Al-Nahrain Journal for Engineering Sciences **NJES** 22(1)31-36, 2019
http://doi.org/10.29194/NJES.22010031

Comparative Studied of Degradation of Textile Brilliant Reactive Red Dye Using H_2O_2, TiO_2, UV and Sunlight

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Paper History:

Received: 26th Sep. 2018

Revised: 1st Jan. 2019

Accepted: 18th March. 2019

Abstract

In this study sunlight and UV radiation were used to compare the efficiency of decolorization of textile wastewater containing brilliant reactive red dye K-2BP (λmax = 534 nm) by the advanced oxidation process (AOP) using (H_2O_2/sunlight, H_2O_2/UV, H_2O_2/TiO_2/sunlight, and H_2O_2/TiO_2/UV). The results studied the effect of solution pH, applied H_2O_2 concentration, TiO_2 concentration (nanoparticle), and initial dye concentration were studied. The experimental results showed that decolorization percentage with H_2O_2/sunlight and TiO_2/H_2O_2/sunlight under the following conditions: - reaction time 150 of minutes, [500 ppm] H_2O_2, [100 ppm] TiO_2, pH=3, initial dye concentration =15 ppm and at ambient temperature were 95.7% and 98.42% respectively. For the same conditions using H_2O_2/UV, H_2O_2/TiO_2 /UV, the percentage of decolorization were 97.85% and 96.33% respectively. The results also indicated that the sunlight is more economic and cost-effective than UV radiation.

Keywords: Sunlight; Photochemical oxidation; Brilliant Reactive red; Water Treatment.

دراسة مقارنة لازالة الصبغة الحمراء المتفاعلة باستخدام (H_2O_2, TiO_2, UV and Sunlight)

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الخلاصة:

في هذه الدراسة استخدمت أشعة الشمس والأشعة فوق البنفسجية لمقارنة كفاءة إزالة اللون من مياه الصرف الصناعية النسيجية التي تحتوي على صبغة حمراء تفاعلية ذات الطول الموجي 534 نانوميتر بواسطة عملية الأكسدة المتقدمة (AOP) باستخدام (H_2O_2/sunlight,H_2O_2/UV, H_2O_2/TiO_2/sunlight, H_2O_2/TiO_2/UV).

وتمت دراسة تأثيرالمتغيرات الرقم الهيدروجيني للمحلول وتركيز بيروكسيد الهيدروجين (H_2O_2) وتركيز ثاني أكسيد التيتانيوم (TiO2) وتركيز الصبغة الأبتدائي. أظهرت النتائج التجريبية أن نسبة إزالة اللون مع H_2O_2 /sunlight و H_2O_2/TiO_2 /sunlight في افضل الظروف وقت التفاعل 150 دقيقة , تركيز بيروكسيد الهيدروجين 500 ملغ\مل , الرقم الهيدروجيني 3 , تركيز ثنائي اوكسيد التيتانيوم 100 ملغ\مل وتركيز الصبغة 15 ملغ\مل وفي درجة حرارة الغرفة 95.7 ٪ و 98.42 ٪ على التوالي. لنفس الظروف باستخدام H_2O_2/UV، H_2O_2/TiO_2 / UV ، كانت النسبة المئوية لإزالة اللون 97.85 ٪ و 96.33 ٪ على التوالي. كما أشارت النتائج إلى أن ضوء الشمس اقتصادي واكفئ من الأشعة فوق البنفسجية وخفض تكاليف التشغيل لمعالجة المياه الصناعية النسيجية.

1. Introduction

Many industrial processes use totally different chemical dyes for numerous functions (textile, cosmetics, food, pharmaceutical, paper, dying of fabric, printing, etc.). The presence of dyes in water is most unwanted, therefore an awful bit of these coloring agents are extremely visible and will be poison to the aquatic surroundings [1]. Dye compounds are artificial organic compounds with complicated molecular structures and huge molecular weights, therefore treatment difficulties were a raised of dye waste product. Textile dyes can be classified into many types, reactive, basic, disperse, fat, direct, acid and sulfur dyes according to their application in the dying process. Reactive dyes are used in the various textile stages industry that related to fibers by reacting with OH group in fiber. Some of them contain typical azo-based chromophores (N=N band) combined with forms of reactive teams. This property makes them hard to degrade in waste product[2].

