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Development of direct blue 15 dye removal combined adsorption process with Bionano-Fenton

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Dye removal processes have gained importance with the developing industries. Among these, the fenton process, known as one of the advanced oxidation processes, is also very important today. In our research, the bionano-fenton catalyst was prepared by attaching nano iron to the polymer prepared using sunflower and chitosan, which are biological materials. Subsequently, using this reagent, it was aimed to remove DB 15 dye from water and this procedure was investigated. For this purpose, determination of optimum time, pH, temperature, fenton reagent and catalyst amounts for dye removal was studied. In addition, different techniques were used to examine the interactions between the obtained bionano-fenton reagent and the dye. In dye removal studies, the maximum absorbance of the dye was found by scanning it with a 598 nm spectrophotometer. In addition, using this method and calculations, optimum time: 15 min., pH: 2 temperatures: 25ºC, H_2O_2 amount: 600 uL (30%), and catalyst amounts were determined as 60 mg/L. It has been shown that 95.89% of the paint can be removed from the environment by using this method. In addition, changes occurring before and after dye removal were explained by SEM, TEM and photographs.

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1. Introduction

Paints used in industries such as textile, plastic, food, paper, leather, cosmetics, medicine, coating, dyeing and printing are among the main sources of environmental pollution, especially water pollution [1]. Considering that approximately half of the dyes produced are azo dyes and 1-10% of these dyes are thrown into the environment without being used in production, the dimensions of the pollution become easier to understand. In fact, the pollution that these industries give to the environment can be easily understood from the colors of the wastewater [2-3]. Due to these dyes and their metabolites, the living conditions of aquatic organisms are negatively affected and environmental pollution can cause mutation, toxic, carcinogenic and teratogenic diseases and deaths in living species. One of the dyes that can cause these effects is Direct Blue 15 [4-5]. Among the dyes used in textiles, color strength is a desired property, and azo dyes are preferred over other dyes due to their different advantages in use. DB15 is used in the textile industry [6] because it has a strong affinity for cellulose fibers. Direct Blue 15, an anionic direct diazo dye, is used to dye cellulose, leather, paper, cotton, silk and wool and to make biological materials visible. DB15 produces carcinogenic amines during degradation. They are the most widely used azo dyes among synthetic organic dyes, and they account for 60-70% of the total dye consumption. Azo dyes are characterized by the azo group in their structure (-N = N-) and the azo group is attached to an aromatic ring. Azo-paint wastes because great problems in their removal from water due to their high color, high organic content, complex composition and poor biodegradability [7-8]. As a result of researches on various dyes, it shows that azo dyes, which are aromatic amines and acrylamides

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and benzamine derivatives in their structures, have serious carcinogenic effects on the metabolism process. For these reasons, removing azo dyes from water is an important environmental approach.

In order to remove these industrial effluents from the environment, various innovative, efficient, cheap and effective colour removal techniques are required. To this end, it has become essential to develop many methods that combine chemical, physical and biological methods, as well as chemical, physical and biological methods. In addition to the characteristics mentioned above in the selection of the method for dye removal, the reactive decomposition products that may be formed during dye removal can cause various types of damage to the environment, and if the reactants used cannot be removed from the water, it is necessary to prevent them from harming the environment. There are studies using microorganisms for this purpose [9].

Many studies have shown that the physical, chemical and biological methods commonly used to remove waste dyes from water are not sufficiently effective in removing dyes. It is therefore important to investigate different methods for removing azo dyes and others from water. Advanced Oxidation Processes (AOP) are used in the Fenton reaction to degrade dye molecules in the presence of metal (iron) and hydrogen peroxide [10]. This method is used in more advanced treatment processes. Fenton processes using such as nano iron are very important research areas today. In reactions like Fenton and Fenton, iron or different metals were also used as an oxidizer (to form OH) H_2O_2 to perform the reaction. With the Fenton reaction, organic contaminants such as DB15 dye can be decomposed and removed from the reaction medium [11-13]. The catalytic power of nanoparticles has been well demonstrated in a variety of fields, and recent advances in bio-inspired synthesis methods have provided a sustainable approach to using these nanoparticles for the degradation of dyes [14-15].

