# INVESTIGATION OF COLOR REMOVAL PERFORMANCE IN DYEHOUSE REACTIVE DYEING WASTEWATER USING DENDRIMER TECHNOLOGY

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***ABSTRACT:*** *In this study, the color removal performance of polyamidoamine (PAMAM) dendrimer was examined in real reactive dyeing bath wastewater (that is, waste water in which the dye is in hydrolyzed form and contains other auxiliary chemicals used in dyeing besides the dye). These experiments were carried out on three reactive dye bath wastewaters, one for trichromatic light color, one for trichromatic dark color, and one for turquoise color dyeing, supplied from a dyehouse. Studies conducted on real plant dyeing wastewater showed that the optimum conditions were 50-100 mg/L dendrimer and 15-30 minutes centrifugation. Color removal efficiency was between 75-90%. In the light of all these results, it can be said that dendrimer technology can be an alternative to other existing techniques in decolorizing reactive dye bath wastewater.*

***Keywords:*** *reactive dye, color removal, dendrimer, dyehouse.*

# ISTRAŽIVANJE PERFORMANSE UKLANJANJA BOJE U OTPADNIM VODAMA ZA REAKTIVNO BOJENJE KORIŠĆENJEM DENDRIMER TEHNOLOGIJE

***APSTRAKT:*** *U ovoj studiji ispitan je učinak uklanjanja boje poliamidoaminskog (PAMAM) dendrimera u stvarnoj reaktivnoj otpadnoj vodi kupke za bojenje (odnosno otpadnoj vodi u kojoj je boja u hidrolizovanom obliku i sadrži druge pomoćne hemikalije koje se koriste u bojenju pored boje). Ovi eksperimenti su izvedeni na tri otpadne vode iz*

*kupatila sa reaktivnim bojama, jednom za trihromatsku svetlu boju, jednom za trihromatsku tamnu boju i jednom za farbanje u tirkiznoj boji, koje se snabdevaju iz farbanja. Studije sprovedene na otpadnim vodama pravih biljnih boja pokazale su da su optimalni uslovi bili 50-100 mg/L dendrimera i 15-30 minuta centrifugiranja. Efikasnost uklanjanja boje bila je između 75-90%. U svetlu svih ovih rezultata, može se reći da tehnologija dendrimera može biti alternativa drugim postojećim tehnikama u dekolorizaciji otpadnih voda iz kupatila sa reaktivnim bojama.*

***Ključne reči:*** *reaktivna boja, uklanjanje boje, dendrimer, farba.*

## 1. INTRODUCTION

In the textile industry, reactive dyes, which have a wide range of color options due to their high fastness and brightness, are widely used in the dyeing process [1, 2]. Since dyes are generally stable and contain complex aromatic molecular structures, their biological purification is quite limited, and when discharged into the environment without purification, it causes toxic and carcinogenic effects on living things [3].
Therefore, color removal from wastewater containing dye is a very important issue.
Dendrimers consist of branched polymer compounds of various sizes containing different functional groups and whose functionality can be adjusted, and they have physical properties such as flexibility, viscosity and density distribution compared to polymers [4, 5]. Among dendrimers, poly(amidoamine) (PAMAM) is a dendrimer consisting of an ethylenediamine core, a certain number of repeating units and certain endings, and is one of the dendrimers used in water and wastewater treatment [6].
Studies show that dendrimers are effective in the removal of reactive dyes [3, 4, 7-10]. With chitosan-polypropylene imine (PPI) dendrimer, Reactive Black 5 and Reactive Red 198 dye removal was achieved as 97.0% and 99.4%, respectively [4]. Reactive Blue 19 dye removal was achieved as 72% and 88% with PAMAM dendrimer and PPI dendrimer, respectively [9]. In Reactive Black 5 dye removal with magnetic PAMAM dendrimer, the adsorption capacity was obtained as 70.4 mg/g [7]. In the study investigating Reactive Blue 21 removal with Chitosan/PAMAM dendrimer microparticles, it was stated that 89.3% Reactive Blue 21 removal could be achieved, while the adsorption capacity was 556 mg/g [3]. It has been stated that the adsorption capacity of Reactive Red 3BS with PAMAM dendrimer increases depending on the generation of PAMAM dendrimer and can increase up to 323 mg/g with the 4th generation [8].
However, when these studies are examined, it is seen that dye removal in synthetic dye solution has been investigated and no studies have been conducted with real dyehouse wastewater. In this study, the color removal performance of dendrimer was examined by taking real reactive dyeing wastewater from a dyehouse. For this purpose, the effects of dendrimer concentration and centrifuge time on color removal in three different wastewaters taken from a dyehouse were examined. Since there is no study in this scope and with this approach in the literature, it can be said that the study is innovative and original.

