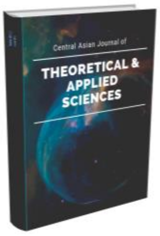

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Article

Degradation of Acidic Dyes by Advanced Oxidation Processes

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Abstract: This study looks at how acid dyes, often used in the textile industry, break down using advanced oxidation processes (AOPs) like the hydrogen peroxide (H_2O_2) system and the H_2O_2/UV system. The research evaluates the efficiency of these processes in breaking down dye molecules, which reduces their environmental impact when released into wastewater. The H_2O_2/UV system, which combines hydrogen peroxide with ultraviolet light, generates highly reactive hydroxyl radicals that enhance degradation. Researchers analyzed key parameters like dye concentration, pH, reaction time, and the dosage of H_2O_2 to determine optimal conditions for effective dye removal. The results indicate that the H_2O_2/UV system works better at breaking down dyes than using H_2O_2 by itself, making it a good option for cleaning wastewater with industrial dye pollution. This research looks at how Advanced Oxidation Processes (AOPs) can remove and break down acidic dyes in polluted water by examining different factors, like the kind of oxidizing agent used, the pH level, the concentration of the dye, and how long the treatment lasts to make these processes more effective and lessen the environmental harm from pollutants.

Keywords: Acidic dyes, Environmental impact, AOPs, UV, H2O2

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1. Introduction

Water pollution with dyes is a significant environmental issue, especially in areas with heavy industrial activities, such as textiles and dyeing industries. These dyes can be synthetic or natural, often finding their way into water bodies through various discharge points. The dying process is one of the most significant contributors to dye pollution. During the dyeing process, large quantities of water are used, and a substantial amount of dye is often released into wastewater. Similar to textiles, the leather industry uses various chemicals and dyes that can contaminate water sources. Some dyes and pigments used in paper production can also contribute to water pollution. Cosmetics and pharmaceuticals production and consumption can also be a source of pollution of water systems [1].

Dyes can be toxic to aquatic life as many dyes are not biodegradable and can persist in the aquatic environment, affecting the health of ecosystems. Contaminated water can pose serious risks to human health, mainly if it is used for drinking or irrigation. Many dyes can be carcinogenic or have other adverse health effects. Water bodies with high dye concentrations can become discolored, affecting their aesthetic appeal and usability for recreational activities [2].

Industrial effluents can be treated using pre-treatment processes to remove dyes before wastewater is discharged. This might include physical, chemical, or biological treatments. Traditional wastewater treatment methods have been used for centuries and form the basis of many modern wastewater treatment systems [3]. These methods typically involve a series of physical, chemical, and biological processes to remove contaminants from wastewater. These methods can be used alone or in combination, depending on the specific requirements and characteristics of the treated wastewater. Modern techniques often build on these traditional methods, incorporating advanced technologies to improve efficiency and effectiveness [4].

Recently, attention has been concentrated on utilizing extremely effective "advanced oxidation processes (AOPs)" techniques to eradicate persistent organic contaminants from polluted water. In advanced oxidation processes (AOPs), the oxidative destruction of organic pollutants is facilitated by the production of hydroxyl (•OH) radicals using a combination of ultraviolet light (UV), semiconductor photocatalysts, ozone, hydrogen peroxide, ultrasound, and Fenton reagents [5].

The oxidation potential of the hydroxyl radical ("•OH) is 2.85 eV. This value exceeds the oxidation potentials of ozone (2.07 eV), hydrogen peroxide (1.77 eV), and hypochlorous acid (1.49 eV") [6]. Consequently, •OH radicals are highly reactive oxidants that break down almost all organic molecules into benign inorganic products, including water and carbon dioxide. In practical terms, •OH radicals cannot persist for extended periods under typical environmental circumstances. Ultraviolet light may degrade organic molecules, enhancing the oxidative capacity of free radicals due to its short wavelengths of less than 287 nm, which can cleave organic C-H bonds [7]. A significant number of AOP research studies have used "H_2O_2/UV" procedures [8;9], photocatalytic processes [10], and AOPs grounded in Fenton [11;12], electro-Fenton [13;14], and photo-Fenton [15;16] methodologies. Combinations of various oxidants with ultraviolet light are frequently employed to break down unwanted organic molecules, as these combinations may eliminate a broad spectrum of organic contaminants [17].