Dyeing wastewater leads to a serious environmental problems including high pH, low biodegradable, high temperature, suspended solid (SS), high COD, high Total Dissolved Solids (TDS), high color and organic materials [3].These substances cause great harm to the environment, and many countries are conducting research to treat industrial water, especially the water of textile and dyeing plants, to decrease the substances before they flow into the rivers or sewage [4].There are many ways to treat textile wastewater (physical, biological and chemical) or in some cases a combination treatment of these processes are used. Physical treatment involves isolation, adsorption, ion exchange, membrane filtration or separation of the waste material from the mainstream. In the biological treatment, the main purpose involves microbes to be feed on organic waste. Chemical treatment includes coagulation/Flocculation and Advanced oxidation processes [5]. Coagulation and flocculation, adsorption on activated carbon and reverse osmosis are varied chemical/ physical processes. These processes are inadequate to decay the coloured compounds in textile wastewater. More of sludge formation could be a major issue related to these processes [6]. Advanced oxidation Processes are applied to treat dye-contaminated waste product of textile industries. This technique produces a powerful oxidizing species such as OH* radicals, that break down them into little and non-harmful substances. In several cases the organic compound is totally mineralized into water and CO_2. The AOP technique has drawn significant attention by many scientific community because it is easy to be handled and it produces considerably fewer residuals as compared to the classical approaches. The various strategies applied within the advanced oxidation approach are the UV photolytic technique, photo-Fenton, Fenton, ozonation, photocatalytic, biodegradation and also the radiation induced degradation of dyes [7].The mechanism of AOPs is simply formation of hydroxyl radicals OH*, that may oxidize a large variety of organic compounds [8]. The UV–H_2O_2 method has many benefits over different AOPs: the ambient conditions were used and no sludge formation [9]. The dosage of H_2O_2 and pH plays important role within the discoloration of dyes by H_2O_2/UV method. The method has been found to be more practical in an acid medium in context to discoloration [1]. The decomposition rate of dye will increase with the increase in ultraviolet radiation intensity [10]. TiO_2 concentration in suspension within the presence of low concentrations of hydrogen peroxide supported the established increase in the rates of decolorization and mineralization of the several pollutants in standard state [11, 12, 13]. Those researches studied the effects of amount of catalyst, contact time, effect of pH for many methods of AOP. UV light has been tested together with H_2O_2 and TiO_2 for the degradation of textile wastewater [14]. [15], investigation of Methylene Blue (MB**)** decolorization from synthetic wastewater using H_2O_2/UV as an advanced oxidation process. [16] stated that the effect of peroxide to TiO_2/UV process will increase in the formation OH* radical, because it prevents the electron–hole recombination. Titanium dioxide "TiO_2" is more economical catalyst for photocatalytic for pollutants removal because of faster electron transfer to the molecular oxygen furthermore, essentially available, cheap, non-toxic and comparatively high chemical stability [17]. There are four mineral type of titanium oxide: anatase, rutile, brookite, titanium dioxide (B) or TiO_2 (B) and degussa P-25. Anatase form is used mainly as a photo-catalyst under UV irradiation. But degussa P-25 is more active than pure anatase:- It is used as a photocatalyst with particle size 20-30 nm [18].

Solar radiation was also used within the AOP systems. [19], studied the treatment of textile effluent exploitation artificial solar radiation. The target of this study is to discover the efficiency of decolorization of the wide used textile brilliant reactive red dye by sunlight and UV radiation within the presence of H_2O_2 and TiO_2 nanoparticles during a laboratory reactor. Many parameters will be investigated like initial pH, initial H_2O_2 dosage, TiO_2 amount initial dye concentration and ultraviolet light intensity so as to determine the optimum operational conditions.

