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Optimizing the Operational Parameters of Nanographene-based Cathode Electrode in Electro-fenton Process for Treatment of Textile Industry Wastewater Containing a Mixture of Dyes

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Abstract

This study aimed to evaluate the effectiveness of the electro-Fenton process in the treatment of textile wastewater using carbon felt modified with graphene nanoparticles as the cathode and a thin film of platinum as the anode. The primary characteristics of wastewater, including COD, color, BOD₅, pH, electrical conductivity (EC), and chlorides, were measured. Factors affecting the efficiency of the electro-Fenton process were studied. The optimum conditions were determined as follows: the inlet airflow of 1 (L/min), pH=2.5, the current intensity of 200 mA, and ferrous ion concentration of 1.5 mM. Based on the results maximum system decolorization and COD removal rates were 94.31% in 120 minutes and 57.47% in 30 minutes of reaction respectively. Dye removal efficiency increases due to graphene particles on the carbon felt and increasing surface area. Also, the application of the platinum electrode and the role of this electrode in anode oxidation causes an increase in the efficiency of dye removal. Because the electro-Fenton process is carried out at acidic pH, it is necessary to conduct pH modification on the final effluent of this process.

Keywords: Electro-fenton, Textile Sewerage, Dye, Cathode Electrode, Nanographene, Carbon Felt

1. Introduction:

Water wastage is a serious problem worldwide, due to the massive consumption of water in industrial and agricultural sectors. As one of the important chemicals, dyes are extensively used in different industries such as textiles, paper, cosmetics, and food. The textile industry is one of the largest consumers of water and chemicals, which subsequently discharge huge quantities of dye wastewater to the reservoirs [1].

Discharged effluents from textile industries are a mixture of different dyes that differ in quality and quantity [2]. Various physical, chemical, and biological methods have been used to treat textile wastewater [3]. Textile wastewaters resist to conventional biological treatment methods due to the complex molecular structure of synthetic dyes and the low ratio of Biochemical Oxygen demand to Chemical Oxygen demand (BOD / COD) ratio [4, 5]. On the other hand, physiochemical methods such as

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filtration, adsorption, ion exchange, etc. are not able to decompose and degrade colorants completely which results in a considerable amount of sludge and causes secondary contamination that needs to be managed [6, 7]. Therefore, creating and developing a treatment and decolorization method to protect water resources is very important.

Studies show that advanced oxidation processes (AOPs) effectively remove toxic and resistant compounds, including dyes, from textile wastewater based on the production of free hydroxyl radicals with high oxidation potential [4, 5, 8].

Electrochemical-assisted advanced oxidation processes (EAOPs) have recently been considered in wastewater treatment with the ability to generate in-situ hydroxyl radicals through electrochemical procedures with no primary toxic reactants in a controlled atmosphere. Among these, the electro-Fenton process is widely recognized as one of the most frequently employed EAOPs due to its notable efficiency in the degradation and mineralization of pollutants [9].

The nature of this process involves the electrochemical production of H_2O_2 in an acidic environment through the reduction of two O_2 molecules in a carbon cathode electrode and then the catalytic decomposition of hydrogen peroxide to hydroxyl radical by Ferrous ion (Fe^{+2}) [10].

The produced hydroxyl radicals can cause the non-selective decomposition of organic pollutants and organically based metals to complete mineralization, converting the dye to carbon dioxide, water, and mineral ions [11].

Electro-Fenton processes are desirable because of their high oxidation power. Nevertheless, their effectiveness is significantly restricted by the low pH levels required for the procedure and elimination of iron compounds previously introduced to the system [12]. This process is also affected by parameters such as current intensity, catalyst concentration, reaction time, pH, and cathode material [13].

Carbonaceous materials are widely used in electro-Fenton systems due to their non-hazardous nature,

high conductivity, and stability [14].

Carbon felt also exhibits a conspicuous level of efficacy as a result of its 3-D structure, numerous surface-to-volume ratios, and remarkable specific area and has been used widely as the cathode in electro-Fenton systems [13].

