

M. ŞABAN TANYİLDİZİ¹, YAVUZ DEMİRCİ²

ADSORPTION OF REACTIVE ORANGE 4 ON SESAME STALKS. MODELING, KINETICS AND EQUILIBRIUM

Placket–Burman design (PBD) and central composite design (CCD) were employed to study the adsorption of Reactive Orange 4 (RO4) on sesame stalk. In the study conducted with the PBD, a total of seven parameters (initial dye concentration, initial pH of solution, temperature, amount of adsorbent, particle size, contact time, and shaking speed) were studied, and four of these were found to influence the adsorption of dye. A mathematical model equation was developed by using the CCD. Analysis of variance (ANOVA) indicated a high coefficient of determination ($R^2 = 0.93$). The initial dye concentration, amount of sesame stalk, contact time, and initial pH were shown to be very significant ($p < 0.05$) for RO4 adsorption. The data for the adsorption of RO4 at equilibrium on sesame stalk were analyzed by the Langmuir, Freundlich, and Tempkin models. Temperature increase from 20 to 60 °C enhanced the adsorption capacity of the monolayer from 84.75 to 178.57 mg/g. The rate constants were calculated for various initial concentrations of the dye by using pseudo-first and pseudo-second order kinetic and particle diffusion adsorption models. The kinetic evaluations showed that the experimental data were in accordance with the pseudo-second order model.

1. INTRODUCTION

Dyes are natural and synthetic compounds making the world more beautiful through colored products. Large quantities of wastewater associated with the use of dyes are produced in many industries such as textiles, food, paper, rubber, plastics, and dye manufacturing. According to incomplete statistics, there are more than 10 000 types of dyes in commercial use [1]. Azo dyes that contain reactive groups are used in great quantities in the Turkish textile industry. 10–25% of textile dyes is lost during the dyeing process, and 2–20% is discharged directly as aqueous effluents that seriously pollute the environment and affect aquatic organisms. A great deal of research has indicated that reactive

¹Firat University, Engineering Faculty, Department of Bioengineering, 23119, Elazığ, Turkey.

²Adiyaman University, Engineering Faculty, Department of Environmental Engineering, 02040 Adiyaman, Turkey, corresponding author, e-mail address: yavuzdemirci@gmail.com

dyes are highly toxic to the biotic communities in the ecosystem [2]. In particular, the discharge of dye-containing effluents into water is undesirable due to their color and because decomposition products of many dyes have toxic, carcinogenic, or mutagenic effects on living organisms. For example, it was reported that some carcinogens such as benzidine, naphthalene, and other aromatic compounds, originated from dyes [3, 4].

Numerous treatment methods have been developed, including coagulation, flocculation, biological treatment (aerobic and anaerobic), the use of ozone, membrane filtration, colloidal gas aphrons, chemical oxidation, photocatalytic removal, adsorption, and ion exchange [5]. However, most commonly used and cost-effective biological treatment methods cannot degrade the effluent dye completely because of the complex and refractory nature of dye molecules.

Both physical and/or chemical adsorption is an effective technique for effective removal of color from wastewater, however activated carbon used as an adsorbent in the purification process is expensive. Thus many studies were conducted to identify other viable, low-cost adsorbents such as biosorbents, agricultural waste, bacteria, clay minerals, and organoclays [6]. Several recent studies focused on the potential use of different agricultural materials, and their effectiveness as inexpensive biosorbents for the removal of dyes from aqueous solutions were investigated [7].

Sesame is an important agricultural crop in Turkey. Currently, sesame crop is cultivated in a total area of 5.1×10^4 ha, and 2.8×10^4 t of the crop are produced per year in Turkey. Unfortunately, the stalks of this crop are not used for any other beneficial applications, thus their usefulness as bio sorbents has been considered. Sesame stalk, a complex material consisting of lignin, hemi-cellulose, cellulose, and some proteins, has the potential to be an effective adsorbent for contaminants [8].

Response surface methodology (RSM) is an experimental approach that is used to identify optimum conditions of a multivariable system, and it first was described by Box and Wilson [9]. Various statistical experimental design methods were used recently in the optimization of experimental studies. RSM was used in the design in some experimental adsorption studies for various dyes such as Methylene Blue, Acid Orange 52, Reactive Black 5, and Disperse Orange 30 [10].

The purpose of this study was to investigate the adsorption of Reactive Orange 4 on sesame stalk by using experimental design procedures such as Placket–Burman (PB) and Central Composite Design (CCD). The RSM was used to describe the adsorption process mathematically, thermodynamic and kinetic parameters of the adsorption process have also been analyzed.

