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TREATMENT OF TEXTILE WASTEWATER WITH CHERRY LAUREL LEAVES AND WASTE POTATO PEELS

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ABSTRACT

In this study, a research was carried out on the removal of dyestuff, which is a big problem in the textile industry. The adsorption method was used for the removal of Maxilon Yellow 4GL dyestuff. Cherry laurel leaf (*Prunus laurocerasus*) and waste potato peels were used as adsorbent, and the removal efficiency was determined as 76.64% at pH 7 and with 2 g adsorbent, 80% dyestuff removal efficiency was achieved in the specified conditions for cherry laurel leaves. For experiments in which waste potato peels were used as adsorbent, the optimum conditions were found as follows: Contact time: 60 minutes, adsorbent concentration of 0.75 grams and initial concentration of 25 mg/L. The Freundlich isotherm model was suitable for our study, since the regression number was found to be 0.999 for cherry laurel leaves and 0.995 for waste potato peels as a result of isotherm studies. According to the cost analysis, the materials supplied free of charge, due to mixing, the electricity cost for treatment (0.128 TL) and the chemical material cost is 17 TL, and it has been determined that these adsorbents are quite economical in dyestuff treatment. As a result, the fact that there is no study on the removal of cherry laurel leaves with the mentioned dyestuff in the literature shows that this study can be further developed.

Keywords: Adsorption, Dye removal, Cherry Laurel leaf, Waste potato peels.

1. INTRODUCTION

Increasing environmental concerns have led scientists to use natural materials for the environment. The rise in population has increased the demand for textile products. Therefore, more production caused more water pollution. The main environmental problem for the textile industry is colored wastewater. Since dyestuffs have toxic properties and have a carcinogenic effect on metabolism, they must be purified from wastewater. In addition, when these waters are mixed with the discharge environment, the dyestuffs in it reduce the photosynthesis by blocking the sun rays. The presence of these substances in the aquatic environment causes great damage to the aquatic ecosystem [1]. Most of the dyes are organic and consist of chromogen and auxochrome groups. Of these, auxochrome groups provide binding to textile products. When these groups are bonded with molecules, a shift can occur in the visible region and these groups are called "chromophore groups" or "color forming groups". The main ones are as follows: [2]:

Nitroso group: -NO or =N-OH

Nitro group : -NO₂

Azo group : -N=N

Ethylene group : -C=C

Carbonyl group : -C=O

One of the most commonly used methods for dye removal from textile wastewater is adsorption. When an atom, ion or molecule is brought into contact with a solid, some of the atoms, ions or molecules are held by the solid. If this holding process takes place on the surface of the solid, it is called adsorption. The substance adsorbed to the substance whose concentration increases on the liquid or solid surface is called adsorbate, and the substance that adsorbs is called adsorbent [3].

Usage areas of the adsorption process:

- Dechlorination
- Removal of persistent organic pollutants found in industrial waste
- Dye removal
- Reducing the need for chlorine
- Removal of undesirable odor and taste
- Removal of toxic compounds [4].

In this study, powders of cherry laurel leaves and waste potato peels were used as adsorbent material. The cherry laurel plant, which is grown in the Black Sea region of Turkey, has an antioxidant effect due to its phenolic contents. It is found in many

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countries in the world, especially in Europe and Iran, and it is frequently used as an ornamental plant [5]. Potato is an antioxidant like other adsorbent and is widely consumed [6]. Therefore, it creates a large amount of domestic waste potential. It will be very useful to use the waste potato peels, which are turned into adsorbent by a simple process, in the removal of the color parameter in the textile industry wastewater.

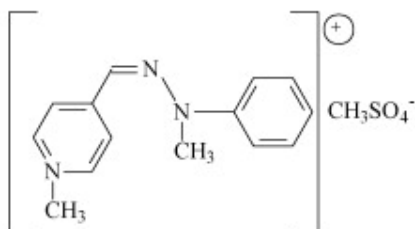


Figure 1. Maxilon yellow 4GL [7]

Maxilon yellow 4GL (Figure 1) which is used in experimental a cationic dye. Since their colored parts are in the form of cations, these dyes are defined as cationic dyestuffs. Cationic dyes are currently used in large quantities for dyeing acrylics and modified acrylics [8]. The reason for choosing this dye in the study is that it is a reactive dye. The difference of reactive dyes from other dyes is that they can react with large molecules in the fibers and form real bonds. [2,9]. The characteristics of the dye are shown in Table 1 [10,11].

