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Adsorption modeling of Orange G dye on mesoporous activated carbon prepared from Algerian date pits using experimental designs

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ABSTRACT

Activated carbon was prepared from Algerian date pits using physicochemical activation method consisted of zinc chloride ($ZnCl_2$) treatment and carbon dioxide (CO_2) gasification. The activated carbon produced was characterized by BET surface area, porosity development (total pore volume and micropore fraction). Adsorption of Orange G dye (OG) from water was studied using the prepared activated carbon. A three-factor central composite design (CCD) combined with response surface modeling (RSM) was employed for maximizing OG removal from aqueous solution by the activated carbon based on 20 different experimental data obtained in a batch study, the effects of various parameters such us agitation time, initial dye concentration and adsorbent dosage were studied. The significant factors on experimental designs response were identified from the analysis of variance (ANOVA). FTIR spectral result indicated all the functional groups were involved in the adsorption process. SEM results showed that the surface of the activated carbon was turned from dark to light color after dye adsorption.

Keywords: Activated carbon; Adsorption; Orange G; Central composite design; Response surface modeling

1. Introduction

Textile industries produce large volume of effluents, which are very toxic, resistant to physic-chemical treatments and not easily biodegradable. The non-biodegradability of textile wastewater is due to the high content of dyestuffs, surfactants and other additives, which are generally organic compounds of complex structure [1]. It is estimated that more than 100,000 commercially available dyes with over 7 × 105 t of dyestuff produced annually [2]. Among several chemical and physical methods, the adsorption has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design. Colour removal from industrial wastewaters by adsorption techniques has been of growing importance due to the chemical and biological stability of dyestuffs to conventional water treatment methods and the growing need for high quality treatment [3]. In adsorption based methods, it is desirable to have knowledge of the process variables and their influence on adsorption capacity in order to maximize the contaminants removal efficiency of the adsorbents. The liquid–solid interface adsorption process is mainly influenced by the initial concentration of the adsorbate, initial PH of the solution, adsorbent

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dose, surface area of the adsorbent, contact time, operating temperature and the agitation speed. Optimization of the process variables is required to achieve the maximum adsorption capacity, and hence, the removal efficiency of the adsorbent [4]. Currently, the most widely used and effective physical method in industry is activated carbon [5]. However, commercially available activated carbons are still considered as expensive materials for many countries due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [6,7]. Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products, such as apricot shell [8], male flower of coconut tree [9], jute fiber [10], rubber wood sawdust [11,12], corncob [13], bamboo [14] and oil palm fibre [15] cotton stalk [16].

In this study the following objectives were undertaken (1) to study the adsorption of Orange G dye (OG) by activated carbon prepared from Algerian date pits (2) to optimize the maximum adsorption of OG using response surface methodology (RSM) and (3) to study the effect of various parameters on OG adsorption.

2. Materials and methods

2.1. Preparation of activated carbon

Date pits (Deghlet Nour) coming from the Algerian south are washed, dried in the oven with 110°C during 12 h and then crushed. With the aim of improving the mesoporosity we proposed to carry out mixed activation according to the protocol of reference [17]. Thus, the particles whose diameter lies between 0.5 and 1 mm were mixed with $ZnCl_2$ powder, with a 1:1 mass ratio. The mixture is subjected to a rise of temperature of 10°C min^{-1} until 800°C under an inert gas flux with a flow of 20 l h^{-1}. When the temperature is reached, the nitrogen is replaced by CO_2 and the activation is maintained during 4 h. The excess of $ZnCl_2$ was first extracted in refluxing HCl (0.1 M) during 3 h, and then washed with hot water until silver nitrate test becomes negative. Thereafter, active carbon was dried in an oven at 110°C.

2.2. Physico-chemical characterization

The surface area and the porosity of the AC prepared were characterized by N_2 adsorption–desorption isotherms. ASAP2010 (Micromeritics Ltd., USA) was used to determine the surface areas and total pore volumes. The S_{BET} was calculated by the BET equation, micropore volume, micropore and external surface areas were obtained using the t-plot method.