2. MATERIALS AND METHODS

Experimental design. RSM can be summarized as a collection of statistical tools and techniques for constructing and exploring an approximate functional relationship

between a response variable and a set of design variables [11]. By using RSM, it is possible to derive an expression for the performance measure based on the response values obtained from experiments for some particular combination of the input variables

$$x_i = \frac{X_i - X_0}{\Delta X_i}, \quad i = 1, 2, 3, \dots, k \quad (1)$$

where x_i is the dimensionless value of an independent variable; X_i is the real value of an independent variable; X_0 is the real value of an independent variable at the central point, and ΔX_i is the step change. Codification of the levels of the variable consists of transforming each real value that is to be studied into coordinates inside a scale with dimensionless values, which must be proportional at its localization in the experimental space [10].

The adsorption yield was chosen as a response in the PBD having 7 independent variables. These factors were the initial concentration of the dye, initial pH of the solution, amount of adsorbent, temperature, particle size, shaking rate, and contact time. As shown in Table 1, the parameters were changed within two levels and minimum and maximum ranges selected for the parameters. The PBD required at least 12 runs, in total 24 experiments were conducted for the adsorption of RO4 with replicates.

Table 1

Factors and levels used in the PBD

Level	Sesame stalk dose [g/dm ³]	Initial pH	Temperature [°C]	Dye conc. [mg/dm ³]	Particle size (mesh)	Shaking rate [rpm]	Contact time [min]
-1	0.75	1	20	50	-30 (149 μm)	100	10
1	1.25	3	40	150	-100 (595 μm)	200	420

According to the results of the PBD, four important parameters (initial concentration of the dye, initial pH of the solution, amount of adsorbent, and contact time) were studied using CCD for the adsorption of RO4. The remaining parameters that could affect the adsorption were kept constant, i.e., the temperature of 25 °C, the particle size of 297 μm, and the shaking rate of 150 rpm. Each of the design parameters was investigated at five different values as shown in Table 2. We designed our experiments to obtain a quadratic model consisting of 2⁴ trials plus a star configuration and six center points. Then, the results of the CCD were used to fit a quadratic equation by a multiple regression procedure. The following quadratic equation explains the behavior of the system:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j \quad (2)$$

where β_0 is a constant, β_i is the slope or linear effect of input factor, β_{ii} is the quadratic effect on the input factor, and β_{ij} is the effect of the linear interaction between the input factors [12].

Table 2

Experimental range and levels of the independent variables for CCD

Symbols coded	Variables	$-\alpha$	-1	0	1	α
x_1	sesame stalk dose, g/dm ³	0.25	0.5	0.75	1	1.25
x_2	initial pH	0.5	1	1.5	2	2.5
x_3	dye concentration, mg/dm ³	100	150	200	250	300
x_4	contact time, min	30	120	210	300	390

Equation (2) is an empirical model that summarizes the relationships to the response of measured independent variables of the experiment. Data obtained from the experimental runs were analyzed using the statistical package of the Design Expert software (version 8.0, Stat-Ease, Inc., Minneapolis, USA). Analysis of variance (ANOVA) was performed, and three-dimensional response surface curves were plotted to show the interaction between various independent parameters.

Adsorbent and adsorbate. Sesame stalk was obtained from a local agricultural plant. Deionized water was used to wash the sesame stalks to remove soluble impurities, after which the stalks were dried at 105 °C for 4 h. The dried samples were ground and sieved to obtain various size fractions. The fractions were stored at room temperature in a desiccator that contained CaCl₂.

Table 3

General characteristics of sesame stalks [8]

Component	Contents [wt. %]
Hemicellulose	32.50
Lignin	32.60
Cellulose	28.50
Ash	6.63
Moisture	8.70

Table 3 provides the general characteristics of sesame stalks. The specific surface area and the nature of the surface are very important characteristics because they strongly affect the sorptive capacity. The single-point BET surface area of the adsorbent was measured

by the nitrogen adsorption method (Micromeritics ASAP 2020). The commercial azo dye, RO4 containing ca. 50% of the dye (Fig. 1), was obtained from a local textile firm in Turkey and was used as received. Table 4 provides a general characteristics of the RO4 dye.

