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Crystal violet removal from aqueous solutions using dry bean pods husks powder – optimization and desorption studies

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Abstract. In this study the Taguchi method was used to establish the optimal conditions for the adsorption of crystal violet dye on an adsorbent obtained from dry bean pods husk. Six factors, at three level, were considered in establishing the L27 Taguchi orthogonal array. The ANOVA analysis was performed to calculate the each factor percentage contribution on the dye removal efficiency. A desorption study was carried out to evaluate the regeneration possibility of the used adsorbent. The removal efficiency ranged from 5.91 to 94.48 % depending on the controllable factors combination set by Taguchi design. The results showed that the factor with the highest percentage contribution on the dye removal efficiency was the ionic strength (48.85 %). The correlation between the predicted values of the dye removal efficiency with those obtained experimentally indicate a good accuracy of Taguchi approach.

***Keywords*:** dye adsorption; crystal violet: dry bean pods husks; Taguchi optimization.

1. Introduction

The development of the industry has led to an increase in the quality of human life but has generated many problems related to environmental pollution. Dyes are a category of chemical compounds with numerous applications in the textile, leather, plastics, food and paper industries. The resulting industrial wastewater contains significant amounts of dyes that have toxic, carcinogenic and mutagenic effects. Improperly treated, these waters can cause serious environmental problems [1-3].

Several methods of removing dyes from water have been used, but of these the adsorption is very often applied because it has numerous advantages: easily applicable even at low dye concentration, high-quality of the treated effluents, minimum amounts of sludge, low cost, fliexibility and high efficiency [1-6].

The costs related to the adsorbent material are largely reflected in the total cost of the adsorption process. The use of low-cost adsorbents, such as various plant wastes resulting from agricultural activities, make the process very economically advantageous [6-12].

Common bean (*Phaseolus vulgaris* L.) is an important legume widely cultivated in many regions of the world. The seeds have beneficial nutritional properties and represents an important source for human food [13,14]. After harvesting and separation of the grains, a significant amount of dry pod husks results. This vegetable waste was used in this study to obtain the adsorbent material for crystal violet dye removal from aqueous solutions.

The most important factors that influence the adsorption process are: time, initial dye concentration, pH, adsorbent dose, temperature and ionic strength. To achieve the maximum dye removal efficiency these parameters should be optimized. The optimization of experimental conditions is essential in the adsorption field [15, 16].

Taguchi approach is one of the most efficient methods capable of finding an optimized design configuration for multifactor conditions. This method have some significant advantages: keeping the experimental cost at a minimum level through a small number of trials, reducing the time of experimental investigation and determine the most effective parameter that influence the process [1, 15-17].

The main objective of this study was to use the Taguchi method to establish the optimal conditions for the adsorption of crystal violet dye on an adsorbent obtained from dry bean pods husk. Also, the most effective parameter that influence the process was determined. The ANOVA analysis was performed to calculate the percentage contribution of each factor on the crystal violet removal efficiency. In addition, a desorption study was carried out to evaluate he regeneration possibility of the used adsorbent.

2. Experimental

Dry bean pods husks were provided by a local agricultural farmer from Timis County, Romania. The adsorbent obtaining process from dry bean pods husks which includes grinding, sieving, washing and drying has been described previously in detail [18].

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In order to characterize the surface of the adsorbent material, the SEM analysis was performed using a Quanta FEG 250 microscope. A color analysis (*CIEL*a*b** system) was also carried out, using a Cary-Varian 300 Bio UV-VIS colorimeter (D65 illuminant under 10° observer angle).

All experiments were performed in the batch system, at constant stirring intensity. Diluted solutions of NaOH (0.1 N) and HCl (0.1 N) were used for pH adjustment. To study the influence of ionic strength, NaCl was used as the background electrolyte. The dye concentration was determined using a UV-VIS spectrophotometer (Specord 200 PLUS) at 590 nm.

The dye removal efficiency, R(%), was calculated with Equation (1):

$$R(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where: C_i is the initial crystal violet concentration (mg/L) and C_f is the crystal violet concentration after adsorption (mg/L).

The Taguchi method was used to determine the optimal conditions for removing the dye from the solution. An orthogonal L27 matrix with six factors at three levels was applied (Table 1). The analysis of variance (ANOVA) was used to evaluate the results of the Taguchi method and to calculate the each factor percentage contribution on the crystal violet removal efficiency. The required mathematical calculations were performed with the Minitab 19 Software.

