**Research Article**

**Removal of Maxilon Red GRL dye in continuous system adsorption column using waste pine sawdust**

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**ABSTRACT**

In this study, the effect of various design parameters on the removal of the Maxilon Red GRL dye, used in textile dyeing, in continuous system adsorption column was investigated using pine sawdust that were pre-treated with sulfuric acid. In each selected study parameter, the values read at certain times for the ratio of the output water concentration to the input concentration (C/Ci) were recorded into the graph and the breakthrough curves were drawn. The adsorption capacity (q) obtained under the best conditions (10 cm bed height, 6 mL/min flow rate and 100 mg/L initial concentration) selected according to breakthrough curve data is 483.32 mg/g. In the latest stage, with a 0.4 M NaOH solution, the applicability of regeneration to the adsorbent bed was examined. The results of the study showed that the adsorbing capacity of the used adsorbent continued for another even after regeneration. Furthermore, the data obtained from the breakthrough curve was adapted to the Adams-Bohart, Thomas, and Yoon-Nelson models. It was understood that compared to other models, the Thomas model was more appropriate for the identification of breakthrough curves.

1. Introduction

In many industries such as leather, textiles, plastics, food, cosmetics, dyes in different structures are often used to color products. However, if the dyes that are mixed into wastewater after the dyeing process are discharged into the receiving waters without removal, they cause both color formation, which is not acceptable from an aesthetic point of view, and carcinogenic and mutagenic effects on aquatic life. Therefore, such colored wastewater must be treated with appropriate treatment methods before discharge to the receiving environment.

Basic dyes, acid dyes, azo dyes and disperse dyes are commonly used in the textile industry. Most of these dyes, such as Maxilon Red GRL (MR GRL), are an azo dye and used for dyeing wool, fibers, silk, and carpet [1]. Azo group dyes are one of the most problematic dyes found in industrial wastewater. Their presence in the waters may be a potential threat to the life of the living organisms [2]. Moreover, many of the reaction products of azo dyes, such as aromatic amines, are also highly carcinogenic. Therefore, removal of these dyes from the aquatic system is of primary importance for the environment.

Although there are many methods used for the removal of dyes, most of the traditional wastewater treatment methods are insufficient for the removal of such dyes and by-products [3]. Therefore, researchers are investigating alternative treatment methods that are more environmental and effective. Among alternative treatment methods, adsorption is gaining more and more attention, especially because of the advantages it presents related to the removal of color and dissolved molecule [4]. The choice of efficient, cheap, easily obtainable adsorbent materials makes the method even more advantageous. Therefore, many researchers study on the use of low-cost or no-cost agricultural and industrial wastes as adsorbents for the removal of dyes from wastewater [5].

Sawdust produced in abundance from furniture production, industrial activities, and forestry activities are preferred as adsorbents in adsorption studies. Sawdust have several important advantages such as cost, quantity, renewability, and biodegradability. Because they mostly
consist of cellulose, hemicellulose, and lignin, these properties convert the sawdust into a suitable adsorbent for adsorption [6,7]. Researches has shown that sawdust can be used as an efficient adsorbent to remove various types of dyes and other undesirable pollutants from wastewater mixtures.

Recent search have headed on the application of different modification agents to improve the adsorption capacity of the adsorbent. Several chemical activating agents are used by researchers, such as zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄), potassium hydroxide (KOH), calcium chloride (CaCl₂), sulfuric acid (H₂SO₄), sodium hydroxide (NaOH), hydrochloric acid (HCl), nitric acid, etc. [8]. These activating agents are used to modify the adsorbent inorganic acid (stronger acid) (HCl, H₂SO₄, and HNO₃); the treatment has shown that the addition of H₂SO₄ increases adsorbent efficiency, surface area, and porosity [9]. The same results were obtained in our previous study [10].

