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Optimization of methyl orange bioremoval by *Prunus amygdalus* L. (almond) shell waste: Taguchi methodology approach and biosorption system design

Fatih Deniz

Nigar Erturk Trade Vocational High School, Gaziantep 27590, Turkey
Tel. +90 342 3291194; Fax: +90 342 3291529; email: f_deniz@windowslive.com

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ABSTRACT

This study presents a systematic procedure to define optimal operational conditions for optimizing methyl orange biosorption by almond shell waste using the Taguchi method. Several biosorption experiments were conducted using the L_9 orthogonal array with four factors in three levels. The optimum set of parameters was obtained as reaction time of 80 min, initial dye concentration of 100 mg L^{-1}, pH of 3, and temperature of 20˚C, considering the larger is better pattern. Analysis of variance displayed that the initial dye concentration was the dominant factor affecting the dye biosorption. Verification experiments were performed to confirm the optimized results. Further, a regression model was developed as a function of the process parameters mentioned. Finally, a single-stage batch biosorption process design was presented based on the Langmuir isotherm. Thus, the Taguchi statistical approach provided a pleasing success in specifying the optimum conditions for the dye removal process.

Keywords: Almond shell waste; Biosorption; Methyl orange; Optimization; System design; Taguchi method

1. Introduction

The presence of residual dyes in surface water is esthetically undesirable and causes annoyance to the aquatic biosphere due to the reduction in sunlight penetration and depletion of dissolved oxygen. Besides, some dyes are toxic and mutagenic and have potential to release the carcinogenic amines [1]. Many industries like textile use dyes to color their products, and thus, they produce wastewater with a strong color; where in the dyeing processes, the percentage of dye lost could be up to 50% because of the low level of dye–fiber fixation [2]. With regard to environmental protection and safety regulations, it is crucial to treat dye-contaminated wastewaters prior to discharge.

Various techniques, including chemical oxidation, ion-exchange, membrane separation, etc., have been examined for the treatment of effluents containing dyes, but these methods are mainly expensive or incomplete [3]. In recent years, biosorption has attracted great interest for treating dye-bearing effluents. The biosorption is a separation process and can be explained with the adsorption principles [4]. Dye removal by activated carbon is a common practice, but its high production cost and regeneration difficulty limit its frequent usage [2]. Hereby, interests are now growing in the use of alternative non-conventional waste materials from agriculture and industry. One of such agricultural solid waste resources is *Prunus amygdalus* L. (almond) shell. Agricultural and industrial sectors dispose of large amounts of untreated wastes, which may pollute the land, water, and air, and as a result, these wastes damage the ecosystem. Moreover, improper treatment of these wastes also causes similar problems. So, within the last few decades, many ideas have been introduced to properly dispose of them, such as intensive use as sorbents for dye removal. Agricultural wastes are very low or no cost, renewable and great availability. Furthermore, they require no or little processing and thus reduce cost [2,5].

P. amygdalus L. (Rosaceae) is one of the most popular tree nuts on a worldwide basis and ranks number one in the tree nut production [6]. It is commercially cultivated in various countries like Iran, Italy, Morocco, Spain, Syria, Tunisia, Turkey, and USA. Worldwide almond production in 2010 was 2,56 metric tons from a total of 1,68 Ha [7]. Almond shell, which represents more than 50% of the dry weight of almond fruit, is generated in large quantities as a residue of the fruit processing and has no significant industrial and commercial uses [6]. A survey of the literature revealed that only a little study has been carried out so far on utilization of almond shell waste as a dye biosorbent.