2. Experimental

The chemicals used in this study were Brilliant reactive red which is used in textile as a pollutant, H_2O_2 (50% w/w) was obtained from Merck.TiO_2 degussa P-25 (80% anatase, 20% rutile with particle size 30±5 nm). H_2SO_4 and NaOH were used to adjust the pH of the solutions. A batch reactor with magnetic starrier was used in this work. The Advanced oxidation methods decolorization experiments were conducted in 600 mL batch reactor which is contained 500 mL of the simulated wastewater. The distilled water was used to prepare the desired concentration of brilliant reactive red dye. Initial concentration of dye was 50mg/L. The equivalent stirring velocity of magnetic starrier was around 200 rpm at room temperature for 10-150 min with sunlight as energy source, other experiments with UV chamber equipped two UV lamps (11W 4P-SE, Philips, England). Samples were collected every 10 min. The decolorization efficiency of dye under exposure (sunlight-H_2O_2, UV-H_2O_2, sunlight-TiO_2-H_2O_2 and UV-TiO_2-H_2O_2) were investigated. Three brilliant reactive red dye concentrations (15, 30, 50) mg/L were tested at a different residence times (10, 20, 30, 45, 60, 90, 120, 150) min using two UV lamp and the same techniques were used by sunlight rather than UV lamps. Firstly the dosage of hydrogen peroxide was changed with concentration of (50, 100, 150, 250, 500, 700) mg/L at pH=6.3, then the optimum concentration of H_2O_2 was used at different concentration of nano TiO_2 catalyst (25, 50, 75, and 100) ppm, also pH was varied (3, 5, 6.3, and 8). The pH was adjusted before adding the reagents by using NaOH or H_2SO_4. Finally, the initial dye concentration was varied to obtain the optimum conditions. The decolorization rate of degradation of red dye was measured by UV-Spectrophotometer at 534nm absorption maxima. The decolorization rate (%) was calculated using equation 1:

Decolorization rate is:

$$(\%) = (C_o - C)/ C_o \times 100 \qquad (1)$$

Where C_o is the initial concentration of contaminants (dyes) in the samples wastewater (mg/L).C is the concentration after photo irradiation (mg/L).

3. Results and discussion

3.1 Effect of H_2O_2 concentration

Figure 1 shows the effect of initial concentration of H_2O_2 in the range (50-700ppm) on the decolorization rate. At pH= 6.3, time=150min, increasing the H_2O_2 amount from 50 to 500 mg/L increases the decolorization rate from 45.51% to 65.88%. Further increase of H_2O_2 from 500 to 700 mg/L decreases the decolourisation rate to 58.4% for the red dye. Hence 500 mg/L H_2O_2 concentration was the optimal for the photo-oxidation. Increasing of the hydrogen peroxide concentration from 500 to 700 ppm decreases the rate of decolourization to 58.004% for the brilliant reactive red dye. Hence 500 ppm H2O2 amount is the best dosage for the photo oxidation. Increasing of H_2O_2 concentration accelerate the decolorization speed and decreased the required reaction time for the complete decolorizetion. The mechanism is represented by the following equations: [1]

$$H_2O_2 + h\nu \longrightarrow 2OH^* \qquad (2)$$

$$OH^*+dye \longrightarrow \text{dye-intermediate} \qquad (3)$$

$$OH^*+dye \longrightarrow \text{intermediate} + CO_2+H_2O + \text{mineralization products} \qquad (4)$$

The ultraviolet light, represented as hv, causes the dissociation of the H2O2 into two hydroxyl radicals (OH*). The hydroxyl radicals are strong oxidants that can readily oxidize organic compounds. The higher initial hydrogen peroxide concentration produces higher hydroxyl radical concentration (Eq. 2), which decomposes more target compound. However, an optimal hydrogen peroxide concentration exists because overdosing of hydrogen peroxide would lead to reaction with hydroxyl radical and formation of HO_2^*, then the hydroxyl radical react with HO_2^* to form water and oxygen. These results agree with [1,20]

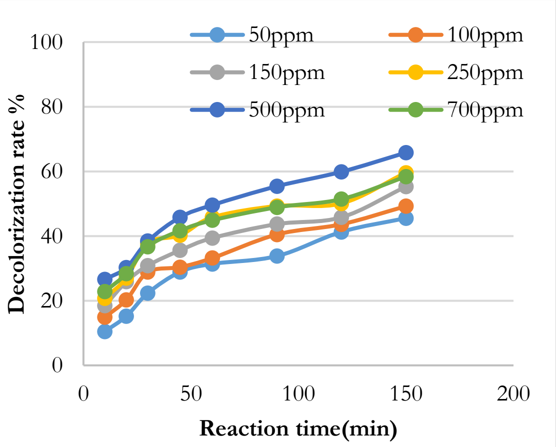

Figure (1): Effect of H_2O_2 on the dye removal: [dye] = 50 mg/L, pH=6.3, 2 UV lamp, reaction time= 150min and All the experiments were at room temperature.

