Removal of Acid Red 151 dye by Advanced oxidation processes

Elsayed A. Khalawy, A. M. Radwan, Sahar M. Ibraheem and Gamal O. El-Sayed*

1Qalyubia drinking water and wastewater company
2Faculty of Science, Benha university, Benha, Egypt
E-mail: gamaloelsayed@yahoo.com

Abstract

The presence of synthetic dyes in wastewater is a great problem as they are relatively stable and most of them are carcinogenic. An intense and successful treatment plan is required to remove dyes from water. By converting organic pollutants into carbon dioxide and water, advanced oxidation processes (AOPs) have demonstrated exceptional efficacy. An intense and successful treatment plan is required to remove dyes from water. By converting organic pollutants into carbon dioxide and water, advanced oxidation processes (AOPs) have demonstrated exceptional efficacy. Acid Red 151 (AR151) is an azo dye used for dying wool, silk, polyamide, and wool fabrics. Additionally, polyamide plastic shading is made with it. Some reagents including H2O2, O3, and Fenton were used to remove AR151 from aqueous medium in absence and presence of UV radiation. Different parameters controlling color disappearance were studied and optimized. The most effective system is UV/O3/H2O2 which cause a complete removal of the dye in few minutes.

Keywords: acid red 151, ozone, hydrogen peroxide, UV radiation, AOPs.

1. Introduction

The textile, pharmaceutical, leather, ink, paper, food, drink, and cosmetic industries utilize a wide variety of dyes to color items [1,2]. These dyes can be categorized as sulphur, reactive, metal complex, acid, basic, direct, vat, and azoic colors. Over 100,000 dyes are marketed commercially, and the number is growing each [3]. The most prevalent of these dyes, accounting for over 70% of global dye output, are azo dyes [4]. The presence of a nitrogen double bond (-N=N-), which together with another element known as a chromophore, is what distinguishes azo dyes from other types. [5]. Numerous companies release copious amounts of colored industrial waste with high concentrations of an azo dyes into bodies of water including lakes and rivers. Numerous aesthetic issues result from this, and natural waters are penetrated by light retardation. Since azo dyes and their breakdown byproducts are cancerous, poisonous, and hazardous, they may cause a variety of health issues in living things [6]. The reason azo dyes are resistant to biodegradation and are difficult for biological treatments in wastewater treatment plants to remove is because of their high stability in the aquatic environment [7]. Traditional treatment methods are used for removal of azo dyes from water, which including adsorption [8-11], electrocoagulation [12,13], and electrooxidation [14,15].

Conventional treatment techniques for dye removal are either not effective and/or expensive [16]. Therefore, research is required to create stronger and more efficient techniques for eliminating these contaminants and their byproducts from wastewaters for the purpose to stop the potentially harmful effects on the planet. Advanced oxidation processes (AOPs) are one of these techniques that have been the subject of extensive research in recent decades. In order to effectively eliminate water contaminated by organic contaminants, AOPs is dependent on the creation of potent oxidizing agents which include hydroxyl radicals (•OH) and persulfate radicals (S2O82-) in substantial quantities. Due to their larger reduction potential (2.8 V) than other oxidizing agents, hydroxyl radicals are the most prevalent and widely recognized oxidizing agents.

Numerous varieties of aliphatic and aromatic amines, medications, dyes, and different insecticides have all been found to degrade via advanced oxidation mechanisms [17–21]. With the exception of Fenton-based processes, advanced oxidation techniques that are capable of fully mineralizing organic pollutants are frequently referred to as “zero sludge” procedures. The attack of oxidizing radicals produced during AOPs on organic molecules may differ based on the specifics of the process, including the catalyst utilized, the chemical structure, the qualities of the pollutant, and the applied technique. In situ OH radical production has led to the development of numerous types of AOPs. •OH radicals have been produced using chemical, sonochemical, photochemical, and electrochemical techniques. The main advantage of AOPs techniques
is the possibility of total breakdown and mineralization of the desired organic contaminants.

Very few works have been concerned to the removal of AR151 including aerobic degradation [22], ozonation [23], and ozonation followed by treatment by activated sludge [24]. So, this research sought to examine the degradation efficiency of several AOPs for the aqueous solution degradation of AR151 dye.

2. Materials and Methods
2.1. Materials
The textile dye AR151 (commercial grade) was selected as a probe pollutant for this study. The chemical structure of the dye is shown in Scheme 1. All chemicals employed in this work (FeSO₄·7H₂O and H₂O₂) were of AR grade and were applied as received. All experiments were carried out using second distilled water.

Scheme 1. Chemical structure of acid red 151 dye.