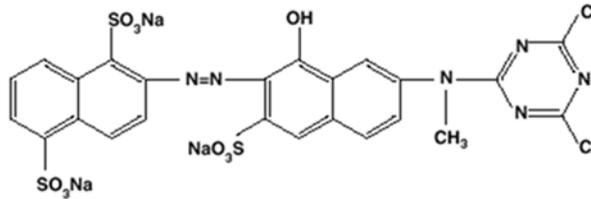


Fig. 1. Chemical structure of Reactive Orange 4 [3]

Table 4

Characterization of Reactive Orange 4 (C.I. No. 18260)

Generic name	C.I. Reactive Orange 4
Molecular formula	$C_{23}H_{13}N_6O_{10}S_3Cl_2Na_3$
Molecular weight	769 g/mol
λ_{max} , nm	490 nm
pK_a	6.14 at 20 °C

Adsorption experiments. Dye solutions of various concentrations were prepared using distilled water, and the initial pHs of the solutions were adjusted by the addition of dilute HCl. In each of the experiments, 50 cm³ of the dye solution and a certain amount of sesame stalks were placed into a 150 cm³ airtight conical flask sealed with a rubber stopper. The flasks were shaken at a constant rate at a specified temperature (Selecta Rotabit) for a specific period of time and centrifuged afterwards (Hettich EBA21). The concentration of RO4 in the aqueous solution was determined by using a Chebios optimum one UV spectrophotometer. The maximum molecular absorbances of dye solutions were measured at the wavelength of 490 and pH 1, 2 and 3. The calibration curve was linear over a reactive dye concentration range of 0.5–100 mg RO4/dm³ (at pH 2) with the correlation coefficient $r > 0.98$. The color of RO4 dye was independent of pH in the investigated range. All of the experiments were conducted twice, and average values were used for the subsequent calculations. If the difference between the two values exceeded 5%, the experiments were repeated. In the study, the adsorption yield (%) was calculated by using the following equation:

$$\text{Adsorption yield} = \frac{C_i - C}{C_i} \times 100\% \quad (3)$$

where C_i is the initial concentration of RO4, and C is the concentration of RO4 at any time (mg/dm^3), respectively.

Theory. To determine the controlling mechanism of adsorption process, pseudo-first and pseudo-second order kinetic models were used to test the experimental data.

A linear form of the pseudo-first-order kinetic model, known as the Lagergren rate equation, can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e and q_t (mg/g) are the amounts of RO4 adsorbed per unit weight of sesame stalk at equilibrium and at any other time t , respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption.

The pseudo-second order kinetic model can be expressed in a linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) is the rate constant of the pseudo-second order adsorption.

The intra-particle diffusion model commonly is used to identify the adsorption mechanism for design purposes [13]. It can be expressed as:

$$q_t = k_{\text{int}} t^{1/2} + I \quad (6)$$

where k_{int} is the intra-particle diffusion rate constant ($\text{mg}/(\text{g} \cdot \text{min}^{0.5})$), and I is the intercept.

Equilibrium data are basic requirements for the design of adsorption systems. In order to investigate the dye adsorption isotherm, we used the following models:

- Langmuir model:

$$\frac{C_e}{q} = \frac{1}{K q_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (7)$$

- Freundlich model

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

- Tempkin model

$$q_e = B \ln A + B \ln C_e \quad (9)$$

where C_e is the equilibrium concentration of adsorbate (mg/dm^3) in solution, q_e is the amount adsorbed per unit mass of adsorbent (mg/g), q_{max} is the maximum adsorption

capacity (mg/g), K (dm^3/mg) is a constant related to affinity of binding sites or bonding energy, K_f ($(\text{mg}/\text{g})(\text{mg}/\text{dm}^3)^{1/n}$) and n are the Freundlich constants, A (dm^3/g) is the Tempkin isotherm constant and B is related to heat of adsorption. q_{\max} is a practical limiting adsorption capacity when the surface of the adsorbent is covered completely by the adsorbate. A favorable sorption experiment can be described in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = \frac{1}{1 + KC_0} \quad (10)$$

where C_0 is the highest initial concentration of the dye (mg/dm^3), and K (dm^3/mg) is the Langmuir constant.

3. RESULTS AND DISCUSSION

Sesame stalks consisting of lignin, hemicellulose, cellulose, and some proteins (Table 3) are an effective adsorbent for contaminants [8]. These components include various polar functional groups such as OH^- , COOH^- , and phenol, which are involved in dye binding. The BET-nitrogen specific surface area for sesame stalks has low value ($1.48 \text{ m}^2/\text{g}$), but they have polar functional groups that remove dyes effectively.