3.2 Effect of TiO_2 Concentration

Figure 2 shows the degradation of brilliant reactive red dye by combining dosing of TiO_2 and H_2O_2. The experiments were achieved at 500 mg/l of H_2O_2, pH 6.3, two UV lamps and carried out for different TiO_2 concentration (25 mg/l to 100 mg/l) with reaction time 150 min. At 100 mg/l concentration of nano TiO_2 catalyst, the maximum of 76.84% removal was achieved in UV/H_2O_2/TiO_2. However, increasing of catalyst amount lead to increase the rate of decolorization. Also, the addition of H_2O_2 in photo-catalysis, the fraction of light absorbed by the photo-decomposition increases and thus the photolysis rate also increased. TiO_2 was considered as suitable to combine with H_2O_2, because in the presence of H_2O_2 the reaction is clearly accelerated due to the production of hydroxyl radical that attract the organic pollutants. This is an agreement with[11, 21]. The mechanism are represented by the following equations:

$$TiO_2+UV \longrightarrow TiO_2(e^- + h^+) \qquad (4)$$

$$TiO_2\,(e^-) + H_2O_2 \longrightarrow O_2^- \qquad (5)$$

$$TiO_2\,(h^+) + H_2O \longrightarrow OH^*+H^+ \qquad (6)$$

$$H_2O_2 + e^- \longrightarrow OH^* + OH^- \qquad (7)$$

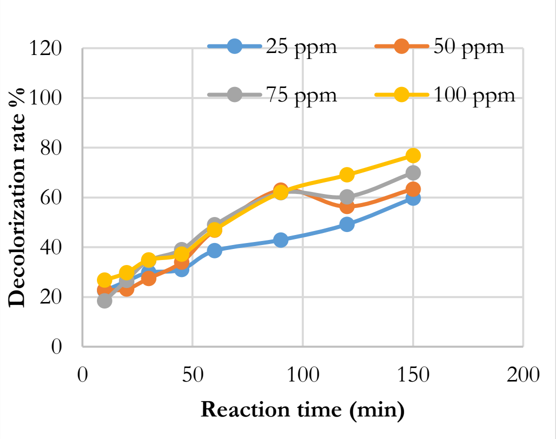

Figure (2): Effect of TiO_2 on the dye removal: Initial concentration [dye] = 50 mg/L, [H_2O_2] = 500mg/l, pH= 6.3, 2 UV lamp, reaction time= 150min, and at room temperature.

3.3 Effect of pH

Figures 3, 4, 5 and 6 show the effect of the pH (3-8) on the rate of the decolorization of brilliant reactive red dye by (H_2O_2/sunlight, H_2O_2/UV and H_2O_2/TiO_2/sunlight, H_2O_2/TiO_2/UV) using a series of experiments. For the four processes at pH =3, the removal efficiency were (81.3%, 89.49%, 93.6%, 87.25%) respectively and at pH = 8, the removal efficiency were (47.15%, 51.09%, 58.35%, 53.18%) respectively. The maximum removal efficiency is achieved at pH 3 with H_2O_2/TiO_2/sunlight process. For H_2O_2/UV and H_2O_2/sunlight at pH=3, the results show increasing in the removal efficiency compared with pH= 8, due to which acidic pH improves the formation of hydroxyl radicals with strong oxidation efficiency. The lowering decolorization rate in the pH 8, may be due to decrease of hydroxyl radical concentration. So, the photolysis of H_2O_2 produced water and oxygen instead of hydroxyl radical. Also, in alkaline conditions the (HO_2^-) is formed. This HO_2^- anion reacts with OH* radical and a residual H_2O_2. The mechanism shows in equations 8 and 9. For the photocatalytic the highest removal efficiency is achieved at pH = 3. At pH= 3, the result show slightly increases in the removal efficiency compared with pH= 8, due to which acidic pH the TiO_2 surface is negatively and repulsive forced lead to increased adsorption, however the formation of hydroxyl radical is increased. The decreasing in the decolorization rate at the pH= 8, may be due to decrease in the production of hydroxyl radical concentration. The UV irradiation and sunlight can bring high efficiency, however sunlight, because of its abundance and non-hazardous nature. This is agreement with [20]