2.2. Apparatus
A batch mode glass beaker reactor with 50 mL of dye solution was employed to examine the dye's degradation behaviour. Ozone generator model Aqua-6 (A2Z Ozone Inc., USA) was used as the source of ozone gas with a capacity 600 mg/h O₃. The gas was bubbled in the working solution through a stone diffuser. A UV-Lamp (PHILIPS) was the source of UV radiation, which was fixed at a distance of 30 cm.

The remaining dye concentration was followed by measuring its absorbance and compared with the initial absorbance using a JASCO V-350 UV/Vis a spectrum analyzes. A magnetic stirrer (100 - 700 rpm) was used for experiments not using ozone. with Using a pH device (HANNA instruments HI 8014, USA), the pH of the dye solutions was determined.

2.3. Degradation Processes
Eight different systems were applied for dye degradation experiments: H₂O₂, UV/H₂O₂, O₂, UV/O₂, O₂/H₂O₂, UV/O₂/H₂O₂, H₂O₂/Fe²⁺, and UV/H₂O₂/Fe²⁺. The efficiency of removal of the dye was determined by using the formula below:

\[
\text{Removal\%} = \frac{A_0 - A_t}{A_0} \times 100
\]

Where, A₀ and Aₜ are absorbances at the beginning and the end of treatment time t (min).

3. Results and discussion
In order to extract CR from water through an oxidation process via interactions with hydroxyl radicals (•OH), four distinct systems of AOPs processes were created.

3.1. H₂O₂ and UV/H₂O₂ system
When various amounts (20 - 100 mM) of H₂O₂ were added to the dye solution (10 mg/L), the dye removal percent reached a maximum (21.7 %) at 40 mM H₂O₂. Hydrogen peroxide decomposes slowly into water and elemental oxygen when exposed to normal light. In UV/H₂O₂, the generation of •OH radicals is directly aided by the photolysis of H₂O₂. The homolytic portion of the oxidant's O-O bonds shapes the radicals, which alter the target organic agent's chemical structure [25]. The initial step that precedes subsequent reactions is the generation of the •OH radical via direct photolysis of H₂O₂. Equations [26] that show the reactions describing UV/H₂O₂ are as follows:

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot\text{OH} \quad (2)
\]

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (3)
\]

\[
\text{HO}_2^- + \cdot\text{OH} \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (4)
\]

\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (5)
\]

The mechanistic pathways of reactions (2) and (3) suggest that the creation of •OH and HO₂• is responsible for the oxidizing ability of UV/H₂O₂. The attack of an organic molecule's preferred carbon, which results in the removal of hydrogen, the addition of electrons to an unsaturated bond electrophilically, or electron transfer (redox reactions) are the predicted events caused by the •OH radical [27]. Compared to other procedures that use UV radiation, this one demands a comparatively high concentration of H₂O₂ and/or a substantially extended UV exposure time [28]. On the other hand, Hydrogen peroxide photolysis has been found to be pH-dependent, with higher rates occurring in more alkaline environments.

In order to investigate how UV affects the rate of breakdown at various doses of hydrogen peroxide, the same doses of H₂O₂ (20 - 100 mM) were added to a solution of AR dye containing 10 mg/L and exposed to UV radiation. The rate of change of remaining dye concentration compared to the initial concentration were followed till equilibrium at 60 min. As shown in Fig. 1, applying UV radiation enhanced the breakdown of dye and the maximum removal occurred at 40 mM of H₂O₂ in absence of UV, while maximum removal in the presence of UV was observed at 80 mM, then the removal efficiency decreased.
icals in a largely 3 - 171 dye, ozone gas was 2 mutants, they accelerate 3 time under radiation H values (2.4, 2 2 2 2 2). As shown, the removal increases with increasing pH and maximum removal is observed at pH 10.2. It is well known that temperature, light, and pH all have a significant impact on hydrogen peroxide's stability [29]. Both under the impact of appropriate energy radiation and at higher temperatures, breakdown is encouraged. For optimum stability of pure H2O2, the pH range below 4.5 is convenient and above pH 5, the decomposition increases sharply [30]. Also, the presence of impurities in the H2O2 solution accelerates its decomposition. In UV/H2O2, the photolysis of H2O2 marginally promotes the production of -OH radicals [31], as a complete dye removal was attained at shorter time under radiation (Fig. 4).