In the performed literature review, any study on the effect of pre-treated sawdust as waste material for MR GRL on the batch and continuous system adsorption potential was not encountered. In terms of industrial, for the fixed bed adsorption system, the evaluation of adsorbent efficiency is more useful than batch system studies. The reason for this is that the data obtained from batch system studies may show inconsistencies with the data obtained from column studies. Therefore, it is very important to investigate the adsorption system by using fixed-bed systems [11]. Large amounts of colored wastewater are treated in the adsorption column to ensure the adsorption of the dye onto the adsorbent surface. The dye-loaded solid adsorbent mass obtained at the end of this process will yield a less dense dye when regenerated. This dye can be re-evaluated within an ‘Industrial Ecology’ framework. If such a system is not available, it will be sent back to the adsorption column to be treated. If regeneration of the adsorbent is not possible, the dye-loaded adsorbent will be disposed of as a hazardous waste.

The most important advantage of the adsorption process is to ensure that toxic and dangerous dyes in large wastewater masses are removed by holding onto the solid surface. Thus, both the volume of waste to be treated is reduced and the solid mass obtained can be disposed of more easily or can be used as a fuel in boilers.

In this study, removal from the aquatic environment of MR GRL was performed in the continuous system adsorption column by using pre-acid-treated pine sawdust. By investigating the effect of different operating parameters such as adsorbent bed height, input dye concentration, flow rate, and regeneration efficiency, the MR GRL removal efficiency of pre-treated pine sawdust in the continuous system adsorption column was investigated.

2. Materials and Methods

2.1 Adsorbent

Primarily, natural pine sawdust, obtained from an industry engaged in woodworking, were washed with pure water 5-6 times to be free from dirt, dust, and impurities contained within it. Then, they were dried in a drying-oven at 80°C for 24 hours. The sawdust in a large grain fraction ranging from +0.38 -2 mm (USA standard) were made suitable for pre-treatment. 20 g was taken from the sawdust prepared for pre-treatment and transferred to 500 mL Erlenmeyer flask; then, 200 mL 1 N H₂SO₄ solution was added on it. While the mouth of the Erlenmeyer flask closed, the mixture was kept in the oven at 150°C for 24 hours. After the material, brought to room temperature, was washed several times with pure water, it was kept overnight in a 1% NaHCO₃ solution to remove the remaining acid. The material was then washed again with pure water and dried in the drying-oven at 80°C for 24 hours. The resulting adsorbent material was named as pre-acid-treated sawdust and stored in a brown glass bottle for use in studies [12,13].

2.2 Dye (Adsorbate)

In Table 1, the properties of the dye used in the study are given. The stock dye solution was prepared by weighing the dye and dissolving it in distilled water in a way that it would be at a concentration of 1 g/L. Images of the adsorbent before and after adsorption are given in Figure 1.

![Figure 1](image)

Figure 1. Unloaded adsorbent and the adsorbent loaded with MR GRL

2.3 Continuous System Adsorption Experiments

Continuous system adsorption studies were conducted in a 37 cm long transparent plexiglass column with an inner diameter of 1.4 cm. The experiment assembly is equipped with a peristaltic pump (Shenchen Pump, YZ1515x) for continuous flow rate. After the lower base of the column was supported with glass wool, the desired amount of adsorbent material was placed in the column in a way that there was no space between them, and the top of the adsorbent was again supported by glass wool. After the adsorbent bed was prepared in this way, the bed was washed with distilled water for a certain period of time to get rid of air bubbles and to ensure proper distribution of fluid in the colon [15].
The MR GRL dye solution, prepared in different concentrations, was pumped to down from the adsorbent bed at the specified flow rate. The output concentration of the dye solution taken from the column output at specific times was analyzed spectrophotometrically. The system was operated until the output dye concentration matches the input dye concentration. The different operating parameters such as bed height, flow rate, and initial dye concentration on the column treatment efficiency was studied. It was studied at three different flow rates (4, 6, and 8 mL/min), at 5, 10 and 15 cm bed height (1.2, 2.4 and 3.6 g of adsorbents were used, respectively), and at three different dye concentrations (50, 100 and 150 mg/L). Studies were continued on the determined optimum condition for each parameter and the effect of the next parameter was examined. With desorption studies, the reusability of adsorbent substance has also been investigated. Time-breakthrough curves of C/Ci were drawn for different column operating parameters (where Ci is the dye concentration at the column output at the end of the t (min) period and C is the input concentration).