Table 5

PBD for the effect of factors in the adsorption experiments

Run	A	B	C	D	E	F	G	Adsorption yield [%]
1	-1	-1	1	1	-1	1	-1	25.95
2	1	-1	-1	1	1	-1	1	49.48
3	1	1	1	1	1	-1	-1	33.88
4	1	-1	-1	-1	1	1	-1	44.56
5	-1	1	-1	1	-1	-1	1	26.89
6	-1	1	1	-1	1	-1	-1	20.87
7	-1	-1	-1	-1	-1	-1	-1	28.09
8	1	-1	1	-1	-1	-1	1	69.51
9	-1	-1	1	1	1	1	1	36.32
10	1	1	-1	1	-1	1	-1	23.28
11	-1	1	-1	-1	1	1	1	39.93
12	1	1	1	-1	-1	1	1	59.56

Seven independent variables were analyzed in 12 trials using PBD for the adsorption of RO4. Table 5 shows the design matrix selected for screening the variables for

the adsorption of RO4 and the corresponding responses. A–G are symbols uncoded. The determination coefficient (R^2) of the model was found to be 0.974, suggesting that the predicted values were in agreement with experimental data. Four variables had significant effects on adsorption as proved by their P -values (<0.05 , significant at 5% level) obtained from regression analysis of PBD, as shown in Table 6.

Table 6

Regression analysis of PBD criterion data for adsorption of RO4

Source	Coefficient	Sum of squares	Mean square	F -ratio	P -value
Constant	38.19	2466.96	352.42	21.486	0.0051
Sesame stalk dose, g/dm ³	8.52	870.74	870.74	53.086	0.0019
Initial pH	-4.13	204.19	204.19	12.449	0.0243
Temperature, °C	2.82	95.54	95.54	5.825	0.0733
Dye concentration, mg/dm ³	-5.56	370.96	370.96	22.616	0.0089
Shaking rate, rpm	-0.69	5.66	5.66	0.345	0.5885
Particle size, mesh	0.07	0.06	0.06	0.004	0.9530
Contact time, min	8.76	919.80	919.80	56.077	0.0017
Residual		65.61	16.40		
Cor total		2532.57			

$$R^2 = 0.974, R^2_{\text{adj}} = 0.928, CV = 10.60.$$

Table 7

Experimental design for CCD and the observed results

Run	x_1	x_2	x_3	x_4	Adsorption yield [%]		Run	x_1	x_2	x_3	x_4	Adsorption yield [%]	
					Exp.	Predicted						Exp.	Predicted
1	-1	-1	-1	-1	21.07	23.81	16	1	1	1	1	16.81	16.73
2	1	-1	-1	-1	29.54	30.01	17	-2	0	0	0	12.99	7.87
3	-1	1	-1	-1	8.85	10.03	18	2	0	0	0	18.51	19.37
4	1	1	-1	-1	11.21	13.91	19	0	-2	0	0	36.11	33.45
5	-1	-1	1	-1	14.89	17.69	20	0	2	0	0	11.53	9.93
6	1	-1	1	-1	22.89	23.18	21	0	0	-2	0	31.85	28.41
7	-1	1	1	-1	5.48	7.52	22	0	0	2	0	19.15	18.33
8	1	1	1	-1	11.36	10.68	23	0	0	0	-2	17.36	13.71
9	-1	-1	-1	1	23.43	25.70	24	0	0	0	2	22.26	21.65
10	1	-1	-1	1	33.43	34.04	25	0	0	0	0	17.78	17.68
11	-1	1	-1	1	12.32	14.68	26	0	0	0	0	18.61	17.68
12	1	1	-1	1	21.90	20.69	27	0	0	0	0	17.57	17.68
13	-1	-1	1	1	18.89	18.85	28	0	0	0	0	17.68	17.68
14	1	-1	1	1	26.06	26.48	29	0	0	0	0	16.53	17.68
15	-1	1	1	1	10.31	11.44	30	0	0	0	0	17.89	17.68

The dosage of sesame stalks (x_1), initial pH (x_2), dye concentration (x_3), and contact time (x_4) exhibited low P -values according to PBD. Therefore, these parameters were selected for optimization for maximum dye adsorption onto sesame stalks using CCD. The experiment was conducted 30 times according to CCD, as shown in Table 7. In these experiments, CCD was used first to generate quadratic equations described by the parameters that are effective on adsorption and then to determine the optimum values of these parameters.

Using the Design Expert software, the experimental data were analyzed for their linear, quadratic, and interactional effects on the variables. From the software, the following model equation (in the coded factors) was proposed for the adsorption of the dye:

$$\begin{aligned}
 Y = & 17.68 + 2.88x_1 - 5.88x_2 - 2.52x_3 + 1.99x_4 \\
 & -1.01x_1^2 + x_2^2 + 1.42x_3^2 - 0.58x_1x_2 - 0.18x_1x_3 + 0.53x_1x_4 \\
 & + 0.90x_2x_3 + 0.69x_2x_4 - 0.19x_3x_4
 \end{aligned} \tag{11}$$

where Y is the predicted response variable, the adsorption yield (%), and x_1 – x_4 are the values of independent variables, i.e., sesame stalk hull dose, initial pH, initial dye concentration, and contact time, respectively.