Homogeneous photo-Fenton processes only utilize Fe (2+/3+), H_2O_2, and UV light in acidic environments. Due to the facile oxidation of Fe^{2+}, most iron species are found as Fe^{3+}. A pH level between 2 and 3 is best for uniform Fenton reactions to stop the formation of insoluble Fe $(OH)_2$+[18]. Possible sources of UV radiation include UVA (315–400 nm), UVB (285–315 nm), and UVC (less than 285 nm); in each case, the amount of hydroxyl radicals produced changes depending on how strong the light source is [19]. The AOP technique has remediated many pollutants, including pesticides, dyes, and medicines [20;21]. The stability of iron salts and H_2O_2 decreases as the pH increases, making the Fenton reaction very sensitive to pH changes[22;23]. This study used Acid Black RM dye as a test pollutant to see how well it could be removed by hydrogen peroxide and Fenton reagents, both with and without UV light. The study looked at how different factors that affect dye removal, like pH, H_2O_2 concentration, and Fe (II) ions, were examined and changed.

2. Materials and Methods

2.1. Experimental

2.1.1. Materials and Components

Acid Black dye was procured commercially from the market. "Hydrogen peroxide (30% w/w)" and Fe^{2+} ions were obtained from ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) as a source of Fe^{2+} ions. NaOH and H_2SO_4 were procured from Merck. Other compounds were of analytical reagent grade and utilized without further purification. All solutions were produced using double-distilled water. Acid Black RM dye is used to represent organic contaminants in aqueous environments. It is a dark brown powder that is water-soluble and utilized for dyeing and printing wool, polyamide fibres, silk, and mixed fabrics. Nylon fabric exhibits excellent dye absorption capabilities. It can also be utilized for colored leather. Figure 1 illustrates the chemical structure of the dye. The chemical formula is C20H12N3NaO7S.

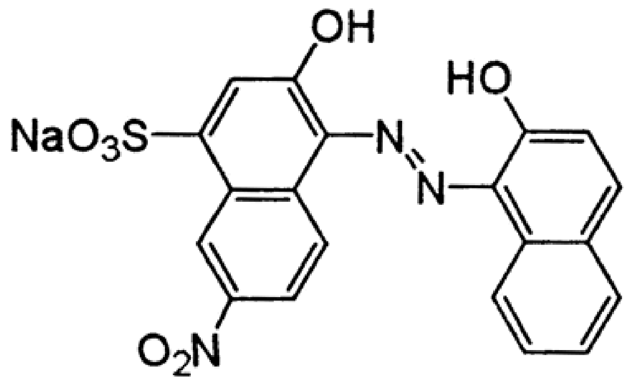

Figure. 1. Chemical structure of Acid Black dye RM.

2.1.2. Apparatus

The UV–Vis spectra were obtained utilizing a UV–Vis spectrophotometer (Jasco V-630). The pH levels of the solutions were assessed utilizing a digital pH meter (HI 98107). A magnetic stirrer was employed to agitate the dye solution and the analytical balance. A Sartorius Balance (cp153) was employed to measure the standards.

2.1.3. Photochemical Reactor

Photochemical reactions took place in a 100 mL glass beaker placed under a low-pressure mercury vapor lamp (45 cm long and 15 W, Osram) that produces UV light at 254 nm. The processes transpired at ambient temperature (23–27 °C). A precise volume of dye solution (25 mL) matching the desired concentration was deposited in the glass beaker.

2.1.4. Decolorization studies

Dye removal was achieved in batch mode by adding ferrous sulfate heptahydrate as a source of Fe^{2+} and hydrogen peroxide as an oxidizing agent to the dye solution. The pH of the “50 mL dye sample was calibrated to the designated value, after which Fenton reagents (H_2O_2 and Fe_2^+) were added to the stirred dye solution. The solutions were put into the photoreactor for the photo-Fenton reaction. Following the addition of Fenton’s reagent and mixing the dye solution (50 mL”), samples were collected at various intervals, and the absorbance of each sample was quantified using a UV-Vis spectrophotometer at λmax.

2.1.5. Kinetic studies

In the Fenton reaction, many < UNK> •OH radicals are produced during the first stage of decay of the dyes. Subsequently, the reaction slowed down due to the consumption of most of the H_2O_2 in side reactions. We conducted the kinetic study from the reaction's first step onward. The following first-order reaction kinetics could represent the removal of the dye in the photo-Fenton reaction:

$$\ln\left(\frac{C}{C_o}\right) = -kt \qquad (1)$$

Co represented the starting concentration of the dye. This equation indicates that a graph of ln(C/Co) vs. t will provide a linear representation with a slope of k. The reaction rate constants and correlation coefficients were computed.

