



Treatment of Contaminated Textile Factories' Wastewater by Photocatalyst Degradation

Ahmed K. Hassan*, Adnan F. Hasan, Alaa Jasim, Salam Nassar Owaiyd

Environment and Water Directorate, Ministry of Science and Technology – Iraq

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*Corresponding Author:

Ahmed K. Hassan

ahmedkhh71@gmail.com

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Abstract

The aim of this work is remove the textile factories' wastewater such as dyes via the Advanced Oxidation Processes (AOPs) that on using the nano titanium dioxide photocatalytic degradation. The degradation of C. I. Reactive black 45 (RB 45) in aqueous medium by the photocatalysis process has been studied. The effects of several parameters such as pH, the concentration of TiO₂, irradiation time, and dye concentration have been examined. The optimal parameters were found to be [TiO₂] = 0.75 g/L, irradiation time 480 min and pH=3.0. The results shown that the photocatalytic degradation could be enhanced by adding hydrogen peroxide H₂O₂ or potassium persulfate K₂S₂O₈, for example, the efficiency increased from 68.9% to 88.7% and 95.4% when added 0.027 M or 1.5 g/L of H₂O₂ and K₂S₂O₈ respectively. Also, the effects of inorganic salts Na₂SO₄, Na₂CO₃, and NaCl on the degradation efficiency of the photocatalysis process were investigated.

1. Introduction

Mostly, industrial actions are responsible for surface water contamination. In specific, effluents of these activities are discharged directly or indirectly by the factories into the water resources without suitable treatment [1]. Textile effluent consists of a variety of organic dyes, alkalis, and inorganic salts that make the chemical composition of textile industry wastewater a very complex mixture and environmental challenge [2, 3]. To have a green, clean, and healthy environment, there is an urgent need to search for a method, which applies to achieve higher removal at room temperature, is safe to handle, low cost, and eco-friendly. And above all, the main requirement of the remediation method is that it should not be harmful to the environment in any manner [4, 5]. An advanced oxidation process (AOPs) is defined as "Oxidation processes, which generate highly reactive radicals (especially hydroxyl radicals) in sufficient quantity to affect the water treatment" [6]. These processes of oxidation can degrade almost all chemical organic pollutants [7]. It is clear from standard redox potential data that "hydroxyl radical" •OH is the strongest known oxidant (2.8 V), second to fluorine (3.03 V) [8]. Therefore, the complete degradation of the generality of organic pollutants by hydroxyl radical is one of the most advantages of AOPs [7-9]. Among the photocatalysts used, titanium dioxide (TiO₂) is considered a very effective catalyst that, unlike other photocatalysts, is nontoxic, stable to photo corrosion, economical cost, and suitable to work using solar light. Various research works have been conducted on dye wastewater treatment by nano TiO₂ catalyst under UV-irradiation due to TiO₂ having the capability to remove dyes from water as early as possible and show a speedy response time during dye decolorization [10-12]. To date, most works implemented the photocatalytic degradation of dyes by UV/TiO₂ technology using nano-Degussa P25 (a mixture of 80% Anatase, and 20% Rutile crystallites).

In addition to nano-Degussa P25, several commercially available TiO₂ catalyst materials could be used for textile dyes' degradation. However, the plurality of research on TiO₂ reported that P25 appeared to be the most effective catalyst for the degradation of azo dyes [13] and Acid Orange 7 and Methyl Orange [14]. When nano TiO₂ is excited by UV radiation with a wavelength below 380 nm, that means the photons excite the valence band electrons across the bandgap into the conduction band, leaving holes behind in the valence band; then the produced holes will react with water molecules (H₂O) or hydroxide ions (HO⁻) to produce hydroxyl radicals (•OH) [15]. The resulting •OH radical, being a very strong oxidizing agent can oxidize most of the azo dye molecules to the mineral final products such as CO₂, H₂O, and mineral acids [16]. Besides, azo bonds also can be oxidized or reduced by a positive hole in the valence band or electrons in the conduction band, respectively. Sulfate radicals (SO₄^{•-}) which are generated from persulfate (S₂O₈²⁻) have a high redox potential of 2.6 V. So, they can oxidize organic pollutants into small molecules [17]. Generally, S₂O₈²⁻ can be activated by UV, heat, or transition elements [18]. Photocatalytic degradation of the water contamination is mainly dependent on the type of organic chemical pollutants, pH, their concentration, catalyst amount, temperature, and UV-light intensity. The effects of various parameters on photocatalytic degradation efficiency are very important to select a sustainable and efficient treatment method for the degradation of pollutants [19].