The adsorption technique is widely used, particularly for the removal of dyes from textile industry wastes. One of the main reasons why this method is preferred is to remove the dyes to be removed from the environment and the reactants remaining in the reaction medium. For this purpose, high surface area absorbents such as activated carbon and clay are widely preferred [16]. Another group synthesized Fe3O4poly(methacryloxyethyltrimethylammonium chloride) to remove a DB15 dye from water. Using this absorbent, they explained the adhesion of the dye to the surface using equations[17].

As a result of our research, we have seen that DB15 dye is tried to be removed from wastewater by using different and combined procedures. Together with our research group, we aimed to use iron nanoparticles synthesized in an environmentally friendly approach and to use them as fenton reagent by binding them on the waste material sunflower and chitosan in the same way. Using the bionano-fenton reagent we obtained, we aimed to effectively remove the dye DB15 from water. This method aims to remove both the azo dye DB15 and its degradation products, the reactants, from water.

2. Material and method

2.1. Supply of chemicals and plant materials

In this study, the sunflower (*Helianthus annuus*) plant was used for the green synthesis of bionano-fenton substances as Turgut et al. Sunflower and *Euphorbia amygdaloides* were grown in the Dr. Alayli gardens of Erzurum City. The plants were collected in September, washed with pure water, dried and then stored in the deep freezer (20°C) until use. The bowl part of the sunflower was dried in the oven at 40 °C and turned into powder with the help of a blender. *Euphorbia amygdaloides* plant was used for the green synthesis of iron nanoparticles added to bionano-fenton catalyst [18]. Chemicals used in the studies and Direct Blue 15, ≥%40 were obtained from Merck and Sigma Aldrich companies. Solutions were prepared using purified water.

Iron oxide nanoparticles were synthesized by green synthesis method using *Euphorbia amygdaloides* plant as reducing and stabilizing agent. Nano-iron oxide in the size range of 30-80 nm was synthesized under the same conditions using the method of Turkoglu et al. [19].

Bionano-fenton reagent to be used in the study was prepared by using sunflower waste material and chitosan like Turgut et al, and then used after being modified with iron nanoparticles synthesized by green synthesis method. The plan was to synthesize a high surface area absorbent from sunflower waste and chitosan, and the environment required for the Fenton reaction was naturally created by adding nanoiron to the reaction vessel during synthesis. For the Fenton process, studies have been carried out to determine the optimum conditions by adding bionano-fenton catalyst and H_2O_2 to the reaction medium. Optimizing the bionano-fenton reaction where DB15 dye is best removed; temperature, pH, catalyst amount, dye concentration and hydrogen peroxide H_2O_2 concentration parameters were examined separately and optimum conditions were determined. FT-IR, XRD, SEM and TEM analyzes were used to show the changes in the surface and structure of the catalyst before and after dye removal. In addition, dye removal was shown by photographing visually [19-20].

3. Results and discussion

In this study, the sunflower plant waste, chitosan, nanoiron and H_2O_2 were used for the removal of DB15 dye from water. For the same purpose, The Fenton reaction was used to remove DB15 dye from water by Sun et al. [2]. Hassan et al. were used for the removal of DB15 dye with bimetallic iron/copper nanoparticles loaded on bentonite clay as heterogeneous catalysts with the use of eucalyptus leaf extract [21].

3.1. Dye removal

In the experimental stage, absorbance values were measured using UV-spectrophotometer. For DB15, the wavelength of the dye to be studied was determined as 598 nm by scanning between 400-800 nm in fig. 1a. The amount of dye was calculated using the dye amount absorbance chart for DB15 and the following equation was used to calculate dye removal (%)(Figure 1b).