Table 1. The characteristics of dye

Name	Color	Color Index	Molecular Weight	Molecular formula
Maxilon Yellow 4GL	Basic Yellow	87	337.39	$C_{15}H_{19}N_3O_4S$

The aim of this study is to investigate the use of some materials found in nature in wastewater removal. Harmful chemicals are used in the removal of color parameter from the colored wastewater of the textile industry, which is one of the main environmental problems, and new materials are used as alternatives to these harmful chemicals. For this purpose, cherry laurel tree leaves and potato peels were used in the study.

2. MATERIAL AND METHOD

Cherry laurel leaves were freshly collected from Düzce, Turkey. Afterwards, it was thoroughly washed with tap water in order to avoid any residue (dust, insects, etc.) on it. Then the leaves were washed with deionized water and dried in a sunny room for 1 week. Thoroughly dried leaves were passed through a kitchen grinder and stored in an airtight container. In this way, it is ready for the experimental stage. The chemical materials used in the study were of analytical purity and ultrapure water was used at every stage to prevent any unwanted interference. The same procedure was followed for waste potato peels. Digital scale (Radwag), shaker incubator (JSR), pump (Rocker), spectrophotometer (Hach lange dr3900) and pH meter (Hach lange hd30d) were used in the analysis phase.

Before starting the experiments, the target pollutant prepared at certain concentrations was measured in the spectrophotometer in order to understand the results. In this context, certain amounts of dilution were made from the stock solution prepared as 100 mg/L then, solutions were prepared at concentrations of 5 mg/L, 10 mg/L, 15 mg/L and 25 mg/L, and adsorbance readings were made in the device at 410 nm.

After the solutions prepared at the concentrations stated in the second section were read in the spectrophotometer, a calibration graphic was drawn. In this context, experiments were carried out. In the next experiments, the adsorbent values read in the spectrophotometer were converted to concentration using this equation.

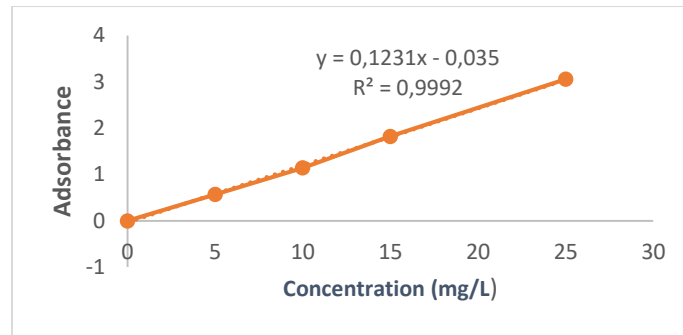


Figure 2. Calibration graphic

The relevant graphic is shown on the Figure 2. The correlation coefficient was found to be 0.999. The linearity of the graph indicated that good calibration solutions were prepared.

2.2. Adsorption Studies

In order to investigate the effect of pH on dyestuff removal, the initial dyestuff solution was using 0.1 N NaOH and 0.1 N HCl solutions at pH of 3, 5, 7, 9 and 11 set at room temperature. In order to examine the effect of temperature on dye removal, samples were taken at 25, 35 and 45 degrees. The effect of initial concentration was determined by experimenting with concentrations between 5-25 mg/L. In order to determine the contact time of the cherry laurel leaves and waste potato peels in the removal of the dyestuff, samples were taken and measured at certain times different minutes. In order to determine the effect of the amount of the adsorbents on the removal of the dye, 0,1-2 grams of leaves were added.