Dye removal by biosorbent is dependent on various factors/parameters/variables (these terms are synonymously used throughout the study), including initial dye concentration, pH, reaction time, and temperature [2]. In most of the previous reports, traditional one variable at a time technique was used by majority of researchers to specify the individual effect of various factors on dye biosorption process. Contrary to this conventional technique, the design of experiment (DOE) methodologies can be employed to minimize the number of experiments, time, and research costs. The DOE techniques define which factors have significant effects on a response as well as how the effect of one factor varies according to the level of the other factors. Taguchi approach is one of the most powerful methods of DOE. Nevertheless, only a few works have been reported in the dye biosorption field by applying the Taguchi method. The purpose of this study is to optimize the biosorption of methyl orange by almond shell waste employing the Taguchi statistical method, to find the optimal operational conditions for achieving maximal biosorption and to present the parameters having the most influence on the biosorption process based on the analysis of variance (ANOVA) method. The key factors examined are the pH, initial dye concentration, temperature, and reaction time. Methyl orange is a common azo dye used in many industries such as textile, printing, paper, pharmaceutical, food, and also in the research laboratories [8]. Because of harmful impacts, it is important to remove the dye from waste streams before discharge. Besides, in the research, validation tests were conducted for confirming the reliability of the analysis results. A regression equation was also obtained to define relationship between the process parameters and the dye removal performance. Lastly, using the Langmuir isotherm equation, a single-stage batch system was designed to predict the required biosorbent mass for certain percentage of dye removal at a fixed solution volume. Thus, this work could be useful in practical applications of almond shell waste for further studies.

2. Materials and methods

2.1. Preparation of biosorbent

Almond shell waste was acquired from the farmland after almond harvest in Gaziantep province, Turkey. This waste material was washed with distilled water to remove soluble impurities. It was then dried in an oven for 24 h at 80˚C, powdered, and sieved to get particle size range of 230–120 mesh (no). It was finally stored in an airtight plastic container to use as biosorbent without any pre-treatments for the biosorption studies.

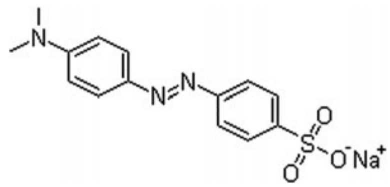
2.2. Dye solution

All chemicals used were of analytical grade and used without further purification. Methyl orange was obtained from Merck KGaA (Darmstadt, Germany). Some properties of methyl orange are given in Table 1 [9]. A stock solution of $500\,\mathrm{mg\,L^{-1}}$ was prepared by dissolving accurately weighed quantity of the dye in distilled water. The working solutions of desired concentrations were then obtained by diluting the dye stock solution with distilled water. The initial pH of solutions was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.3. Biosorption operation

Batch studies were conducted with the biosorbent concentration of $1\,\mathrm{g\,L^{-1}}$ in 100-mL Erlenmeyer flasks with 50 mL of the total working volume of known pH, initial dye concentration (C_0, mg $\mathrm{L^{-1}}$), temperature (T, ˚C), and reaction time (t, min). The flasks were

Table 1
General characteristics of methyl orange dye

Molecular structure	
Synonyms	Gold orange, Helianthine, Orange III
Molecular formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass	327.34 g mol^{-1}
C.I. number	13,025
CAS number	547-58-0
Type	Anionic
LD 50 (oral, rat)	60 mg kg^{-1}

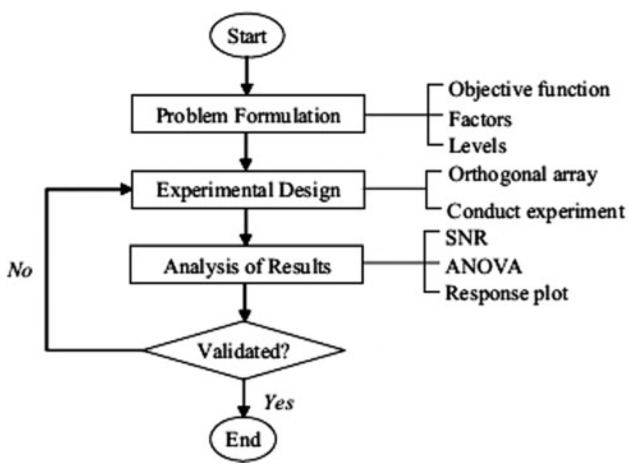


Fig. 1. Taguchi method flow chart.

agitated at a constant speed in a water bath at desired temperatures for the required time period. A portion of the samples was collected at proper reaction times and centrifuged. The dye concentration in the solution was defined by a UV–vis spectrophotometer at the maximum wavelength of 464 nm.

The dye amount sorbed by biosorbent (q, mg g^{-1}) and percentage dye removal efficiency (R, %) were determined by Eqs. (1) and (2), respectively.

$$q = \frac{(C_0 - C_t)V}{M} \tag{1}$$

$$R\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 is the initial dye concentration (mg L^{-1}), C_t is the residual dye concentration at any time (mg L^{-1}), V is the volume of solution (L), and M is the mass of adsorbent (g). q and C_t are equal to q_e and C_e at equilibrium, respectively.