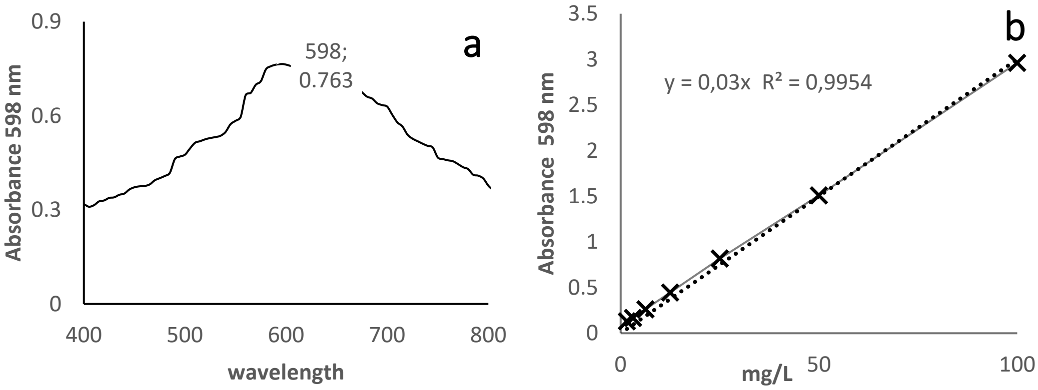

Fig. 1. (a)Wavelength scan and (b) standard curve of the DB15 dye.