Table 8

ANOVA for the quadratic model

Source	Sum of squares	Degrees of freedom	Mean square	F -value	$P > F$
Model	1430.33	13	110.03	16.30	<0.0001
Residual	108.02	16	6.75		
Lack of fit	105.77	11	9.62	21.33	0.0017
Pure error	2.25	5	0.45		
Cor total	1538.36	29			

$$R^2 = 0.93, CV = 13.8\%, R_{\text{adj}}^2 = 0.87.$$

The ANOVA of the quadratic regression model indicated that the model was highly effective based on Fisher's f -test with a very low probability value ($(P_{\text{model}} > F) = 0.0001$) (Table 8). At the same time, a relatively low coefficient of variation CV (13.81%) signaled a better precision and reliability of the experiments that were conducted. The fit of the model was assessed by the determination of the coefficients (R^2) and the adjusted R^2 (R_{adj}^2). The high R^2 (0.929) and R_{adj}^2 (0.872) values show a close agreement between the values predicted by the model and the experimental results. The residual plots were examined by approximating the model. Figure 2 shows the normal

probability and studentized residual plots for the adsorption of RO4 onto sesame stalks. The probability density plot indicates whether the residuals follow a normal distribution, in which case the points should be in a straight line. In Figure 2 an S-shaped curve was not formed, indicating that response transformation was not needed and that there was no apparent problem with normality [14].

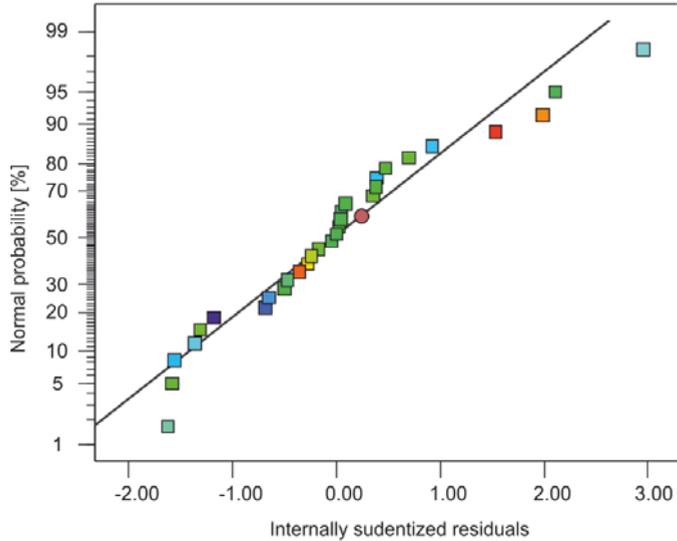


Fig. 2. The studentized residuals and normal % probability plot of RO4 adsorption

Table 9

Least-squares and parameters estimations (significance of regression)

Term	Parameter estimation	Standard error	Computed <i>t</i> -value	<i>P</i> > <i>F</i>
Constant	17.68	0.90	16.30	<0.0001
x_1	2.87	0.53	29.38	<0.0001
x_2	-5.88	0.53	122.90	<0.0001
x_3	-2.52	0.53	22.56	0.0002
x_4	1.99	0.53	14.02	0.0018
x_1^2	-1.01	0.49	4.26	0.0555
x_2^2	1.00	0.49	4.18	0.0578
x_3^2	1.42	0.49	8.40	0.0105
x_1x_2	-0.58	0.65	0.80	0.3832
x_1x_3	-0.18	0.65	0.08	0.7867
x_1x_4	0.53	0.65	0.68	0.4233
x_2x_3	0.90	0.65	1.92	0.1843
x_2x_4	0.69	0.65	1.12	0.3048
x_3x_4	-0.19	0.65	0.08	0.7779

The significance of each coefficient was determined by t -values and P -values, which are listed in Table 9. The values of $P > F$ less than 0.05 indicated that the model's terms were significant, whereas values greater than 0.100 do not indicate a systematic relationship. Regression analysis of the experimental data showed that the dosage of sesame stalks and the contact time had significant, positive, and linear effects on the adsorption of RO4 onto the sesame stalks. However, the initial pH and the initial dye concentration had negative linear effects on the adsorption of RO4 onto sesame stalks. Table 9 also shows that the quadratic effect of the initial dye concentration was more significant than other factors ($P < 0.05$).