Therefore, this work has aimed to assess the performance of photocatalyst as part of AOPs, for the degradation of polluting dyes, studying specifically the effects of TiO₂, pH, irradiation time, and dye concentrations on the color removal efficiency. And further enhancing photocatalyst by adding hydrogen peroxide (H₂O₂) or potassium persulfate (K₂S₂O₈) was also investigated. Moreover, dye mineralization at the optimum condition in the present inorganic salts was evaluated.

2. Experimental

2.1. Materials

Nano Titanium dioxide (TiO₂) used in this work was obtained from Nanjing XFNANO Materials Tech Co., Ltd, CHINA. The TiO₂ particle size (15-25 nm), and has a BET surface area of 77.37 m²/g. The TiO₂ suspension was stirred for 30 minutes every time before use. C. I. Reactive black 45 (RB 45) was a gift from Al-Kut Textile Factory, Iraq. H₂O₂ (30% W/W), and K₂S₂O₈ were obtained from (Merck and BDH). NaOH and H₂SO₄ were used to adjust the pH which was purchased from Appli Chem (GmbH). NaCl, Na₂CO₃, and Na₂SO₄ were obtained from Fluka. All solutions were prepared using distilled water. The main characteristics and chemical structure of RB 45 dye are listed in Table (1).

Table (1). Characteristics of Reactive Black 45 dye.

Properties	Value
Chemical formula	C ₃₉ H ₂₆ ClN ₁₀ Na ₅ O ₁₆ S ₅
Molar Mass(g/mol)	1201.41
Chemical Structure	
Functional group	Diazo
Color, λ max (nm)	Black, 600

2.2. Procedure

A photoreactor equipped with a UV lamp (254 nm) as shown in Figure (1). The reactor is cylindrical, with a UV lamp placed in a quartz tube cylinder, taking up all its length. The tight positioning of the lamp enabled the treatment of polluted water with low UV transmittance. A pump will be used for the recirculation of the wastewater dye solution. The flow system is collected with plastic tubing. The degradation of RB 45 was carried out by photocatalyst process using a continuous reactor (Beaker total volume of 1L) under constant agitation with a magnetic stirrer and room temperature ranging from $35 \pm 2^\circ\text{C}$. Samples for analysis are taken from the synthetic solution. After an experiment was conducted, the system was cleaned with 1.0 M sulfuric acid, rinsed with distilled water, and air-dried before starting a new experimental run. The color removal of the diazo dye RB 45 solutions was followed quantitatively by measuring the decrease in absorbance at $\lambda_{\text{max}} = 600\text{nm}$ using (UV/Vis, Model SP-3000 OPTIMA) spectrophotometer. A linear correlation was founded between the dye concentration and the absorbance at $\lambda_{\text{max}} = 600\text{nm}$, in the range (1-100 mg/L) with a correlation coefficient, $R^2 = 0.9997$. Eq (1) was used to calculate the photocatalytic degradation efficiency ($DE\%$) in the photocatalyst experiments.

$$DE\% = \left[1 - \frac{C_t}{C_0} \right] \times 100 \quad (1)$$

Where C_t and C_0 (mg/L) are the concentrations of RB 45 dye at reaction times t and 0, respectively.

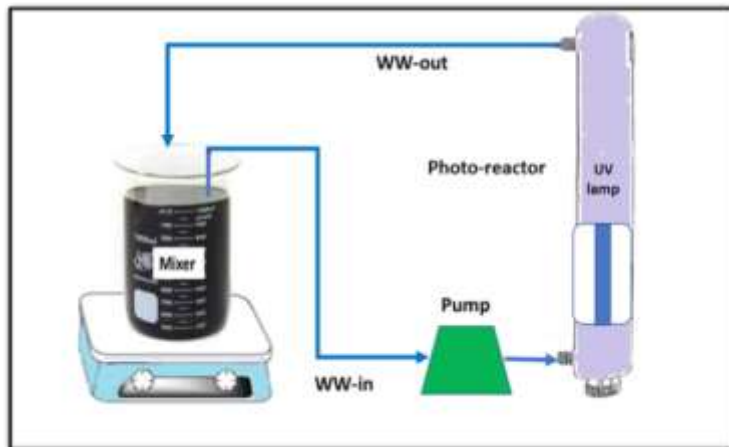


Figure (1). Representation of the photocatalytic degradation system used in this research. (WW, is synthetic wastewater polluted with RB 45 dye).