$$\%Dye\ removing = \frac{Co-Ct}{Co} \tag{1}$$

Co: Dye absorption
Ct: Result dye adsorption

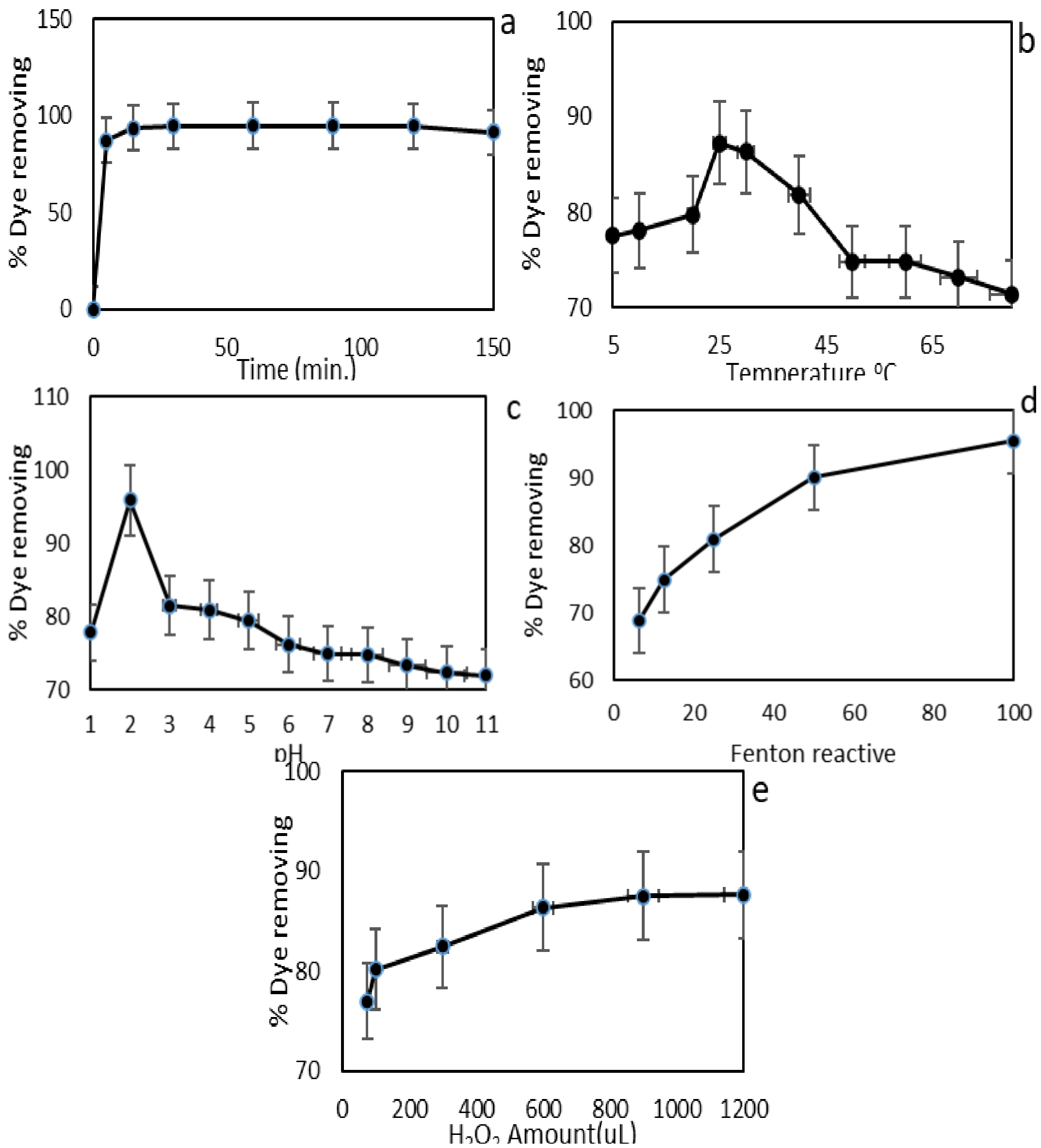

Fig. 2. Determination of optimum conditions for bionano fenton reaction

In order to determine the effect of contact time on the bionano-fenton of dyestuffs and to determine the optimum contact time, samples were taken from the reaction medium at regular intervals for 150 minutes and the absorbance value was read using a spectrophotometer. By using the data obtained, the dye removal was calculated with the help of equation (I), as a result, it was understood that the dye was removed in a very short time such as the first 15 minutes (Fig 2a). In order to determine the most suitable temperature at which we can provide dye removal, samples were taken from the reaction mediums set up at different temperatures and measurements were made with the help of a spectrophotometer at 589 nm and the dye removal values were calculated.

As a result of the investigations, it was understood that the maximum efficiency occurred at a temperature close to room temperature, which is a moderate condition such as 25 °C. This shows that the bionano-fenton reagent designed for the dye removal systems planned to be installed is highly preferable in Fig. 2b. In our study, it was observed that the bionano-fenton reaction of 25 mg/L direct blue dyestuff by Fenton reaction reached 95.89% in a shorter contact time of 30 minutes. Hassan et al., were examined combined method for removing DB15 dye. As a result of this work, 100 mg/L of DB15 was completely degraded within 60 min. with optimum pH 3.5, H_2O_2 dosage of 7.5 µmol/L, and UV intensity of 15 W/m^2. Sun et al were found the optimal conditions for the decolorization of DB15 were determined as pH = 4.0, H_2O_2, 2.8 μmol/L, and temperature, 30 °C [2,3].

In figure 2c, the reaction results for determining the best pH for dye removal are shown. Samples were taken from the established reaction media between pH 3.0 and 11.0, and the absorbance was measured, and the pH was determined as 2, where maximum dye removal was achieved. In order to determine the appropriate amount of bionano-fenton reagent for dye removal, reaction environments using different amounts of reagent were established and it was determined that the best removal would be obtained as a result of the reaction using 60 mg/L catalyst (fig 2d). It is very important to determine the efficiency of the bionano-fenton reaction in determining the amount of H_2O_2 used as an oxidation agent in the experimental environment. For this purpose, 0-1200 ul of oxidation agent was added to the reaction medium and then the % amount of the dyes removed in the reaction medium was calculated and it was observed that the best dye was removed in the medium with 600ul 30% H_2O_2 added in fig 2 e. Different methods were used to understand the interaction of the biofenton reagent and the dye. Using optimized method and calculations, optimum time: 15 min., pH: 2 temperatures: 25°C, H_2O_2 amount: 600 uL (30%), and catalyst amounts were determined as 60 mg/L. It has been shown that 95.89% of the paint can be removed from the water. In their research, Li and his group aimed to remove methylene blue and rhodamine B dyes with lignin-based magnetic adsorbents and investigated their adsorption properties. In this study, in contrast to our experiments, it was found that maximum removal was achieved at basic pH [22].

The group working on dye removal from water by the Fered-Fenton method carried out the Fenton reaction by applying electric current to the environment through electrodes and found that 90% colour removal was achieved by this process [23]. The group investigating the method using DB15 dye, ultrasonic irradiation and Fenton together achieved 99% colour removal [24].