## 2. MATERIAL AND METHODS

In this study, to determine the optimum dendrimer dosage in the decolorization of real reactive dyeing wastewater with PAMAM dendrimer (Figure 1), 6 different dendrimer concentrations (5-10-25-50-75-100 mg/L) and 3 different centrifuge times (15-30-60 min.) (to determine the optimum time) were used. After adding the required amount of dendrimer to the real reactive dyeing wastewater, the solution pH was adjusted and the solutions were stirred in a mechanical mixer at 90 rpm. At the end of the determined periods, samples were taken from the upper waters of the solutions, centrifuged, and color measurements were made with a UV/Vis spectrophotometer.

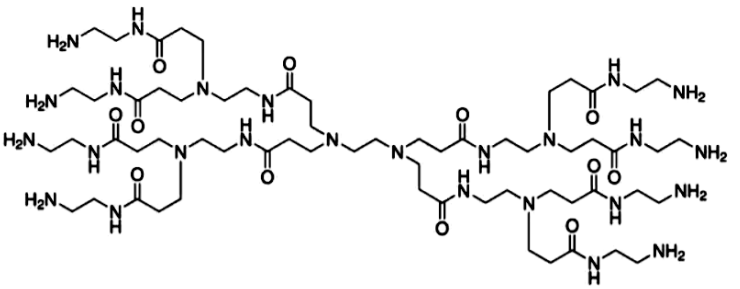


**Figure 1.** Chemical structure of the dendrimer used in the study [11]

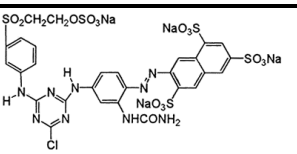
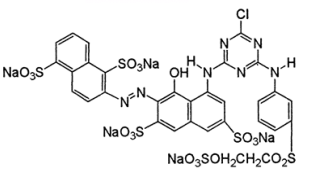
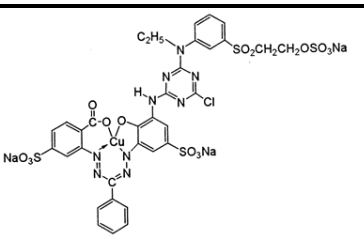
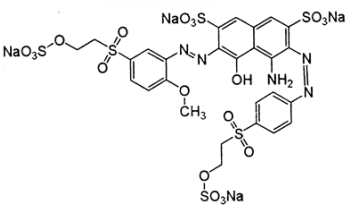
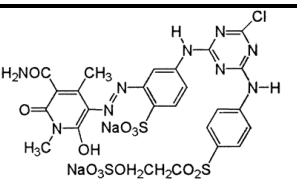
Within the scope of the study, the color removal performance of PAMAM dendrimer was examined in real reactive dyeing bath wastewater (that is, waste water where the dye is in hydrolyzed form and contains other auxiliary chemicals used in dyeing besides the dye). These experiments were carried out on three reactive dyebath wastewaters, one of which was obtained from Özen Mensucat company with thrichromatic light color, the other with thrichromatic dark color and the third with turquoise color dyeing. In fact, it is important to determine the color removal efficiency of dendrimer in the final waste water of the operation. However, a wide variety of dyes are mixed in the final wastewater of a dyehouse. In order to evaluate the color removal performance of dendrimer in our study, it is necessary to know what dyes the wastewater contains. For this reason, in the experiments, after the dyeing in the enterprises, final wastewater samples were taken directly from the dyeing machine and their color removal with dendrimer was studied. However, normally the wastewater generated after a dyeing process is highly concentrated. In the actual operation, the final wastewater contains dyebath waste water as well as various washing baths, bleaching baths, and many more baths are mixed and dilution occurs. For this reason, the real enterprise dye bath wastewater collected in this experimental group was diluted and then subjected to color removal studies with dendrimer. The dyes used in these dyeing recipes and their usage percentages are given below.