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + OH^* \qquad (8)$$

$$OH^* + HO_2^- \longrightarrow H_2O + O_2^- \qquad (9)$$

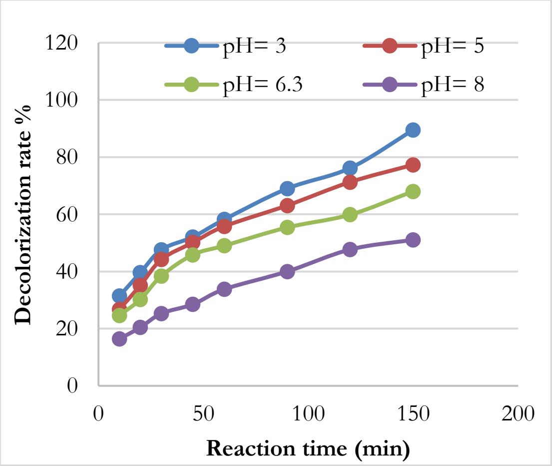

Figure (3): Effect of pH on the dye removal: dye concentration = 50 mg/l [H_2O_2] = 500mg/l, sunlight and reaction time=150min.

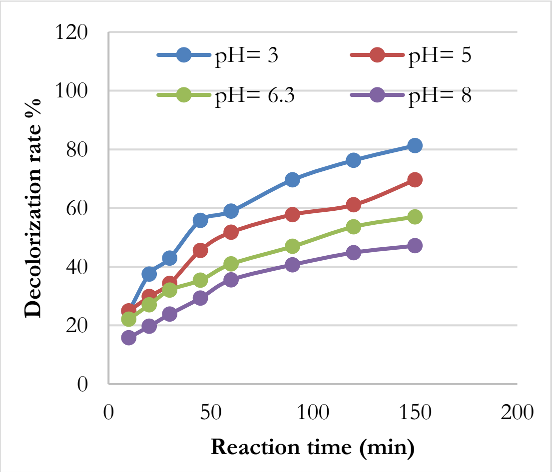

Figure (3): Effect of pH on the dye removal: [dye] = 50 mg/l H_2O_2=500mg/l, 2 UV lamp, reaction time= 150min.and at room temperature.

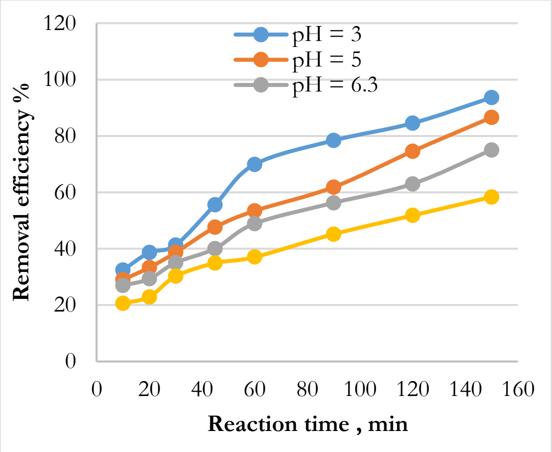

Figure (5): Effect of pH on the dye removal: [dye] = 50 mg/l [H_2O_2] = 500mg/l, [TiO_2] = 100mg/l, sunlight, and at reaction time = 150min.

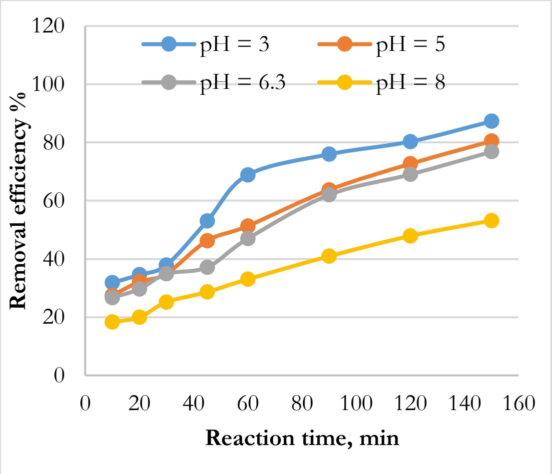

Figure (6): Effect of pH on the dye removal: [dye] = 50 mg/l, [H_2O_2] = 500mg/l, [TiO_2] = 100mg/l, 2 UV lamp, reaction time = 150min and at room temperature.

3.4 Effect of dye concentration

The effect of various initial concentrations on the photochemical decolourisation has been investigated from 15 to 50 mg/l for (H_2O_2/sunlight, H_2O_2/UV, H_2O_2/TiO_2/sunlight, and H_2O_2/TiO_2/UV) processes. The results are shown in Figures 7, 8, 9 and 10. At pH 3 increasing in the initial concentration of dye from 15 to 50 mg/l decreases the decolorization rate from 95.7% to 81.34% for H_2O_2/sunlight, 97.5% to 89.49% for H_2O_2/UV, 98.4% to 89.6% for H_2O_2/TiO_2/sunlight and 96.33% to 87.25% for H_2O_2/TiO_2/UV. The transfer of photons decreases when the concentration increased, so it will lower the hydroxyl radical concentration. This agree with Ref. [20].