3.2. O3, UV/O3 and UV/O3/H2O2 system

The gas ozone is highly reactive and poorly soluble in water. It is an unstable gas with a poor utilisation rate because it can break down fast into molecular oxygen [32]. Strong oxidant (2.07 V), it can break down organic contaminants by molecular ozone's direct electrophilic attack as well as -OH radicals' indirect attack. The efficiency of ozone oxidation is primarily reliant on the structure of organic molecules and is selective [33]. Most organic compounds react with -OH radicals in a largely diffusion-controlled manner [34]. Sometimes the organic component is not completely oxidised by ozone on its own. Numerous dyes have been reported to be successfully removed from textile effluents by ozonization [35]. Many researches have shown that reactive dyes degrade with O3 to a high degree, whereas basic dyes degrade with an intermediate degree and disperse colours with a low degree of efficiency [36].

Three tests were conducted at three distinct pH values (3.4, 8.8, and 11.7) in order to investigate the influence of O3. As Fig. 3 illustrates, there is a modest impact of pH variation on dye degradation. Since 8.8 was found to be the ideal pH, UV light was utilized to cause the dye to deteriorate at the same pH. In case of UV/O3 system, the rate at which dyes deteriorated increased slightly with UV exposure and complete degradation was observed after about 15 min of treatment (Fig. 4). It has been noted that while rising ozone concentrations slow down the breakdown of some other pollutants, they accelerate the breakdown of certain organic pollutants. This may be attributed to the mode of direct reaction between ozone and the polluting molecule which includes oxidation—reduction, cycloaddition, electrophilic and nucleophilic reactions [37].

When ozone gas and UV are coupled, exposure to UV causes more free -OH radicals, which speeds up the dye's breakdown. [38] according to the following equations:

\[ O_3 + \text{uv} \rightarrow O_2 + O \]  \hspace{1cm} (6)

\[ O + H_2 O \rightarrow 2 -OH \]  \hspace{1cm} (7)

\[ 2O^- + H_2 \rightarrow -OH + H_2O \rightarrow H_2O_2 \]  \hspace{1cm} (8)

At all pH levels, azo dye is more likely to degrade when O3 and UV are combined [39] and as expected, The UV/O3 process's decolorization efficiency was higher than the O3 system's. [40].

In the UV/O3/H2O2 system, the presence of H2O2 can speed up ozonolysis and produce more hydroxyl radicals (-OH) in the UV/O3/H2O2 system, the oxidation process of -OH takes centre stage. Different concentrations of H2O2 (20 - 100 mM) were added to a fixed amount of dye and exposed to UV during O3 bubbling. As shown in Fig. 5, the change of H2O2 content slightly deteriorated increased slightly with UV exposure and complete degradation was observed after about 15 min of treatment (Fig. 4). It has been noted that while rising ozone concentrations slow down the breakdown of some other pollutants, they accelerate the breakdown of certain organic pollutants. This may be attributed to the mode of direct reaction between ozone and the polluting molecule which includes oxidation—reduction, cycloaddition, electrophilic and nucleophilic reactions [37].

When ozone gas and UV are coupled, exposure to UV causes more free -OH radicals, which speeds up the dye's breakdown. [38] according to the following equations:

\[ O_3 + \text{uv} \rightarrow O_2 + O \]  \hspace{1cm} (6)

\[ O + H_2 O \rightarrow 2 -OH \]  \hspace{1cm} (7)

\[ 2O^- + H_2 \rightarrow -OH + H_2O \rightarrow H_2O_2 \]  \hspace{1cm} (8)

Three tests were conducted at three distinct pH values (3.4, 8.8, and 11.7) in order to investigate the influence of O3. As Fig. 3 illustrates, there is a modest impact of pH variation on dye degradation. Since 8.8 was found to be the ideal pH, UV light was utilized to cause the dye to deteriorate at the same pH. In case of UV/O3 system, the rate at which dyes deteriorated increased slightly with UV exposure and complete degradation was observed after about 15 min of treatment (Fig. 4). It has been noted that while rising ozone concentrations slow down the breakdown of some other pollutants, they accelerate the breakdown of certain organic pollutants. This may be attributed to the mode of direct reaction between ozone and the polluting molecule which includes oxidation—reduction, cycloaddition, electrophilic and nucleophilic reactions [37].

