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Preparation of High-Performance Adsorbent From Low-Cost Agricultural Waste (Peanut Husk) Using Full Factorial Design: Application to Dye Removal

Asmadi Ali [1,*], Alex Wong Chung Ing [1], Wan Rafizah Wan Abdullah [1], Sofiah Hamzah [1], Fazureen Azaman [1]

[1] Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu 21030, Kuala Nerus, Terengganu, Malaysia; thunderking93@hotmail.com; wanrafizah@umt.edu.my; sofiah@umt.edu.my; fazureenazaman92@yahoo.com;
* Correspondence: asmadi@umt.edu.my;

Scopus Author ID 54790692100
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Abstract: Dye pollution becomes one of the significant environmental concerns nowadays. The adsorption technique is a potent method for the removal of the dye from wastewater effluents. Conventional activated carbon is one of the best adsorbents for dye removal. However, it is constraint due to high cost, and problems with regeneration hamper large scale applications. The alternative method using low-cost adsorbent is being introduced to replace the activated carbon since they are available in large quantities, renewable and inexpensive. Hence, peanut husk (*Canavalia Ensiformis*) as absorbent was investigated for its potential in Malachite Green (MG) dye removal. The effects of dye concentration (25 and 100 mg/L), temperature (30 and 60 °C), and adsorbent dosage (25 and 100 mg) on MG dye removal percentage were designed and optimized using two levels full factorial design. Based on the optimization process, it was determined that the 25 mg/L of dye concentration, 60 °C of temperature, and 100mg of adsorbent dosage resulted in the highest removal efficiency of 84.85 % and 91.83 % for untreated and treated adsorbent, respectively. In conclusion, treated peanut husk has shown its great potential as low-cost adsorbent based on the removal efficiency.

Keywords: dye pollution; adsorbent; full factorial design; optimization.

1. Introduction

Water from the textile industries is an ecological problem that causes serious problems for living beings. Approximately one-fifth of industrial water pollution is due to textile processing and dyeing. The textile industry is known to be the largest polluter of clean water with the use of over a thousand chemicals in different coloring and printing processes [1, 2]. With that, several techniques have been investigated to remove the dye molecules from the effluents such as ion exchange, adsorption, biodegradation, membrane filtration, and others. Adsorption has received considerable attention among the techniques in terms of cost, ease of use, flexibility, and simplicity of design [3,4]. Activated carbon (AC) is one such adsorbent that has excellent potential for dye removal since it has a micro-porous nature, larger surface area, micro-porous nature, and high adsorption capacity [5, 6].

However, activated carbon is restricted due to high prices, high operating costs, and problems with regeneration hamper larger-scale applications. Hence, there is a constant need to find a better adsorbent with renewable, low cost and locally available materials for the

removal of dye [7, 8]. Numerous low-cost adsorbents for removing dyes have been proposed. These include agricultural waste (sawdust, bark, fruit peel), industrial wastes products (fly ash, red mud, metal hydroxide sludge), clay materials (zeolites, diatomite, dolomite), bio-adsorbents (biomass, peat) and others (cotton, starch) [3]. Due to environmental considerations, agricultural wastes are considered an essential precursor. This is because they are cheap in terms of cost, renewable resources, safe, available in large quantities, and easily accusable sources. These are also high in carbon and have low ash content [9].

Besides, the adsorption process depends on several parameters such as pH, temperature, initial solute concentration, and adsorbent dosage used [10, 11]. A popular approach to researching and maximizing the effect of adsorption factors is to use the experimental one-factor-at-a-time (OFAT), which considers measuring the response against one factor, keeping contents for other factors. However, it involves multiple experiments and very time consuming, besides being unable to study the effects of interactions between the factors, rendering a conclusion about optimization unreliable [12]. To draw the effective method, the design of experiment (DoE) can be applied to replace the stated conventional method. Thus, the main objective of this study is to determine the optimum adsorption of dye removal using low-cost peanut husk adsorbent based on initial dye concentration, temperature, and adsorbent dosage via full factorial design.

2. Materials and Methods

2.1. Materials.

Malachite Green (MG) dye with molecular formula $C_{23}H_{25}N_2Cl$ (molecular weight = 364.92g/mol, λ_{max} = 617nm) was procured from Bendosen Laboratory Chemicals and was used as the adsorbate. NaOH pellet with a molecular weight of 40g/mol was prepared to modify untreated peanut husk as treated adsorbent under alkali treatment and pH adjustment. All reagents were used without further purification, and the study utilized double distilled water.