2.2. Isotherm and Kinetic Studies

The kinetic study was carried out considering the optimum conditions where the highest dyestuff removal was achieved. In this context, Freundlich isotherm model, which is one of the most frequently used isotherm models in adsorption studies, was used. The formula for the relevant model is shown in Equation (1) and Equation (2). Here, the correlation coefficient (R^2) must be taken into account. The closer this number is to 1, the closer it is to linearity [12].

$$q = \frac{x}{m} = Kf \cdot Ce^{\left(\frac{1}{n}\right)} \quad (1)$$

The equation is expressed logarithmically as:

$$\log\left(\frac{x}{m}\right) = \log Kf + \left(\frac{1}{n}\right) \log Ce \quad (2)$$

Ce (mg/L) is the equilibrium concentration, q (mg/g) is the adsorption amount at equilibrium, x (mg/L) is the concentration of adsorbed solute, K_f is adsorption capacity, n is adsorption intensity [12].

As the kinetic model, 1st order, 2nd order and additionally the kinetic model they studied in Behnajady et al. (2007) was used [13,14].

$$1. \quad \text{order kinetic model: } Ct = Co e^{-k_1 t} \quad (3)$$

$$2. \quad \text{order kinetic model: } \frac{1}{Ct} = \frac{1}{Co} + k_2 t \quad (4)$$

In the equations given in Equations 3 and 4, C is the concentration of maxilon yellow 4gl and t is the time. k_1 and k_2 are 1st and 2nd order kinetic constants, respectively. Co is the starting concentration of maxilon yellow 4 GL.

The kinetic model formula used by Behnajady et al. in their study is shown in Equation 5. Here, the b represents the degradation value of the pollutants.

$$\frac{Ct}{Co} = 1 - \frac{1}{b} \quad (5)$$

3. RESULTS AND DISCUSSION

3.2. pH Effect

As it is known, pH is an important parameter in adsorption. For this purpose, adjustments were made at different pH values. First of all, initial concentration (C_0) was adjusted 25 mg/L, amount of adsorbent (A_a) was 1 g/L and contact time was 60 minutes. According to the data obtained from the adsorption studies performed at acidic, neutral and basic values, the highest dyestuff removal was obtained in neutral conditions. As seen in Figure 3, the best dye removal efficiency was achieved at pH 7.

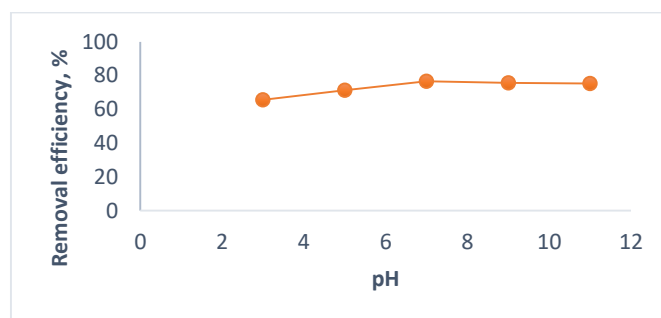


Figure 3. pH effect (C_0 :25 mg/L, A_a : 1 g/L, Time: 60 min.)

The reason why the removal efficiency is higher at high pH values is that the adsorbent is more effective in removing cations because OH^- ions are coated on the surface of the adsorbent at high pH [15]. In addition, with the increase in pH, the adsorbent surface is negatively charged and attracts Maxilon Yellow 4GL, a cationic dye. Therefore, it is thought that dye removal is higher at neutral and basic pH values. [16].

3.3. Temperature Effect

According to the results obtained, the dye removal of the adsorbent little decreased as the temperature increased. As the reason for this, it can be concluded that the efficiency decreased because of the deterioration of the temperature on the adsorbent. Figure 4 shows that, high temperature is not suitable for this adsorbent. However, the effect of temperature is negligible as the reduction is very small.