Microscopic appearance and chemical properties of activated carbon (before and after dye adsorbed) were studied by Scanning Electron Microscope (SEM) and Fourier transform infrared (FTIR).

SEM and EDX analyses of activated carbon (adsorbent) were conducted using a JEOL-JSM 840 SEM. The SEM enables the direct observation of the changes in the surface microstructures of the adsorbent due to the adsorption of OG.

FTIR spectroscopy was used to determine the vibrational frequency changes in the functional groups of the activated carbon. The spectra were collected by FTIR Perkin Elmer (Spectrum One) within the range of wavenumber of 400–4000 cm^{-1}. Specimens of activated carbon was first mixed with KBr and pressed into tablet form. The FTIR spectrum was then recorded. The background obtained from scan of pure KBr was automatically subtracted from the sample spectra.

2.3. Sorbate

Orange G, an azo dye ($C_{16}H_{10}N_2Na_2O_7S_2$) was purchased from Sigma- Aldrich, USA. The chemical structure of Orange G is given in Fig. 1.

2.4. Adsorption studies

Batch adsorption studies were performed in 20 sets of 100 ml Erlenmeyer flasks containing 50 ml of OG solution with initial concentration of 10 to 30 mg l^{-1}.

Appropriate amount of activated carbon (0.1–0.3 g) was added to each flask and was kept in a shaker (150 rpm, 25°C) for a desired time (2.5–6 h), All aqueous samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of OG in the supernatant solution before and after adsorption were determined using a double beam UV–Vis spectrophotometer (JASCO-530) at its maximum wavelength of 477.8 nm (Fig. 2.) The percent dye concentration reduction was calculated by the following equation:

$$\text{Dye adsorption}(\%) = \frac{Co - Ct}{Co} \times 100 \tag{1}$$

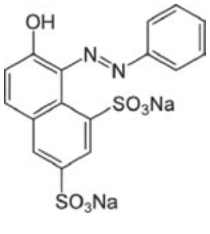

Fig. 1. Structure of Orange G dye.

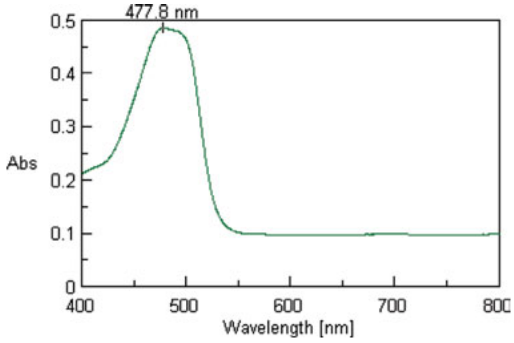

Fig. 2. Maximum wavelength of Orange G dye.

where C_o is the initial adsorbate concentration (mg l^{-1}) C_t the adsorbate concentration (mg l^{-1}) after time t.

2.5. Design of experiments

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions [18]. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables [19]. A standard RSM design called a CCD was applied in this work to study the independent variables for maximum adsorption of OG. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [20]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and nc center runs (six replicates).

The dependant variables selected for this study were time (X_1), carbon (X_2) and concentration of OG (X_3). A statistical optimization was conducted by using CCD. For each categorical variable, a 2^3 full factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments were required, as calculated from the following equation [20]:

$$N = 2^n + 2n + nc = 2^3 + 2 \times 3 + 6 = 20 \qquad (2)$$

where N is the total number of experiments required and n is the number of factors.

The center points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the (−1, 1) interval where the low and high levels are coded as −1 and +1, respectively. The axial points are located at (± α, 0, 0), (0, ±α, 0) and (0, 0, ±α) where α is the distance of the axial point from center, makes the design rotatable, generate the quadratic terms, and replicate tests at the center; in this study, the α value was fixed at 1.682 (rotatable), $\alpha = (k)^{1/2}$, where k is number of variables.

The experimental data were analyzed using (JMP 7 statistical software) for regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations.