After the dye removal process was carried out by determining the optimum conditions, the absorbent used in the absorbent and bionanofenton reaction was filtered through filter paper and dried in an oven at 30 ^{0}C for 48 h. to determine the change on the surface. FT-IR, XRD, SEM and TEM chromatographies were used to examine how DB 15 dye changes the adsorbent surface and morphology, and the results are shown below.

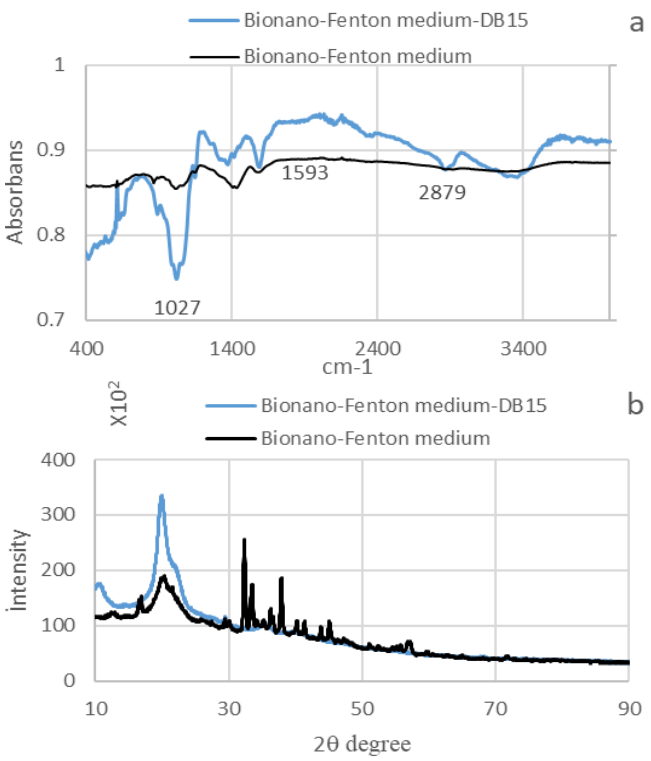

Fig. 3. (a) FT-IR spectra of absorbents 3(b) XRD spectra of adsorbents

FT-IR 3(a) and XRD 3(b) spectra were compared to investigate how the structure of the biosorbent entering the Fenton Reaction and subsequently changing with the dye on the surface changes. When the FT-IR spectra are examined, spectra in the range of 2800-3000 cm^{-1} for the DB15 dye show the characteristic N-H and CH aromatic stretching vibration bands around 2879 cm^{-1}. The N=N-bonded aromatic rings of the dye-derived azo cluster, generally attributed to C=C, appear around 1593 cm^{-1}. Several bands attributed to N-H and CH bending vibrations were also observed at around 1460-1300 cm^{-1}. The interaction formed by the absorption of the dye on the surface and the intermediates formed by Fenton could not affect the properties of the double bonds and enhanced the properties of the single bonds. The result is a broad band at 1027 cm^{-1}. [16]. In Figure 3(b), the XRD spectrum of the absorbent before the bionano-fenton reaction and the absorbent whose surface was covered with dye after the reaction was completed were taken and compared. It was understood that the intense dye peak around 20 θ degree was caused by DB 15 dye.