2.2. Preparation of adsorbents.

2.2.1. Preparation of untreated peanut husk.

Peanut husks were collected from Material Laboratory located in FTKKI, UMT, Kuala Nerus, Terengganu. The raw peanut husks were thoroughly rinsed with distilled water to get rid of soil, dust, and impurities [13]. After that, peanut husk was bottomed with aluminum foil and put into a universal oven for drying purposes at 105˚C for 24 hours until crisp. Then, the dried peanut husk was ground into fine powder in an analytical mill [14] and sieved to obtain particles of diameter ranging between 250-500µm by using laboratory sieve [15]. Ziplock bags were prepared to store the sieved pea husk powder, labeled clearly, and placed into desiccator for further purpose.

2.2.2. Preparation of treated peanut husk.

A similar procedure was followed for the preparation of treated peanut husk. After the peanut husks were dried and grinded, they were soaked into 0.1M sodium hydroxide (NaOH) solution for 24 hours at room temperature so that they could fully adsorb all the reagents [16].

The alkali solution was filtered off and washed with distilled water to remove any possible residue of NaOH solution [13]. The pH was adjusted to nearly neutral. The treated peanut husks were dried again in a universal oven for 24 hours [14]. The preparation was ended with storing the dried peanut husk into a zip lock bag with clearly labeled and placed into desiccator for further purpose.

2.3. Adsorption experiments.

The experiment was carried out by batch adsorption method to investigate the effect of temperature, adsorbent dosage, and initial dye concentration [17]. Peanut husk was contacted with 100mL Malachite Green (MG) solutions in a sealed 250mL conical flask agitated vigorously by using a water bath shaker. The shaken speed was kept constant at 150rpm until equilibrium [18]. The sealed flasks were agitated for time intervals (10, 20, 30, 40, 50, 100, 150, and 200minutes) until equilibrium reached. Influence of temperature (30 and 60˚C), initial dye concentration (25 and 100mg/L), and adsorbent dosage (25 and 100mg) was examined during this research. Samples were collected from the flasks for analysis of the residual dye concentration in each flask at predetermined time intervals. The suspensions were filtered through the Whatman filter paper, and the supernatant was analyzed by measuring absorbance at maximum wavelength = 617 nm using UV-Vis Spectrophotometer. The removal capacity of MG dye by peanut husk was calculated using Equation (1):

$$\text{Percentage removal efficiency}(\%) = \frac{C_o - C}{C_o} \text{ x } 100\% \qquad (1)$$

Where C_o is an initial concentration of MG, mg/L, and C is MG concentration after adsorption at a certain time interval, mg/L. The adsorption experiments were repeated in triplicate to reduce any possible random errors.

2.4. Characterization of adsorbent.

Characterization techniques of absorbent involve the morphological study by SEM, FTIR, and Micromeritics ASAP. SEM was used to characterize the surface morphology of the adsorbent materials. The analysis was conducted at 1000x magnification using SEM (JEOL-JSM-6610L) in Centralized Lab UMT. FTIR (Shimadzu IR Tracer-100) used to detect the surface functional groups of untreated and treated peanut husk. The specific surface area and pore volume were determined by using nitrogen adsorption-desorption isotherm properties. The analysis was carried out by using Micromeritics ASAP 2000 in Centralized Lab UMT.

2.5. Design of experiment (DoE).

The design of the experiment was carried out using Minitab 16.0 software using a two-level (23) complete factorial design with 3 replicates. The three selected factors were temperature, initial dye concentration, and adsorbent dosage, while the response was MG dye removal percentage, %. The studied ranges for initial dye concentration, temperature, and adsorbent dosage were between 25 to 100mg/L, 30 to 60°C, and 25 to 100mg, respectively. Table 1 summarizes the code levels and their corresponding actual values for three factors.

