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Systematic approach for the optimal process conditions of Reactive Red 198 adsorption by pistachio nut shell using Taguchi method

Fatih Toprak[a], Bulent Armagan[b,*], Avni Cakici[a]

[a]*Ataturk University, Faculty of Engineering, Environmental Engineering Department, Erzurum, Turkey*
[b]*Istanbul University, Faculty of Engineering, Environmental Engineering Department, 34320 Istanbul, Turkey*
Tel. +90 212 473 70 70; email: bulent.armagan@istanbul.edu.tr

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ABSTRACT

A new adsorbent, the pistachio nut shell was investigated as an inexpensive and effective adsorbent for adsorption of the commercially important reactive azo dye, Remazol Rot RB (C.I. Reactive Red 198) from its aqueous solution. Taguchi method was applied to determine optimum conditions for the removal of dye from synthetic textile wastewater. After the parameters were determined to remove Remazol Rot RB (C.I. Reactive Red 198) from synthetic textile wastewater, the experimental studies were realized. For this purpose, a series of batch adsorption tests were carried out to address the effect of various experimental parameters and their ranges such as adsorbent concentration, contact time, initial dye concentration, pH, temperature, adsorbent particle size, agitation speed, respectively. An orthogonal array L27 (7^3) for experimental plan and the smaller the better performance statistics formula were selected to define optimum conditions. The optimum conditions were found to be as follows: contact time (min), 10; agitation speed (rpm), 100; initial dye concentration (mg/L), 25; pH, 2; temperature (°C), 20; adsorbent particle size (mm), $0.025 < x < 0.5$; adsorbent concentration (mg/L), 100, respectively. Under these optimum conditions, it was determined that the Remazol Rot RB removal efficiency from textile wastewater was 88%. Also, it was thought that pH, adsorbent particle size and initial dye concentration were important parameters for the performance statistics. Langmuir and Freundlich adsorption isotherms were also studied to model the adsorption mechanism data for Remazol Rot RB (C.I. Reactive Red 198).

Keywords: Pistachio nut shells; Adsorption; Reactive dye; Taguchi method; Non-linear method; Isotherm

1. Introduction

Many industries have been widely using dyes and pigments for various purposes and their effluents include high color, high suspended solids, and dissolved organics. A considerable amount of high quality water is needed in textile industry for dyeing and finishing operations. Color and recalcitrant compounds are among the vital environmental concerns in effluent treatment [1]. Reactive azo dyes are presently the most important compounds, constituting about 20–40% of the total dyes used for coloring [2]. Such voluminous quantities pose considerable environmental problems. Besides, reactive dyes are highly soluble in water, it needs to be removed or decolorized before the wastewater can be discharged. This is important especially in regions where water resources are scarce [3–5].

*Corresponding author.

One of the main problems in the treatment of textile dyeing wastewater and dye manufacture wastewater is the removal of dye color [6]. In order to remove dyes from aqueous solutions, many chemical or biological treatments have been used either individually or together [7]. Adsorption has been an effective separation process for a wide variety of applications, especially for removal of non-biodegradable pollutants (including dyes) from wastewater [8,9]. In the recent years, for the removal of different type of substances from wastewater, several materials have been evaluated as adsorbents like silicagel [10], perlite [11], hydroxyapatite [12], fly ash [13], dried waste sludge [14], coir pith carbon [15], pulp fibers [16], wheat straw [17], silkworm pupa [18], hazelnut shells [19], saw dust [20], mesoporous carbon [21], wheat shells [22], tree leaf [23], natural or modified minerals such as montmorillonite [24], zeolite [25], sepiolite [26], and bentonite [27]. In this study, the pistachio nut shell was chosen as an adsorbent because of its high availability and carbon contents, low ash content and reasonable good hardness property. It contains around 23 % protein, 56% fat, 19% carbohydrate and 5% moisture, respectively. Pistachio nut also contains high amounts of K, P, Ca, Mg and Fe at different proportions [28,29].

The novelty of the present study consists of Taguchi optimization method for the removal of Remazol Rot (C.I. Reactive Red 198) dye from aqueous solution and experimental data are presented in order to demonstrate the practical usage of the pistachio nut shell. The optimum conditions with the higher pollutant removal efficiency for batch adsorption studies were determined using the Taguchi method. For this purpose, seven controllable factors were identified for the removal of dye. The parameters used in the optimization are pH, adsorbent particle size, contact time, adsorbent concentration, agitation speed, temperature and initial dye concentration respectively. Furthermore, Langmuir and Freundlich adsorption isotherms were also studied to explain the adsorption mechanism.