The 3D response surface and the 2D contour plots are the graphical representations of the regression equation. Both plots are presented in Figs. 3–5. The main goal of the 3D response surface plots is to efficiently determine the optimum values of the corresponding variables at the maximum response. Each contour curve shown below the surface represents the set of an infinite number of combinations of two test variables provided that the other two were maintained at their respective optimum levels.

The initial pH of the solution was one of the most important factors influencing the adsorption of the dye, as discussed in most related studies published in the literature. Figure 3 shows the dependence of the percentage adsorption on the initial pH and initial dye concentration for a pair of optimum contact times and adsorbent dose parameters.

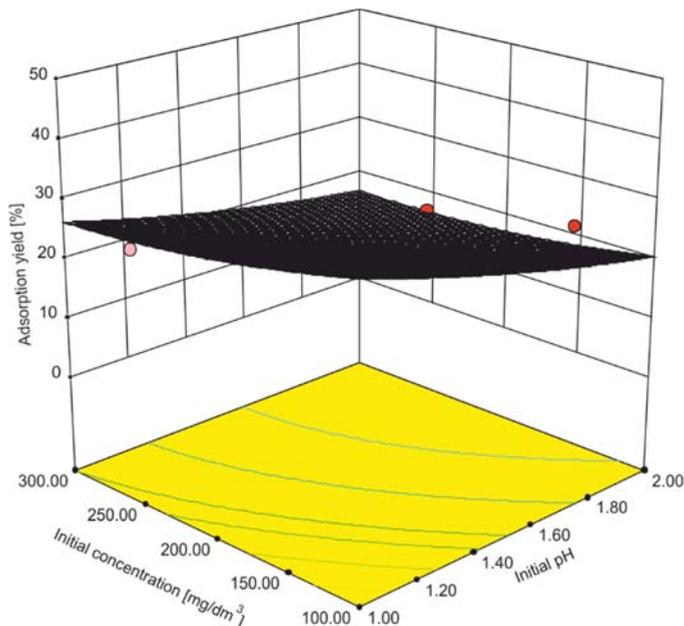


Fig. 3. Response surface plot showing the effect of initial pH, dye concentration and their mutual effect on the adsorption of RO4 onto sesame stalk

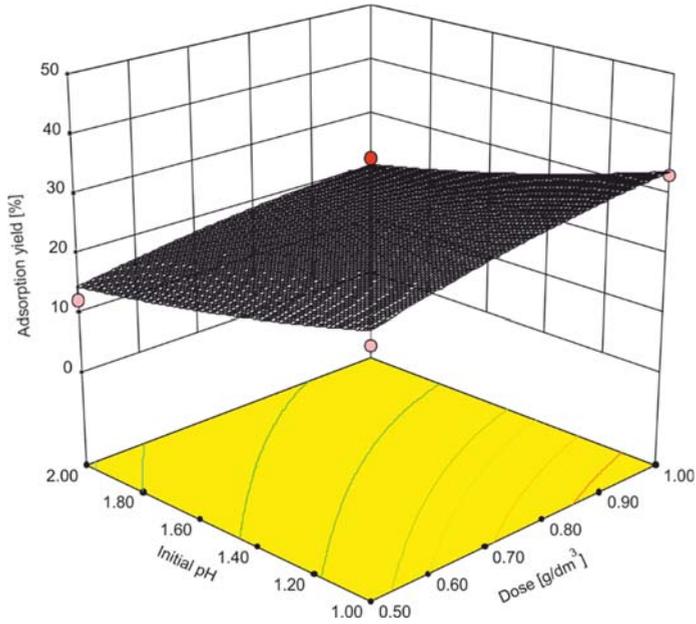


Fig. 4. Response surface plot showing the effect of dose, initial pH and their mutual effect on the adsorption of RO4 onto sesame stalk