The experiments were conducted as the following:

1. To achieve the effects of the initial TiO_2 concentration (ranging from 0.25 to 1.0 g/L) on the color removal of RB 45, photocatalyst experiments were conducted at a fixed pH of 3.0. The pH was adjusted to the required value using either (1 M H_2SO_4 or 1 M NaOH); a desired amount of TiO_2 was added to the 1 L of solution with dye concentration (90 mg/L). The slurry solution contains RB 45 dye and the catalyst was stirred magnetically to maintain TiO_2 in suspension. The suspension was left for 30 min in the dark to perform the maximum adsorption of the dye onto the catalyst surface. For monitoring the RB 45 concentration during the color removal process, 10 mL of sample was taken out at -30, -20, -10, 0, 5, 10, 15, 20, 30, 60, 90, 120, 180, and 240 min and the photocatalysts were removed by centrifugation (4000 rpm) for 10 min, then filtrated using $0.22 \mu\text{m}$ membrane filter and the concentration of the RB 45 was analyzed by checking the absorbance at 600 nm with a UV-vis spectrophotometer.
2. The effects of pH were carried out at three pH values acidic (pH= 3), neutral (pH=7), and basic (pH=10.0), to compare their photocatalytic efficiency.
3. The influence of irradiation time on photocatalytic degradation of RB 45 was investigated under 480 min of light irradiation.

- To enhance the photocatalytic efficiency of the dye RB 45 by adding different concentrations of H_2O_2 (0.009 to 0.027 M) or $\text{K}_2\text{S}_2\text{O}_8$ (0.0018 to 0.0055 M) to assess the color removal of RB 45 (90 mg/L), photocatalytic oxidation experiments were conducted at a fixed TiO_2 concentration of 0.75 g/L, and initial pH=3.0.
- The influence of various inorganic salts solutions (NaCl , Na_2SO_4 , and Na_2CO_3) on the photocatalytic efficiency process were evaluated by adding 1% of the inorganic salt to the aqueous solution of RB 45 (90 mg/L) at optimum conditions: $[\text{TiO}_2] = 0.75$ g/L, and pH=3.0.

3. Results and Discussion

3.1. Effect of TiO_2 Concentration on Photocatalytic Degradation Efficiency of RB 45 Dye in Aqueous Media

The effect of nano TiO_2 concentration on the photocatalytic degradation of RB 45 was studied in the range of 0.25–1 g/L with (90 mg/L) RB 45 at pH = 3.0 under UV irradiation. In this research, about 6.2 % of RB 45 was adsorbed on the TiO_2 surface after 30 min of equilibration time “without UV irradiation” at the optimum loading of catalyst (0.75 g/L). As can be seen from Figure (2), photocatalytic degradation efficiency appeared to increase with increasing the catalyst concentration from 0.25 to 0.75 g/L. It was found that the increase in the amount of nano TiO_2 increased the color removal of the dye, achieving maximum color removal at the TiO_2 concentration equal to 0.75 g/L. The photocatalytic degradation efficiencies were 32.5%, 50.3%, and 60.6% after 240 min of irradiation at catalyst concentrations of 0.25, 0.5 and 0.75 g/L respectively. Any further increase in the TiO_2 concentration resulted in an insignificant effect or a decrease in color removal (58.1% after 240 min of irradiation at a TiO_2 dose of 1.0 g/L) which may be explained by the decreased number of photons reaching the adsorbent active sites due to screening influence by the excess catalyst [11]. Furthermore, the increasing of nano- TiO_2 catalyst loading increases the turbidity of the treated contaminated water and decrease the amount of UV light reaching the active surfaces of nano titanium oxide [10, 12]. Therefore, 0.75 g/L was chosen as the optimum amount of Nano TiO_2 .