2. Materials and methods

2.1. Preparation of pistachio nut shell

The pistachio nut shell is grown mainly in Iran, USA, Syria, Turkey, Greece and Italy and is one of the most popular nuts in the world with high nutritional values and its very unique flavor as a snack and a food ingredient [30]. The sample pistachio nut shell used in the experiments was obtained commercially from Sanliurfa, Turkey and was used for the preparation of adsorbent. A pistachio is composed of internal and external shells. In this study, internal pistachio nut shells sample was used. It was washed several times with distilled water to remove surface impurities and then dried at 110 °C in an oven for 12 h to reduce the moisture content. The development of porous materials with large surface areas is currently an area of extensive research, particularly with regard to potential applications as environmental remediation [31]. The pistachio nut shells were crushed, grounded and sieved in the range of 250–2000 μm with a coffee grinder to increase the surface area. The surface of adsorbent was characterized by scanning electron microscopy (SEM, Zeiss). Fig. 1 shows that the adsorbent had an irregular and porous surface, which indicated high surface areas. After adsorption, the pores were packed with dyes.

2.2. Analytical methods

A commercial textile dye Remazol Rot RB (C.I. Reactive Red 198) was provided from Bursa, Turkey and used in all adsorption experiments without further purification. The chemical structure of Remazol Rot RB is illustrated in Fig. 2. It contains anionic sulfonate groups

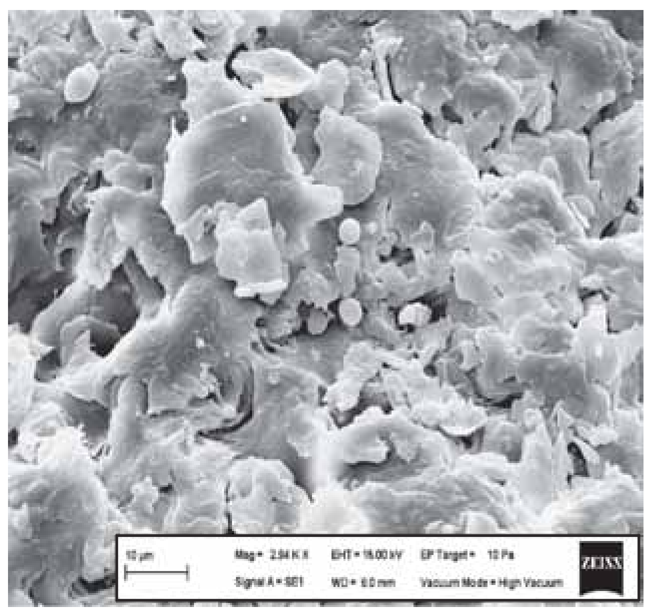

Fig. 1. SEM micrograph of the pistachionut shells with Remazol Rot RB adsorbed.

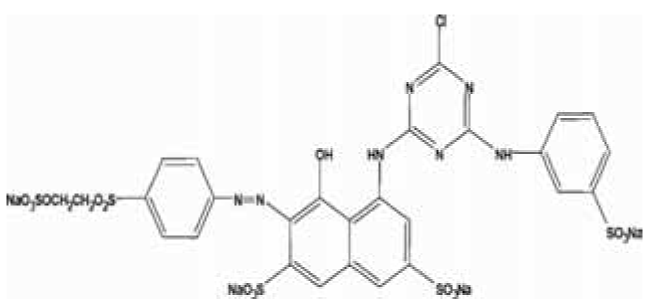

Fig. 2. The chemical structure of Remazol Rot RB (C.I. Reactive Red 198).

to various degrees. The equilibrium concentration of Remazol Rot RB was respectively determined at 520 nm using a visible spectrophotometer (Shimadsu T_{70}). Distilled and deionized water with a conductivity value of $2\cdot10^{-6}$ mhos/cm was used in all experiments. The pollutant removal efficiency is calculated using the following relationships:

$$\text{Removal efficiency} = \frac{(C_\mathrm{i} - C_\mathrm{r})\cdot 100}{C_\mathrm{i}} \tag{1}$$

where C_i = initial dye concentration in mg/L, C_r = equilibrium (residual) dye concentration in mg/L.

2.3. Taguchi method

Conventional experimental design techniques are too complex and hard to implement. Besides, these methods require a large number of experiments when the number of process parameters increases [32,33]. In order to minimize the number of tests required the Taguchi method, which was developed by Taguchi, was used. This is a systematic application of design and analysis of experiments for the purpose of designing and improving product quality. This is a type of fractional factorial design which uses an orthogonal array to study the influence of factors using only a small number of experiments. The design of experiment using Taguchi method provides efficient and systematic approach to determine the optimum conditions [21,34,35]. The advantage of the Taguchi method over the conventional experimental design methods, in addition to keeping the experimental cost at a minimum level, is that it minimizes the variation in product response while keeping the mean response on target. Its other advantage is that the optimum working conditions determined from the experimental study can also be reproduced in the real production environment [36,37]. In this study, seven experimental parameters were used to determine optimum process conditions and each parameter was designed to have three levels, denoted 1, 2 and 3 (Table 1).