Table 1. Coded levels and its actual variables for 2^k Factorial Design Method

Factors	Coded Symbol	Level	
		-1(min)	+1(max)
Initial dye concentration (mg/L)	A	25	100
Temperature	B	30	60
Adsorbent dosage (mg)	C	25	100

2.6. Statistical analysis.

Multiple regression techniques were used to establish the relationship between the response (Removal rate, R) and three factors (initial dye concentration, temperature, and adsorbent dosage). The model equation is expressed in Equation (2):

$$R\ (\%) = X_0 + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7ABC \quad (2)$$

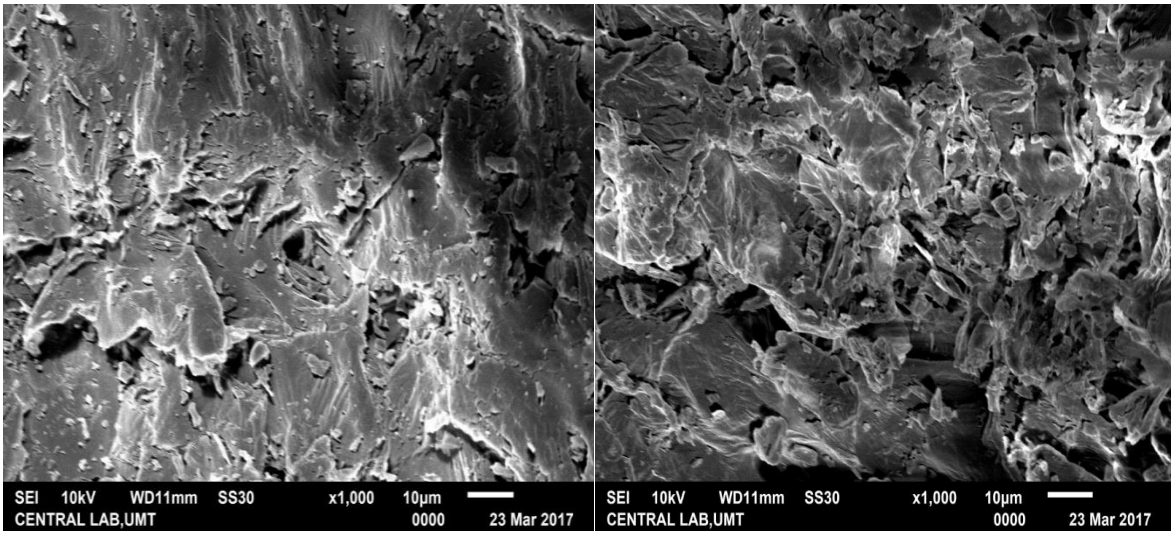
R is the response, X_0 is the global mean, X_i is the other regression coefficients and A, B, C is the initial dye concentration, temperature, and adsorbent dosage, respectively. 2^3 factorial design cube plot diagrams with high and low three factors are shown to give a better understanding of optimum dye removal conditions. Analysis of variance (ANOVA) was performed to analyze the reliability of the model with a 95% significance level (p-values<0.05). All data analysis was analyzed by using Minitab version 16.0 software.

3. Results and Discussion

3.1. Characterization of adsorbents.

3.1.1. Scanning Electron Microscope (SEM).

The morphological features and surface characteristics of peanut husk untreated and after treated with NaOH were examined using SEM, as shown in Figure 1. These images were used to test for potential changes in morphological characteristics before and after being modified by NaOH. Figure 1 (a) shows that the surface of the given untreated peanut husk presented is irregular, smooth, and compact. Even though there are existed pores and cavities, the number of pores is limited and can be considered as less porous.



(**a**) (**b**)

Figure 1. SEM micrographs of a) untreated, and b) treated peanut husk.

The treatment of peanut husk with NaOH has shown improvement in physical characteristics, as shown in Figure 1 (b). The surface of treated peanut husk is rougher compared to untreated conditions. The pores and cavities can be easily observed, and the pores are the deep and more open structure, which indicated that the treated peanut husk has more porous structure. Such characteristics are important for the adsorption process since it makes active sites more accessible and allows larger dye molecules to be diffused [19]. Alkali treatment induced the cracking of pores, and surface roughness increment. It also results in open compact structures indicating the partial removal of the outer non-cellulose layer consisting of materials like hemicellulose, pectin, lignin, wax, and other impurities contained in the adsorbent. Among these materials, wax and pectin are known as a protective layer that surrounds the surface of natural fibers [20].

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR).