3. Results and Discussion

3.1. H_2O_2 and H_2O_2/UV system

Varying amounts of H_2O_2 (70-280 mM) were added to the dye solution (10 mg/L). The dye content was followed with time; it was observed that the dye removal percentage reached a maximum (54.79 %) at 280 mM H_2O_2 after 90 min (Fig. 2). Hydrogen peroxide decomposes slowly to produce water and oxygen when exposed to normal light. In the case of UV/H_2O_2, the formation of •OH radicals is enhanced by the photolysis of H_2O_2.

The breakage of O–O bonds form radicals that alter the chemical structure of the organic pollutant [24]. The direct photolysis of H_2O_2 yields •OH radicals, the primary step followed by a series of reactions. The reactions describing H_2O_2/UV are displayed by the following equations [25]:

“$H_2O_2 + h\nu \rightarrow 2\ ^{\bullet}OH$ (2)

$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$ (3)

$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O$ (4)

${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ (5)”

The oxidizing ability of “UV/H_2O_2” may be attributed to the formation of •OH and HO_2• as indicated by the eqs. (2) and (3). The formation of •OH radicals causes a rapid attack of specific carbon atoms of the organic molecule, resulting in several mechanisms, including hydrogen removal, addition by electrophilic attack to some unsaturated bonds, or electron transfer (redox reactions) [26].

To examine the influence of UV on the degradation efficiency at different hydrogen peroxide doses, the same doses of H_2O_2 (70 - 280 mM) were added to a solution of Acid Black RM dye containing 10 mg/L under the influence of UV radiation. The change of the remaining dye concentration compared to the initial dye concentration was followed until equilibrium occurred at 90 min. As shown in Figure 2, the use of UV radiation enhanced the degradation of dye. Maximum removal occurred at 280 mM of H_2O_2 in the absence and presence of UV. The UV radiation caused an increase in dye removal from 54.97% to 74.25% in the absence and presence of the radiation, respectively.

This reaction mechanism requires a comparatively high concentration of H_2O_2 or a significantly extended duration of UV exposure [27]. The photolysis rate of hydrogen peroxide is pH-dependent, rising under more alkaline circumstances, see Figure 3.

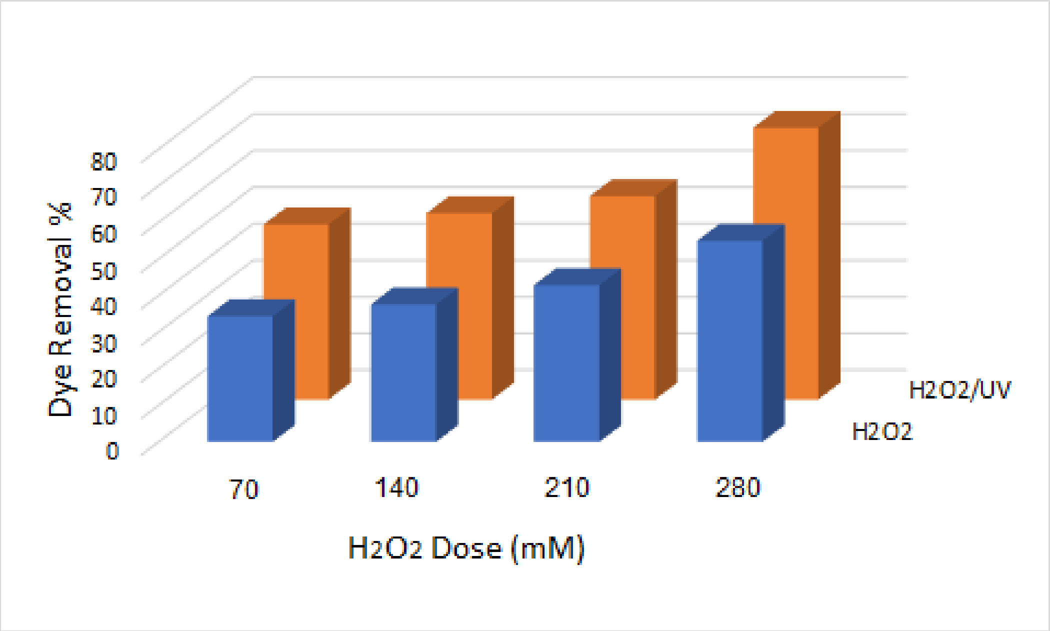

Figure. 2. Effect of H_2O_2 dose on Acid Black RM dye degradation in the absence and presence of UV radiation.