The experimental design was according to an L27 array based on Taguchi method, which markedly reduced the number of experiments from 343 to 27 (Table 2) [32,38]. The validity of this assumption was checked by confirmation experiments conducted at the optimum conditions. In order to observe the effects of noise sources on the dye removal, each experiment was repeated twice under the same working conditions.

There are three categories of performance statistics, the larger-the-better, the smaller- the-better and the nominal-the-better. In this study, the performance statistics of the-smaller-the-better was used to define the optimum conditions [39,40]. The smaller-the-better performance statistics was given by Eq. (2).

$$\mathrm{SN}_S = -10\mathrm{Log}\left[\frac{1}{n}\sum_{i=1}^{n} y^2\right] \tag{2}$$

where SN_s is performance statistics, n the number of repetition done for an experimental combination, and Y_i the performance value of ith experiment.

In the Taguchi method, the experiment corresponding to optimum working conditions might not have been done during the whole period of the experimental stage. In such cases, the performance value corresponding to optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this, the additive model may be used Eq. (3) [41]:

Table 1
Experimental parameters and their levels

Parameters		Levels		
		1	2	3
A	pH	2	4	8
B	Adsorbent particle size (mm)	$0.025 < x < 0.5$	$0.5 < x < 1$	$1 < x < 2$
C	Contact time (min)	10	30	60
D	Adsorbent concentration (mg/L)	100	500	1000
E	Agitation speed (rpm)	100	120	150
F	Temperature (°C)	20	30	40
G	Initial dye concentration (mg/L)	25	100	200

Table 2
Chosen L27 (7^3) experimental plan table and results of experiment

Experiment No	A	B	C	D	E	F	G	The results of experiment Y_i		
								1	2	
1	1	1	1	1	1	1	1	4,627	4,698	–13.3726
2	1	1	1	1	2	2	2	22,461	22,391	–27,015
3	1	1	1	1	3	3	3	95,073	95,993	–39.6032
4	1	2	2	2	1	1	1	5,476	5,901	–15,106
5	1	2	2	2	2	2	2	54,379	55,724	–34,816
6	1	2	2	2	3	3	3	143,623	143,552	–43,1423
7	1	3	3	3	1	1	1	5264	5405	–14,5426
8	1	3	3	3	2	2	2	46,311	46,241	–33,3071
9	1	3	3	3	3	3	3	131,096	131,308	–423,588
10	2	1	2	3	1	2	3	139,639	140,084	–42,914
11	2	1	2	3	2	3	1	17,012	17,224	–24,6692
12	2	1	2	3	3	1	2	75,257	76,602	–37,6086
13	2	2	3	1	1	2	3	200	200	–46,0206
14	2	2	3	1	2	3	1	25	25	–27,9588
15	2	2	3	1	3	1	2	94,719	94,649	–39,5255
16	2	3	1	2	1	2	3	199,674	198,966	–45,991
17	2	3	1	2	2	3	1	25	24,868	–27,9359
18	2	3	1	2	3	1	2	93,445	94,79	–39,4736
19	3	1	3	2	1	3	2	93,87	93,516	–39,4342
20	3	1	3	2	2	1	3	162,66	162,802	–44,2294
21	3	1	3	2	3	2	1	21,4	21,754	–26,6801
22	3	2	1	3	1	3	2	94,719	93,941	–39,4931
23	3	2	1	3	2	1	3	197,834	197,753	–45,9242
24	3	2	1	3	3	2	1	25	25	–27,9588
25	3	3	2	1	1	3	2	98,116	98,046	–39,8317
26	3	3	2	1	2	1	3	200	200	–46,0206
27	3	3	2	1	3	2	1	25	25	–27,9588

$$Y_i = \mu + X_i + e_i \tag{3}$$

where μ is the overall mean of performance value; X_i the fixed effect of the parameter level combination used in ith experiment and e_i the random error in ith experiment. Because Eq. (2) is a point estimation, which is calculated by using experimental data in order to determine whether results of the confirmation experiments are meaningful or not, the confidence interval must be evaluated. The confidence interval at chosen error level may be calculated by Eq. (4) [36]:

$$Y_i \mp \sqrt{F\alpha;1,\mathrm{DFMSe}\left(\frac{1+m}{N}+\frac{1}{n_i}\right)} \tag{4}$$

where F is the value of F-table, α the error level, DFMSe the degrees of freedom of mean square error, m the degrees of freedom used in the prediction of Y_i, N the number of total experiments, and n_i the number of repetitions in the confirmation experiment. The order of the experiments was obtained by inserting parameters into columns of OA, L27 (7^3), chosen as the experimental plan given in Table 2. The experiments were conducted in random order to avoid noise sources which had not been considered initially and could occur during an experiment and affect results in a negative way. A confirmation experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and the additive model is a good approximation [38].