On the other hand the remarkable electrochemical properties of Graphene, such as rapid electron transfer rates and high conductivity; serve it as a promising candidate for utilization as an electrode material [15].

In this study, graphene nanoparticles were employed to modify carbon felt electrodes; an action anticipated to augment both the specific surface area and the electrochemical performance related to oxidation-reduction processes within the cathode of the electro-Fenton framework. The impact of the modified carbon felt material on the cathode plates was investigated. Various factors including electric current intensity, amount of catalyst, reaction time, pH, as well as air flow were analyzed in relation to COD and dye removal efficiency.

2. Material & method:

2.1. Chemicals:

Sulfuric acid, ferrous sulfate, sodium hydroxide, phenanthroline monohydrate, and ammonium Ferro sulfate were provided by Merck, and silver sulfate, mercury sulfate, and potassium dichromate were purchased from Sigma Aldrich USA.

2.2. Sampling and sample transfer :

Sampling was performed on the day when a mixture of several different colors was used from the output of the yazdbaf textile factory. At the time of sampling, the factory's production conditions were examined regarding the type of dyes used. The pH and temperature of the effluent were also measured. The samples were collected according to the standard methods [16] in plastic containers and transferred to the laboratory away from sunlight. The samples were examined for physicochemical properties immediately after transfer to the laboratory. It should be noted that the samples were kept at 4 ° C before performing the necessary tests.

2.3. Tests to determine the physicochemical properties of wastewater:

All tests related to wastewater's initial properties including COD, BOD, Color, total suspended solids (TSS), electrical conductivity (EC), and chloride, were performed in accordance with the procedures established in the standard methods for the examination of water and wastewaters [16]. The color concentration was measured using the American Dye Manufactures Institute (ADMI) method and HACH-DR5000 spectrophotometer. Experiments were repeated twice for each parameter, and finally, 14 experiments were performed.

2.4. Fabrication of carbon felt cathode electrode modified with graphene nanoparticles:

Graphene nanoparticles were purchased from the Nano Research Institute of the Sharif University of Technology. These nanoparticles were coated on carbon felt. For this purpose, 0.1 g of graphene nanoparticles with 0.42 g of polytetrafluoroethylene powder were dissolved in 60 ml of distilled water containing 3% by volume of n-butanol. The sample then was transferred to an ultrasonic bath for 20 minutes to homogenize and obtain a uniform solution. The sample was then mixed at 80 °C until a clear oil solution was obtained. A piece of carbon

fiber with dimensions of 9*10 cm was prepared. First, this piece of carbon was soaked in the prepared oil solution for 15 minutes. The bonded fabric with graphene nanoparticles was then exposed to 350 °C for 30 minutes.

2.5 Dye removal experiments:

Before performing the test, the samples were filtered through a 0.45-micron filter to eliminate any potential interference from impurities. The optimal pH in most studies of the electro-Fenton process is 2.8-3. First, the sample's pH was adjusted using 0.5 M sulfuric acid (H_2SO_4) and 0.5 M NaOH. To study the electro-Fenton process, a split cell with a volume of 250 ml for a 200 ml sample of textile wastewater was used at ambient temperature. A modified carbon cathode electrode with graphene nanoparticles measuring 10*9*0.3 cm was installed in the cell's inner wall.

Commercial platinum with dimensions of 1*2 cm was used as an anode in this study. The platinum electrode was placed in the center of the cell at 3 cm from the cathode electrode. Zhaoxin 5A, 60V digital power supply was used to supply electricity. The air required for injection into the cell was supplied through a ceramic splitter and an SKC air pump. The amount of incoming air was measured using a flow meter during the process. The experimental setup scheme is shown in Figure