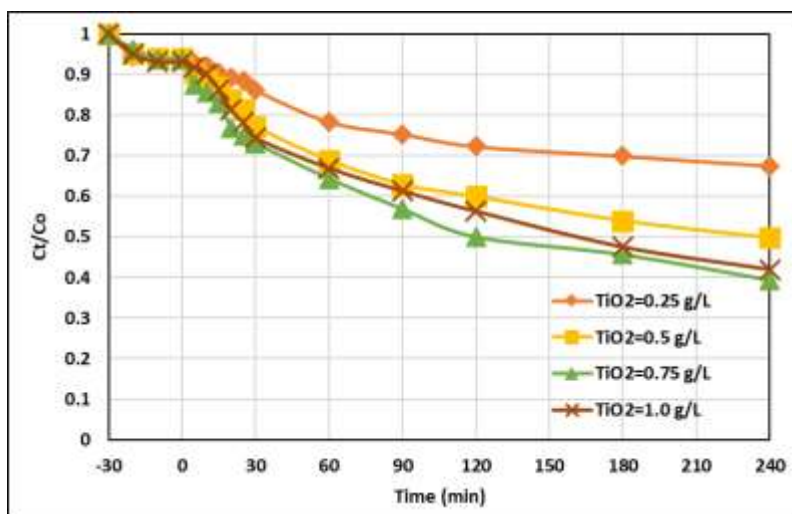


Figure (2). Effect of nano TiO_2 concentration on photocatalytic degradation efficiency of RB 45 dye. Experimental conditions: $[\text{RB 45}] = 90$ mg/L and pH=3.0.

3.2. Influence of pH on Photocatalytic Degradation Efficiency RB 45 Dye in Aqueous Media

As mentioned in previous studies, the pH value plays a very important role in the degradation of some organic pollutants in the photocatalytic process [19, 20]. Figure (3) illustrates the photocatalytic degradation of RB 45 at acidic (pH=3), neutral (pH=7), and alkaline (pH=10) solutions, and displays that the best results were gained in acidic solution (pH=3). Consequently, for the diazo dye with the sulfonic group in their structure, at acidic pH value, electrostatic interactions between the positively charged catalyst surface and dye anions lead to the very strong adsorption of the dye on the titanium dioxide support and are more effective than neutral and alkaline solutions which the photocatalytic degradation efficiencies were 33.1% and 29.8% after 240 min of irradiation, respectively for removal of dye.

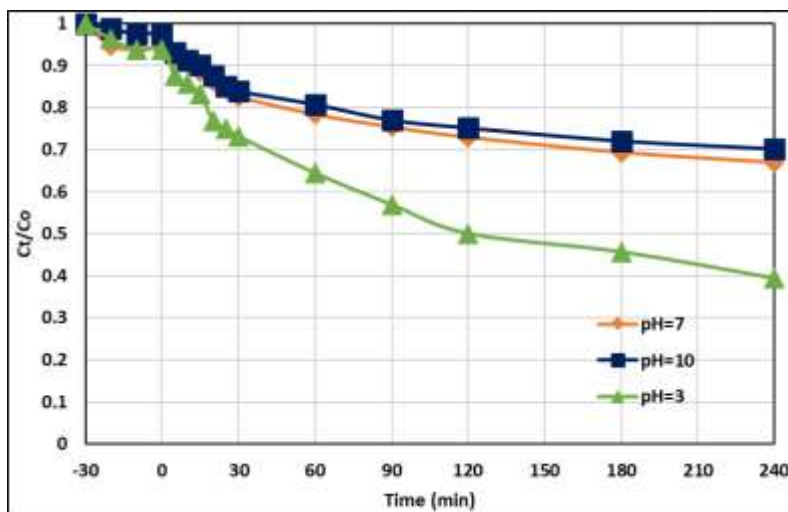


Figure (3). Effect of pH on photocatalytic degradation efficiency of RB 45 dye. Experimental conditions: $[\text{TiO}_2] = 0.75 \text{ g/L}$ and $[\text{RB 45}] = 90 \text{ mg/L}$.

3.3. Influence of Irradiation Time on Photocatalytic Efficiency of RB 45 Dye in Aqueous Media

The photocatalytic degradation efficiency was evaluated by the color removal of RB 45. Figure (4) shows the variations of RB 45 concentration (C_t/C_0) as a function of irradiation time. It can be noted that the photocatalytic degradation enhanced with a longer time contributed. The results point out that degradation increases by increasing the irradiation time and reaches a constant level after 480 min of reaction. Maximum photocatalytic degradation of RB 45 achieved at 480 min under UV-irradiation was 68.9 %. The decolorization efficiency of RB 45 dye was higher during the first 120 min of effective irradiation time. After 120 min, the degradation rate of RB 45 dye gradually decreased. This may be attributed to the consumption of hydroxyl radicals ($\cdot\text{OH}$) and the low remaining concentration of dye, a similar effect was shown by Alalm, and et al [21].