2.4. Adsorption isotherm studies

Adsorption isotherms experiments for pistachio nut shell were undertaken by a batch equilibrium technique by placing a known quantity of the adsorbent (0.3%) in a glass bottle containing 50 mg·L^{-1} of an aqueous solution of Remazol Rot RB with a predetermined concentration. After such solution preparation, the bottles were placed on an orbital shaker at 150 rpm at room temperature for 1 h followed by centrifugation at 4000 rpm for 10 min. The equilibrium adsorption uptake, q_e (mg/g), of Remazol Rot RB was calculated using the following relationships:

$$\text{Equilibrium adsorption uptake, } q_e = \frac{(C_i - C_r)\cdot V}{1000\cdot m} \qquad (5)$$

where q_e = amount of dye adsorbed per gram of adsorbent in mg/g, C_i = initial dye concentration in mg/L, C_r = equilibrium (residual) dye concentration in mg/L, V = the volume of the solution in mL, and m = mass of adsorbent (g).

Adsorption isotherm data of Remazol Rot RB dye was investigated to fit the models of Langmuir and Freundlich. In first instance, Langmuir model assumes that adsorption occurs in a monolayer where the actives sites are identical and energetically equivalent. This isotherm is given by

$$q_e = \frac{q_{\max} K_L C_r}{1 + K_L C_r} \qquad (6)$$

where $q_{\max}$ is the maximum adsorption capacity (mg/g) and K_L (L/mg) represents the Langmuir equilibrium constant, respectively. Both $q_{\max}$ and K_L are obtained from data correlation. Alternatively, Freundlich model is an empirical expression used to describe a heterogeneous system, which is defined as

$$q_e = K_F C_r^{(1/n)} \qquad (7)$$

where K_F and n are Freundlich constants as indicators of adsorption capacity and adsorption intensity, respectively. Linear regression was frequently used to determine the most fitted isotherm. The linear least-squares method to the linearly transformed isotherm equations was widely applied to confirm the experimental data and isotherms using coefficient of determination [42]. However, several studies have shown that the transformation of nonlinear adsorption models to linear forms usually results in parameter estimation errors and uncertainties [43]. Thus, in this study, a nonlinear regression approach employing a stochastic global optimization method was used to determine the model parameters of isotherm equations.

3. Results and discussion

3.1. Taguchi results

The collected data were analyzed by PC to evaluate the effect of each parameter on the optimization criteria. In order to see effective parameters and their confidence levels on the dye removal process, an analysis of variance was performed. A statistical analysis of variance (ANOVA) was then applied to determine the significant parameters and the main effect plot was used to set the optimal level for each parameter in the dye removal process. For this, the MINITAB 15.0 software was used to analyze the experimental data. F-test is a tool to see which process parameters have a significant effect on the dye removal value. The F-value for each process parameter is simply a ratio of the mean of the squared deviations to the mean of the squared error.

The degrees of the influences of parameters on the performance statistics are given in Figs. 3–10. The numerical value of the maximum point in each graph corresponds to the best value of the particular parameter. As seen in Fig. 3, the increase of the solution pH from 2 to 8 shows the decrease of performance statistics. The increase of solution pH did not show a positive effect for the performance statistics because of OH^- radicals. Since the reactive dyes have negative sulphonate groups, they are repelled by the negatively charged the pistachio nut shell surface.

Adsorption from solution to solid surface starts to take place when dipole or charged species of adsorbent

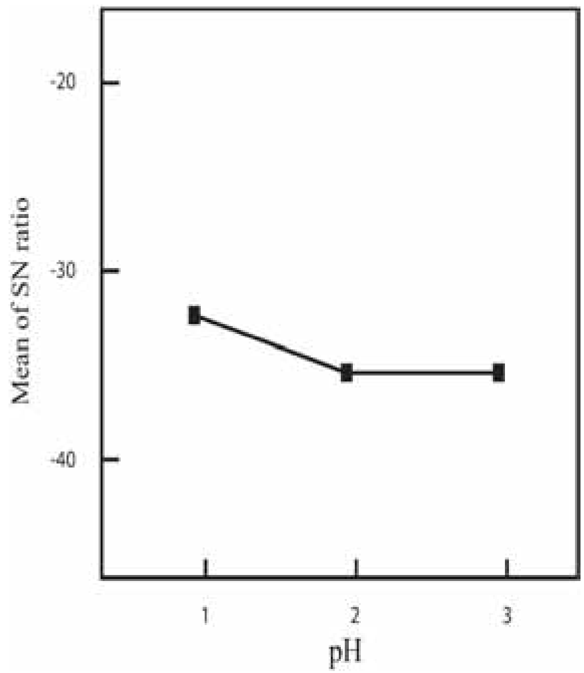

Fig. 3. The effect of pH on the S/N ratio in the removal with pistachionut shell. (T = 20 °C, adsorbent particle size= 0.025 < x <0.5, C_i = 50 ppm, agitation speed = 150 rpm)