2.4. Taguchi DOE methodology

The Taguchi technique is a simple and robust method for optimizing the process parameters involving reducing of process variation. The aim of analysis is to investigate how different process parameters affect the mean and variance of process performance characteristics and which variables contribute significantly [10]. The Taguchi DOE uses orthogonal arrays to organize the factors affecting the processes and the levels of factors should be also varied. It is tested only a limited collection of factors combinations instead of check all possible combinations like factorial design.

Table 2
L_9 (3^4) orthogonal Taguchi array and analysis results obtained

Exp. no.	Parameters and levels				Dye removal (q) (mg g^{-1})			SNR
	A t (min)	B C_0 (mg L^{-1})	C pH	D T (℃)	q_1	q_2	Mean	
1	20(1)	50(1)	3(1)	20(1)	15.80	16.03	15.91	24.03
2	20(1)	75(2)	6(2)	30(2)	19.40	19.63	19.51	25.81
3	20(1)	100(3)	9(3)	40(3)	19.59	19.96	19.78	25.92
4	40(2)	50(1)	6(2)	40(3)	11.32	11.26	11.29	21.06
5	40(2)	75(2)	9(3)	20(1)	23.28	22.90	23.09	27.27
6	40(2)	100(3)	3(1)	30(2)	33.29	34.10	33.69	30.55
7	80(3)	50(1)	9(3)	30(2)	12.05	12.21	12.13	21.68
8	80(3)	75(2)	3(1)	40(3)	24.87	24.60	24.73	27.86
9	80(3)	100(3)	6(2)	20(1)	36.42	35.93	36.18	31.17

Such technique also allows determination of factors which most affect system performance with a minimum number of experiments. Thus, the method reduces work time and cost in the processes [11]. The flow diagram of the Taguchi DOE is illustrated in Fig. 1 [12]. Taguchi L_9 (3^4) orthogonal array as reported in Table 2 was employed based on the total degree of freedom (df_t) in the present investigation. The procedure used was provided by the software Minitab (ver. 16.2.1, Minitab Inc., PA, USA). L and 9 mean Latin square and the number of experiments, respectively. Else, 4 and 3 denote the numbers of factors and their levels, respectively. The four parameters and three levels of each one are also shown in Table 2. The parameters selection is a main step to obtain precise and reliable results. The process parameters (pH, initial dye concentration, temperature, and reaction time) and their ranges (low, medium, and high) were determined based on the previous dye biosorption studies.

3. Results and discussion

3.1. Analysis of Taguchi method

According to the Taguchi L_9 orthogonal array, nine experiments were performed, and each experiment was replicated twice. In the Taguchi approach, it is used as a statistical measure of performance known as signal-to-noise ratio (SNR) to analyze the results. Briefly, the SNR is the ratio of the mean response (signal) to the standard deviation (noise). Generally, the SNR performance characteristics can be categorized as "larger is better," "nominal is best," and "smaller is better". The goal of this study is to maximize the response (dye biosorption, q (mg g^{-1})). Thus, the larger is better type of SNR was chosen, and it can be defined by Eq. (3).

$$\mathrm{SNR} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \tag{3}$$

where n is the number of samples for performance response corresponding to the number of design parameter combinations, and y_i is the performance response for the set of factor combination. The variability characteristic is inversely proportional to the SNR. It means that a larger SNR corresponds to a better performance [11]. For this work, the SNR was computed using Eq. (3) for each of the nine experimental combinations and the values are reported in Table 2 along with their experimentally defined values

Table 3
Response table of SNR and mean data for four factors in three levels

Level	Factors			
	A t	B C_0	C pH	D T
SNR values				
1	25.26	22.26	27.48	27.49
2	26.29	26.98	26.01	26.01
3	26.90	29.21	24.96	24.95
Delta	1.65	6.96	2.53	2.54
Rank	4	1	3	2
Mean data				
1	18.4	13.11	24.78	25.06
2	22.69	22.45	22.33	21.78
3	24.35	29.88	18.33	18.60
Delta	5.94	16.77	6.45	6.46
Rank	4	1	3	2