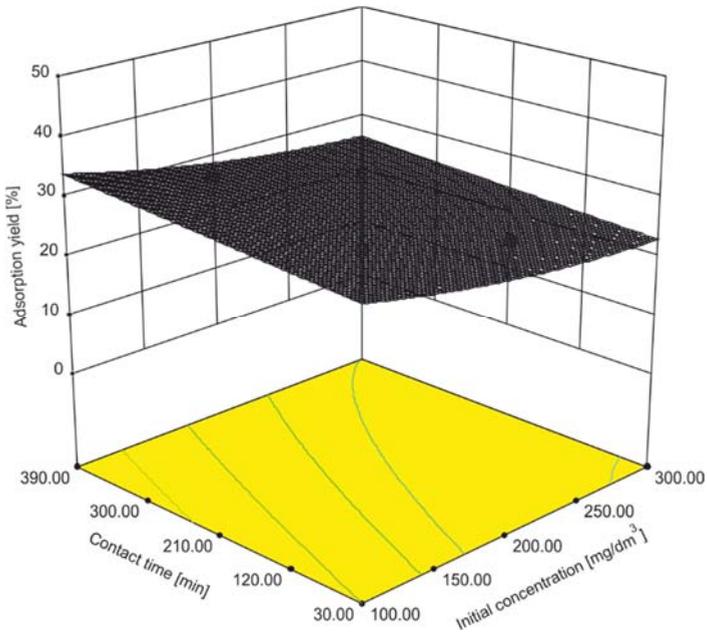


Fig. 5. Response surface plot showing the effect on contact time, initial dye concentration and their mutual effect on the adsorption of RO4 onto sesame stalk

Sesame stalks are composed of complex constituents and contain a large number of active sites. The uptake of the dye ions could be related to the active sites and also to the chemistry of the solute in the solution. The adsorption increased as initial pH and the dye concentration decreased. Depending on the initial pH of the solution, active sites may change their valences. At lower pH, the surface of the adsorbent may have a positive charge. Adsorption increases due to the increasing electrostatic interactions between the negatively charged, anionic dye molecules and the positively-charged active groups of the sesame stalks.

Figure 4 shows the effects of dose and dye concentration on the adsorption of RO4 onto sesame stalks. Adsorption decrease depicts a considerable increase at the point at which there was the maximum amount of adsorbent (1.25 g/dm^3) and the initial pH of the solution was less than 1.5. However, this increase begins at $\text{pH} < 1$, when the amount of the adsorbent is at its minimum level (0.25 g/dm^3).

The adsorption of dye did not change much as the concentration of the adsorbent was increased from 1.0 to 1.25 g/dm^3 . This observation was anticipated given that adsorption increases as the concentration of the adsorbent increases, which is due mainly to the impact of the concentration on adsorption frequency and the adsorption constant.

Figure 5 shows the effect of the initial dye concentration and the contact time on the adsorption yield (%). In all experiments, adsorption of dye occurred rapidly in the first 30 minutes (α point). Subsequently, the rate of adsorption decreased. This observation can be explained by the rapid adsorption that occurred on the outer surface, which was followed by the slower adsorption inside the pores. According to the 3D surface plots, the maximum adsorption yield (%) was obtained at lower pH, lower dye concentrations, and higher adsorbent doses and contact times.

We used the numerical method given by Meyers and Montgomery to solve the regression equation (Eq. (4)). The optimal values of the test variables were determined as follows: sesame stalk dose – 1.23 g/dm^3 , initial pH – 0.5, dye concentration – 100 mg/dm^3 , contact time – 380 min. 56% of the RO4 was adsorbed on sesame stalks when the above optimized parameters of the variables were used. We obtained the adsorption efficiency of 51% in our experiment. This percentage was in close agreement with the model's prediction. The results obtained by numerical methods for the adsorption process were as expected. The adsorption yield increased as the concentration of the adsorbent increased and decreased as the initial concentration of RO4 increased. The dye removal efficiency increased as the initial pH of the dye decreased due to the anionic nature of the reactive dye.

Adsorption kinetic models are used to explain the adsorption mechanism and adsorption characteristics. The experimental data were analyzed using pseudo-first and pseudo-second order adsorption models and the intraparticle diffusion model.

Table 10 gives the values of the constants and correlation coefficients of the adsorption kinetic model. It is apparent that the values of R^2 (larger than 0.95) were only slightly different for the pseudo-first and pseudo-second order equations. The calculated values of q_e obtained from the pseudo-second order model were in better agreement

with the experimental values; therefore, we concluded that the pseudo-second order model provided results closer to the values obtained experimentally. These results suggest that the sorption was not a first order process; hence the second order model, based on the assumption that the rate limiting step may be chemisorption, provided the best correlation with the experimental data for the removal of the dye [15]. The intraparticle diffusion model is important for determining the controlling step in the adsorption process [16]. The adsorption of RO4 dye onto sesame stalks depends on intraparticle diffusion but some other mechanism also may be involved due to the relatively low values of the correlation coefficients.