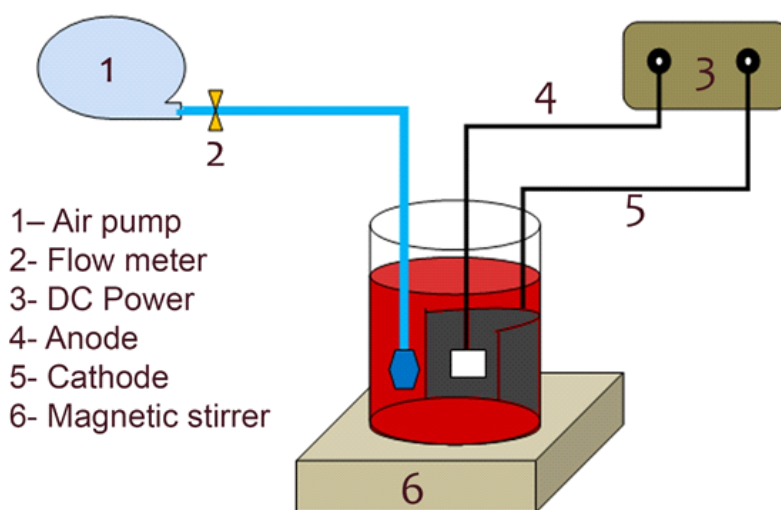


Figure 1. Schematic diagram of the electrochemical reactor

Before electrolysis, the sample was aerated for 10 minutes to increase the dissolved oxygen concentration. Then a certain amount of Ferro ion was added to the sample using ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to combine with the produced hydrogen peroxide to form hydroxyl radicals. During the process, the solution was mixed with a magnetic stirrer. After applying the electric current and performing the reaction at the desired time, the applied electric current was cut off. The reactor was sampled, and the dye was measured using a spectrophotometer to determine the percentage of dye removal.

3. Results and discussion:

3.1. Real textile wastewater statistics:

Textile industry wastewater contains various compounds due to the consumption of many types of dyes and chemicals. The basic specifications of Yazdbaf Textile Factory wastewater are given in Table 1. The BOD/COD ratio in the textile industry's wastewater is low (0.15).

Due to synthetic dyes' complex and resistant nature, conventional treatment methods, including biological and physicochemical methods, are ineffective in removing dyes from wastewater [4, 5]. So developing effective and efficient methods is needed to remove the dye from the sewage.

Table 1. Initial parameters of Yazdbaf Textile wastewater

Parameter	Amount
COD	1150 mg/l
BOD ₅	175 mg/l
BOD/COD	0.15
color	3780 ADMI
EC	3.73 ms/cm
pH	8.2
TSS	25.6 mg/l
cl ⁻	1140 mg/l

3.2. Deposition of Graphene Nanoparticles On Carbon Felt:

As is evidenced in the electron microscope images shown in Figure 2, graphene nanoparticles are well placed on carbon fibers due to the porous structure and interstitial void of fibers. Graphene nanoparticles were homogenously dispersed on the surface of the fiber of carbon felt. The results exhibit vast differences in the surface morphologies of modified and pristine carbon felt fibers. Coating nanoparticles with carbon felt fibers led to an increase in the specific surface area of carbon felt and improved its conductivity. The modified carbon felt fibers showed much better performance than pristine carbon felt electrodes in the removal efficiency due to increased hydrogen peroxide produced in the process.