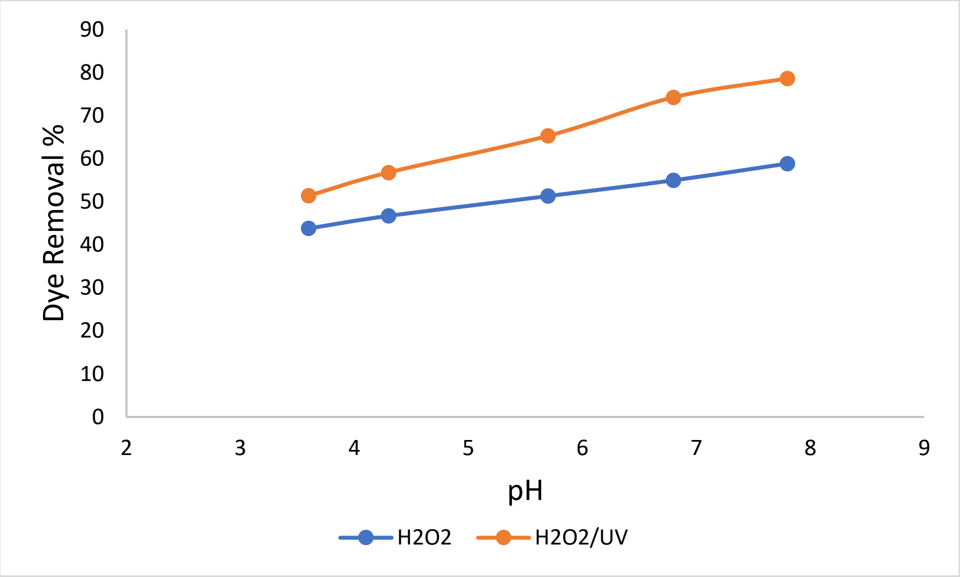

Figure. 3. Effect of pH on degradation of Acid Black RM dye in absence and presence.

3.2. Fenton and photo-Fenton systems

Fenton's reagent is a powerful oxidizing agent used primarily for degrading organic pollutants. It consists of a mixture of hydrogen peroxide "(H_2O_2) and an iron salt, typically ferrous sulfate ($FeSO_4$). The reaction between hydrogen peroxide and Fe (II) ions creates hydroxyl radicals (•OH), which are very reactive and can break down complicated organic molecules into simpler, less harmful ones". This process is known as Fenton's reaction and is represented by the following equations:

Fenton's reagent is a powerful oxidizing agent used primarily in environmental chemistry to degrade organic pollutants. Fenton's reagent involves the complex mechanisms of the reactants. It consists of a mixture of hydrogen peroxide (H_2O_2) and an iron salt, typically ferrous sulfate ($FeSO_4$). The following equations represent Fenton's reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOOH^+ + {}^\bullet OH \qquad (7)$$

The hydroxyl radicals produced are very effective at oxidizing a wide range of organic compounds, making Fenton's reagent a valuable tool in wastewater treatment and soil remediation. However, the process needs careful control because it can be highly exothermic and generate heat.

The most important problem in Fenton reaction is the choice of the optimal concentrations and Fe(II)/H_2O_2 ratio [28]. To examine the effective ratio between Fe(II) ions and H_2O_2, a series of dye solution of the same concentration (10 mg/L) at pH 4.3, was used with a constant concentration of H_2O_2 (280 mM) and varying amounts of Fe(II) ions (0.075 – 0.25 g/L). The remaining dye concentration was measured by spectrophotometry for 90 min. the highest removal percent was obtained at 0.2 g/L Fe(II). Figure 4 and 5, represent the change of dye removal when Fenton and photo-Fenton techniques were applied, respectively. As shown in the Figure 6, the exposure to UV radiation increased the removal percent remarkedly.