FTIR spectra analysis was used mainly to identify the existence of available functional groups (carbonyl, hydroxyl, and carboxyl) that were capable of dye adsorption [21]. Figure 2 shown the comparison of FTIR spectra between untreated and treated peanut husk. From this figure, it is evident that some of the peaks have shifted after the peanut husk underwent NaOH modification. For example, the O-H stretching shifted little from 3402.43cm^{-1} to 3419.79cm^{-1} and C-O stretching from 1041.56cm^{-1} to 1045.42cm^{-1}. Modification of NaOH can cause swelling that leads to a breakdown of structural connections between lignin and carbohydrates, disruption of the lignin structure, increased internal surface area, decrease in polymerization, and crystallinity [22]. It is believed that MG dye molecules had possessed ion-exchange mechanisms which increase the adsorption capacity after alkali treatment. From the FTIR spectra analysis, there existed a large number of hydroxyl and carboxyl groups on the surface of peanut husk. This indicated that these functional groups had the potential to act as active sites for interaction with dye molecules [23].

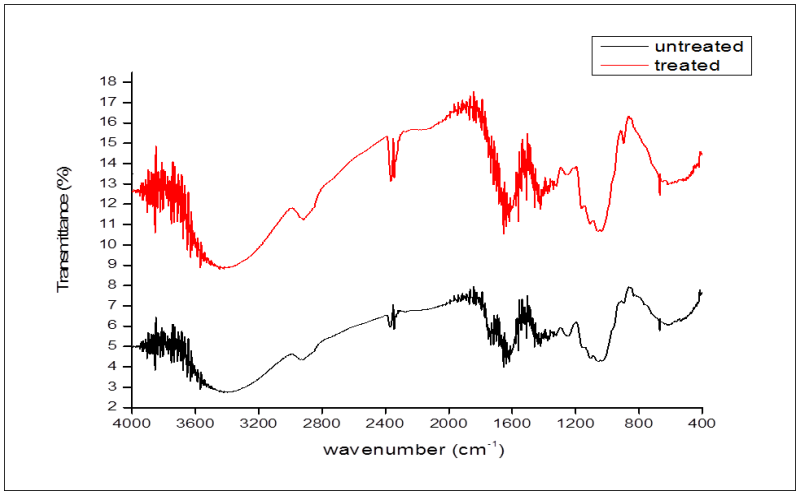


Figure 2. FTIR spectra between untreated and treated peanut husk.

3.2. Analysis of Surface Area and Pore Size (ASAP).

The texture properties, such as surface area play an important role in the sorption process of dye molecules [24]. Surface area and pore distribution of untreated and treated peanut husk were measured using BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) as shown in Table 2.

Table 2. BET and BJH analysis results for untreated and treated pea husk

Sample	BET surface area (m^2/g)	BJH adsorption average pore diameter (nm)
Untreated peanut husk	1.0191	18.5149
Treated peanut husk	0.6431	37.8083

From Table 2, BET surface area has shown decrement from 1.0191m^2/g to 0.6431m^2/g while the BJH average pore diameter shown increment from 18.5149 nm to 37.8083nm. The reduction of surface area can be due to the modification of peanut husk using NaOH, which resulted in the surface of modified samples has been covered by the NaOH layer. This causes, in part, the observed reduction in the specific surface area by increased mass and partial porosity filling [25]. According to IUPAC classification [26], pore size lies between 2-50nm falls under the mesoporous category. For both samples, they are having mesoporous structure but treated peanut husk has been observed to have a bigger pore size. The tendency of NaOH activation to produce mesoporous adsorbent was also observed by Ding et al. [27]. The presence of a large number of mesoporous features facilitates the uptake of a larger amount of dye molecules from the liquid phase [24].

3.3. Results of factorial experimental design by 2^k full factorial design.

The results of the adsorption experiment by untreated and treated peanut husk have been tabulated in Table 3. The main effects plot, typical plot, interaction plot, and cube plot have been analyzed and shown in Figure 3. Analysis of Variance (ANOVA) has been tabulated in Table 4. After discarding any insignificant terms, the empirical modeling equation can be represented as in Equation (3) and (4):

$$R1\ (\%) = 72.363 - 2.171A + 3.152B + 6.286C - 1.926AB + 2.693AC + 0.677BC - 0.965ABC \quad (3)$$

$$R2\ (\%) = 77.549 - 1.978A + 3.892B + 7.253C - 2.225AB + 3.14AC + 1.117BC - 0.955ABC \quad (4)$$

Where R1 and R2 are the removal rate of untreated and treated peanut husk, respectively, A is initial dye concentration, B is temperature, and C is adsorbent dosage. At the same time, AB, AC, BC, and ABC are the cross product of factors.