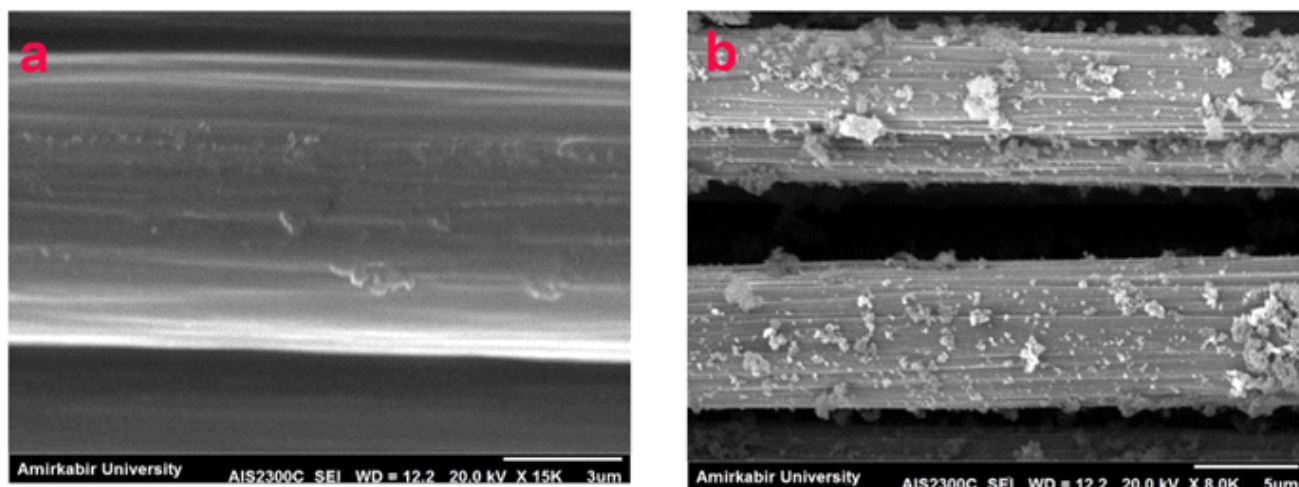


Figure 2: SEM images of carbon felt: (a) Unmodified carbon felt, (b) Modified carbon felt with graphene nanoparticles

3.3. Effect of airflow on dye removal efficiency:

Oxygen is one of the main limiting factors in the electro-Fenton process. Increasing the amount of air entering the solution results in the higher oxygen transfer rate which ultimately leads to increased production of hydrogen peroxide. The dissolved oxygen of the sample is converted to H₂O₂ by cathodic reduction according to the following

reaction (reaction1) [5, 11].



As illustrated in Figure 3, the dye removal efficiency has also increased by increasing the inlet airflow rate from 0.2 to 1 (L/min) in the presence of 2 mM Ferro, the current intensity of 200 mA, pH = 3 in 30 minutes. The highest color removal efficiency was reached at 88.82% in the inlet airflow rate of 1(L/min)

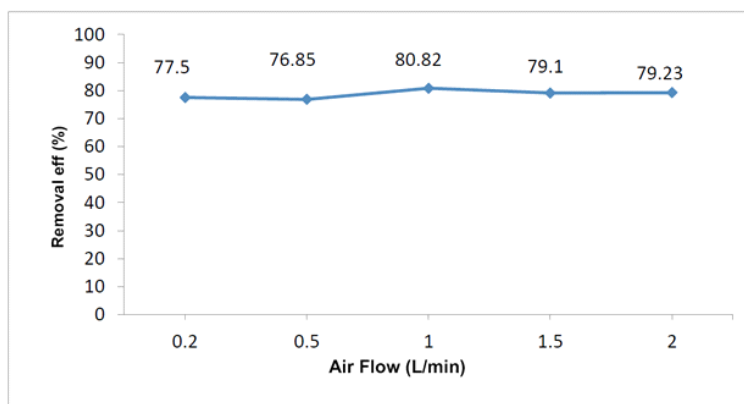


Figure 3. Effect of incoming airflow on dye removal in textile wastewater treatment under optimal conditions (current intensity 200 mA, ion Ferro concentration 2 mM, pH = 3 in 30 minutes)

3.4. Effect of pH on dye removal efficiency

Since the best pH range for the Fenton process is 2-4, the dye removal efficiency was measured in this range. Dye removal efficiencies at pH values of 2, 2.5, 3, 3.5, 4, and 7 were 80, 88.34, 87.69, 83.9, and 75.92%, respectively (Figure 4). The maximum dye removal was reached at pH 2.5, and this pH was considered as the optimal pH in the following steps. This result is consistent with the results of Brillas et al. In 2003 [17] and Zhu et al. In 2007 [18] on the degradation of organic pollutants by the electro-

Fenton process. The optimum pH in their studies was valued as 3.