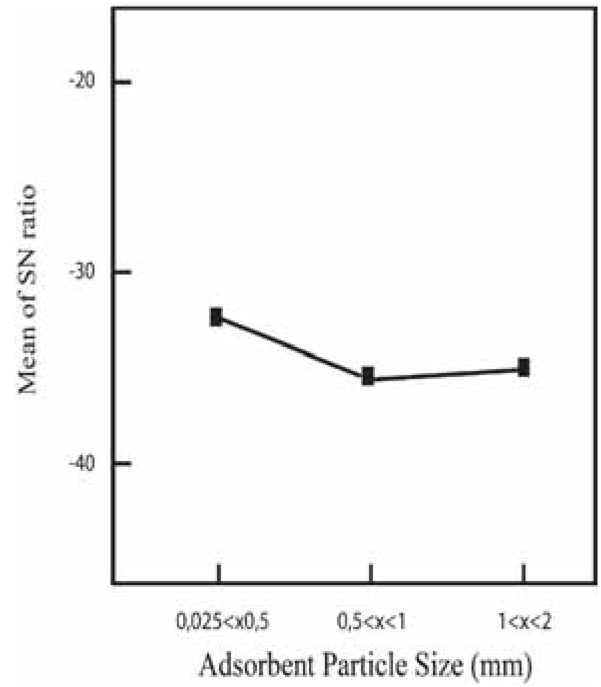

Fig. 4. The effect of adsorbent particle size on the S/N ratio in the removal with pistachionut shell. (T = 20 °C, adsorbent concentration= 0.3 g, C_i = 50 ppm, agitation speed = 150 rpm).

and adsorbate mutually interact with each other. Anion or cation exchange also takes place as the neutral molecules come closer to each other. Interactive effects between adsorbent particle size and dye molecules on the performance statistics for the dye removal are shown in Fig. 4. The performance statistics value was high at the level of 0.025 < x <0.5 mm, but it decreased with the increase of the adsorbent particle size substantially. As a result, redoubling adsorbent particle size results in a little effect.

The distribution of adsorbate between adsorbent and solution is influenced by contact time. Fig. 5 shows the change of the contact times respectively (from 10 to 60 min) according to performance statistics values. The performance statistics value was high at the level of 10 min. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake,the rate of adsorption is found to be nearly constant [44].

As seen in Fig. 6, the dye removal performance statistics value decreased substantially with the increase of adsorbent concentration from 100 to 500 mg/L. Then, it remains almost constant as the adsorbent concentration reaches to 1000 mg/L. Increase in adsorption with adsorbent concentration can be explained to increased adsorbent surface area and availability of more adsorption sites. Nevertheless, for quantitative removal of dye, the unit adsorption decreased with the increase in the amount of adsorbent [45].

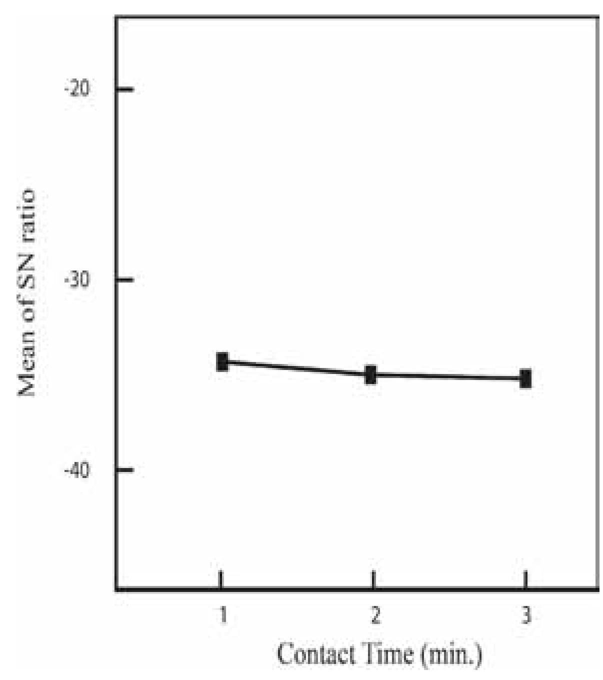

Fig. 5. The effect of contact time on the S/N ratio in the removal with pistachionut shell (T = 20 °C, pH = 2, adsorbent concentration = 0.3 g, C_i = 50 ppm, agitation speed = 150 rpm).