Table 3. Results of adsorption experiment by untreated and treated peanut husk.

Run	Variables			Dye removal of untreated peanut husk (R_1) (%)	Dye removal of treated peanut husk (R_2) (%)
	A	B	C		
1	100	30	25	59.46	63.56
2	100	30	25	59.62	63.40
3	100	30	100	78.80	84.10
4	25	60	100	84.92	91.46
5	100	30	25	60.01	64.06
6	100	60	25	63.63	66.40
7	25	30	25	68.03	70.95
8	25	60	25	74.54	79.03
9	100	60	25	62.41	67.35
10	25	60	25	73.97	80.11
11	25	30	25	67.81	71.65
12	25	60	25	74.62	79.24
13	25	30	100	71.46	75.38
14	100	30	100	78.03	84.21

Run	Variables			Dye removal of untreated peanut husk (R_1) (%)	Dye removal of treated peanut husk (R_2) (%)
	A	B	C		
15	25	60	100	84.49	91.43
16	100	60	100	80.46	88.13
17	25	60	100	85.14	92.59
18	100	30	100	77.87	84.10
19	25	30	100	71.51	75.59
20	100	60	100	79.85	87.18
21	25	30	100	71.24	75.38
22	25	30	25	66.68	71.51
23	100	60	25	62.14	66.29
24	100	60	100	80.02	88.07

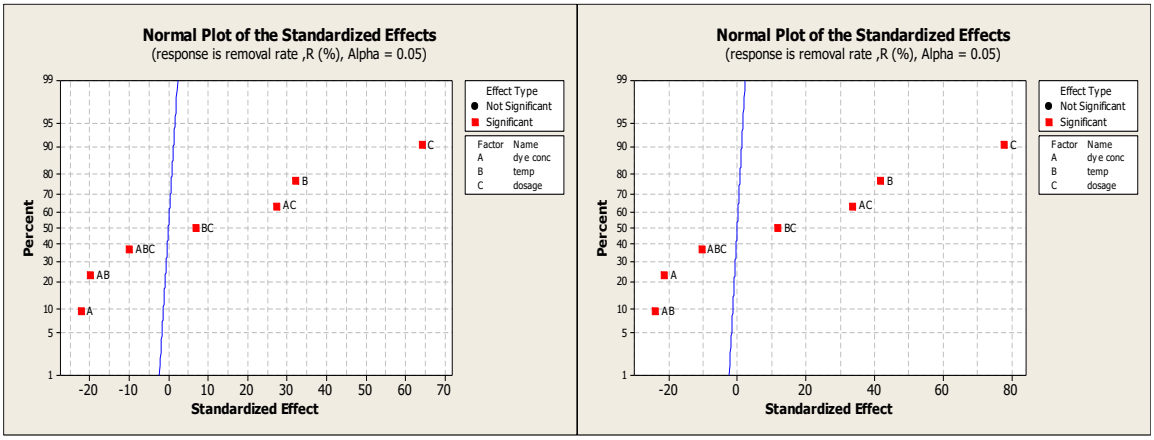
Table 4. Analysis of Variance (ANOVA) for removal rate, R (%) of untreated and treated peanut husk.

Source	Seq. SS	Adj. SS	Adj. MS	F	P	R^2	R^2 (pred.)
Untreated peanut husk (R_1)							
A	113.112	113.112	113.119	490.61	0.000	0.9970	0.9948
B	238.50	238.50	238.502	1034.42	0.000		
C	948.24	948.24	948.238	4112.66	0.000		
AB	89.07	89.07	89.068	386.30	0.000		
AC	174.10	174.10	174.099	755.10	0.000		
BC	10.99	10.99	10.993	47.68	0.000		
ABC	22.35	22.35	22.354	96.95			
Treated peanut husk (R_2)							
A	93.88	93.88	93.88	451.59	0.000	0.9984	0.9965
B	363.54	363.54	363.54	1748.72	0.000		
C	1262.44	1262.44	1262.44	6072.68	0.000		
AB	118.81	118.81	118.81	571.50	0.000		
AC	236.67	236.67	236.67	1138.47	0.000		
BC	29.95	29.95	29.95	144.06	0.000		
ABC	21.88	21.88	21.88	105.25			

The interaction factors influencing the removal of MG dye were calculated by conducting the analysis of variance (ANOVA), as shown in Table 4. All the factors were potentially significant, with a 95% confidence level and the P-value of less than 0.05 ($P<0.05$). Also, the model presented a real square correlation coefficient R-square of 99.7%, indicating that the data are fitting the statistical model well.