Table 1. The six controllable factors and their levels used in Taguchi method

Factor	Level 1	Level 2	Level 3
Time (min)	2	30	60
Initial dye concentration (mg/L)	50	150	300
pH	3	7	11
Adsorbent dose (mg/L)	0.5	1.5	2.5
Temperature (K)	284	294	307
Ionic strength (mol/L)	0	0.1	0.2

The desorption study was realized in batch mode, where the adsorbent resulted after adsorption was mixed with different regeneration reagents (0.1 N HCl, distilled water, 0.1 N NaOH) at constant stirring for 2 h.

The desorption percent D(%) was calculated with equation (2):

$$D(\%) = \frac{m_d}{m_a} \times 100 \qquad (2)$$

where: m_d is the amount of dye liberated by regeneration reagent and m_a is amount of dye adsorbed on adsorbent.

3. Results and discussion

3.1. Adsorbent surface characterization

The SEM images (6000 × magnification) of the adsorbent material surface, before and after adsorption, are shown in Figure 1. Initial, the adsorbent surface have many pores and voids with different shapes indicating a favorable structure for dye adsorption (Figure 1A). After adsorption (Figure 1B), the adsorbent surface becomes more homogeneous with pores and voids filled by dye molecules.

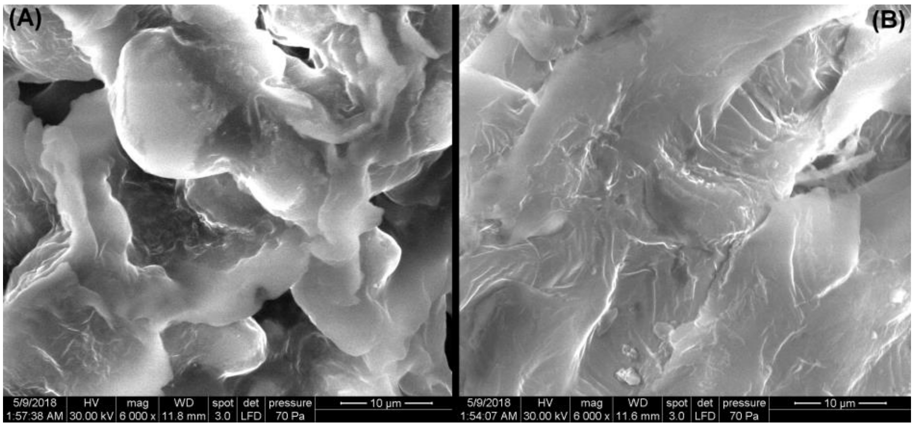

Figure 1. SEM images of adsorbent surface before (A) and after (B) adsorption

The color of the adsorbent materials before and after adsorption was analyzed using the *CIEL*a*b** color parameters (Figure 2). After adsorption, the color of adsorbent is modified. Luminosity L^* decrease and the parameters a^* and b^* change their value. The point 3 characteristic of the adsorbent color after adsorption appears in the color quarter of crystal violet dye (characterized by point 2). The color analysis confirms the dye adsorption on the material surface.

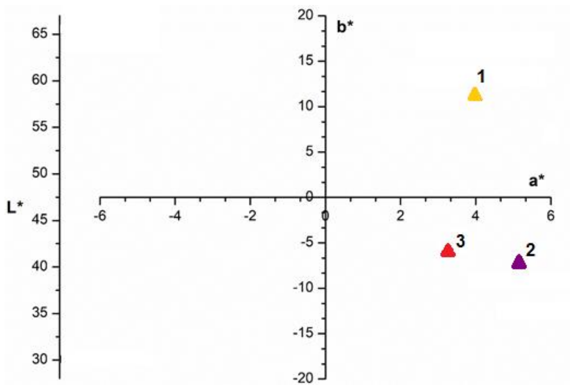

Figure 2. *CIEL*a*b** color parameters of: **1** – dry bean pods husk powder before adsorption; **2** – crystal violet dye; **3** – dry bean pods husk powder after adsorption

3.2. Optimization using Taguchi design

Six controllable factors (time, initial dye concentration, pH, adsorbent dose, temperature and ionic strength) at three level were used in the Taguchi L27 orthogonal array to determine the optimal condition for dye removal. The effect of these factors on crystal violet removal efficiency was evaluated by the signal/noise ratio (S/N) analysis. The "larger is the better" option (equation 3) was taking into consideration because the goal was to maximize efficiency [19,20].

$$\frac{S}{N} = -log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{1}{y_i}\right)^2\right] \quad (3)$$

where: n is the number of repetitions under the same experimental conditions and y_i is the experimental response.

Table 2 shows the L27 orthogonal array and the value for removal efficiency and S/N ratios determined in each of the 27 experiments carried out. The removal efficiency ranged from 5.91 to 94.48 % depending on the controllable factors combination set by Taguchi design. The order of the controllable factors' significance (Table 3) was establish based on the rank of S/N ratio and the delta values. The factors with the highest influence on the dye removal efficiency was the ionic strength, followed by time, adsorbent dose, pH, initial dye concentration and temperature.