The breakthrough time (t0) in this study is the time elapsed when the output dye concentration reaches 5-10% of the feed concentration. The exhaustion time (t1) is the time elapsed when the output dye concentration reaches 90% of the input dye concentration [16].

The maximum adsorption capacity qm (mg/g) is defined as the ratio (m) of the adsorbed dye mass (q) to the adsorbent mass in the column [Eq 1] [15,17].

\[ q_m = \frac{q}{m} \]  

2.4. Continuous System Desorption Studies

By being passed 100 mg/L concentration of dye solution from the column, which had 10 cm bed height, at a flow rate of 6 mL/min, adsorption of dye by the column bed was ensured. Subsequently, the exhausted material after adsorption was regenerated with a 0.4 M NaOH solution at a flow rate of 6 mL/min. After the regeneration process, the adsorbent substance was washed with pure water until the pH was neutral. After the original cycle, three more cycles of adsorption-desorption studies were conducted, and the reusability of the adsorbent substance was examined.

3. Results and Discussion

3.1. Effect of Flow Rate (Q)

With pre-treated pine sawdust, the effect of flow rate on MR GRL adsorption was studied at three different flow rates (4, 6, 8 mL/min). Figure 2 shows the effect of the flow rate on the breakthrough curve under the determined operating conditions. It is seen that adsorption is faster at a low flow rate. When the flow rate is low, the adsorption efficiency is better because enough time is provided for the dye ions to reach and pass through numerous reaction sites on the adsorbent surface. The contact time between the adsorbent and the adsorbent decreases as the increased flow rate will allow the dye molecules to move faster in the column. Thus, the removal rate and mass transfer rate of the dye decreases [18].

As the flow rate rises, the breakthrough point was reached in a shorter time and a smoother and steeper curve was obtained. For an effective adsorption, the length of time the dye molecules stay in the colon is very important. Because, there is always a threshold value for each sorption process [19]. As seen in Figure 2, the column adsorption capacity (qm) decreased from 674.15 mg/g to 431.79 mg/g as the flow rate increased from 4 mL/min to 8 mL/min. As can be seen, the highest removal rate was obtained at a flow rate of 4 mL/min and a larger volume of dye solution was treated.

![Figure 2](image-url)
3.2 Effect of the Adsorbent Height (H)

Depending on the amount of adsorbent used in the column, the removal efficiency varies. Therefore, the adsorbents of 1.2, 2.4 and 3.6 g, corresponding to the bed height of 5, 10 and 15 cm, were placed in the column in a way that there is no space between them. The breaking curves obtained for different bed heights are given in Figure 3. Since dye molecules are more in contact with the adsorbent surface as bed height (i.e. adsorbent mass) increases, the dye removal efficiency has increased. Because a larger mass transfer region is formed along with the increased adsorbent mass, the increase in dye removal is probably due to the obtainability of additional active binding sites for the sorption of MR GRL dye [20,21]. Similar results were also obtained in the column study conducted by Li et al. [21]. Also the same results were also observed by Cruz et al. [22] for removal of crystal violet with bone char. In fact, Gupta and Babu [23] obtained similar breakthrough curves for Cr (VI) removal. Such results are frequently encountered in liquid phase adsorption systems where mass transfer is limited by diffusion.

The MR GRL dye in the input wastewater was adsorbed by the adsorbent in the early minutes, and this trend continued with the increase in bed height. However, after a certain period of time, the MR GRL dye concentration in the water coming out of the column increased and eventually adsorption reached equilibrium. It was seen that dye adsorption was proportional to the amount of adsorbent in the column. When the adsorbent height in the column was increased from 5.0 cm to 15.0 cm, the MR GRL adsorption capacity increased from 434.48 mg/g to 554.02 mg/g. The adsorbing capacity of the adsorbent bed and the spreading rate of the pollutant increased with increasing bed height. The same results were reported by Alardhi et al. [24].

3.3. Effect of Dye Concentration (C_i)

The breakthrough curves obtained at different initial concentrations (50, 100 and 150 mg/L) by keeping the other operating parameters such as pH, bed height and flow rate constant are given in Figure 4. As seen in the Figure 4, when the input dye concentration was reduced, the break time was significantly increased and a better column performance was achieved. The reason could be that at lower concentrations, there will be lower competition between dye molecules that will be adsorbed to the surface of the adsorbent due to a decrease in mass transfer or diffusion coefficient. Based on this, it can be said that the diffusion process depends on the input dye concentration [20,21,25].