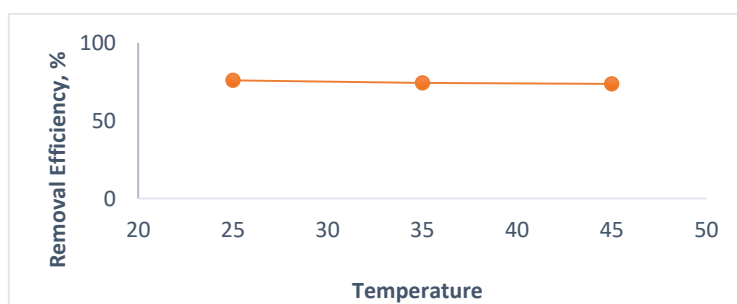


Figure 4. Temperature effect (pH: 7, C_0 :25 mg/L, A_a : 1 g/L, Time: 60 min.)

pH and temperature values was studied for cherry laurel leaves. These parameters were not studied in other adsorbent to see how much efficiency can be obtained without using much chemicals and spending energy for extra heating.

3.4. Contact Time Effect

As seen in the Figure 5, for cherry laurel leaves, adsorption increased with increasing contact time. However, after the 90th minute, the reaction reached equilibrium, that is, there was no significant increase. It can be said that the reason for this is that the pores of the leaves are filled with adsorption in the first stage, and then these pores cannot achieve more dyestuff retention.

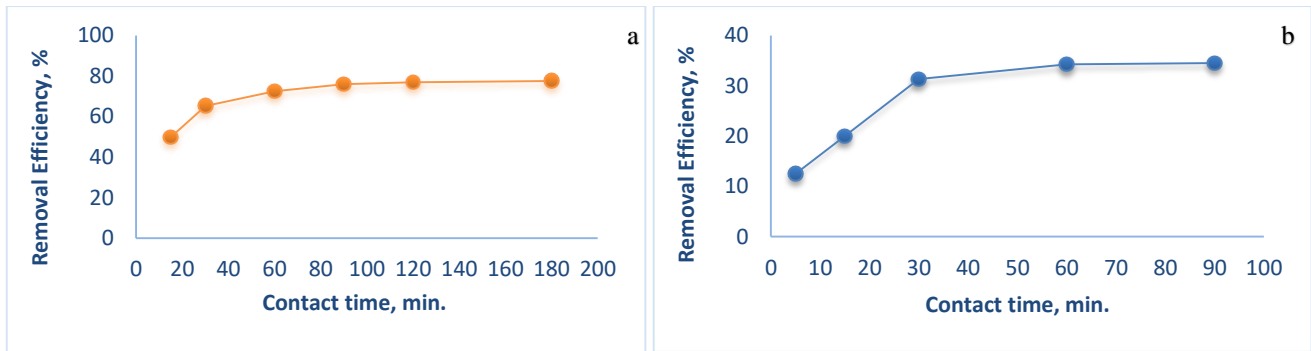


Figure 5. Contact time effect, cherry laurel leaf (a), waste potato peel (b)

For the studies in which waste potato peels were used as adsorbent, pH 7, initial dyestuff concentration of 25 mg/L and temperature were adjusted as room temperature. As seen in Figure 5 (b), an increase in removal efficiency is observed until the 60th minute, then the solution reaches equilibrium. At first, a rapid adsorption was observed because the pores on the surface of the adsorbent were open, while a slowdown in adsorption was observed as the pores filled over time [16]. Therefore, cherry laurel leaves reached equilibrium at 90 minutes and waste potato peels reached equilibrium at 60 minutes. However, the dye removal efficiency was lower than the other adsorbent (waste potato peels).

3.5. Adsorbent Concentration

According to the results obtained for cherry laurel leaves, 40.8% color removal was observed when 0.1 grams of adsorbent was added, 62.6% when 0.5 grams was added, 76% when 1 gram was added, and 80% when 2 grams were added, 78.76 when 2.5 grams were added. With the addition of adsorbent up to a certain amount, the removal efficiency increases and it is fixed after a point, indicating that the adsorbent has reached saturation for cherry laurel leaves.