Also, the optimal pH in our study is very close to the optimal pH of 2.8 in a study conducted by Sean and Pignatella in 1993 [19].

As the pH increases, it is observed that the color removal efficiency decreases. This is due to the reduction of OH radical oxidation potential. Also, ferric hydroxide formation at high pH prevents the regeneration of Ferro ions and thus prevents the production of more hydroxyl radicals [20].

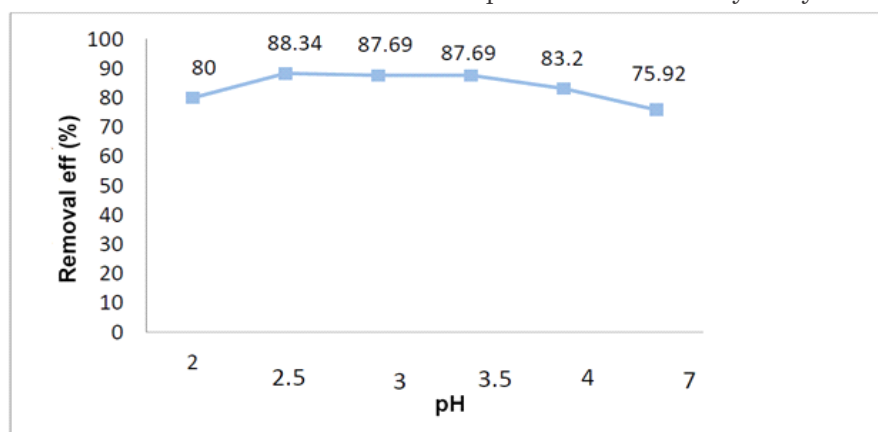


Figure 4. Effect of pH on dye removal in textile wastewater treatment under optimal conditions (inlet air 1 liter per minute, current intensity 200 mA, ion Ferro concentration 2 mM and time 30 minutes)

3.5. Effect of current intensity on dye removal efficiency:

To investigate the effect of current intensity on the electrochemical production of hydrogen peroxide different current intensities in the range of 60-500 were considered. As it is shown in Figure 5 the dye removal efficiency increases with increasing current intensity. The dye removal efficiency increased from 82.8% at 60 mA to 91.26% at 200 mA as a result of increase in hydrogen peroxide production. After the current intensity of 200, the dye removal efficiency gradually decreases. This

may be due to the decomposition of hydrogen peroxide as the result of oxidation of hydrogen peroxide in the electrode according to reactions (2) and (3). Spontaneous decomposition of hydrogen peroxide produced in solution may also occur according to reaction (4) [21].