Table 1 shows the complete design matrix of the experiments carried out, together with the results obtained. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The three variables were time (X_1), activated carbon (X_2) and concentration of OG (X_3). Each response was used to develop an empirical model which correlated the response to the dye adsorption variables using a second degree polynomial equation as given by the following equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j \qquad (3)$$

Table 1
Experimental design matrix and results

Run	Pattern	Time (X_1) (h)	Carbon (X_2) (g)	Dye (X_3) (mg l^{-1})	Dye adsorption (%) (actual data)
1	−−−	2.5	0.1	10	35.10
2	−−+	2.5	0.1	30	62.23
3	−+−	2.5	0.3	10	72.22
4	−++	2.5	0.3	30	73.44
5	+−−	6	0.1	10	55.54
6	+−+	6	0.1	30	73.47
7	++−	6	0.3	10	73.54
8	+++	6	0.3	30	75.85
9	−α00	1.30	0.2	20	44.85
10	+α00	7.19	0.2	20	78.09
11	0−α0	4.25	0.031	20	46.57
12	0+α0	4.25	0.368	20	78.85
13	00−α	4.25	0.2	3.18	44.80
14	00+α	4.25	0.2	36.81	78.12
15	0	4.25	0.2	20	78.01
16	0	4.25	0.2	20	78.00
17	0	4.25	0.2	20	78.00
18	0	4.25	0.2	20	78.00
19	0	4.25	0.2	20	78.00
20	0	4.25	0.2	20	78.00

where Y is the predicted response, b_0 the constant coefficient, bi the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and X_i, X_j are the coded values of OG adsorption variables.

3. Results and discussion

The elementary composition of date pits (Deghlet-Nour) is shown in Table 2, like any lignocellulosic material, the principal content is allotted to cellulose that constitutes approximately 37% of the total composition. While the rate of ash is less than 2%. This is a significant characteristic in the preparation of activated carbon.

3.1. Optimization of dye adsorption by response surface methodology (RSM)

Regression analysis was performed to fit the response function of % adsorption OG. The results are given in Table 3.

We have derived a second order mathematical model, presented in Eq. (4), for the experimental results obtained for the Orange G adsorption using JMP 7 statistical software:

$$Y = 77.863 + 6.686X_1 + 9.006X_2 + 7.661X_3 - 3.493X_1X_2 - 1.013X_1X_3 - 5.191X_2X_3 - 4.943X_1^2 - 4.504X_2^2 - 4.947X_3^2 \quad (4)$$

The square regression is more adequate for our purposes than the linear regression given that the Prob > F value less than 0.0001 (Table 4) and R^2 of 0.94, which shows that our theoretical model is good fit with the experimental data for the adsorption of OG.

Table 2
The elementary composition of date pits (Deghlet-Nour) [21]

Characteristics	Value (%)
Moisture	15.76
Lipid	4.39
Proteins	10.71
Total sugars	11.75
Reducing sugars	6.50
Cellulose brute	37.00
Ash	1.74
Sodium	0.20
Potassium	0.67
Calcium	0.23
Phosphorus	0.32
Magnesium	0.06
Non determined matters	10.67

Table 3
Regression coefficients for the response dye adsorption % for experimental designs of 3 variables (Time, Carbon and Dye)

Source	DF	Sum of squares	F -Value	Prob > F
Time (h) (2.5–6)	1	610.5378	27.4778	0.0004
Carbon (g) (0.1–0.3)	1	1107.7643	49.8559	<0.0001
Dye (mg l^{-1}) (10–30)	1	801.5667	36.0752	0.0001
Time (h) * carbon (g)	1	97.6503	4.3948	0.0625
Time (h) * dye (mg l^{-1})	1	8.2215	0.3700	0.5566
Carbon (g) * dye (mg l^{-1})	1	215.5926	9.7029	0.0110
Time (h) * time (h)	1	352.1712	15.8498	0.0026
Carbon (g) * carbon (g)	1	292.4763	13.1632	0.0046
Dye (mg l^{-1}) * dye (mg l^{-1})	1	352.6751	15.8725	0.0026

DF: degree of freedom.

Table 4
Analysis of Variance (ANOVA) for experimental designs for dye adsorption %

Source	DF	Sum of squares	Mean square	*F*-value
Model	9	3673.9277	408.214	18.3720
error	10	222.1932	22.219	Prob > *F*
C. Total	19	3896.1209	–	<0.0001

Fig. 3 Shows the correlation between the model predicted values of % dye adsorption and experimental data (observed values). As can be seen the predicted values obtained by Eq. (4) provide a good description of the experimental results. The significance of the estimated effects was tested by analysis of variance (ANOVA).