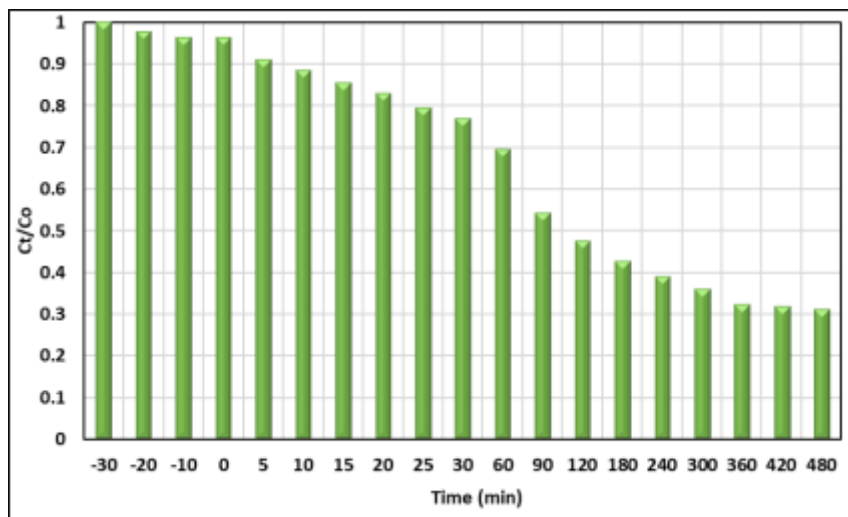


Figure (4). Influence of irradiation time on photocatalytic efficiency of RB 45 dye. Experimental conditions: $[\text{TiO}_2] = 0.75 \text{ g/L}$, $[\text{RB 45}] = 90 \text{ mg/L}$ and $\text{pH}=3.0$.

3.4. Effect of Initial RB 45 Dye Concentration on Photocatalytic Degradation Efficiency

Using optimum photocatalyst amount (0.75 g/L) and different initial concentrations of RB 45 dye, the plots of concentration (C_t/C_0) as a function of irradiation time are presented in Figure (5). The photocatalytic degradation efficiency of different concentrations of RB 45 was studied. It was observed from Figure (5) that the color removal of dye increases with the decrease in initial RB 45 concentration. As the concentration of dye decreased from 120 to 50 mg/L, the photocatalytic degradation efficiency of dye increased from 55.4% to 100% at 360 min of

irradiation time. This was probably due to a higher dye concentration will increase the path length of a photon entering the dye solution and absorb a significant amount of UV-light rather than the TiO₂ catalyst [22].

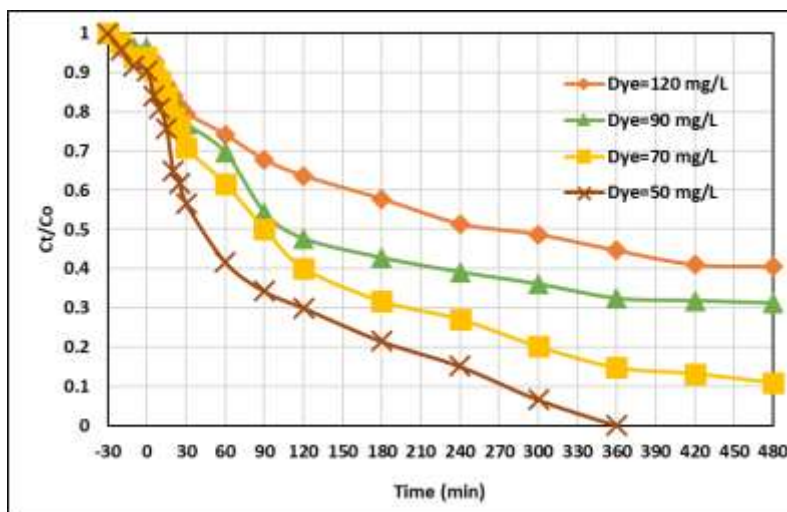


Figure (5). Influence of dye concentration on photocatalytic efficiency of RB 45 dye. Experimental conditions: [TiO₂] = 0.75 g/L, and pH=3.0.