Table 2. The L27 orthogonal array and the value for removal efficiency and S/N ratios determined in each experiment

Time (min)	**Initial dye concentration (mg/L)**	**pH**	**Adsorbent dose (g/L)**	**Temperature (K)**	**Ionic strength (mol/L)**	**Removal efficiency (%)**	**S/N ratio**
2	50	3	0.5	284	0	14.86	23.44
2	50	3	0.5	294	0.1	6.08	15.67
2	50	3	0.5	307	0.2	5.91	15.43
30	150	3	1.5	284	0	48.98	33.80
30	150	3	1.5	294	0.1	20.04	26.03
30	150	3	1.5	307	0.2	19.47	25.78
60	300	3	2.5	284	0	41.06	32.26
60	300	3	2.5	294	0.1	16.80	24.50
60	300	3	2.5	307	0.2	16.33	24.25
2	300	7	1.5	284	0.1	12.04	21.61
2	300	7	1.5	294	0.2	12.65	22.04
2	300	7	1.5	307	0	36.22	31.17
30	50	7	2.5	284	0.1	31.41	29.94
30	50	7	2.5	294	0.2	33.03	30.37
30	50	7	2.5	307	0	94.48	39.50
60	150	7	0.5	284	0.1	17.76	24.98
60	150	7	0.5	294	0.2	18.67	25.42
60	150	7	0.5	307	0	53.43	34.55
2	150	11	2.5	284	0.2	14.93	23.48
2	150	11	2.5	294	0	46.21	33.29
2	150	11	2.5	307	0.1	17.48	24.85
30	300	11	0.5	284	0.2	13.74	22.75
30	300	11	0.5	294	0	42.52	32.57
30	300	11	0.5	307	0.1	16.09	24.13
60	50	11	1.5	284	0.2	29.16	29.29
60	50	11	1.5	294	0	90.26	39.10
60	50	11	1.5	307	0.1	34.15	30.66

Table 3. Response table for signal-to-noise S/N ratios considering option "larger is better"

Level	**Time**	**Initial dye concentration**	**pH**	**Adsorbent dose**	**Temperature**	**Ionic strength**
1	23.45	28.16	24.58	24.33	26.84	33.30
2	29.43	28.02	28.85	28.84	27.67	24.71
3	29.45	26.15	28.91	29.17	27.82	24.32
Delta	6.01	2.01	4.33	4.83	0.98	8.99
Rank	2	5	4	3	6	1

The maximum mean of S/N ratio indicate the optimal conditions for crystal violet removal. Correlate the result with the data's from Table 1, the best adsorption conditions were: contact time 60 minutes, initial dye concentration 50 (mg/L), pH = 11, adsorbent dose 2.5 (g/L), temperature 307 K and ionic strength 0.0 (mol/L).

The variation of characteristic S/N ratio mean with the change in controllable factors levels is illustrate in Figure 3. This figure offer a suggestive representation of the trend of controllable factors influence on the process.

The increase of pH, time, adsorbent dose and temperature positively influences the adsorption process efficiency, while the initial dye concentration and ionic strength have a negative effect. The same observation was reported in scientific literature by other researcher which used, for the removal of violet crystal from aqueous solutions, similar adsorbent materials obtained from vegetable waste such as: *Artocarpus altilis* skin [21], *Terminalia arjuna* sawdust [2], *Artocarpus odoratissimus* leaf-based cellulose [22], cedar cone [3], pinus bark powder [23], *Ananas comosus* leaf powder [7], *Moringa oleifera* pod husk [24], eggshells [4] and crosslinked grafted xanthan gum [25].

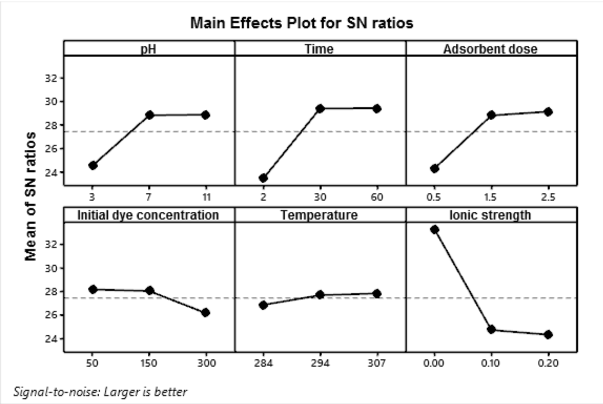

Figure 3. The mean of S/N ratio variation with the change in controllable factors levels

Analysis of variance (ANOVA-General Linear Model) was used to calculate the percentage contribution of each controllable factor on the crystal violet dye removal efficiency. The results confirm the order of controllable factor influence establish by Taguchi method (Figure 4). The factor with the highest percentage contribution on the dye removal efficiency was the ionic strength (48.85 %), while the factor with the lowest percentage contribution was temperature (0.52 %).