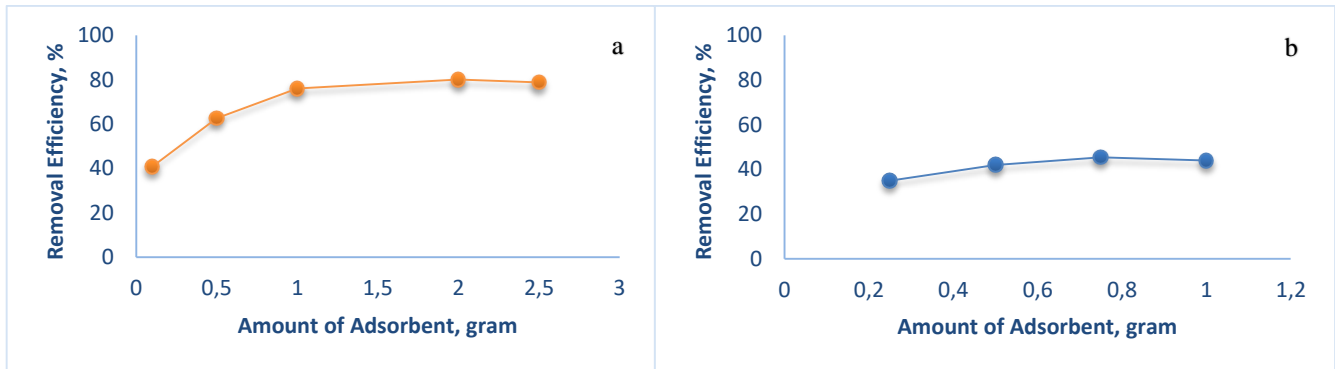


Figure 6. Amount of adsorbent effect

As seen in Figure 6 (b), the adsorbent added as 0.25, 0.5 0.75 and 1g/L reached the most efficient value at 0.75 g/L. Since the small amount of adsorbent could not adsorb the dyestuff, the dyestuff removal efficiency increased as the amount of adsorbent increased. However, there was a slight decrease in the dye removal efficiency afterwards. The reason for this suggests that the waste potato peels may give a yellowish color in the solution due to its structure.

3.6. Initial Concentration

Components in low concentration dyestuffs have difficulty interacting with each other. Thus, the adsorption rate of the dye increases. In the case of an increase in dye concentration, the dye removal efficiency decreases as the mentioned components compete with each other [17].

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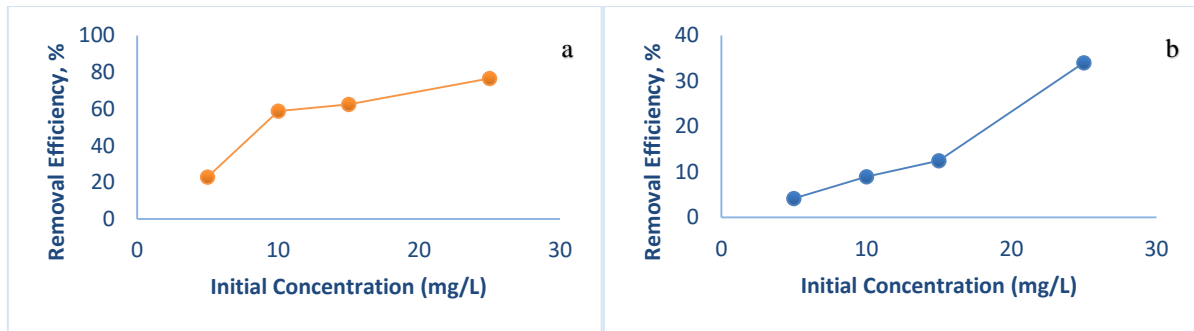


Figure 7. Initial concentration effect

Figure 7 shows a leap in dye removal after an initial concentration of 15 mg/L for both adsorbents. Therefore, for both adsorbents, the dye removal efficiency increased as the dye concentration increased.

