Removing The Acid Orange 12 Azo Dye from Aqueous Solution Using Sodium Hypochlorite, A Kinetic and Thermodynamic Study

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Abstract. This study investigated the feasibility of using sodium hypochlorite as an advanced oxidation process to remove Acid Orange 12 azo dye from wastewater. For this purpose, batch reactor experiments were done. Several variables to address the efficiency of using this process were considered. These variables are initial pH (5, 7, and 9), the concentration of hypochlorite (50 – 250 mg/l), temperature (20-50) degrees Celsius, and time of electrolysis (1-75) min. also investigate the effects of UV on the process was done. Experimental results showed that the color removal efficiency using NaOCl with UV is more effective than NaOCl alone. The highest removal efficiency was obtained by increasing the concentration of NaOCl from (50-250mg/l) at PH=5. When the solution temperature was increased from (20-50) ℃, the removal efficiency increased, and at the same time, the time required was reduced from (20-5) minutes to obtain the highest removal efficiency. The kinetic study also showed that the oxidation process follows a second-order reaction. The thermodynamic functions indicate that the response is spontaneous, endothermic, and increases randomness.

Keywords: Acid Orange 12, Sodium Hypochlorite, Azo dye, Advanced Oxidation.

1. Introduction

Water is a natural and fundamental resource for the development of life and human activities. Due to the enormous number of pollution elements that contribute to water contamination, rendering it is inappropriate for the living creatures that dwell in it [1]. The shortage of clean water is currently one of the most pressing issues in our society [2]. As a result of recent rapid industrial progress and population growth, there has been a significant increase in the problems associated with environmental pollution, as human life has become increasingly threatened, forcing engineers and workers in this field to treat and work to control and reduce its harmful effects. There are several forms of pollution. It might be air, soil, or water pollution. Water pollution is one of the most hazardous forms of pollution because water plays such an essential part in everyday life and is also a significant source of industry, the world's greatest polluters. The textile business is one of the most polluting sectors for water since it employs a variety of synthetic dyes that have diverse impacts on the aquatic environment [3]. Because there are over 100,000 commercially accessible dyes with yearly production volumes of over 700 thousand tons [4]. The World Bank estimates that fabric dyeing and processing contributes 7-20% of industrial water pollution [5]. Many types of dyes are difficult to dissolve due to their manufacturing sources and complicated structures. These dyes can keep their structural formula and hues and biodegradation
resistance when exposed to sunlight [6,7]. Nitrogen dyes are among the most often used color in the textile, cosmetics, tanning, and food sectors, accounting for 70% of all dyes used in the textile industry, where these dyes are stable [8]. Furthermore, because the textile business uses much water in many industrial processes like (scaling, washing, dyeing, printing), which all utilize water in the presence of chemicals like detergents or bleaches, or to set the dye on the cloth, and the residues are removed from the chemicals. The water discharged by the textile businesses pollutes the water supply, resulting in poor water quality [9]. The nature of textile industry pollution, which is primarily attributed to the production of large amounts of industrial water, as well as the presence of high concentrations of aromatic amines, toxic metals, acids, bases, and carcinogens found in liquid pollutants, which lead to their presence as a threat to environmental life [10]. As a result, dye contamination is a significant cause of environmental pollution [5]. Because many pollutants are difficult to degrade, they must be removed from the aquatic environment before discharge. There are several methods for removing contaminants from wastewater, including electrocoagulation [11], ozone [12], adsorption [13], and advanced oxidation processes because it is characterized by the formation of an effective oxidizing medium and its ability to produce hydroxyl radicals (OH) that attack organic compounds and convert them to their essential elements [14-16], advanced oxidation processes (AOPs) are an alternative and successful solution in the treatment of industrial wastewater containing organic dyes and toxic substances [17-20]. Hydrogen peroxide (H₂O₂) and ozone (O₃) are the most efficient and commonly used oxidizing agents because they have high oxidation efforts, but they are costly. Therefore, we resort to new oxidation processes that are effective and economical, such as sodium hypochlorite (NaOCl). Although it is mainly used as a disinfecting agent, it effectively oxidizes organic dyes because of its high oxidation potential [21]. The current research aims to study the factors affecting the removal efficiency of (Acid Orange 12) dye using sodium hypochlorite (NaOCl). Moreover, in the presence of ultraviolet rays and finding the kinetic and thermodynamic constants.

2. Experimental and Methodology
2.1. Materials
Nitrogen dye (Acid Orange 12), sodium hypochlorite solution (NaOCl), sodium hydroxide (NaOH), hydrochloric acid (HCl).