Table 10

Kinetic constants for dye adsorption at various dye concentrations C_0
(50 cm³, pH = 1, adsorbent dose = 1 g/dm³)

C_0 [mg/dm ³]	q_e exp [mg/g]	Pseudo-first order kinetic model			Pseudo-second order kinetic model			Intraparticle diffusion model		
		k_1 [1/min]	q_e [mg/g]	R^2	k_2 [g/mg·min]	q_e [mg/g]	R^2	k_{int} [mg/(g·min ^{0.5})]	I	R^2
50	3.201	0.031	1.406	0.98	0.4479	3.213	0.99	0.185	5.77	0.96
75	4.021	0.028	1.457	0.98	0.4637	4.044		0.123	4.47	0.95
100	4.570	0.020	1.349	0.98	0.5394	4.444		0.139	2.74	0.92
150	5.828	0.016	1.342	0.95	0.6658	5.559		0.130	3.27	0.97
200	7.669	0.019	1.902	0.96	0.6259	7.413		0.140	1.96	0.94

To determine the equilibrium isotherms for the Langmuir, Freundlich, and Tempkin models, the initial concentrations of RO4 were varied from 50 to 400 mg/dm³, while the adsorbent concentration and contact times were kept constant at 1 g/dm³ and 420 min, respectively, at temperatures of 20, 30, 40, 50 and 60 °C.

Table 11

Coefficients of the Langmuir and Freundlich isotherms at various temperatures

Temperature [°C]	Langmuir model				Freundlich model			Tempkin model		
	K [dm ³ /mg]	q_{max} [mg/g]	R_L	R^2	n	K_f [(mg/g) (mg/dm ³) ^{1/n}]	R^2	A [dm ³ /mg]	B	R^2
20	0.0194	84.75	0.13	0.969	2.98	11.29	0.930	0.3013	16.14	0.899
30	0.0164	98.04	0.15	0.972	2.80	11.16	0.939	0.2516	18.68	0.876
40	0.0175	113.64	0.14	0.976	2.81	13.20	0.927	0.2693	21.70	0.921
50	0.0252	133.33	0.10	0.986	2.72	16.49	0.905	0.3393	26.61	0.890
60	0.0206	178.57	0.12	0.979	2.36	15.99	0.909	0.2687	35.90	0.914

The isotherm constants and correlation coefficients are given in Table 11. The Langmuir model exhibited a better fit to the adsorption data than the Freundlich and Tempkin

ones. The maximum adsorption capacity (178.57 mg/g at 60 °C) defined the total capacity of the sesame stalks for RO4 adsorption upon increasing temperature.

Table 12

Adsorption capacities for the removal of reactive dyes by various adsorbents

Material	Adsorbate	Adsorption capacity [mg/g]	Concentration [mg/dm ³]	Source
Rhizopus arrhizus	Reactive Orange 4	190.00	0–500	[17]
Polyaniline nano composite		200.00	25–100	[18]
Sunflower seed hull	Reactive Orange 16	22.10	–	[4]
Peanut hull	Reactive Black 5	55.55	50–350	[11]
Sesame stalk	Reactive Orange 4	178.57	50–400	Present study

Table 12 gives reported maximum monolayer adsorption capacities for some adsorbates and reactive dyes. The value of q_{\max} in this study corresponded well with data available in the literature. R_L values ($0 < R_L < 1$) indicated that the adsorption process was favorable at studied conditions. Although the Freundlich equation provided the poorest fit of experimental data among the three models, its n values were higher than 1 at all temperatures, indicating favorable adsorption conditions.

4. CONCLUSIONS

The PBD tool was used to determine the parameters influencing the adsorption of RO4 onto sesame stalks. $R^2 > 0.974$ for the mathematical model developed by using PBD indicated that there was a high correlation between the observed and predicted values. Four parameters, i.e., concentration of sesame stalks, initial pH, initial RO4 concentration, and contact time had significant effects on the adsorption according to the PBD. CCD was used to determine the relationships among the active adsorption parameters according to PBD and their effects on the results. It was observed that reduced second order polynomial model by CCD was in good agreement with the experimental results. The reduced second-order polynomial model was used successfully to fit the experimental data. The quadratic equation of this model can be used to determine the value of RO4 adsorption at any values of the independent parameters. The results of the ANOVA analysis indicated that adsorbent concentration and contact time had a negative, linear effect on the adsorption efficiency.

The Langmuir, Freundlich, and Tempkin models were used to investigate the adsorption equilibrium of sesame stalks for RO4 adsorption. The Langmuir isotherm gave a better fit than the other two isotherms. The monolayer adsorption capacities of sesame stalks were found to be 84.75, 113.64, and 178.57 mg RO4/g for 20, 40, and 60 °C,

respectively. Technologies for the removal of dyes are generally expensive. Kinetic measurements showed that adsorption process followed a pseudo-second order model.

Sesame stalks, which are produced as an agricultural waste during the production of sesame are very cheap. In addition, the stalks do not require any pretreatment process, which would increase the cost of using them adsorbents. Thus, from an economic perspective, the use of sesame stalks is a very beneficial and effective means of removing waste dye from aqueous solutions.

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