- **Light color dyeing:** 0,66% Reactive Yellow 145, 0,15% Reactive Red 195, 1,35% Reactive Blue 221

- **Dark color dyeing:** 0,358% Reactive Red 195, 0,453% Reactive Yellow 145, 1,781% Reactive Blue 250, %8,195 Reactive Black Mix
- **Turquoise color dyeing:** 0,735% Reactive Yellow 160, 0,0382% Reactive Blue 221, 2,915% Reactive Blue 21

Information on the properties of the reactive dyes used in this study is given in Table 1.

**Table 1:** Reactive dyes used in dyeings

| C.I. Number | Chromophore group | Formula | Source |
|---|---|---|---|
| Reactive Yellow 145 | Azo |  | [12] |
| Reactive Red 195 | Azo |  | [13] |
| Reactive Blue 221 | Cupper formazan |  | [14] |
| Reactive Blue 250 | Disazo |  | [15] |
| Reactive Yellow 160 | Azo |  | [16] |

## 3. RESULTS AND DISCUSSION

Within the scope of the study, the color removal performance of PAMAM dendrimer in real reactive dyeing bath wastewater was examined. These experiments were carried out on three reactive dye bath wastewaters, obtained from Özen Mensucat company one of which was with thrichromatic light color (Green), the other with thrichromatic dark color (Black) and the third with turquoise color dyeing.
The result of variance analysis regarding the color removal of light colored real reactive dyeing wastewater with dendrimer is given in Table 2.

**Table 2:** Analysis of variance result for color removal of light colored real reactive dyeing wastewater with dendrimer

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Dendrimer Conc. (mg /L) | 5 | 16962.7 | 3392.54 | 1773.58 | 0.000 |
| Centrifuge Time (min.) | 3 | 28.4 | 9.48 | 4.95 | 0.014 |
| Error | 15 | 28.7 | 1.91 | | |
| Total | 23 | 17019.8 | | | |

When Table 2 is examined, it is understood that the effects of both dendrimer concentration and centrifuge time parameters on the color removal of the light colored real reactive dyeing wastewater with dendrimer are statistically significant ($p<0.05$). Tukey analyzes were also conducted to see the source of the difference and the results are given in Tables 3 and 4.

**Table 3:** Tukey analysis result on the effect of dendrimer concentration on the color removal obtained in light colored real reactive dyeing wastewater

| Dendrimer Conc. (mg/L) | N | Average | Grouping |
|---|---|---|---|
| 100 | 4 | 75.0000 | A |
| 75 | 4 | 73.3642 | A |
| 50 | 4 | 68.9198 | B |
| 25 | 4 | 57.8704 | C |
| 10 | 4 | 24.1667 | D |
| 5 | 4 | 5.4321 | E |

**Table 4:** Tukey analysis result on the effect of centrifugation time on the color removal obtained in light colored real reactive dyeing wastewater

| Centrifuge Time | N | Average | Grouping | |
|---|---|---|---|---|
| 60 | 6 | 51.6255 | A | |
| 30 | 6 | 51.4609 | A | |
| 15 | 6 | 51.1523 | A | B |
| 0 | 6 | 48.9300 | | B |

When Table 3 is examined, it can be seen that dendrimer concentrations of 5, 10, 25 and 50 mg/L are each in a separate group, and concentrations of 75 and 100 mg/L are in the same group. Accordingly, it can be said that 75 mg/L is the optimum concentration. When Table 4 is examined, it can be said that color removal is low when centrifugation is not performed, but increasing the centrifugation time beyond 15 minutes does not provide any additional benefit. According to these results, it can be said that the optimum process conditions for light-colored real dye wastewater are 75 mg/L dendrimer and 15' centrifuge. The highest color removal of 76.05% was achieved for this wastewater. All these results can be clearly seen from the "Main Effects Plot for Color Removal" given in Figure 2.