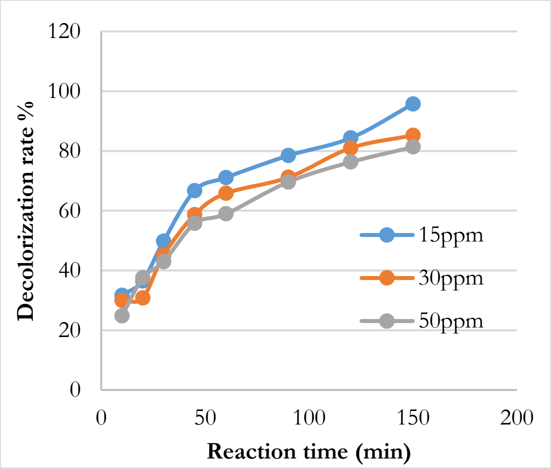

Figure (7): Effect of dye concentration on the removal efficiency: pH=3, $[H_2O_2]$ = 500mg/l, sunlight, and at reaction time=150min

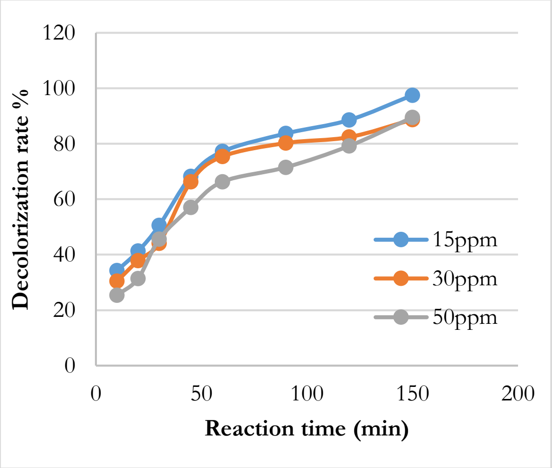

Figure (8): Effect of dye concentration on the removal efficiency: pH=3, $[H_2O_2]$ =500mg/l, 2UV lamp, reaction time=150min

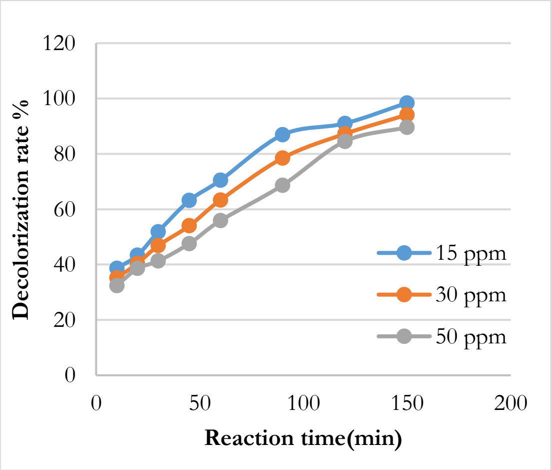

Figure (9): Effect of dye concentration on the removal efficiency: pH= 3, $[H_2O_2]$ = 500mg/l, $[TiO_2]$ = 100 mg/l, sunlight and at reaction time = 150 min.

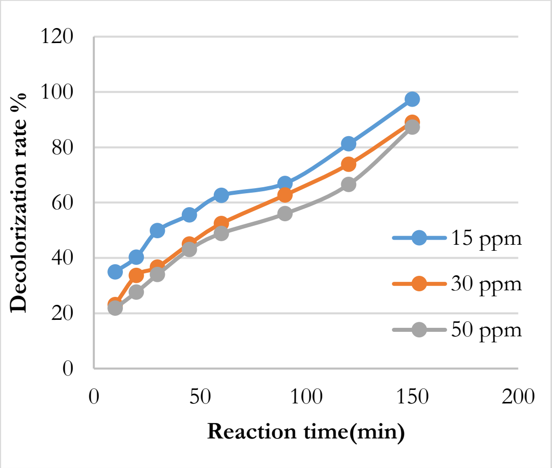

Figure (10): Effect of dye concentration on the removal efficiency: pH= 3, $[H_2O_2]$ = 500mg/l, $[TiO_2]$ = 100 mg/l, 2 UV lamp, reaction time = 150 min and at room temperature.

