained findings show that the heat of adsorption (ΔH: 5339.8 J/mol**)** and the entropy (ΔS≅ 70 J/mol.K) indicate that the current adsorption process is endothermic and random irregularity at the solid-liquid. However, the value of (ΔG≅ −15000 J/mol) refers to the spontaneous status and significant favorable adsorption process [23].

*3.6. Optimization with RSM-BBD*

The optimum conditions for the studied operating variables and the required responses have been estimated using RSM based on BBD and the Minitab-statistical software program. Fig. 8 shows the optimization process of the studied variables and responses by considering the operating variables. As shown, that the optimal values of the operational variables were 5.5 gm, 0.8 gm, 3, and 143 min of the SD-adsorbent, LNL-adsorbent, pH, and contact time, respectively. The optimal variables gave more than 62 % of dye removal at Composite Desirability (D-value) equals 1.

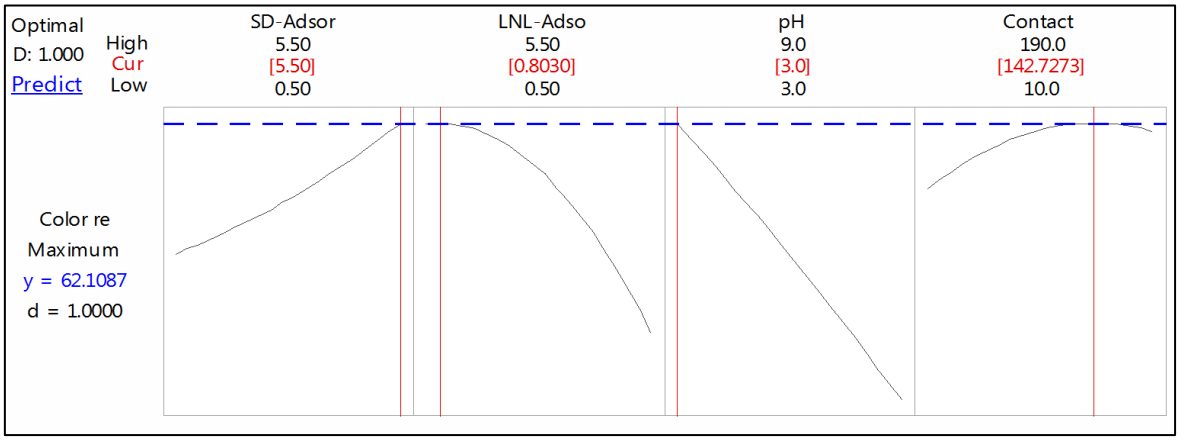



**Figure 8.** The optimization results of the studied variables.

## Conclusion

A huge amount of dye wastewater are annually discharged from industrial activities into the environment without efficient treatment. This study employed two types of natural adsorbents without any pre-chemical modifications. Laurus Nobilis Leaves (LNL) and sawdust (SD) are used as low-cost natural adsorbents to remove 30 ppm of the reactive blue (RB) dye from synthetic wastewater under the impact of their dosages, solution pH, and contact time with constant stirring speed of 150 rpm. Adsorption isotherms study revealed that Langmuir isotherm was more fitted model than Freundlich model. Adsorption kinetic shows that the current adsorption process obeys the Pseudo-Second-Order Model ($R^2$=0.998) compared to the First-Order Model ($R^2$=0.973) and the intraparticle diffusion model ($R^2$=0.915). The obtained results of thermodynamic study show that the values of (ΔH) and (ΔS)

indicate that the current adsorption operation is endothermic and random irregularity at the solid-liquid as well as the the Gibbs energy (ΔG) refers to the spontaneous status and favorable adsorption process. More than 60% of RB- dye removal efficiency was attained at the optimum values of the operating variables which were 5.5 g of SD-adsorbent, 0.8 g of LNL-adsorbent, pH 3, and 141 min of the contact time. The core results proved that the interaction effect of using multi-natural adsorbents was significant and it should be taken into consideration when more than one natural adsorbent performed at the same process of wastewater treatment.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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