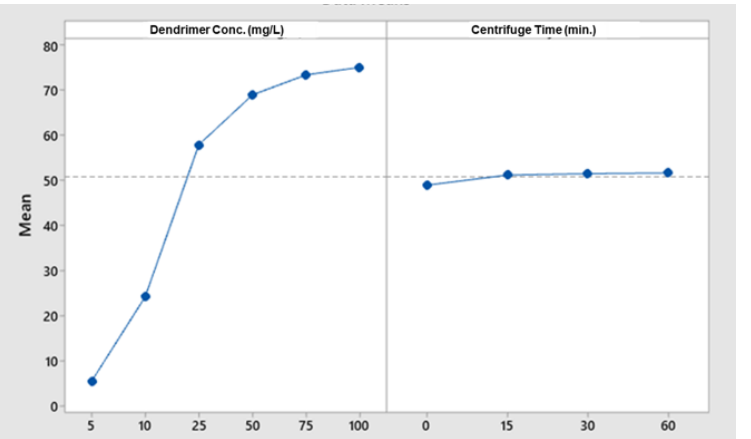



**Figure 2.** Main effects graph for color removal in light colored dye wastewater

The result of variance analysis regarding the color removal of dark colored real reactive dyeing wastewater with dendrimer is given in Table 5.

**Table 5:** Analysis of variance result for color removal of dark colored real reactive dyeing wastewater with dendrimer

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Dendrimer Conc. (mg/L) | 5 | 20794.6 | 4158.91 | 175.21 | 0.000 |
| Centrifuge Time (min.) | 3 | 1371.4 | 457.15 | 19.26 | 0.000 |
| Error | 15 | 356.0 | 23.74 | | |
| Total | 23 | 22522.1 | | | |

From Table 5, it is understood that the effects of both dendrimer concentration and centrifuge time parameters on the color removal of the dark colored real reactive dyeing wastewater with dendrimer are statistically significant ($p<0.05$). Tukey analyzes were also conducted to see the source of the difference and the results are given in Tables 6 and 7.

**Table 6:** Tukey analysis result on the effect of dendrimer concentration on the color removal obtained in the dark colored real reactive dyeing wastewater

| Dendrimer Conc. (mg/L) | N | Average | Grouping |
|---|---|---|---|
| 100 | 4 | 83.4792 | A |
| 75 | 4 | 82.1116 | A |
| 50 | 4 | 80.7713 | A |
| 25 | 4 | 68.7363 | B |
| 10 | 4 | 34.0536 | C |
| 5 | 4 | 5.3884 | D |

**Table 7:** Tukey analysis result on the effect of centrifuge time on the color removal obtained in dark colored real reactive dyeing wastewater

| Centrifuge Time (min.) | N | Average | Grouping |
|---|---|---|---|
| 30 | 6 | 63.7491 | A |
| 60 | 6 | 63.6214 | A |
| 15 | 6 | 62.9832 | A |
| 0 | 6 | 46.0066 | B |

When Table 6 is examined, it can be seen that dendrimer concentrations of 5, 10 and 25 mg/L are each in a separate group, and concentrations of 50, 75 and 100 mg/L are in the other group. Accordingly, it can be said that 50 mg/L is the optimum concentration. When Table 7 is examined, it can be said that color removal is low when centrifugation is not performed, but increasing the centrifugation time beyond 15 minutes does not provide any additional benefit. According to these results, it can be said that the optimum process conditions for dark colored real dye wastewater are 50 mg/L dendrimer and 15' centrifuge. The highest color removal of 87.42% was achieved for this wastewater. All these results can be clearly seen from the “Main Effects Plot for Color Removal” given in Figure 3.

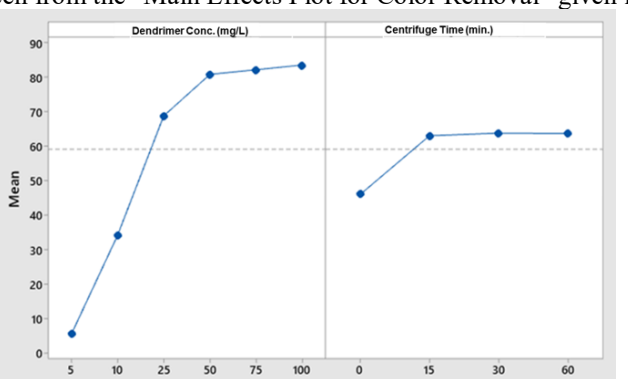



**Figure 3.** Main effects plot for color removal in dark colored dye waste water

The result of variance analysis regarding the color removal of real turquoise reactive dyeing wastewater with dendrimer is given in Table 8.