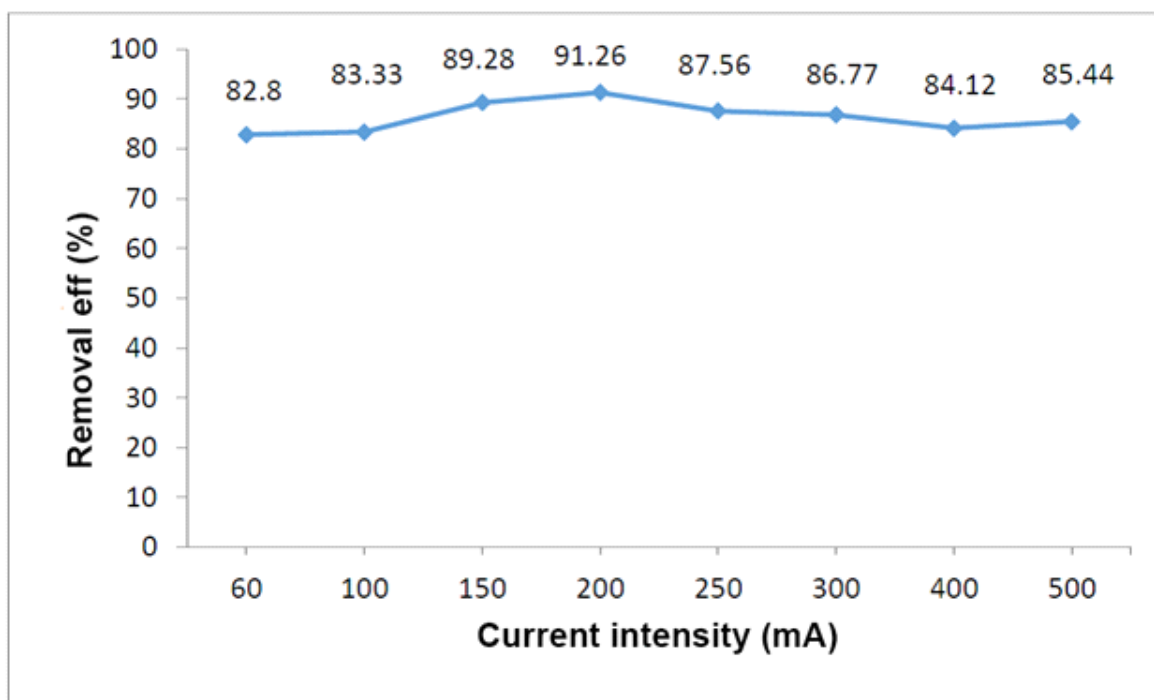
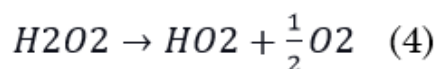
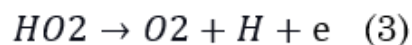
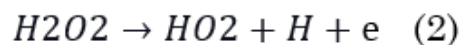


Figure 5. Effect of current intensity on dye removal in textile wastewater treatment under optimal conditions (inlet air 1 liter per minute, pH 2.5, ion Ferro ion concentration 2 mM and time: 30 minutes)

3.6. Effect of Ferro ion concentration on dye removal efficiency:

The efficiency of the electro-Fenton process is greatly affected by the concentration of ions because hydrogen peroxide alone cannot oxidize organic pollutants. The addition of ferrous ions causes the formation of hydroxyl radicals. According to Figure 6 the dye removal efficiency increased with increase of Ferro ion concentration from 0.5 to 1.5 mM.

The highest dye removal efficiency was 94.84% obtained in optimal conditions; the airflow rate was

1 liter per minute, pH = 2.5, the current intensity was 200 mA, and the Ferro ion concentration was 1.5 mM. After that, with the increase of Ferro ion concentration, the dye removal efficiency gradually decreases until it reached to 80.55% at the concentration of 6 mM Ferro ion. This decrease in dye removal efficiency may be related to the consumption of hydroxyl radicals by additional ferrous ions (reaction 5) [22, 23].