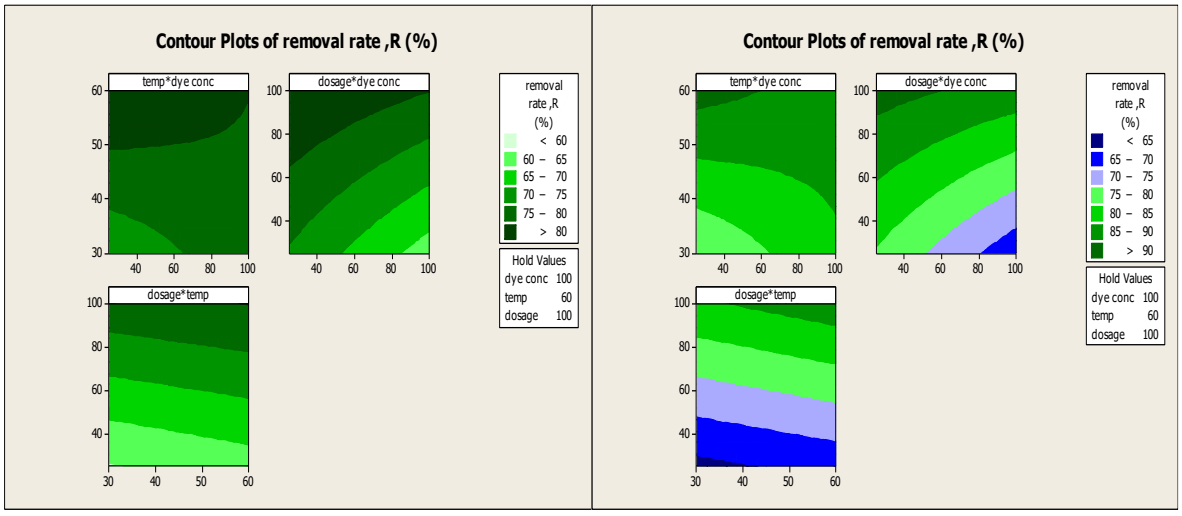
Figure 3 shows that all three factors: A is dye concentration, B is temperature, and C is the adsorbent dosage, and interaction of AB, AC, BC and ABC have a statistically significant effect on removal of MG dye for both untreated and treated peanut husk. In detail, A, AB, and ABC lie on the left side of the line and has a negative effect, while B, C, AC, and BC fall on the right side has a positive effect. Adsorbent dosage (C) had the largest effect on the process of adsorption, followed by B, AC, A, AB, ABC, and BC.

Figure 4 has revealed that the adsorption shown the highest removal rate with the darkest color. For example, the graph of temperature against dye concentration has shown that with increasing temperature and decreasing dye concentration, the removal rate has given the highest value of more than 80%, and the color represented was the darkest green. This concept was applicable to the other graphs. For the optimization process, the results have shown that 25mg/L of dye concentration, 60°C of temperature, and 100mg of adsorbent dosage gave the highest removal efficiency of 84.85% and 91.83% for untreated and treated adsorbent, respectively.



(**a**) (**b**)

Figure 3. Normal Plot of the Standardized Effects of a) untreated; and b) treated peanut husk.



(**a**) (**b**)

Figure 4. Contour Plot of removal rate, R (%) for a) untreated; and b) treated peanut husk.

4. Conclusions

In the present work, a 2^3 full factorial design of experiments are employed to study the removal of MG dye for both untreated and treated peanut husk as an absorbent. SEM, FTIR, BET and BJH analysis were studied to confirm the compatibility of untreated and treated peanut husk. For the optimization process, the results have shown that 25 mg/L of dye concentration, 60 °C of temperature, and 100mg of adsorbent dosage gave the highest removal efficiency of 84.85 % and 91.83 % for untreated and treated adsorbent, respectively. In conclusion, treated peanut husk has shown its great potential as low-cost adsorbent based on characterization and the removal efficiency.

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Conflicts of Interest

The authors declare no conflict of interest.

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