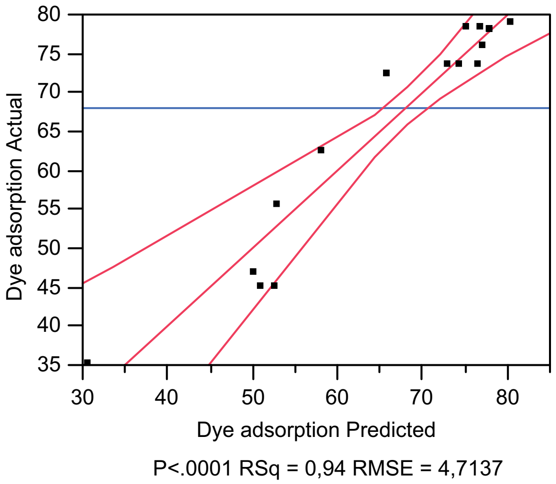

Fig. 3. Correlation between observed and predicted values of % dye adsorption.

The ANOVA test indicates that the model adequately describes the % dye adsorption. The ANOVA of experiment is presented in Tables 3 and 4. Normally, the parameters with Prob > *F* less than 0.05 are considered as significant parameters and correlation factor (R^2) value greater than 0.85 is desired for the mathematical model to be considered as a good approximation of the reaction. [22,23] in this case, initial dye concentration and adsorbent dosage were significant model terms whereas agitation time showed the least effect on adsorption capacity of the prepared activated carbon. From the ANOVA for response surface quadratic model, the model *F*-Value of 18.3720 implied that the model was significant.

3.2. Caracterization of the activated carbon

3.2.1. Caracteristics of porosity in activated carbon

Fig. 4. shows the nitrogen adsorption isotherm obtained at 77 K for the prepared activated carbon. The isotherm takes a shape resembling a combination of type I and II according to the IUPAC classification [24]. Additionally, development of mesoporosity is indicated by the pronounced desorption hysteresis loop.

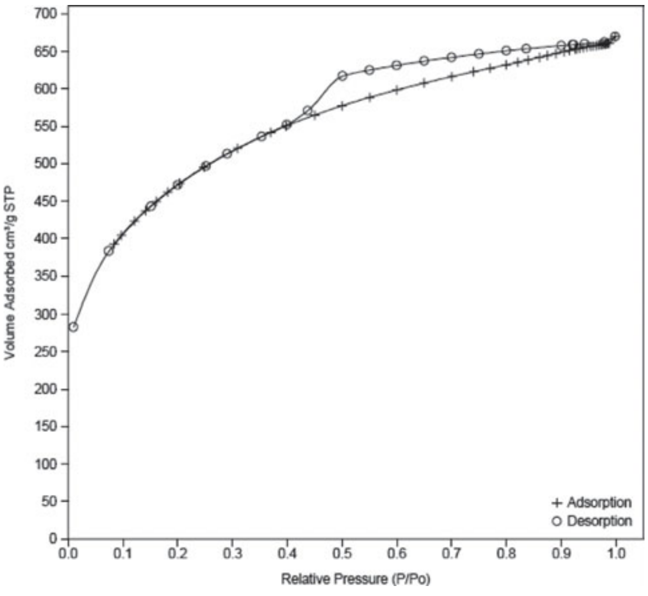

Fig. 4. Adsorption/desorption isotherm of nitrogen at –196°C for AC.

Parameters calculated by the Brunauer–Emmett–Teller (BET) equation [25] and the *t*-plot method [26] from N_2 sorption isotherms are shown in Table 5. Sample possesses mesopore volume greater than 0.9 cm^3 g^{-1} and BET surface area greater than 1500 m^2 g^{-1}. This shows that activated carbon is reasonably good for adsorption.