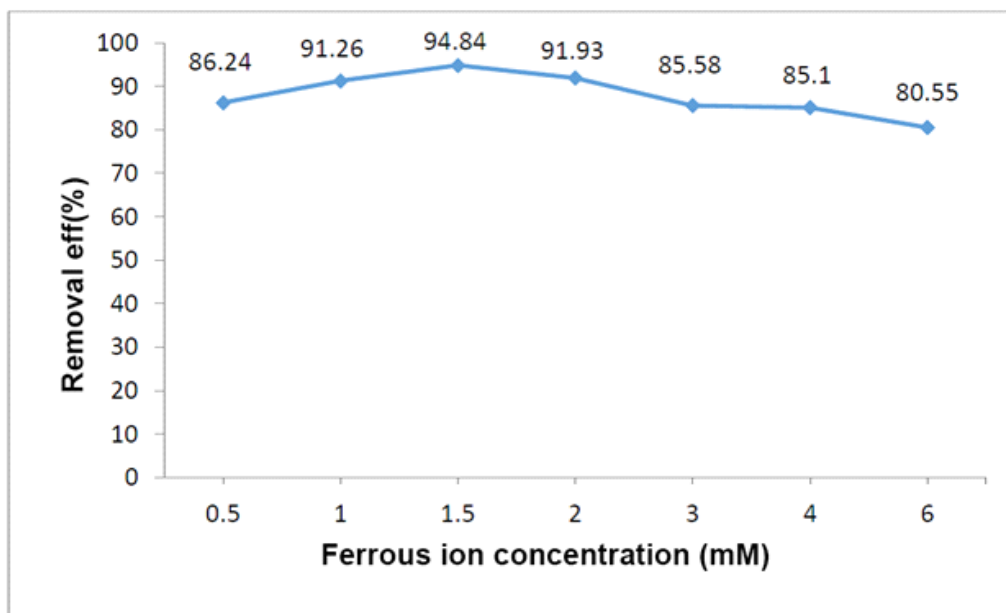


Figure 6. Effect of ferrous ion concentration on dye removal in textile wastewater treatment under optimal conditions (inlet air 1 liter per minute, pH 2.5, current intensity 200 mA, time: 30 minutes)

3.7. Effect of reaction time on dye removal efficiency

The color removal efficiency was examined at different times of 30, 60, 90, 120, and 150. The Effect of reaction time on dye removal and the reduction of COD is represented in Figures 7 and 8 respectively. As it is shown in Figure 7 with the increase of reaction time the color removal efficiency also

increased. The removal efficiency rose from 83.87% in 30 minutes to 94.31% in 120 minutes. After that, there was not much change in the removal efficiency, and 120 minutes was considered optimal in the dye removal process. As it is depicted in Figure 8 at 90 minutes, a drop in the curve is observed which may be due to the intermediates that are generated due to the decomposition of dye molecules.

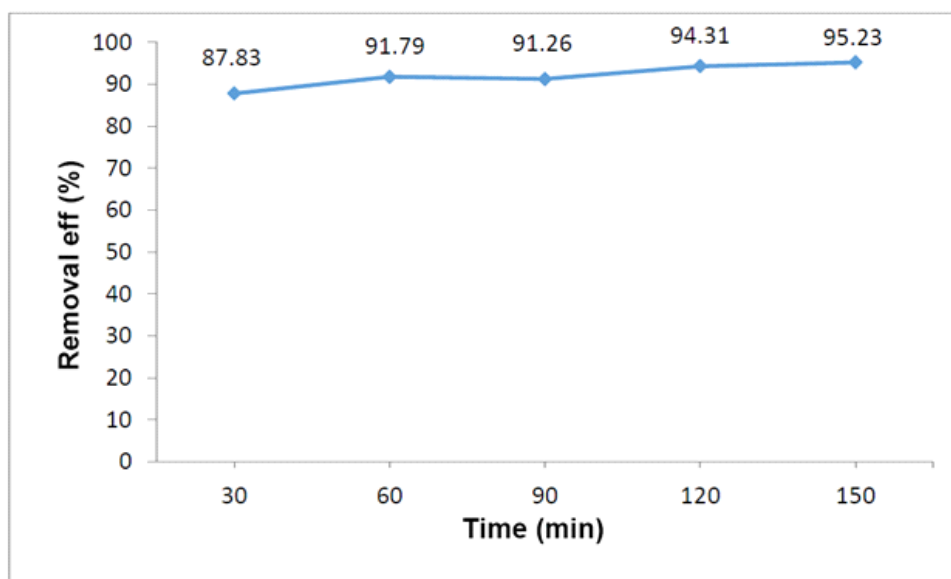


Figure 7: Effect of reaction time on dye removal in textile wastewater treatment under optimal conditions (inlet air 1 liter per minute, pH = 2.5, current intensity 200 mA and Ferro ion concentration 1.5 mM)