When ozone gas and UV are coupled, exposure to UV causes more free -OH radicals, which speeds up the dye's breakdown. [38] according to the following equations:

\[ O_3 + \text{uv} \rightarrow O_2 + O \]  \hspace{1cm} (6)

\[ O + H_2 O \rightarrow 2 -OH \]  \hspace{1cm} (7)

\[ 2O^- + H_2 \rightarrow -OH + H_2O \rightarrow H_2O_2 \]  \hspace{1cm} (8)

Three tests were conducted at three distinct pH values (3.4, 8.8, and 11.7) in order to investigate the influence of O3. As Fig. 3 illustrates, there is a modest impact of pH variation on dye degradation. Since 8.8 was found to be the ideal pH, UV light was utilized to cause the dye to deteriorate at the same pH. In case of UV/O3 system, the rate at which dyes deteriorated increased slightly with UV exposure and complete degradation was observed after about 15 min of treatment (Fig. 4). It has been noted that while rising ozone concentrations slow down the breakdown of some other pollutants, they accelerate the breakdown of certain organic pollutants. This may be attributed to the mode of direct reaction between ozone and the polluting molecule which includes oxidation—reduction, cycloaddition, electrophilic and nucleophilic reactions [37].

When ozone gas and UV are coupled, exposure to UV causes more free -OH radicals, which speeds up the dye's breakdown. [38] according to the following equations:

\[ O_3 + \text{uv} \rightarrow O_2 + O \]  \hspace{1cm} (6)

\[ O + H_2 O \rightarrow 2 -OH \]  \hspace{1cm} (7)

\[ 2O^- + H_2 \rightarrow -OH + H_2O \rightarrow H_2O_2 \]  \hspace{1cm} (8)

Three tests were conducted at three distinct pH values (3.4, 8.8, and 11.7) in order to investigate the influence of O3. As Fig. 3 illustrates, there is a modest impact of pH variation on dye degradation. Since 8.8 was found to be the ideal pH, UV light was utilized to cause the dye to deteriorate at the same pH. In case of UV/O3 system, the rate at which dyes deteriorated increased slightly with UV exposure and complete degradation was observed after about 15 min of treatment (Fig. 4). It has been noted that while rising ozone concentrations slow down the breakdown of some other pollutants, they accelerate the breakdown of certain organic pollutants. This may be attributed to the mode of direct reaction between ozone and the polluting molecule which includes oxidation—reduction, cycloaddition, electrophilic and nucleophilic reactions [37].
and varying amounts of dye (100, 500 and 1000 mg/L). Increasing the dye content decreases the rate and percent of its removal as shown in Fig. 6.

Fig. 3. Effect of pH on dye removal by O₃.

Fig. 4. Effect of treatment time on dye removal by O₃ with and without UV radiation.

Fig. 5. Effect of H₂O₂ concentration on dye removal in presence of O₃ under UV radiation. [dye = 100 mg/L, pH = 8.8]

3.3. H₂O₂/Fe(II) and UV/H₂O₂/Fe(II) system

H₂O₂ is added to the pollutant solution in the Fenton process when Fe²⁺ ions are present. The creation of •OH radicals, a potent oxidizing species, is the reaction's goal. One of the most useful advanced oxidation techniques for getting rid of a lot of dangerous organic contaminants from wastewater is the Fenton reaction. It has several benefits, including less sludge generation and great oxidation efficiency. Since •OH activity is strongly influenced by the pH of the solution, the Fenton process is often carried out in an acidic environment. As pH decreases, •OH's oxidation potential rises [41]. Because inactive iron oxohydroxides and Fe₃O₃ precipitate are formed, there is less Fe²⁺ activity as pH rises, which lowers the Fenton reagent's efficiency. Furthermore, at high pH levels, H₂O₂ seems to auto-decompose [42]. Whereas the concentration of the oxidant directly influences the amount of pollutants destroyed, the dose of iron influences Fenton's reaction rate [43]. The pH level, the H₂O₂/Fe²⁺ ratio, the amount of iron salt injected, and other variables all affect how quickly the Fenton reaction oxidizes [44]. Additional factors that affect the Fenton process's efficiency include the organic pollutant's structure and concentration, the presence of inorganic species, the treatment's duration, temperature, and whether any byproducts are produced as a result of the •OH's lack of selectivity. Numerous scholarly works provide a detailed and equation-based description of the intricate Fenton process mechanism [45–46]. In the absence of organic compounds, the classical Fenton mechanism involves the following reactions [48]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (9) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (10) \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \quad (11) \\
\cdot\text{OH} + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (12) \\
\text{Fe}^{2+} + \text{HO}_2^- & \rightarrow \text{Fe}^{3+} + \text{O}_2 + \text{H}^+ \quad (13) \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (14)
\end{align*}
\]
The catalytic roles of Fe$^{2+}$ and Fe$^{3+}$ are significant in the processes mentioned above. The generation of Fe$^{3+}$ from Fe$^{3+}$ seems to occur through the following equations [49]:

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe–OOH}^{2+} + \text{H}^+ \quad (16)
\]

\[
\text{Fe–OOH}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^- \quad (17)
\]