The accuracy of the Taguchi design, used for crystal violet dye adsorption optimization, has been verified correlating the predicted values of dye removal efficiency with those obtained experimentally. Figure 5 shows this correlation and the value of coefficient of determination R^2 indicates a good accuracy of Taguchi approach.

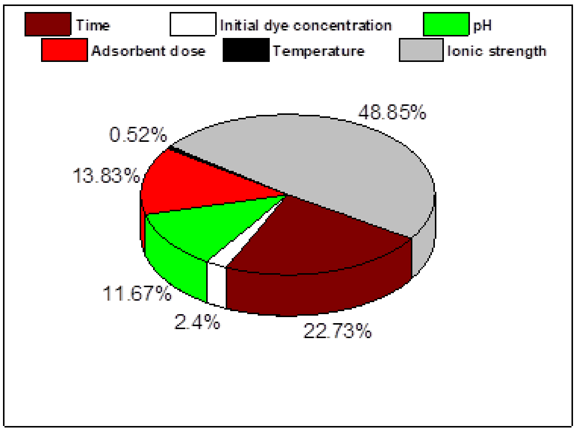

Figure 4. The percentage contribution of each factor on dye removal efficiency, established by ANOVA analysis

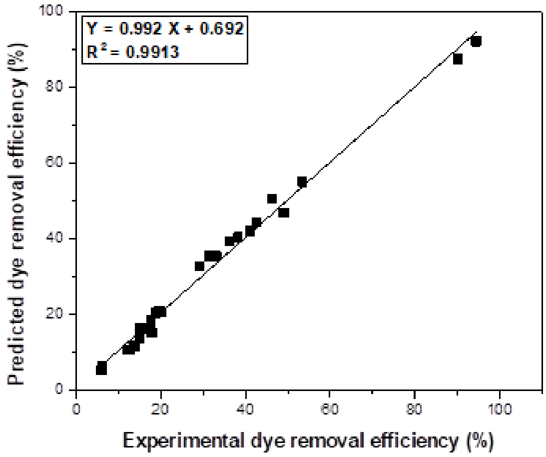

Figure 5. Correlation between the experimental and predicted dye removal efficiency values

3.3. Desorption study

In order to regenerate the adsorbent material, desorption studies were performed in three different media (acid, neutral and basic) using HCl (0.1 N), distilled water and NaOH (0.1 N) respectively. The results are shown in Figure 6. The desorption efficiency, for all desorption reagents, have low values (below 10 %) which shows that the dye is strongly bound to the surface of the adsorbent. Even if the regeneration of the adsorbent material cannot be achieved, this is not a major inconvenience, because the dry bean pods husks is found, every year, in very large quantities and costs little.

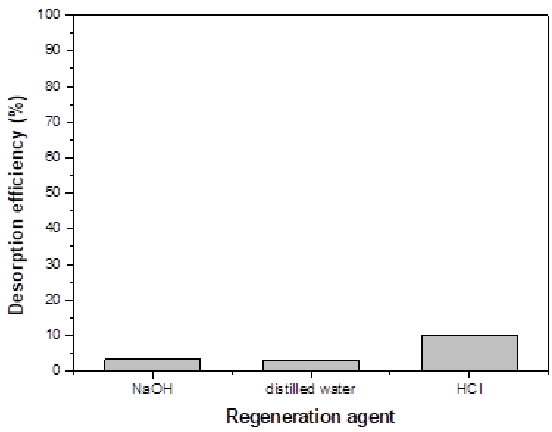

Figure 6. The desorption efficiency of the tested regeneration agents

4. Conclusions

The SEM and color analyzes confirm the crystal violet dye retention on the surface of the adsorbent material obtained from dry bean pods husk. The removal efficiency ranged from 5.91 to 94.48 % function on the controllable factors combination. The optimal adsorption conditions were: contact time 60 minutes, initial dye concentration 50 (mg/L), pH = 11, adsorbent dose 2.5 (g/L), temperature 307 K and ionic strength 0.0 (mol/L).The ionic strength was the factor with the highest influence on the dye removal efficiency (48.85 % contribution), while the factor with the lowest influence was temperature (0.52 % contribution). The accuracy of the Taguchi design was very good. The regeneration of the adsorbent material cannot be achieved, but the dry bean pods husks is found in large quantities and is cheap. This study indicates that the dry bean pods husks powder is suitable for removing crystal violet dye from aqueous solutions.

Conflict of interest

Authors declare no conflict of interest.

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