2.2. Preparing the dye solution:
The dye solution is prepared at a concentration of 100 (mg/l) by dissolving 100 (mg) of the dye in a liter of RO filtered water. Table (1) shows the details of the dye in terms of formula, chemical structure, molecular weight, and other essential properties.

| Acid Orange 12 (AO 12) | Linear formula | Molecular weight | Color spectrum reference | λmax |
|------------------------|----------------|------------------|--------------------------|-------|
|                        | C₁₆H₁₁N₂NaO₅S  | 350.32           |                          | 482 nm |

2.3. Methods
All experiments were carried out in a magnetic stirrer & heat device (type Labnet D0420, USA), the presence and absence of UV/LAMP rays. The materials used in these experiments are characterized by high purity, where five different concentrations of sodium hypochlorite were used. /l (50-250). Moreover, by using a magnetic mixing device that contains a heater for heating to maintain a constant temperature during work, where experiments were conducted at different temperatures (20,30,40,50) degrees Celsius to see the effect of temperature on the reaction, as the
device is used to maintain continuous mixing at a constant mixing speed (300 rpm), three levels of pH values (PH 5, 7, 9) were taken, where the acidity function was measured using a device (PH meter type Hanna). Experiments were carried out by adding 32ml of the dye solution to be treated in a 400ml beaker and then completing the volume to 400ml by adding filtered water using RO technology. Then we add the required amount of sodium hypochlorite to the manufactured water, and then the magnetic mixing device is turned on to start the reaction. Samples are withdrawn at intervals (2, 5, 10, 15, 20, 30, 60, 90) to measure the remaining concentration of the dye in the solution after oxidation using a spectrophotometer, UVD-3000 (UV-Vis, USA).

3. Results and discussion
3.1. Effects of pH
The effect of the pH value on the removal efficiency was examined using sodium hypochlorite solution. (150 mg/l) at a temperature of 20 °C and an oxidation time of 90 minutes. The pH of the dye solutions was adjusted to the appropriate values using solutions with concentrations (0.1 M) of hydrochloric acid and sodium hydroxide, where the efficiency of dye removal at pH (9.7, 5) was 96.9%, 96.3%, 95.6%, respectively. Figure (1) shows the best efficiency of removing color at pH 5 even though the difference is very slight, and this is consistent with the results of researchers Thasilu and Karthikeyan [22] and Beikmohammadi et al. [23]. This is because sodium hypochlorite NaOCl decomposes in Acidic pH to hypochlorous acid HOCl, which is more effective in the oxidation process than hypochlorite anion OCl, which is released at alkaline pH [24,25].

![Figure (1): Effects of pH on removal efficiency.](image)

3.2. Effects of Oxidation Time
Time is one of the main effects of studying the efficiency of (AO12) dye removal, and Figure (1) shows the effect of time on the removal efficiency using acidic pH, which is (5) an initial concentration of (NaOCl) of (150) mg/l, and a temperature of (20) degrees Celsius, the removal efficiency increases rapidly in the first minutes, due to the presence of the oxidizing substance in abundance, as we obtain the highest removal efficiency of 95.49% at minute 20, then slowly increases with time until it becomes almost constant at minute 90, This is to consume most of the oxidant, and this is consistent with the results of researchers Azeroual et al., [26] and Zeng et al., [27]. The experiment was repeated using the same conditions. In the presence of ultraviolet rays, the percentage of removal increased by 96.19% due to the ability of the rays to break the bonds in the dye Sharma et al., [28, 37-38].
3.3. Effects of Concentration

Concentration is one of the critical factors affecting the removal efficiency. Figure (2) shows the effects of sodium hypochlorite concentration on the removal efficiency using dye concentration (100) mg/l, pH of the solution (5), and at a temperature (20) degrees Celsius, the efficiency of dye removal increases from 21% to 95%, and in the presence of ultraviolet rays, the efficiency was about 33% to 97%. It was noted that the removal efficiency increases with an increase in the concentration of sodium hypochlorite from (250-50 mg/l). This is because the increase in the concentration of (NaOCl) would enhance the frequency of collision between oxidizing substances and dye molecules, which is consistent with the results of researchers Xu et al., [29], and Amit, et al.,[30]. In addition, increasing the concentration of (NaOCl) increases the obtaining of hydroxyl radicals in the solution effectively, as shown in the following equations [31]:

\[ \text{HClO} \rightleftharpoons \text{H}^+ + \text{ClO}^- \] \hspace{1cm} (1)

\[ \text{HOCl} \xrightarrow{\text{UV photons}} \text{+} \cdot \text{OH} + \text{Cl}^- \] \hspace{1cm} (2)

**Figure (2):** Effects of time on removal efficiency

**Figure (3):** Effects of concentration on removal efficiency
3.4. Effects of Temperature
Heat is one of the factors affecting removal efficiency (AO12). Figure (4) shows the effect of temperature on the removal efficiency using four temperatures (20, 30, 40, 50) degrees Celsius, an initial concentration of NaOCl (150) mg/l, dye concentration (100) mg/l and pH (5), and a time of 90 minutes. It was noticed that increasing the temperature from 20 to 50 degrees Celsius, the removal efficiency increased from 94.64% to 97.32% because the increase in temperature led to increased mass transfer, this improves the efficiency of removal [32-34]. In the presence of ultraviolet rays, the removal percentage increased from 96.9% to 99.01% because the rays provide several photons needed, which can break the bonds in the dye [31].