When the dye concentration at the column entrance increased from 50 mg/L to 150 mg/L, the adsorption capacity increased from 479.64 mg/g to 497.93 mg/g. This result also means that the MR GRL dye removal efficiency decreased. Based on this, it can be based on the following conclusion that the designed adsorption process is applicable for the removal of more dilute dye concentrations. The same results were also achieved for anionic dye adsorption by waste tea residue [26].

When Table 2 is examined, it seems that when the initial dye concentration increases, the adsorbent's saturation time decreases and adsorption capacity increases. Since the initial dye concentration increases, the adsorption bed will reach saturation more quickly, so the breakthrough curve is achieved in a shorter time (Table 2). When the dye concentration to be treated is increased from 50 mg/L to 150 mg/L, the adsorbent exhaustion time (t_e) decreased from 525 min to 132 min. This situation can be explained in the following way; as the input dye concentration increases, the adsorbent substance needs much more time to achieve adsorption equilibrium. The reason could be that when the input concentration is high, the adsorbent bed reaches the saturation much earlier and the breakthrough moment is reached before all active regions of the adsorbent are not filled by the dye molecules [27].

3.4. Reusability of the Adsorbent Bed

In order for the adsorption study to be economical and efficient, the regenerability of the adsorbent substance used in the continuous system adsorption column is quite important. The regeneration process can be explained as getting back or releasing the substance clinging to the surface of the adsorbent [28].
For this reason, regeneration efficiency was tried to be determined by adsorption-desorption cycles performed consecutively. Washing with desorption fluid was proceed until there was no MR GRL dye stay in the filtrate at the exit of the colon. Then to remove the remaining NaOH solution in the adsorbent bed, the column bed was washed with pure water until the pH was neutral. Adsorption-desorption process was repeated in 3 cycles. The breakthrough curves obtained after each cycle are given in Figure 5.

The adsorption capacities of the raw adsorbent and the adsorbent undergoing the regeneration process are given in Figure 6. While the maximum adsorption capacity \( (q_m) \) in the continuous system was 588.79 mg/g for the original cycle, it was found to be 446.74 mg/g at the 3rd cycle. While the \( q_m \) value showed a significant decrease in the first cycle after the original cycle, a very small decrease was observed in the 2nd and 3rd cycles. The fact that good efficiency and high adsorption capacity were achieved even after the 3rd cycle suggests that the pine sawdust adsorbent, which has undergone acidic treatment, can be used efficiently as several-repetitions in the continuous system for the removal of the Maxilon Red GRL.

### 3.5. Dynamic Mathematical Models Used in Continuous Systems

In order to describe the dynamic behavior of the removal of pollutants in the fixed bed column and to characterize bed performance, mathematical models such as Adams-Bohart, Thomas and Yoon-Nelson were used. Detailed information about the mathematical models used in the study and the equations used in the modeling were given in detail in the study published by Şentürk and Alzein [15]. The results obtained from the breakthrough curves through the specified models are given in Table 3.

As seen in Table 3, the data obtained from the breakthrough curve did not show conformity with the Adams-Bohart model (see \( R^2 \) values). It was understood that the Thomas and Yoon-Nelson models could be used to interpret the colon system (the mean \( R^2 \) value was 0.9557). The Thomas model is one of the most popular models used in colon adsorption studies, where the second-order reaction kinetic model and the Langmuir isotherm are used together. When the \( R^2 \) values gotten under separate working conditions for the Thomas model are examined, it is observed that the \( R^2 \) value obtained at 10 cm bed height, 6 mL/min flow rate and 100 mg/L initial dye concentration is 0.9607.

In addition, according to the data obtained from Table 3, since the input dye concentration increased, the \( q_m \) value of the Thomas model decreased, but the \( k_{th} \) value increased. However, because the contact time between the dye and the adsorbent increased with the increase in bed height, the \( k_{th} \) value decreased this time.