3.5. Enhancement of Photocatalytic Degradation Efficiency of RB 45 Dye Using various H₂O₂ concentrations

To evaluate this effect, experiments were achieved at different concentrations of H₂O₂ in the acidic solution (pH=3.0) and a fixed concentration for both RB 45 dye and TiO₂. The H₂O₂ concentration varied from 0.009-0.027 M as shown in Figure (6). It indicates that the increase in H₂O₂ concentration will increase the photocatalytic degradation efficiency of the UV/TiO₂/H₂O₂ system. It can be seen that at 480min of irradiation with concentrations of 0.009-0.027 M the degradation efficiencies of 79.2%, 84.2%, and 88.7% were obtained, while the degradation efficiency without the addition of H₂O₂ was 68.9% after the same period. We did not increase the concentration of H₂O₂ to more than 0.027 M to avoid the increase in the toxicity solution [23].

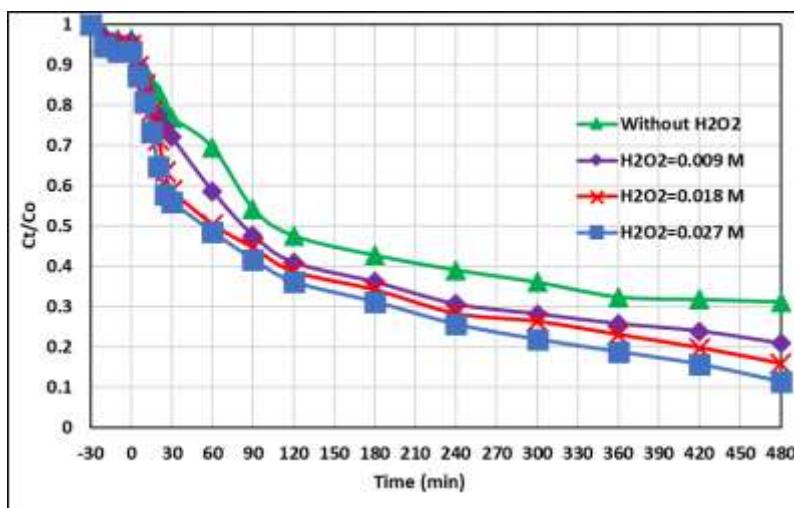
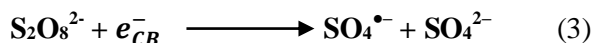
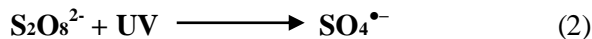


Figure (6). Influence of H₂O₂ concentration on photocatalytic efficiency of RB 45 dye. Experimental conditions: [TiO₂] = 0.75 g/L, and pH=3.0.

3.6. Enhancement of Photocatalytic Degradation Efficiency of RB 45 Dye Using Various $K_2S_2O_8$ Concentrations

In the last years, sulfate radical-based AOPs have been proven to be very promising techniques for the remediation of persistent pollutants [24]. The sulfate radical ($SO_4^{\bullet-}$) has a high redox potential of (2.6V), approximately to hydroxyl radicals (2.8V). It can be produced from persulfate ($S_2O_8^{2-}$), which is activated by UV as shown in Eq. (2). Persulfate can be used as electron acceptors in the photocatalytic degradation process, producing sulfate radical through the following reactions {Eq. (3)}.



To study the effect of $K_2S_2O_8$ concentration, experiments were conducted using various initial oxidant concentrations ranging from 0.5 to 1.5 g/L and the results are shown in Figure (7). With the increase of $K_2S_2O_8$ concentration from 0.5 to 1.5 g/L, the photocatalytic degradation efficiency of RB 45 will increase from 77.4% to 95.4%. This increase is due to more generation of $SO_4^{\bullet-}$ and $\bullet OH$ radicals enhancing the destruction of organic pollutants [25].