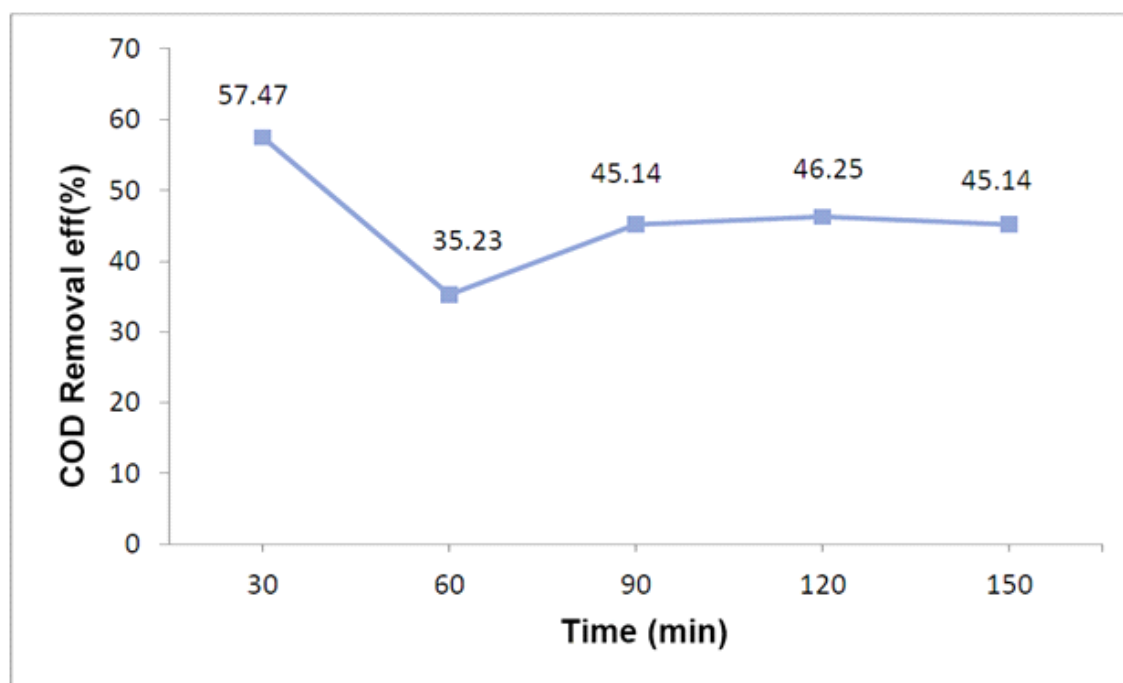


Figure 8. Effect of reaction time on the reduction of COD in textile wastewater treatment under optimal conditions (inlet air 1 liter per minute, the current intensity of 200 mA, pH = 2.5, and ion Ferro concentration of 1.5 mM)

3.8. Removal efficiency with raw carbon felt, and carbon felt modified with graphene nanoparticles:

To assess the effect of the modification of carbon felt with graphene nanoparticles in the treatment of textile wastewater by an electro-Fenton process the dye removal efficiencies were compared before and after of modification of carbon felt. The efficiency reached in the use of modified carbon felt was 94.31 while using raw carbon felt to remove the dye showed 56.3% efficiency.

3.9. COD removal efficiency:

COD removal efficiencies were measured at different 30, 120, 90, 60, and 150 minutes. The highest COD removal efficiency was 57.47 % in 30 minutes and after that little change in COD is observed over time. This may be due to the influence of unknown factors in the wastewater sample. In similar studies, however, the COD removal efficiency increases over time [24].

4. Conclusion

The electro-Fenton process is an effective and efficient technology and environmentally friendly for removing dye from industrial wastewaters. In

this study, the efficiency of dye removal using carbon felt modified with graphene nanoparticles was investigated. The results showed that when this synthesized material was used in the cathode electrode, due to the influential role of carbon felt and also due to the presence of graphene nanoparticles, the production of hydrogen peroxide, and thus the dye removal efficiency increased. The use of a platinum electrode and the role that this electrode plays in the oxidation anode also increases the dye removal efficiency.

The results showed that if the amount of airflow to the sample was 1 liter per minute, pH = 2.5, the current intensity of 200 mA, and the concentration of Ferro ions was 1.5 mM, we achieved 94.31% dye removal efficiency in 120 minutes.

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Declarations:

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