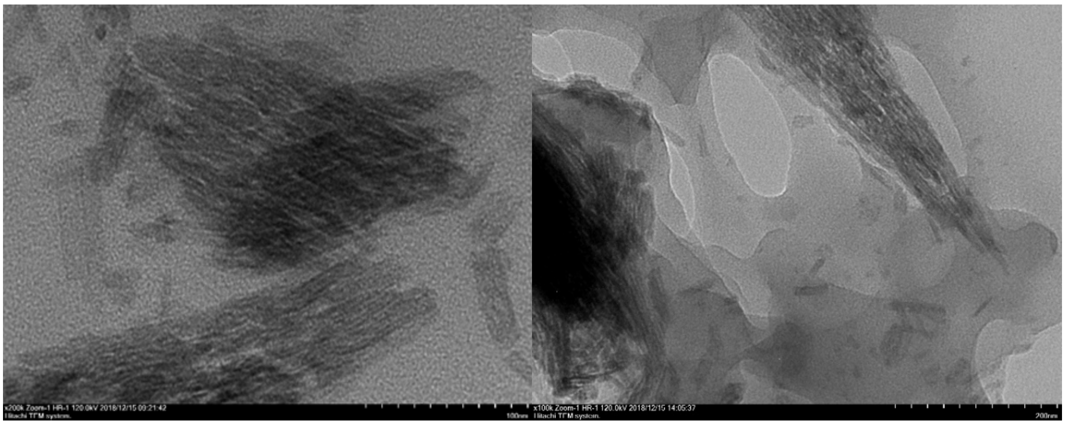

Fig. 4. (a) TEM image of CS-DB15, (b) CS-DB15 after bionano-fenton reaction

First, the TEM image of the surface of the bionano-fenton reagent was taken and then the TEM image showing the interaction of the bionano-fenton reagent with the dye was obtained as a result of the reaction established under optimum conditions. As a result of the TEM analysis, the interaction of the paint and the surface is clearly seen in figure 4 a,b.

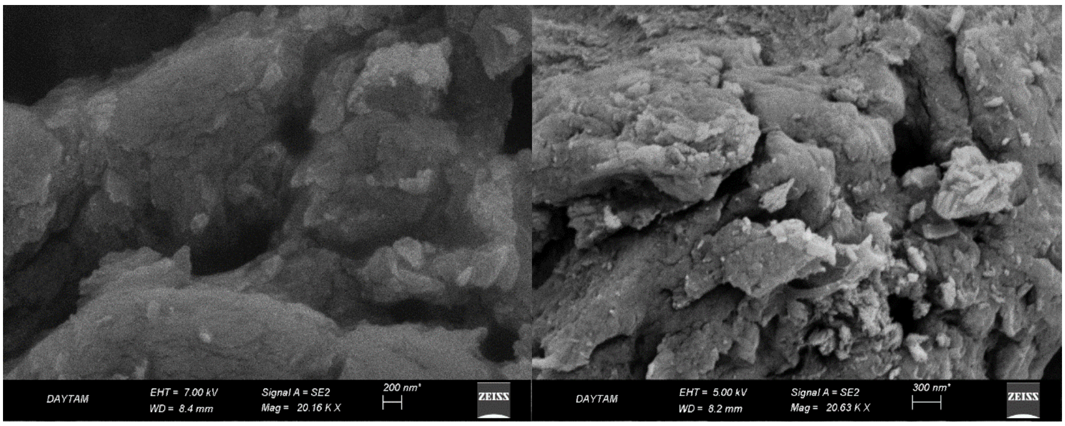

Fig. 5. (a) SEM image of CS-DB15, (b) CS-DB15 after bionano-fenton reaction

With a different method, SEM analysis was applied to better understand the surface change occurring between the bionano-fenton reaction catalyst, chitosan sunflower iron, chitosan sunflower iron H_2O_2 and dye, at nanoscale. As a result of the analyses made, the surface change of the biocatalyst is clearly seen from figure 5 a,b.

(a) *(b)*

Fig. 6. (a) Image of DB 15 (50 mg/L) dye, (b) Image of the DB15 after removal with bionano fenton process.

The initial DB 15 (50 mg/L) dye image is shown in figure 6a. At the end of the reaction, after the bionano-fenton catalyst was filtered and separated from the reaction media established with the reagent in the optimum conditions determined for the experiment, the dye removal was shown as in the photos below when the pictures were taken (Figure 6 a. b).

4. Conclusions

The fact that the green synthesis method is safe, waste-free and has many advantages, such as the use of renewable resources, is very important in terms of waste management in our country, which is rich in agricultural products. This material can be used much more effectively than commercially available absorbents shows that the bionano-fenton reaction we have produced can effectively remove dyes, which shows that it can have commercial applications. In addition, dye removal in the Fenton reaction can be effectively carried out using the catalyst we have synthesized. They also have superior properties such as dye regeneration and prevention of environmental pollution of the bionano-fenton catalyst.

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