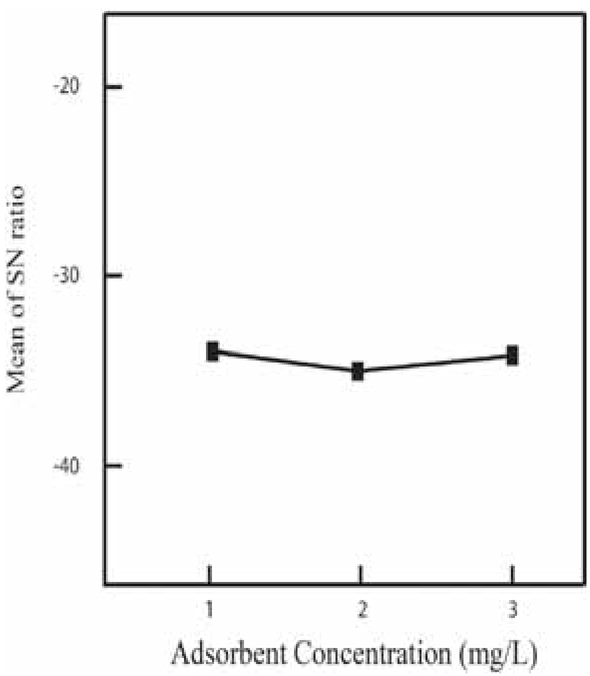

Fig. 6. The effect of adsorbent concentration on the S/N ratio in the removal with pistachionut shell. (T = 20 °C, pH = 2, contact time = 10 min, C_i = 50 ppm, agitation speed = 150 rpm).

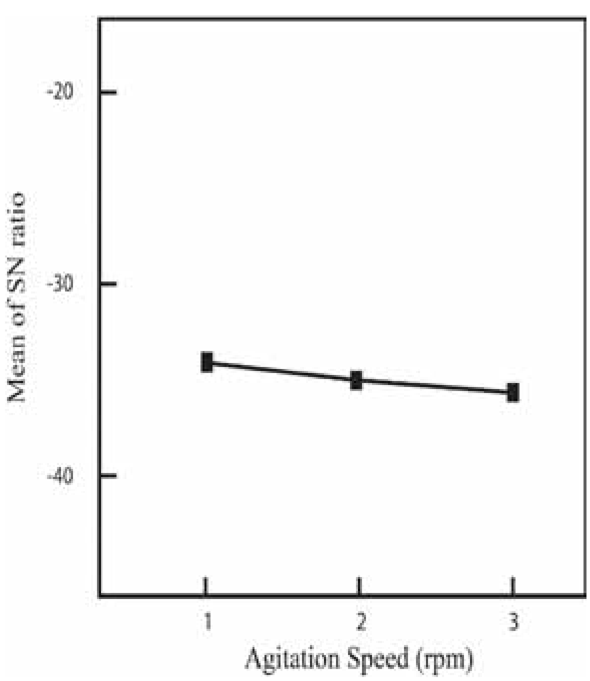

Fig. 7. The effect of agitation speed on the S/N ratio in the removal with pistachionut shell*. ($^*T$ = 20 °C, pH = 2, contact time = 10 min, C_i = 50 ppm, asdsorbent particulate size = 0.025 < x < 0.5).

On the other hand, Fig. 7 respectively, shows the change of agitation speed (from 100 to 150 rpm) according to performance statistics values. The performance statistics value was high at the level of 100 rpm. But it decreased with increasing of agitation speed. It was thought that the reason of decreasing of the performance statistics values at 120 and 150 rpm is that the increase in turbulance and the decrease in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing. This result was also in agreement with Ho and Mckay for the adsorption of dye onto activated clay ash [46].

Fig. 8 shows the effect of temperature ranges from 20 to 40 °C on the performance statistics for dye removal. The dye removal performance decreased with increase of the temperature from 20 °C to 40 °C and therefore the optimum temperature is 20 °C. So the increase in temperature decreases the physical forces responsible for sorption. Similar temperature effects on the adsorption of eggshell had also been observed by Elkady et. al. [45].

Fig. 9 shows the change of the initial dye concentrations respectively (from 25 to 200 mg/L) according to performance statistics values. The performance statistics value was high at the level of 25 mg/L, but it decreased with the increase of the dye concentration. This can explain the increase of the dye concentration in the solution and the decrease of the interaction frequency of adsorbent molecules with the dye molecules. This effect has been attributed to the surface binding of low-affinity surface sites as high-affinity ones begin to reach saturation, leading to a reduction in the removal efficiency.