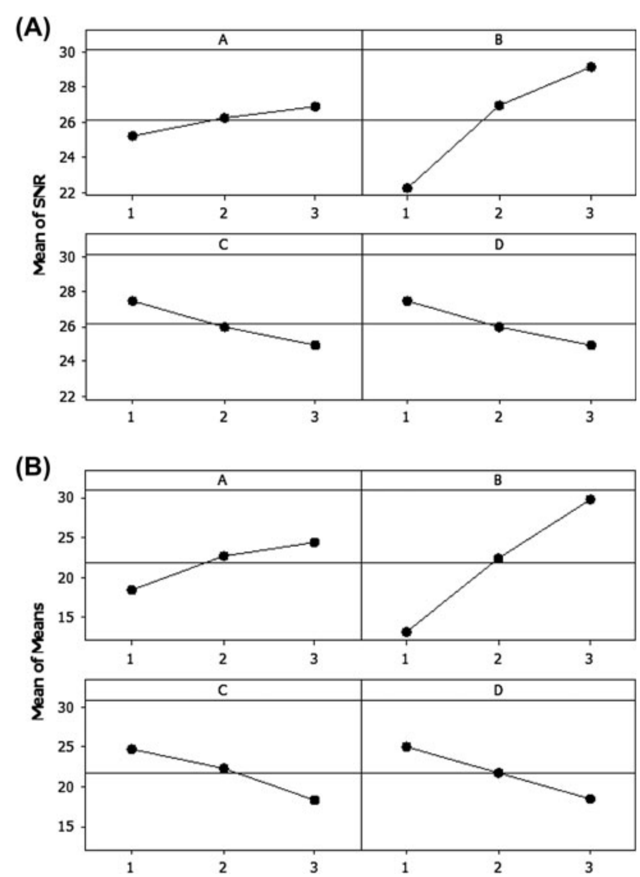


Fig. 2. Main effects of parameters on the dye biosorption for (A) average SNR and (B) mean response (A: t, B: C_0, C: pH, D: T).

and average results. The response table of SNR and mean data for analyzing of the efficacy of each parameter at the three different levels on the dye removal are also presented in Table 3. Besides, the Taguchi DOE also employs main effects graph for the average SNR and the mean response of each factor studied as displayed in Fig. 2. According to these outputs, increasing reaction time and initial dye concentration increased the SNR and the mean response, but increasing pH and temperature showed opposite effect on the SNR and the mean response. Effectively optimizing all the influencing factors is of critical importance for maximizing the dye removal. In current study, "larger is better" pattern was adopted for optimizing the parameters as mentioned previously. Thus, the SNR values are purposed to be large. A high value of the SNR infers that the signal is much higher than the random effect of the noise factors. The parameters having the highest SNR grant the optimal performance with minimum variance [13]. Hereby, in the work, the factors and levels with the highest SNR values resulted in a higher dye biosorption capacity. By selecting performance characteristic "larger is better," the optimal setting of parameters producing the highest dye removal amount was identified as $A_3B_3C_1D_1$. These optimal parameters were reaction time (A) of 80 min, initial dye concentration (B) of $100\,\mathrm{mg\,L^{-1}}$, pH (C) of 3, and temperature (D) of 20℃. In addition to the SNR examination, the same response ($A_3B_3C_1D_1$) was also obtained from the mean response analysis as shown in Table 3 and Fig. 2.

Table 4
ANOVA results for SNR and mean response of all parameters studied

Parameter	*df*	*SS*	*V*	*PC* (%)	Rank
For SNR					
A: *t*	2	4.164	2.082	4.192	4
B: C_0	2	75.709	37.854	76.221	1
C: pH	2	9.674	4.837	9.740	3
D: T	2	9.781	4.890	9.847	2
Error	0	–	–	0.00	–
Total	8	99.328	–	100	–
For mean response					
A: *t*	2	56.466	28.233	9.313	4
B: C_0	2	423.695	211.847	69.881	1
C: pH	2	63.574	31.787	10.485	2
D: T	2	62.577	31.288	10.321	3
Error	0	–	–	0.00	–
Total	8	606.311	–	100	–

3.2. Analysis of variance (ANOVA)

After practicing the SNR and the mean response analyses, an ANOVA was applied to the working data in order to study the relative significance of each parameter more systematically. The main objectives of the ANOVA method are to compute the degree of freedom (*df*), sum of squares (*SS*), variance (mean square) (*V*), and percentage of contribution (*PC*). The results of the ANOVA for the SNR and the mean response are given in Table 4. The contribution percentage of each factor is better shown in Fig. 3. Based on these results, the initial dye concentration (rank: 1) with the highest variance and percentage of contribution values was the most significant factor on the dye biosorption, and this was followed by temperature, pH, and reaction time. The impacts of pH and temperature were almost the same and were larger than that of reaction time (rank: 4).