3.4 Effect of UV-light and sunlight

UV radiation was generated from UV lamps with a diameter of 1.25 cm and length 21 cm sort (TUV 11W 4P-SE, Philips, England).The result of UV-light power on the decolourisation of reactive red is shown in Figure 8. The intensity of UV-C is 680 MW/cm2 with wavelength 254nm, sunlight consists of 3 UV light; UV-A [400-315nm], UV-B [315-280nm], UV-C [280-180nm].The radiation reaching the Earth's surface is UV-A type, wherever the ozone layer absorbs short and medium waves. The development of removal percentage is increased with increasing in the hydroxyl radical OH*. The rate of photolysis of H_2O_2 depends on the incident power. At low concentration the degradation is low. At high intensity extra hydroxyl radicals are produced, therefore removal rate will increase. Figures 11, 12 show the difference between the four processes.

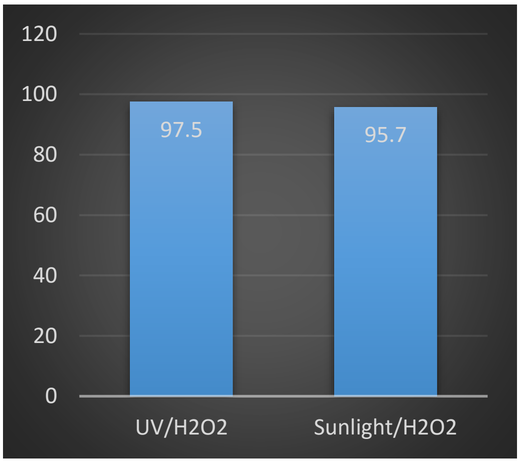

Figure (11): Effect of Light source on the removal efficiency: pH= 3, $[H_2O_2]$ = 500mg/l, [dye] = 15mg/l and reaction time = 150min.

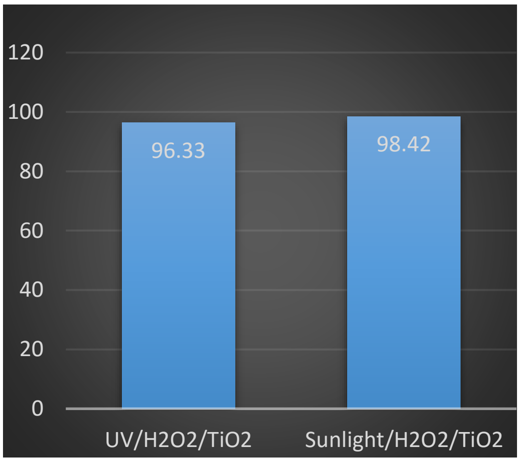

Figure (12): Effect of Light source on the removal efficiency: pH= 3, $[H_2O_2]$ = 500mg/l, [dye] = 15mg/l, $[TiO_2]$ = 100 mg/l and reaction time = 150min.

4. Conclusions

The decolorization of brilliant reactive red dye using four processes (H_2O_2/sunlight, H_2O_2/UV, H_2O_2/TiO_2/sunlight, and H_2O_2/TiO_2/UV) was investigated. It can be use the sunlight with hydrogen peroxide or any oxidant to treat the textile wastewater and it is very low cost, environmental friendly. Sunlight can be used for removal of organic substances. The results indicated that the UV/H_2O_2 and H_2O_2/TiO_2/UV methods can be efficiently for removal of textile wastewater, because H_2O_2 absorb the light <245nm and TiO_2 absorb the light < 365nm .The increasing H_2O_2 amount increased in the decolorization rate to the optimal point. The maximum removal efficiency was achieved at pH 3 to 5 in all AOP experiments. The removal efficiency increases with decreasing of the dye concentration

5.References

[1] A. Al-Kdasi, A. Idris, K. Saed, and C. T. Guan, “Treatment of textile wastewater by advanced oxidation processes—a review,” *Glob. nest Int. J*, vol. 6, no. 3, pp. 222–230, 2004.

[2] B. A. R. TEHRANI and F. L. Amini, “Decolorization of a reactive dye by UV-enhanced ozonation,” 2010.

[3] C. Sahunin, J. Kaewboran, and M. Hunsom, “Treatment of Textile Dyeing Wastewater by Photo Oxidation using UV/H,” *reactions*, vol. 22, p. 23, 2006.