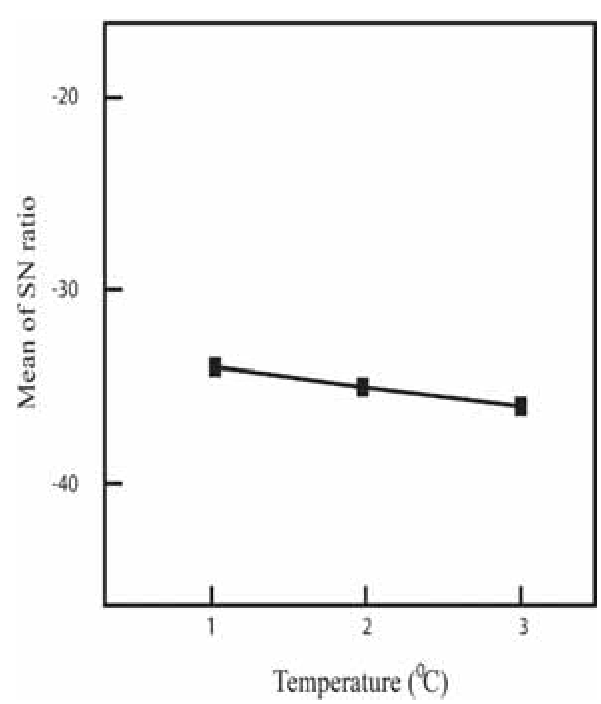

Fig. 8. The effect of temperature on the S/N ratio in the removal with pistachionut shell. (T = 20 °C, pH = 2, contact time = 10 min, C_i = 50 ppm, asdsorbent particulate size = 0.025 < x < 0.5).

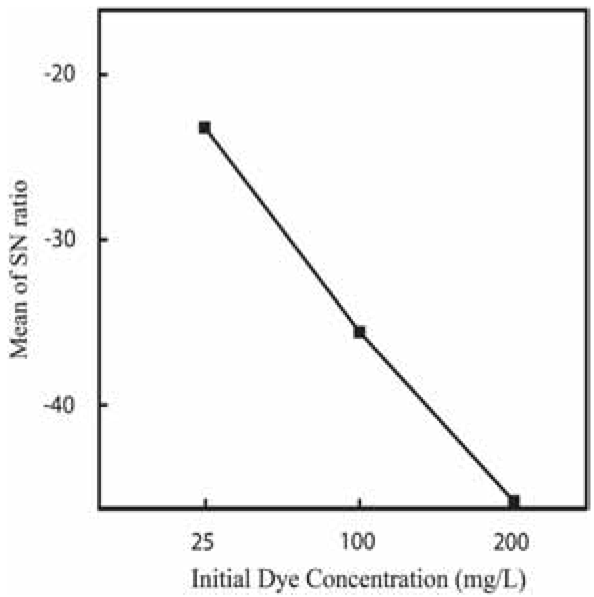

Fig. 9. The effect of initial dye concentration on the S/N ratio in the removal with pistachionut shell*. (*T = 20 °C, pH = 2, contact time = 10 min, agitation speed = 150 rpm, asdsorbent particulate size = 0.025 < x < 0.5).

In order to test predicted results, confirmation experiments were carried out twice at the same laboratory conditions. The fact that the dye removal from confirmation experiments are within the calculated confidence intervals (Table 3) shows that experimental results are within ±5 % in error. Under these optimum conditions, it was determined that the Remazol Rot RB removal efficiency from textile wastewater was 88%.

Table 3
Optimum working conditions, observed and predicted values for the dye removal

Parameters		Optimum working conditions	
		Value	Level
A	pH	2	1
B	Adsorbent particle size (mm)	0.025 < x < 0.5	1
C	Contact time (min)	10	1
D	Adsorbent concentration (mg/L)	100	1
E	Agitation speed (rpm)	100	1
F	Temperature (°C)	20	1
G	Initial dye concentration (mg/L)	25	1

3.2. Adsorption isotherms

The equlibrium adsorption isotherms are important in determining the adsorption capacity of pistachio nut shell [31]. Adsorption isotherm data of Remazol Rot RB dye was investigated to fit the models of Freundlich and Langmuir. For nonlinear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spread-sheet, Microsoft excel. Figs. 10 and 11 shows experimental data and the