3.7. Isotherm and Kinetic Studies

Freundlich isotherm model, which is one of the most used isotherms, has been applied to understand the balance between Maxilon Yellow 4GL dye, which is a residue in aqueous solution, and Maxilon Yellow 4GL dye adsorbed. Figure 8 (a is for cherry laurel leaves and b is for waste potato peels), shows that, a high correlation coefficient was obtained for the Freundlich isotherm. This means that the adsorbent heterogeneous adsorption has taken place and it shows that the adsorption is successful [18]. Also, Langmuir isotherm studies carried out. Although the high correlation coefficient was high for the Langmuir isotherm for cherry laurel leaves, a lower correlation coefficient was found for the Langmuir isotherm for waste potato peels.

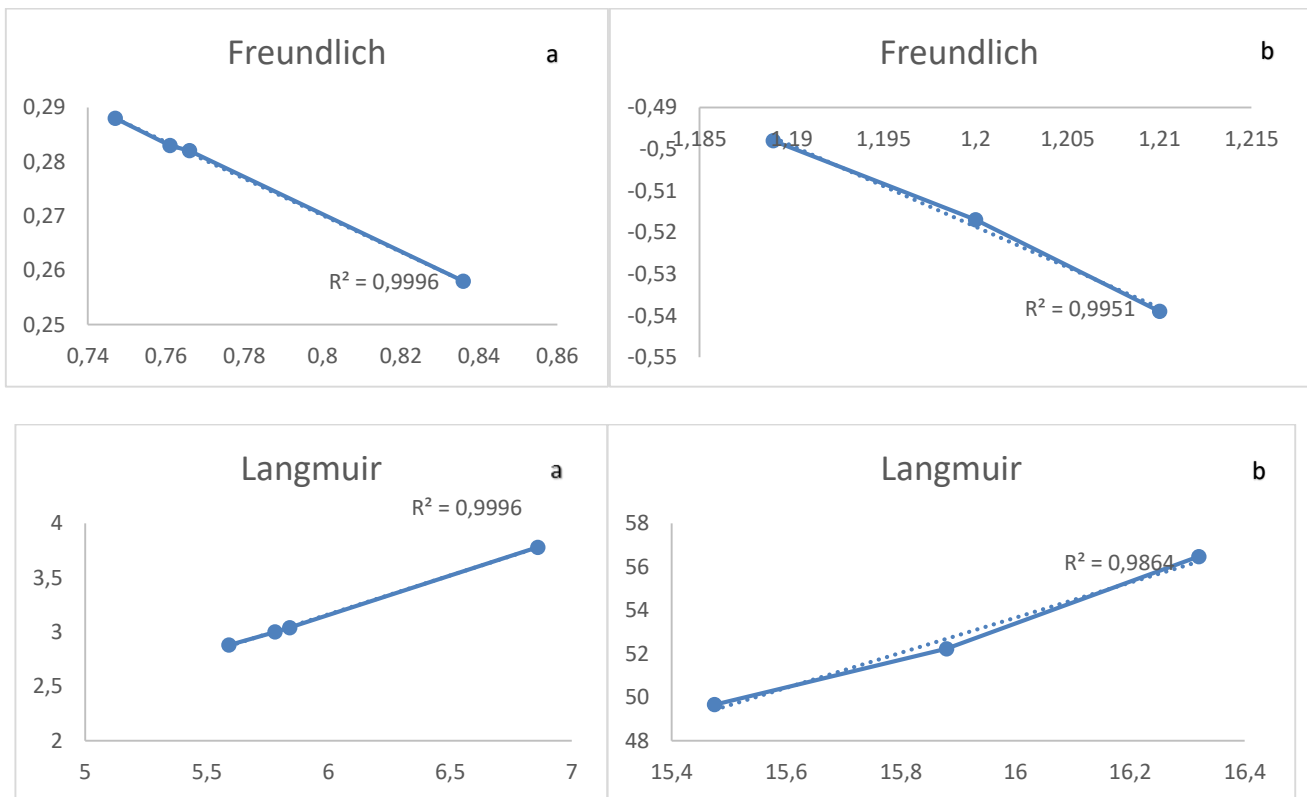


Figure 8. Isotherm graphics

Table 2. Correlation coefficients according to the kinetic model

Adsorbent	First order kinetic	Second order kinetic	Behnjady kinetic model
Cherry Laurel Leaves	0.778	0.776	0.999
Waste Potato Peels	0.984	0.999	0.999

Table 2 shows the kinetic studies. The results show that the Behnjady kinetic model is suitable for both adsorbents.