The dye is destroyed by the hydroxyl radicals created when hydrogen peroxide and ferrous ions interact, as shown below [50]:

\[
\text{RH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{R} \rightarrow \text{further oxidation} \quad (18)
\]

A significant circumstance is the impact of hydrogen peroxide and ferrous sulfate concentrations on dye degradation [51]. The decolorization of polluting dyes was found dependent on Fe(II) content and the H$_2$O$_2$ content [52]. To optimize the H$_2$O$_2$/Fe$^{2+}$ ratio, varying amounts (0.2-1.0 mM) of Fe(II) were added to a fixed concentration of H$_2$O$_2$ (8 mM) at a dye solution contains 10 mg/L AR dye. As shown in Fig. 9 maximum removal is observed at H$_2$O$_2$/Fe$^{2+}$ ratio 20:1 without and under UV radiation. It is clear that UV radiation can accelerate the Fenton reaction. The removal percent reached 96.8% under the effect of UV radiation. UV light can be used to completely mineralize a variety of chemical compounds that are present in aqueous solutions. The process that converts Fe$^{3+}$ to Fe$^{2+}$ ions and creates new •OH with H$_2$O$_2$ is thought to be responsible for the efficiency of UV irradiation [53].

As dyes mostly depend on their own chemical structures, the mechanisms underlying their degradation can differ [54]. During the procedure, a reaction route that doesn’t look as beneficial could occur. Gaining insight into the mechanism will assist future dyes enhance their elimination procedure, attributed to the development of hydroxoferric compounds. The H$_2$O$_2$/Fe$^{2+}$ ratio is the primary determinant of the rank of significance of oxidation and coagulation. At lower H$_2$O$_2$/Fe$^{2+}$ ratios, chemical coagulation is more prevalent, while chemical oxidation is more prevalent at higher H$_2$O$_2$/Fe$^{2+}$ ratios [55]. The synthesis of •OH may be increased and the organic pollutant’s breakdown efficiency raised by adding Fe$^{2+}$ ions at the right concentration. Conversely, self-quenching of •OH is anticipated in the event that the solution contains an excessive amount of Fe$^{2+}$ [56] as a result of production of Fe$^{3+}$ through reaction (12).

When more hydroxyl radicals are present, adding more H$_2$O$_2$ can result in the production of hydroperoxyl radicals (HO$_2$•), which do not contribute to the oxidative degradation of organic molecules and are significantly less reactive [57].

**Fig. 7.** Effect of Fe(II) concentration on AR dye removal at constant H$_2$O$_2$ concentration without UV radiation.

**Fig. 8.** Effect of H$_2$O$_2$ concentration on AR dye removal at constant Fe(II) concentration without UV radiation.

**Fig. 9.** Effect of H$_2$O$_2$/Fe$^{2+}$ ratio on AR dye removal without UV and under UV radiation. (0.4 mM Fe).

**Conclusion**

The application of various advanced oxidation techniques on removal Acid Red 151 from water has
been studied. Many systems were applied for this purpose including \( \text{H}_2\text{O}_2 \), \( \text{UV/UV}_2 \), \( \text{O}_3 \), \( \text{UV/O}_3 \), \( \text{UV/O}_2/\text{H}_2\text{O}_2 \), \( \text{H}_2\text{O}_2/\text{Fe}(\text{II}) \), \( \text{UV/H}_2\text{O}_2/\text{Fe}(\text{II}) \). Different factors affecting the removal efficiency such as oxidant dose, pH, \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio, and exposure time to UV radiation were studied and evaluated. Complete decolorization was attained by using \( \text{O}_3/\text{H}_2\text{O}_2 \) system under the influence of radiation after about 15 min.

References


[18] Recent advances in the removal of emerging contaminants from water by novel molecularly imprinted materials in advanced oxidation processes— A review Yang Zhang, Xiaodong


[26] Wenhui Qiu, Ming Zheng, Jing Sun, Yiquan Tian, Meijuan Fang, Yi Zheng, Ting Zhang, Chunmiao Zheng, Photoysis of enroflloxacin, pefloxacin and sulfamethoxazole in aqueous solution by UV/H2O2, UV/Fe(II), and UV/H2O2/Fe(II) and the toxicity of the final reaction solutions on zebrafish embryos, Science of the Total Environment 651 (2019) 1457–1468.


[54] Review on effect of different type of dyes on advanced oxidation processes (AOPs) for textile color removal Guntur Adisurya Ismail a,b , Hiroshi Sakai, Chemosphere, 291 (2022) 132906.