**Table 8:** Analysis of variance result for color removal of turquoise colored real reactive dyeing wastewater with dendrimer

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Dendrimer Conc. (mg/L) | 5 | 302.485 | 60.4970 | 510.01 | 0.000 |
| Centrifuge Time (min.) | 3 | 11.609 | 3.8698 | 32.62 | 0.000 |
| Error | 15 | 1.779 | 0.1186 | | |
| Total | 23 | 315.874 | | | |

When Table 8 is examined, it is understood that the effects of both dendrimer concentration and centrifuge time parameters on the color removal of the light colored real reactive dyeing wastewater with dendrimer are statistically significant ($p<0.05$). Tukey analyzes were also performed to see the source of the difference and the results are given in Tables 9 and 10.

**Table 9:** Tukey analysis result on the effect of dendrimer concentration on the color removal obtained in real reactive dyeing wastewater in turquoise color

| Dendrimer Conc. (mg /L) | N | Average | Grouping |
|---|---|---|---|
| 100 | 4 | 76.4324 | A |
| 75 | 4 | 73.0710 | B |
| 50 | 4 | 72.7368 | B |
| 5 | 4 | 68.9649 | C |
| 25 | 4 | 67.9240 | D |
| 10 | 4 | 65.9664 | E |

**Table 10:** Tukey analysis result on the effect of centrifuge time on the color removal obtained in real reactive dyeing wastewater in turquoise color

| Centrifuge Time | N | Average | Grouping |
|---|---|---|---|
| 60 | 6 | 71.5877 | A |
| 30 | 6 | 71.3649 | A |
| 15 | 6 | 70.6328 | B |
| 0 | 6 | 69.8116 | C |

When Table 9 is examined, it can be seen that the dendrimer concentrations of 50 and 75 mg/L are in one group, and the concentrations of 5, 10, 25 and 100 mg/L are each in a different group. Accordingly, it can be said that 100 mg/L is the optimum concentration. When Table 10 is examined, it can be said that color removal is low when centrifugation

is not performed, but increasing the centrifugation time beyond 30 minutes does not provide any additional benefit. According to these results, it can be said that the optimum process conditions for turquoise colored real dye wastewater are 100 mg/L dendrimer and 30' centrifuge. The highest color removal of 76.81% was achieved for this wastewater. All these results can be clearly seen from the “Main Effects Plot for Color Removal” given in Figure 4.

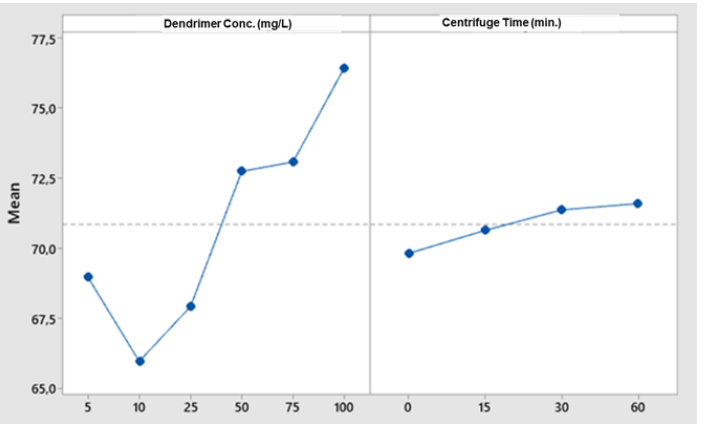



**Figure 4.** Main effects plot for color removal in turquoise dye wastewater

## 3. CONCLUSION

Studies conducted on real plant dyeing wastewater showed that the optimum conditions were 50-100 mg/L dendrimer and 15-30 minutes centrifugation. Color removal efficiency was between 75-90%. In the light of all these results, it can be said that dendrimer technology can be an alternative to other existing techniques in decolorizing reactive dye bath wastewater.

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