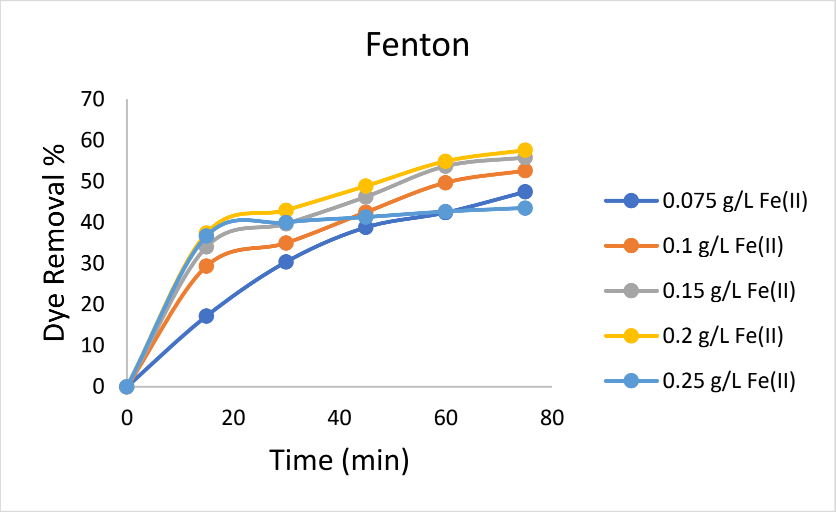

Figure. 4. Effect of Fe (II) dose on dye removal in Fenton reaction. [dye = 10 mg/L, H_2O_2 = 280 mM).

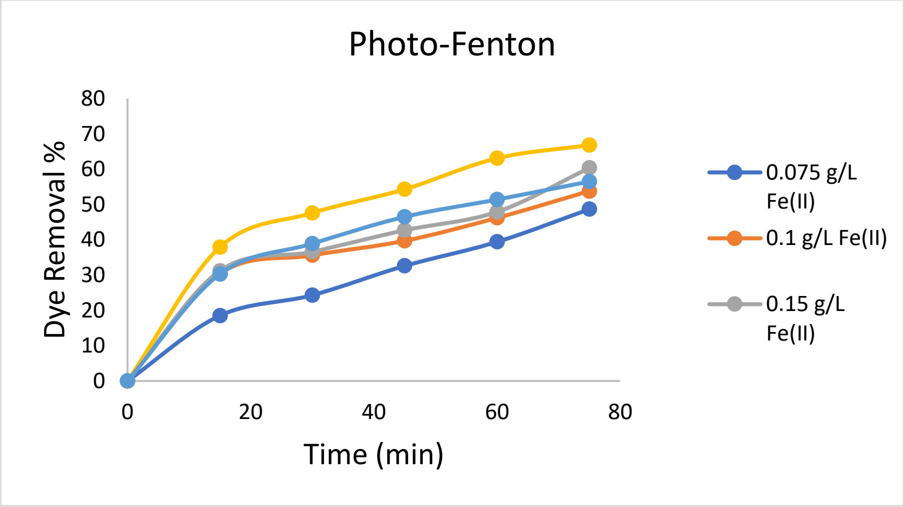

Figure. 5. Effect of Fe (II) dose on dye removal in photo-Fenton reaction. [dye = 10 mg/L, H_2O_2 = 280 mM).

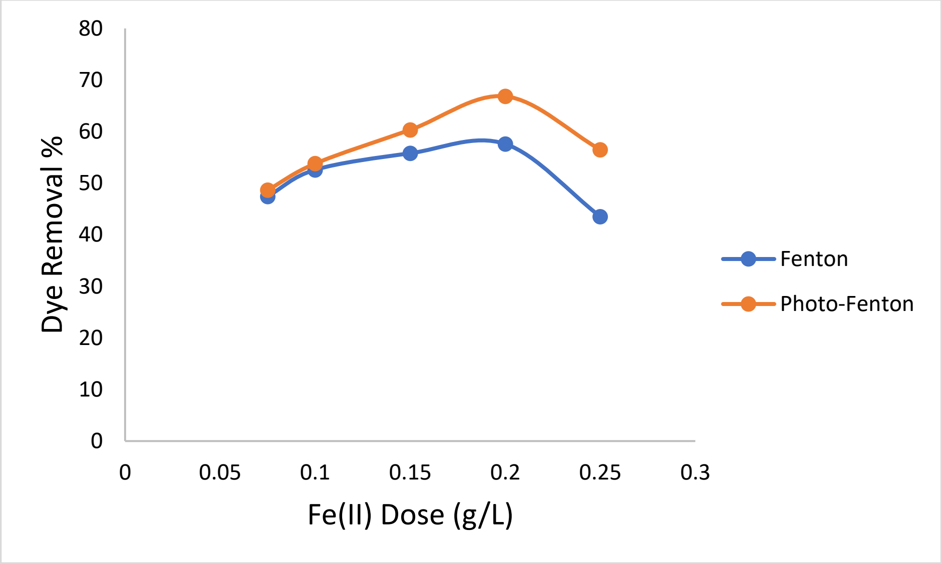

Figure. 6. Comparison between the effect of Fe (II) dose on dye removal in Fenton and photo-Fenton reactions. [dye = 10 mg/L, H_2O_2 = 280 mM).