3.2.2. Fourier transform infrared spectroscopy (FTIR)

FTIR Spectroscopy technique was used to examine the surface functional groups responsible for dye adsorption. The FTIR spectrum obtained for the activated carbon before and after adsorption:

- The band at 3431 cm^{-1} was due to (O–H) vibrations in hydroxyl groups.
- The band located around 1580 cm^{-1} corresponded to (C=C) stretching vibration.
- The band located around 2936 cm^{-1} corresponded to (C–H) vibrations in methyl.
- The spectrum in the region of 1200–1000 cm^{-1} represented (C–O) stretching vibrations of functional groups such as alcohols, ethers, carboxylic acids and esters.
- The band at 2338 cm^{-1} was ascribed to (C≡C) vibrations in alkyne groups and methylene groups and at 663 and 619 cm^{-1} corresponded to (O–H) vibrations group.

Fig. 5 indicates the surface functional groups involvement in adsorption process. The diminished peaks showed that all the functional groups are completely involved in adsorption process.

3.2.3. SEM/EDX analyses

SEM images of activated carbon of date pits (Fig. 6(a)) showed bright dark color on the surface. After OG adsorption the surface of activated carbon was turned to light color (Fig. 6(b)). This may be due to the adsorption of OG on the surface of the activated carbon.

Quantitative EDX analysis showed C and O were the main elemental components, of the oxygen signal on the surface of activated carbon might be large numbers of surface functional groups. And we can observe the presence of Cl that was not completely removed by the cleaning step.

Table 5
Characteristics of activated carbons calculated from BET model and *t*-plot

S_{BET} (m^2 g^{-1})	S_{ext} (m^2 g^{-1})	S_{ext} (%)	S_{mic} (m^2 g^{-1})	S_{mic} (%)	V_t (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	V_{mic} (%)	V_{me} (%)
1587	1419	89.42	168	10.58	1.02	0.108	10.58	72.22

S_{BET}: BET surface area; S_{ext}: external surface area; S_{mic}: micropore surface area ($S_{BET} = S_{ext} + S_{mic}$); V_t: total pore volume; V_{mic}: micropore volume; V_{me}: mesopore volume ($V_t = V_{mic} + V_{me}$).

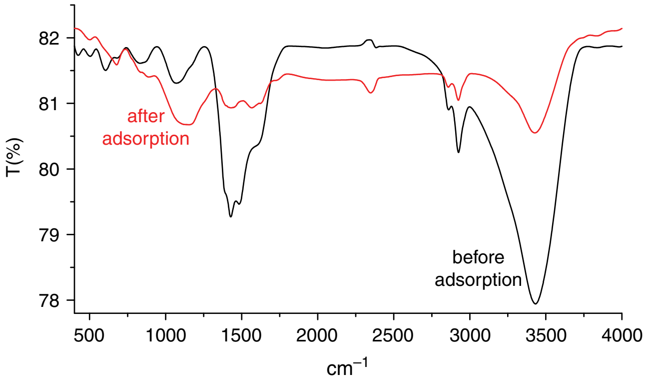

Fig. 5. FTIR spectrum of activated carbon before and after adsorption of Orange G dye.