### Table 2. Parameters of the column breakthrough curve for MR GRL.

| H (cm) | Q (mL/dk) | C_i (mg/L) | t_b (dk) | t_e (dk) | q_m (mg/g) |
|-------|-----------|------------|----------|----------|------------|
| 5     | 4         | 50         | 120      | 300      | 474.17     |
| 5     | 6         | 50         | 95       | 435      | 434.48     |
| 5     | 8         | 50         | 70       | 295      | 431.79     |
| 10    | 6         | 50         | 150      | 525      | 479.64     |
| 15    | 6         | 50         | 265      | 630      | 554.02     |
| 10    | 6         | 100        | 100      | 190      | 483.32     |
| 10    | 6         | 150        | 72       | 132      | 497.93     |

### Figure 5. Column breakthrough curves after regeneration

### Figure 6. Column adsorption capacities \( (q_m) \) of MR GRL dye on raw and regenerated adsorbents after adsorption-desorption cycle

Similarly, at 10 cm bed height and 6 mL/min flow rate, while the \( q_m \) (mg/g) value increased from 41.22 mg/g to 47.12 mg/g when dye concentration increased from 50 to 100 mg/L, it decreased again to value of 38.35 mg/g when the concentration reached to 150 mg/L. Here, it is seen that the column has reached its maximum adsorption capacity at 10 cm bed height, 6 mL/min flow rate and 100 mg/L dye concentration.

When the \( \tau \) values obtained from the Yoon-Nelson model were examined, it is observed that the \( \tau_{0.5} \) value obtained at 10 cm bed height, 6 mL/min flow rate and 100 mg/L dye concentration showed proximity to the \( \tau \) value.
A similar condition was also observed at a dye concentration of 150 mg/L. However, no proximity between these two values was observed for other parameters. Therefore, contrary to the interpretation made above based on the value of $R^2$, the model results given in Table 3 clearly show that the Yoon-Nelson model is not compatible with the breakthrough curve data.

### 4. Conclusion

During this study, in which the continuous adsorption of the Maxilon Red GRL dye in the system was examined using sulfuric acid-activated pine sawdust, no changes were made in parameters such as pH and temperature, and the effects of column height, flow rate and dye concentration on the column breakthrough curve were investigated. Flow rate is an important parameter that should be examined in the design of column systems. It was seen that the MR GRL dye removal and the $q_m$ value in the column decreased with the increase in flow rate. Furthermore, the rise of the flow rate led to low breakthrough capacity, a decrease in retention time, and thus a decrease in the amount of dye adsorbed by the adsorbent bed. The second parameter examined is the column bed height. It was observed that as bed height increased, there was an increase in breakthrough time ($t_b$), exhaustion time ($t_e$) and maximum adsorption capacity ($q_m$) values. Another parameter examined in this study is the dye concentration at the entrance to the column. It was found that efficiency and adsorbing capacity decreased as dye concentration increased. The maximum adsorption capacity ($q_m$) obtained under the selected best conditions (10 cm bed height, 6 mL/min flow rate, and 100 mg/L initial concentration) is 483.32 mg/g.

Changes in the removal efficiency of the adsorbent after the regeneration applied to the exhausted adsorbent were also investigated. While the maximum MR GRL adsorption capacity ($q_m$) of the adsorbent was 588.79 mg/g when studying with the raw adsorbent, which had never been regenerated, $q_m$ of the adsorbent decreased to 446.74 mg/g after the 3rd regeneration.

The Adams-Bohart model, Thomas model, and Yoon-Nelson model were adapted to experimental results obtained from the continuous system. The results showed that the Thomas model was more appropriate for defining breakthrough curves.

Designing of adsorption column with acid activated pine sawdust suggests that activated pine sawdust can be used as low-cost industrial adsorbent in the larger scale. Continuous system adsorption column ensures efficient use of the driving force in the column and more efficient wastewater treatment. Continuous system working columns are a small form of adsorption columns used in the industry and provide very important information for understanding the treatment process. The results obtained from the study showed that MR GRL dye removal with acid-pretreated pine sawdust can be treated in a continuous system adsorption column. However, for industrial application, it should also be worked with real textile wastewater containing MR GRL dye.

### Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

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