[4] U. Pagga and D. Brown, “The degradation of dyestuffs: Part II Behaviour of dyestuffs in aerobic biodegradation tests,” *Chemosphere*, vol. 15, no. 4, pp. 479–491, 1986.

[5] H. Zhou and D. W. Smith, “Advanced technologies in water and wastewater treatment,” *J. Environ. Eng. Sci.*, vol. 1, no. 4, pp. 247–264, 2002.

[6] I. Ahmad Bhatti and S. Irshad, “UV Radiations Assisted Advanced Oxidation Approach for the Degradation of Reactive Azo Dye, Using TiO 2 Photocatalyst.,” *J. Chem. Soc. Pakistan*, vol. 39, no. 5, 2017.

[7] M. A. Rauf and S. S. Ashraf, “Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution,” *Chem. Eng. J.*, vol. 151, no. 1–3, pp. 10–18, 2009.

[8] A. Aleboyeh, M. B. Kasiri, M. E. Olya, and H. Aleboyeh, “Prediction of azo dye decolorization by UV/H2O2 using artificial neural networks,” *Dye. Pigment.*, vol. 77, no. 2, pp. 288–294, 2008.

[9] M. Neamtu, I. Siminiceanu, A. Yediler, and A. Kettrup, “Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H2O2 oxidation,” *Dye. Pigment.*, vol. 53, no. 2, pp. 93–99, 2002.

[10] H. Amin, A. Amer, A. E. Fecky, and I. Ibrahim, “Treatment of textile waste water using H2O2/UV system,” *Physicochem. Probl. Miner. Process.*, vol. 42, pp. 17–28, 2008.

[11] J. C. Garcia and K. Takashima, “Photocatalytic degradation of imazaquin in an aqueous suspension of titanium dioxide,” *J. Photochem. Photobiol. A Chem.*, vol. 155, no. 1–3, pp. 215–222, 2003.

[12] C. Galindo, P. Jacques, and A. Kalt, “Photooxidation of the phenylazonaphthol AO20 on TiO2: kinetic and mechanistic investigations,” *Chemosphere*, vol. 45, no. 6–7, pp. 997–1005, 2001.

[13] B. N. Kumar, Y. Anjaneyulu, and V. Himabindu, “Comparative studies of degradation of dye intermediate (H-acid) using TiO2/UV/H2O2 and Photo-Fenton process,” 2011.

[14] S.-J. Kim *et al.*, “Photocatalyzed destruction of organic dyes using microwave/UV/$O_3/H_2O_2/TiO_2$ oxidation system,” *Catal. Today*, vol. 164, no. 1, pp. 384–390, 2011.

[15] J. C. Garcia, J. I. Simionato, A. E. C. da Silva, J. Nozaki, and N. E. de Souza, “Solar photocatalytic degradation of real textile effluents by associated titanium dioxide and hydrogen peroxide,” *Sol. Energy*, vol. 83, no. 3, pp. 316–322, 2009.

[16] S. A. Mandavgane and M. Yenkie, “Degradation of salicylic acid by UV, UV/H2O2, UV/O3, photofenton processes,” *J Chem*, vol. 4, no. 3, pp. 640–647, 2011.

[17] P. Bansal, D. Singh, and D. Sud, “Photocatalytic degradation of azo dye in aqueous TiO2 suspension: Reaction pathway and identification of intermediates products by LC/MS,” *Sep. Purif. Technol.*, vol. 72, no. 3, pp. 357–365, 2010.

[18] J. Jeni and S. Kenmani, “Solar Nanophotocatalytic Decolorisation od Reactive Dyes Using Titanium Dioxide,” 2011.

[19] D. R. Manenti *et al.*, “Performance evaluation of different solar advanced oxidation processes applied to the treatment of a real textile dyeing wastewater,” *Environ. Sci. Pollut. Res.*, vol. 22, no. 2, pp. 833–845, 2015.

[20] M. Muruganandham and M. Swaminathan, “Photochemical oxidation of reactive azo dye with UV–H2O2 process,” *Dye. Pigment.*, vol. 62, no. 3, pp. 269–275, 2004.

[21] A. Aleboyeh, H. Aleboyeh, and Y. Moussa, “Critical effect of hydrogen peroxide in photochemical oxidative decolorization of dyes: Acid Orange 8, Acid Blue 74 and Methyl Orange,” *Dye. Pigment.*, vol. 57, no. 1, pp. 67–75, 2003.