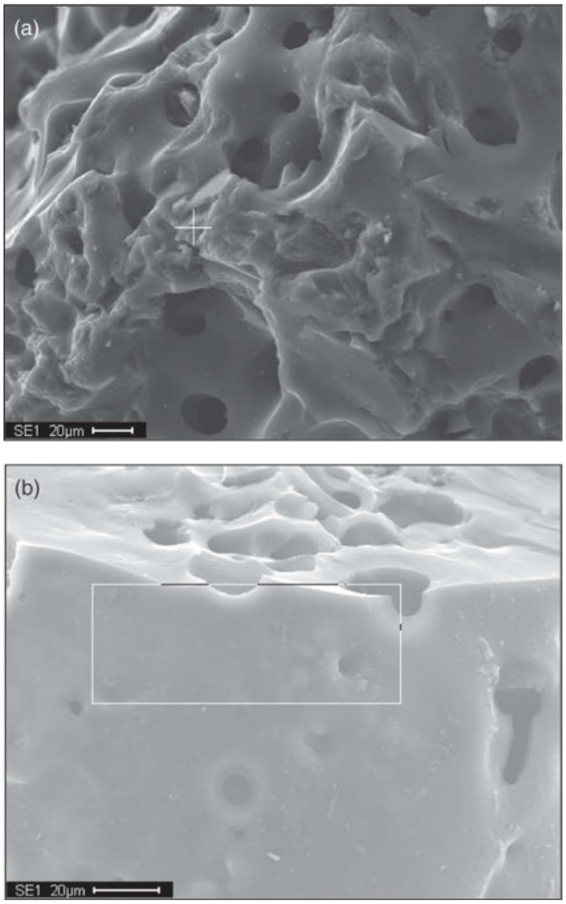

Fig. 6. SEM image of activated carbon of date pits (a) before and (b) after adsorption of Orange G dye.

Slight variation is noticed between the determined S and Na content of the activated carbon before and after adsorption of OG (Fig. 7.) the S and Na are presents in the chemical structure of OG given in Fig. 1, and in the elementary composition of date pits (Deghlet-Nour) given in Table 2.

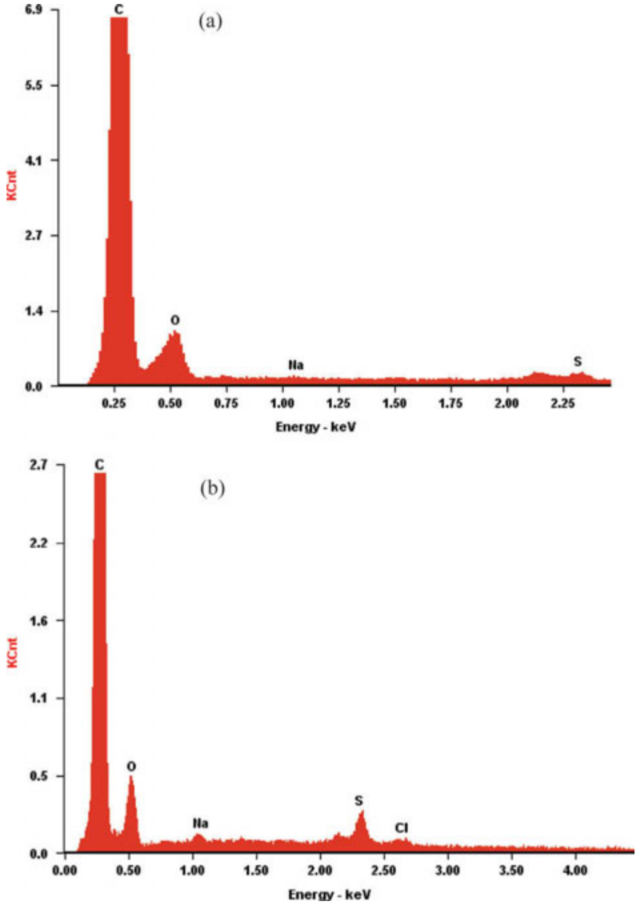

Fig. 7. Elemental compositions of activated carbon of date pits (a) before and (b) after adsorption of Orange G dye.

4. Conclusions

The prepared activated carbon were found to have well-developed pores on its surface. Date pits–based activated carbon was shown to be a promising adsorbent for removal of Orange G dye (OG) from aqueous solution. The effects of various parameters such as agitation time, initial dye concentration and adsorbent dosage were studied using a tree-factor central composite design (CCD) combined with response surface modeling (RSM). The optimum conditions for the maximum adsorption of OG (83.56%) were found as follows: agitation time of 4.99 h, initial dye concentration of 24.19 mg l^{-1} and adsorbent dosage of 0.26 g.

From the analysis of variance (ANOVA) for response surface quadratic model, the model *F*-Value of 18,3720 implied that the model was significant. From the (ANOVA), the most influential factor on experimental design response was identified.

FTIR spectral result indicated all the functional groups were involved in the adsorption process. SEM results showed that the surface of the activated carbon was turned from dark to light color after dye adsorption.

The high adsorption capacity of prepared activated carbon could be used as an alternate for other expensive activated carbon in treating effluents from textiles and dyeing industry.

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