Figure. 7 illustrates the influence of pH on removal efficiency in the photo-Fenton system. As shown in the figure, removal efficiency increased as the pH levels decreased. Previous studies have confirmed this behavior [29, 30].

3.3. Kinetic study using photo-Fenton system

Experimental determination of the kinetics parameters, such as rate constants and reaction orders, is essential to understanding and optimizing the photo-Fenton process for specific applications. This often involves conducting batch experiments under controlled conditions and analyzing the changes in reactant concentrations over time. Overall, the kinetics of the photo-Fenton reaction play a crucial role in determining its efficiency for the degradation of organic pollutants and its applicability in water treatment processes.

In the context of the photo-Fenton reaction, a first-order kinetic model can be applied to describe the degradation of the target pollutant(s) over time.

Using the relation [31], we plotted ln (C/Co) vs. t to determine the order and the rate constant (k) of the degradation process.

$$\ln\left(\frac{C}{C_o}\right) = -kt \qquad (1)$$

Co represents the initial dye concentration (mg/L), whereas C is the dye concentration (mg/L) at time t (min). k denotes the rate constant (min^{-1}).

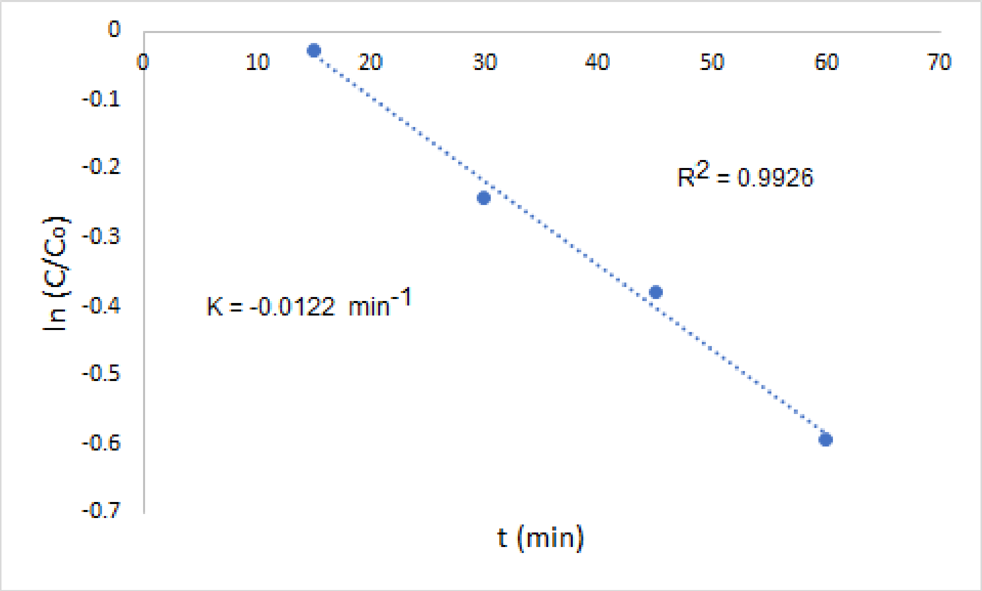

Figure 7. Represents the kinetic plot for photo-Fenton reaction using 10 mg/L of dye and 210 mM of H_2O_2.

This plot gave a correlation coefficient (R^2) of 0.9926 and K with a value of -0.0122 min^{-1}.

4. Conclusion

Some AOP processes for the degradation of a textile dye, Acid Black RM, have been studied using hydrogen peroxide alone and under UV radiation. The use of UV radiation increased the efficiency of the process. Also, Fenton and photo-Fenton techniques were applied and optimized. These reagents were effective and suitable for treating the polluted water with that dye. These methods are fast and easily applied to the studied case.

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