3.3. Verification studies

The final step of the Taguchi DOE is the validation of the experiment results obtained. The verification tests are achieved for controlling the accuracy of the analysis results. Furthermore, these tests also contribute in increasing the efficiency of the method used [13]. According to the Taguchi approach, the prediction of response (*q*) for the optimum set of the

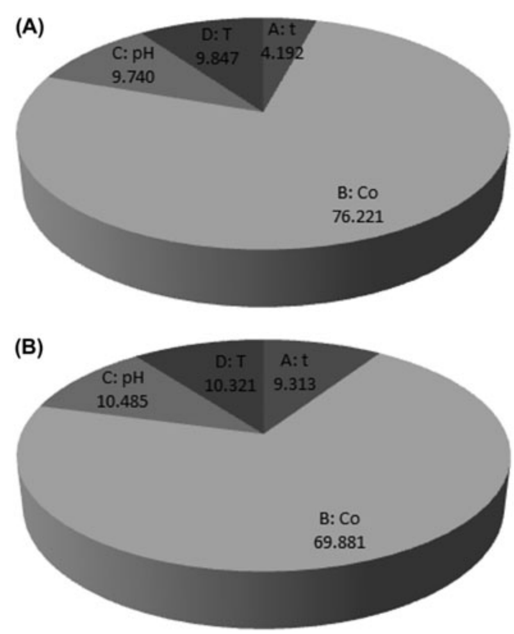


Fig. 3. Contribution percentage of each factor on the dye removal yield for (A) SNR and (B) mean response.

parameters ($A_3B_3C_1D_1$) can be calculated, and thus, it was defined as 38.63 mg g^{-1}. Else, two confirmation experiments were performed at the optimal conditions. Based on the confirmation results, the response values were very similar to the predicted value as shown in Table 5. Thus, these results revealed that the Taguchi methodology could be applied effectively for optimizing the dye removal process.

3.4. Development of regression model

Regression analysis is a statistical tool for the investigation of relationship between the variables. *R Square* (R^2, %) is the correlation coefficient, and the object of the R^2 value is the prediction of future outcomes based on the other related data. It also provides a measure of how well results are properly to be predicted by the regression model [14]. In this study, a regression equation was composed by the mean values of the dye biosorption under different operational conditions, and the equation is represented by Eq. (4).

$$\text{Dye biosorption amount } (q,\ \text{mg g}^{-1}) = 8.56 + 0.0908A + 0.335B - 1.07C - 0.323D \quad (4)$$

Table 5
Confirmation tests

Optimum configuration	q (mg g^{-1})		
	Prediction	Confirmation Replication	
		1	2
$A_3B_3C_1D_1$	38.63 ± 0.47	39.19	38.64

Table 6
Regression analysis results

Statistical data	Value
R^2	97.8%
Adj. R^2	95.6%
Coefficients	
Constant	8.557
A: t	0.09081
B: C_0	0.33542
C: pH	−1.0748
D: T	−0.32293

The regression statistics is presented in Table 6. The value of the R^2 was found to be 97.8% implying a suitable correlation. The predicted data obtained from Eq. (4) were plotted against the experimental data as displayed in Fig. 4. The q values at the same point are very close to each other. In this way, the regression model successfully described the interrelation between the process parameters (initial dye concentration, pH, reaction time, and temperature) and the responses (q data).