![Figure (4): Effects of temperature on removal efficiency](image_url)

3.5. Thermodynamic study
Studying the effect of the temperature change helped determine the values of the essential thermodynamic functions of the oxidation process. The change in free gypsum shot (ΔG°) is determined using the following equation [35]:

\[ ΔG° = nRT \ln K_e \]  

Where R is the general constant for gases (8.314 J mol⁻¹ K⁻¹), T is temperature in Kelvin and Ke represents the equilibrium constant whose value can be found from \((C_0 - C_e)/C_e\), where \((C_0 - C_e)\) represents the concentration of the oxidizing dye. \(C_e\) represents the residual dye concentration in the solution at different temperatures (20, 30, 40, 50) degrees Celsius. Either determine the values of each of the enthalpy change (ΔH°) and the entropy change (ΔS°) using the following equation [34]:

\[ \ln K_e = \frac{ΔS°}{R} - \frac{ΔH°}{RT} \]  

The values of (ΔH°) and (ΔS°) are obtained from slope, and intercept for the plotted relationship between \(\ln K_e\) vs 1/T as shown in figures (5) and (6), where the slope = -ΔH°/R and intercept =ΔS°/R, which gave an excellent linear relationship and correlation coefficient.
Figure (5): The relationship between LnK and 1/T without UV.

Figure (6): The relationship between LnK and 1/T in the presence of UV.

The table shows the values of thermodynamic functions in the presence and absence of ultraviolet rays, where the negative values of (∆G°) indicate the spontaneity of the reaction at all temperatures, and the positive value of (∆H°) indicates that the reaction is endothermic. The positive values of (∆S°) increases randomness.

Table (2): values of thermodynamic functions in the presence and absence of ultraviolet rays

| Transaction               | T (K°) | GΔ      | HΔ       | SΔ       |
|---------------------------|--------|---------|----------|----------|
| Sodium hypochlorite       | 293    | 6997.84-|          |          |
|                           | 303    | -7861.98|          |          |
|                           | 313    | -8959   | 19588.6  | 90.76394 |
|                           | 323    | -9650.6 |          |          |
| Sodium hypochlorite + UV  | 293    | -7965.39|          |          |
|                           | 303    | -10030.80| 44729.3  | 180.3722 |
|                           | 313    | -11995.1|          |          |
3.6. Kinetic study

The kinetics of the reaction for oxidation (AO12) by sodium hypochlorite are studied using the laws of kinetics, including the second-order reaction law, by drawing a relationship between the concentration of the residue and time at an initial conc. of the dye (100 mg/l), an initial conc. of NaOCl (150 mg/l), the pH = 5, at a temperature of 20 degrees Celsius, in the presence and absence of ultraviolet rays, which gave a linear relationship with a suitable bonding strength. Through the obtained relationship, it was found that the reaction is of the second-order, and the reaction rate constant can be calculated as shown in table (3) through the following equation [36]:

\[ K_2t = \frac{X}{a(a-x)} \] ................ (5)

Where \( K \) represents the reaction rate constant, \( t \) represents time in minutes; \( a \) represents the initial concentration of the dye, \( x \) represents the concentration removed, \( (a-x) \) represents the remaining concentration.

| No. | UV Lamp Watt | Concentration of NaOCl (mg/l) | \( K \) L.mol\(^{-1}\).min\(^{-1} \) | \( R^2 \) |
|-----|--------------|-------------------------------|-------------------------------|---------|
| 1   | 0            | 150                           | 0.0019                        | 0.884   |
| 2   | 10           | 150                           | 0.0029                        | 0.9789  |

The following figures (7) and (8) show the values of the slope and the velocity constant that were obtained from applying the second-order law.
4. Conclusion
The results found that the oxidation process using NaOCl with UV is more effective in removing the dye (AO12) than NaOCl alone. The highest removal efficiency obtained by increasing the concentration of NaOCl from (50-250mg/l) at PH=5 when the solution temperature was increased from (20-50) °C, the removal efficiency increased, and the time required to obtain the highest removal efficiency reduced from 20 to 5 minutes. Kinetic study also shows that the oxidation process follows a second-order reaction. Thermodynamic functions indicate that the reaction is spontaneous, endothermic, and has an increase in randomness.

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