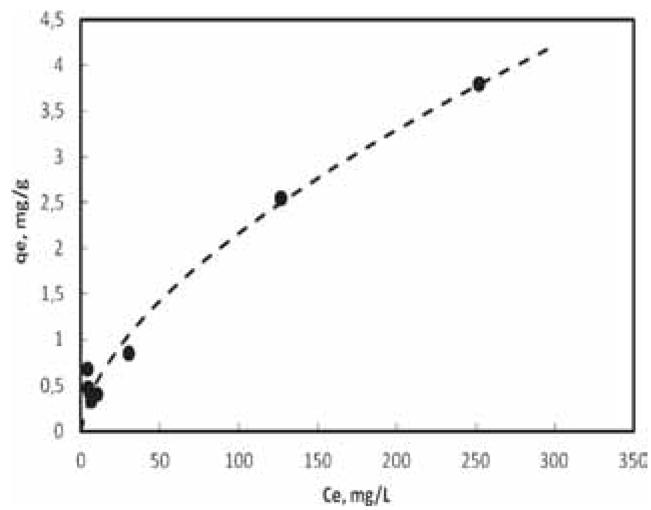

Fig. 10. Freundlich plots for the adsorption of Remazol Rot RB dye onto pistachionut shell.

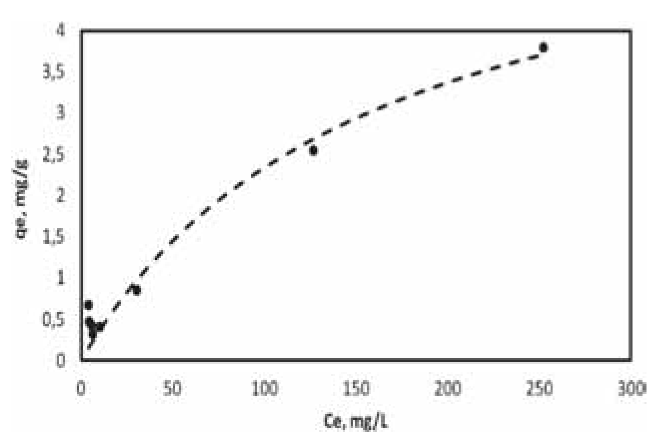

Fig. 11. Langmuir plots for the adsorption of Remazol Rot RB dye onto pistachionut shell.

Table 4
Freundlich and Langmuir parameters for adsorption of pistachio nut shell[a]

Adsorbent	Freundlich			Langmuir		
	K_F	n	R^2	$q_{max,}$ (mg g^{-1})	K_L	R^2
Pistachio nut shell	0.1328	1.65	0.98	108.15	0.006319	0.96

[a]T =20 °C, contact time=10 min., adsorbent particle size= 0.025 < x <0.5, C_i = 50 ppm.

predicted equilibrium curve using nonlinear method for the two-equilibrium isotherm Freundlich and Langmuir at 20 °C, respectively. The calculated isotherm constants by nonlinear method are shown in Table 4. The Freundlich model appears to fit the experimental data better than the Langmuir model as reflected with the correlation coefficients in the range of 0.98 (Table 4). Maximum adsorption capacity of pistachio nut shell was determined as 108.15 mg g^{-1}at 20 °C. In the literature, the maximum adsorption capacity of Remazol Rot RB on eggshell was found 46.9 mg g^{-1} at 22 °C [45]. Besides, Gulnaz et al. [46] found that the maximum adsorption capacities at 20 °C of native acid and alkali pretreated biomass were determined as 14.3, 26.8 and 44.2 mg g^{-1}, respectively [46].

4. Conclusions

This paper has presented an application of the Taguchi method for the dye removal from synthetic textile wastewater. For this purpose, a series of batch adsorption tests were carried out to address the effect of various experimental parameters. An orthogonal array L27 (7^3) for experimental plan and the smaller the better performance statistics formula was selected to define optimum conditions. The optimum conditions were found to be as follows: contact time (min), 10; agitation speed (rpm), 100; initial dye concentration (mg/L), 25; pH, 2; temperature (°C), 20; adsorbent particle size (mm), 0.025 < x <0.5; adsorbent concentration (mg/L), 100, respectively. Under these optimum conditions, it was determined that the Remazol Rot RB removal efficiency from textile wastewater was 88 %.

The higher pH, adsorbent particle size and initial dye concentration values, the lower the performance statistics. On the other hand, the higher adsorbent concentration, the higher the performance statistics. Dye removal increased, but the increase of parameter levels such as agitation speed and temperature did not affect the performance statistics. Finally, dye removal remained unchanged. Also, it was thought that pH, adsorbent particle size and initial dye concentration were important parameters for the performance statistics. Present study shows that both of isotherm equations Freundlich and Langmuir models well represent the adsorption of Remazol Rot RB dye onto pistachio nut shell. Nonlinear method is a better way to obtain the adsorption parameters.

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