3.5. Biosorption system design

A batch biosorption process design can be predicted using the isotherm equations [15]. A visual diagram of a single-stage batch biosorption system is shown in Fig. 5 where the effluent contains V (L) of water and an initial dye concentration, C_0, which is to be reduced to C_t (mg L^{-1}) during the process. In the treatment stage, a mass of M (g) biosorbent is added to the system and the dye loading on biosorbent

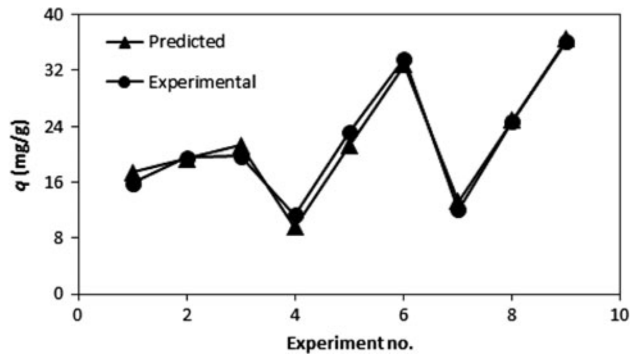


Fig. 4. Predicted values vs. experimental values for the dye biosorption data.

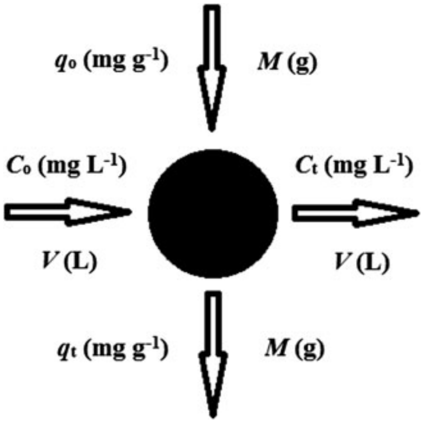


Fig. 5. Schematic diagram of single-stage biosorber for the dye removal.

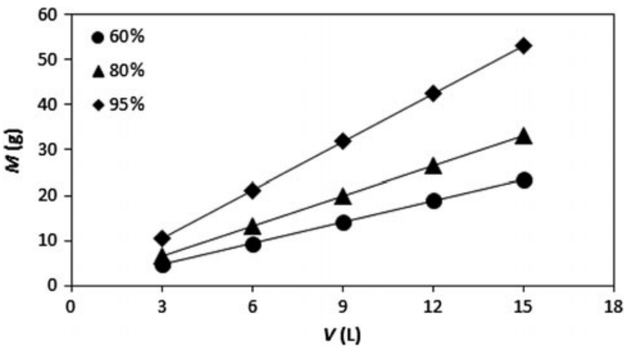


Fig. 6. Biosorbent mass (M) against solution volume (V) for various percentages of dye removal.

changes from q_0 to q_t (mg g^{-1}). The mass balance for the dye in single-stage batch biosorption can be indicated by Eq. (5).

$$V(C_0 - C_t) = M(q_t - q_0) = Mq_t \tag{5}$$

For methyl orange biosorption by almond shell waste, the Langmuir model conferred the better fitness to the experimental data (defined from previous biosorption studies). Thus, the mass balance based on the Langmuir isotherm under equilibrium ($C_t \rightarrow C_e$ and $q_t \rightarrow q_e$) is obtained by Eq. (6).

$$\frac{M}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{bq_m C_e/(1 + bC_e)} \tag{6}$$

where b (L mg^{-1}) is the constant related to the energy of biosorption, and q_m is the maximum monolayer biosorption capacity (mg g^{-1}). Thus, the biosorbent amount required to achieve a specific dye removal percentage at a given solution volume can be predicted using Eq. (6) for methyl orange dye. For different removal percentages of dye, a series of plots of M vs. V is presented in Fig. 6 at optimum working conditions defined by the Taguchi DOE. For instance, the required amount of the biosorbent for 80% dye removal was 26.63 g for dye solution volume of 12 L. Consequently, a design procedure for a single-stage batch biosorption system is outlined, and this information could be useful in practice for almond shell waste.

4. Conclusions

In this work, the optimization of the removal of methyl orange by almond shell waste from aqueous solutions was studied using the Taguchi analytical method. The optimum conditions for maximum biosorption yield were defined as $A_3B_3C_1D_1$ (t: 80 min, C_0: 100 mg L^{-1}, pH: 3, T: 20°C). Based on the ANOVA results, the initial dye concentration was the most significant factor on the dye removal with the 76.221% contribution for SNR. The validation tests confirmed the reliability of the analysis results. These results suggested the practicality of the Taguchi approach for the optimization of the dye biosorption.

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