As can be seen in Table 3, studies in the literature have generally worked with high amounts of adsorbent. The advantage of this study compared to similar studies is that it works at lower adsorbent doses. In addition, dyestuff removal is observed in a short time in this study.

Table 3. Similar studies in the literature

Dyestuff	Adsorbent	Removal Efficiency	Amount of Adsorbent	References
Methylene blue	Rice Straw	91%	1 g/L	[19]
Direct Yellow	Zeolite, wood ash, wood shavings	37%	10 g/L	[20]
Verfix red and Lanasyam brown GRL	Carbon and flyash	100%	10 g/L	[21]
Rodamin B and Malachite Green	Biochar	99.05% and 98.08%	0.1 g/mL	[22]
Malachite green and Methylene blue	Annona skumosa seed	75.66% and 24.33%	0.2 g/50 mL	[23]
C.I.Acid Violet 90 and C.I.Acid Yellow 194	Egg shell	82.3 % and 91.5%	3-25 g/L	[24]

3.8. Cost Analysis

The use of low-cost alternative adsorbents is very important for the environment. Today, the use of adsorbents produced by expensive methods creates an extra burden for the environment and restricts treatment due to some toxic chemicals used in production. The fact that one of the adsorbents selected in this study is a plant grown in nature and the other is a waste food product makes the adsorbent material free. If we take into account only the electricity consumed by the shaker for treatment, the electricity cost is approximately 1,425 TL/kWh *0.09 kWh = 0,12825 TL (excluding taxes) in an hour for May/2023. Since tap water is only used to wash organic materials, there is a consumption of approximately 10 liters. Since 0.2 mL of HCl solution was used per solution to adjust the pH, approximately 25 mL was used in total. According to the current exchange rate, 1 liter of HCl is approximately 665 TL. Therefore, the acid consumption is 17 TL. Thus, it is possible to use Maxilon Yellow 4GL for the removal of dyestuff at a very low cost.

4. CONCLUSION

Maxilon Yellow 4GL removal was done by using leaves of cherry laurel leaves and waste potato peels, and no study was found in the literature in which this dyestuff was removed with the mentioned adsorbents. As a result of a series of experimental studies, the optimum conditions for dye removal were determined as follows: pH, 7; the temperature is 25 degrees; the contact time was 90 minutes and the amount of adsorbent was 1 gram for cherry laurel leaves. The optimum conditions for dye removal were determined as follows: the contact time was 60 minutes, initial concentration was 25 mg/L and the amount of adsorbent was 0.75 gram for waste potato peels. According to the data we obtained, the removal of Maxilon Yellow 4GL, a textile dye, was accomplished with cherry laurel leaves without applying any additional chemical treatment. The highest efficiency was obtained as 80%. In addition, the fact that it is a natural removal is the strongest advantage of this method. For waste potato

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peels, the highest efficiency was 45 %. Although the dye removal efficiency of waste potato peels is lower than other adsorbent, it is thought that the removal efficiency will increase by applying different modifications on it. Here, the adsorbents, which are divided into small pieces, interact with the pollutant and adhere to the surface of the adsorbent. Potato peels appear to have a low effect on the color removal mechanism due to the yellow coloration of the aqueous medium. As a result, under optimum conditions, 76.6% for cherry laurel leaves; 34% removal efficiency was obtained for waste potato peels. There are many pollutants in the content of textile industry wastewater and the main of these pollutants are dyestuffs. These pollutants create a large amount of Chemical Oxygen Demand, especially during dyeing processes, there is a lot of water consumption. For these reasons, the color parameter, which is only one of the parameters that creates the pollution load, was chosen in this study. It is thought that these materials will be studied on the removal of other pollutant parameters in future studies.

SIMILARITY RATE: 10%

CONFLICT of INTEREST

The authors declared that they have no known conflict of interest.

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