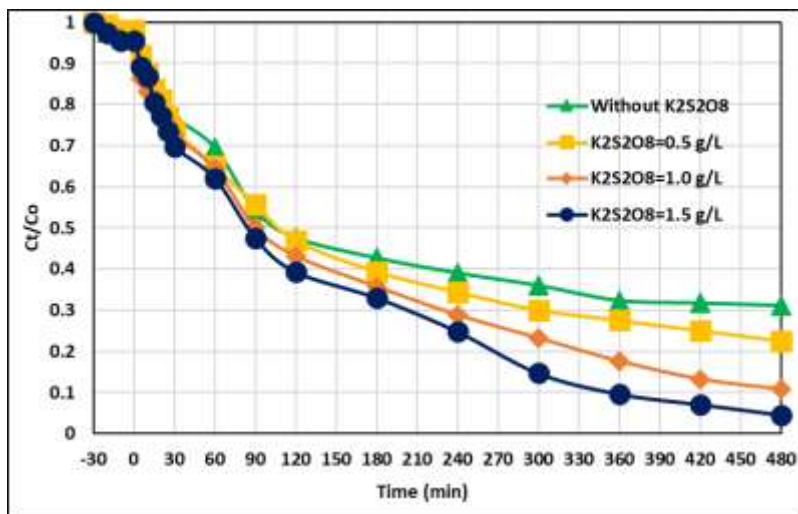


Figure (7). Effect of $K_2S_2O_8$ concentration on photocatalytic efficiency of RB 45 dye. Experimental conditions: $[TiO_2] = 0.75$ g/L, and $pH=3.0$.

3.7. Effect of Added Inorganic Anions on Photocatalytic Degradation Efficiency of RB 45 Dye

The effect of some inorganic anions on the photocatalytic degradation of RB 45 was tested in optimum conditions. To simulate an aqueous solution containing RB 45 at a concentration of (90 mg/L) in the presence of 1.0 % inorganic salt used in this study. Figure (8) show the effect of the studied anions on the RB 45 destruction by the photocatalysis process. Anions suppress the degradation of RB 45 in the following sequence: $Cl^- > CO_3^{2-} > SO_4^{2-}$. The efficiency of RB 45 degradation without the salt solution is 68.9% after 480min of irradiation while with the addition of sodium chloride (NaCl), sodium carbonate (Na_2CO_3), and sodium sulfate (Na_2SO_4) solutions the inhibition in the degradation of RB 45 was 53.7%, 57.6%, and 64.3% respectively.

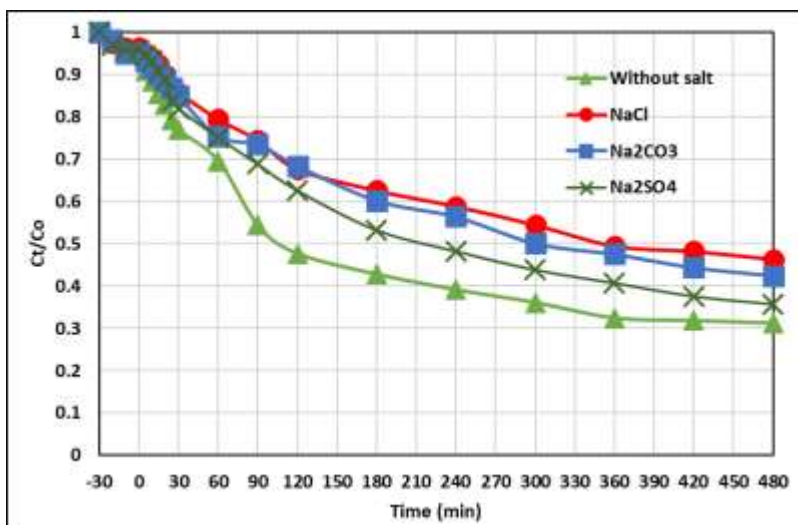


Figure (8). Effect of addition 1% inorganic anions on photocatalytic degradation efficiency of RB 45 dye. Experimental conditions: $[\text{TiO}_2] = 0.75 \text{ g/L}$, and $\text{pH}=3.0$.

4. Conclusions

To conclude, that the photolytic degradation process of RB 45 from aqueous solution is based on several parameters such as, the amount of nano TiO_2 , irradiation time, pH, and dye concentration. Based on the result, the following conclusions were derived: The experiments showed that RB 45 at a concentration of 90 mg/L can be degraded using the optimum conditions, $[\text{TiO}_2] = 0.75 \text{ g/L}$, irradiation time 480 min, and $\text{pH}=3.0$. At this condition, the photocatalytic degradation efficiency was 68.9%. The photocatalytic degradation efficiency of dye increased from 55.4% to 100% after 360 min of irradiation time, when the concentration of dye decreased from 120 to 50 mg/L. The color removal of RB 45 was significantly enhanced by adding H_2O_2 or $\text{K}_2\text{S}_2\text{O}_8$ to the photocatalysis process. The photocatalytic degradation efficiency in the presence of sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), and sodium chloride (NaCl), at an initial concentration of RB 45 dye (90 mg/L), decreased from 68.9% to 64.3%, 57.6%, and 53.7%, at the reaction time of 480 min.

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