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Decolorization of Reactive Yellow Dye by Advanced Oxidation Using Continuous Reactors

Noor A.A. Mohammed [a], Abeer I. Alwared[a] and Mohammed S. Salman[b]

[a]Department of Environmental Engineering/ College of Engineering/ University of Baghdad
[b]Avi-Cenna E-learning Center / University of Baghdad

Abstract

The photocatalytic decolorization of reactive yellow dye from aqueous solution was investigated by using TiO_2 photocatalyst. Heterogeneous photocatalytic processes applied under natural weathering conditions, in the presence of UV lamp show a promising degradation capability. In this study, synergistic effects of factors such as flow rate, and number and intensity of UV lamps were scrutinized in continuous photocatalytic reactor at constant best conditions obtained from the batch reactor tests pH=7, TiO_2 concentration (25mg/l) , 400 mg/l dosage of H_2O_2. Moreover .The maximum removal of dye achieved at 60 minutes, in the presence of two UV-light, 20mg/l dye concentration and at (5 l/h) flow rate was found to be 95.47%, also the reaction was found to be of a first order throughout the system.

Keywords: Reactive yellow dye; Photo-degradation; Heterogeneous catalysis; Water treatment.

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1- Introduction

Wastewater contaminated with toxic organic materials poses a serious threat to the environment [1]. Color is the first pollutant identified in wastewater and must be removed before discharging into land or water. The presence of traces of dye in water (less than 1 mg/l in some dyes) is very clear and affects the aesthetic value of lakes, rivers and other water bodies, water transparency and gas solubility. Decolorization of water is usually more important than the removal of soluble and colored organic matter, which is usually a large part of the biochemical oxygen demand (BOD). However, dyes are more difficult to handle because of their artificial origin and mostly aromatic complex structures [2]. Removal of dyes is difficult and poorly efficient due to the use of conventional physic-chemical and biological methods [3].

Conventional techniques for removing dyes from wastewater are adsorption, biological filtration, coagulation and ozone treatment.

Every technique has its advantages and disadvantages. Such as, adsorption is not destructive because it simply moves the dye from the water to another stage, causing secondary pollution. Therefore, there is a need to reprocess the absorbed materials and solid waste, which is an expensive process. Traditional biological treatment techniques are ineffective for degradation and decolorization due to the presence of large amounts of aromatic hydrocarbons in dye molecules and the stability of modern dyes. Also, most dyes are adsorbed only on the sludge without degradation. Filtration may provide pure water, but pigments with low molar mass may pass through the filtration system. The use of alum, iron salts or lime is also a low cost method. However, it needs waste treatment. Finally, although ozone does not require treatment, it suffers from high operating costs [4].

Through the past few years, advanced oxidation processes (AOP) were chosen as an alternative to water purification. AOP was divided into two classes (heterogeneous catalysis and homogeneous catalysis). Heterogeneous catalysis was successfully used to reduce various hazardous substances [5].

AOPs are based on the generation of hydroxyl radical ($^{\cdot}OH$) which have the ability to decompose organic pollutants into carbon dioxide, water and inorganic materials. Several of AOPs techniques include chlorination, ozonation, Fenton, photo-Fenton, photo-catalytic and wet-air oxidation .Hydroxyl radicals attack the organic molecules causing their destruction and mineralization.Also, another method is the photocatalyst with titanium dioxide that is a wide band gap semiconductor and it is used near- UV light of wavelength shorter than 380 nm or sunlight. Main factor that affects the photo-decolourization of dyes is pH of the reaction solution. It describes the charges on the surface of the photocatalyst and it also manipulates the kinetics of organic compounds degradation. All the three possible reaction mechanisms such as (1) hydroxyl radical attack, (2) direct oxidation by the positive hole and (3) direct reduction by the electron from the conducting band can be influenced by pH.

Corresponding Authors: Name: Noor A.A. Mohammed , Email: mn.r_86@yahoo.com, Name: Abeer I. Alwared, Email: abeerwared@yahoo.com , Name: Mohammed S. Salman, Email: iraqmas68@yahoo.com

The positive hole is seemingly ready to oxidize a water molecule to hydroxyl radical. The hydroxyl radical, in turn, is a powerful oxidant .Hydrogen peroxide has low cost and available which was formed hydroxyl radicals by the photolytic dissociation of hydrogen peroxide in water by UV irradiation at a wavelength of 254nm[6] . Medium Pressure UV lamps produce a higher radical generation. The processes of H_2O_2/TiO_2/UV treatment depend on many conditions that have an effect on the degradation of organic pollutants. The conditions include the type and concentration of the organic materials, hydrogen peroxide concentration, TiO_2 amount, light source, pH, temperature, flow rate and reaction time [7].

Huang et al. [8] studied the parameter of adding the amount of hydrogen peroxide to remove the methyl orange from solution. The removal efficiency was increased with increasing H_2O_2 concentration. Zhiyong et al. [9] studied the addition of hydrogen peroxide with titanium dioxide Degussa P25 (0.5mg/l) catalyst (1mM) to remove methyl orange solution under sunlight irradiation.

Senthil Kumar et al. [10] reported that the increase in the OH concentration will cause the reduction of the hydrogen peroxide [11]. Ali 2017 [12] studied the continuous photo-catalytic reactor using TiO_2/UV process to treat produced wastewater solution, and the results showed that the rate of degradation of organic pollutants decreased with the increase in the flow rate while it increased with increasing the number of the UV lamp. Therefore, the goal of this research is to study the effectiveness of the AOPs in the continuous mode to degrade reactive yellow dye from aqueous solution under the influence of flow rate, intensity of UV lamp and initial dye concentration.

2- Material and Method

2.1. Materials

The Reactive azo Yellow dye (R-Yellow) which is illustrated in Fig. **1**, was supplied by AL-Hilla textile factory south of Baghdad, (Department of Dying and Printing). TiO_2-P25 as powder was supplied by Fluka (China) with 99% purity (molecular weight 79.87g/mol). The hydrogen peroxide H_2O_2 (50% w/w) was obtained from Merck. The pH value of the aqueous solution was adjusted to7 using HCl and/or NaOH.

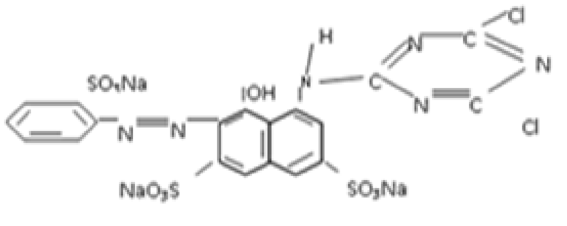


Fig. 1. Chemical Structure of reactive yellow[13]

2.2. UV Lamps

Two types of UV lamp were used in the experiments. Ultraviolent radiation (254 nm) was produced from 1.25 cm diameter and 21 cm length type (TUV 6 W 4P-SE, Philips, England) and the other one was (11W 4P-SE, England). UV lamp was sheathed in quartz sleeve for protection (2.5 cm in diameter and 22 cm in length) as shown in Fig. **2**. The intensity of UV-C of 6w and 11w lamps was 400 Mw/cm^2 and 600 Mw/cm^2 , respectively.

Fig. 2. UV Lamp sheathed in quartz sleeve

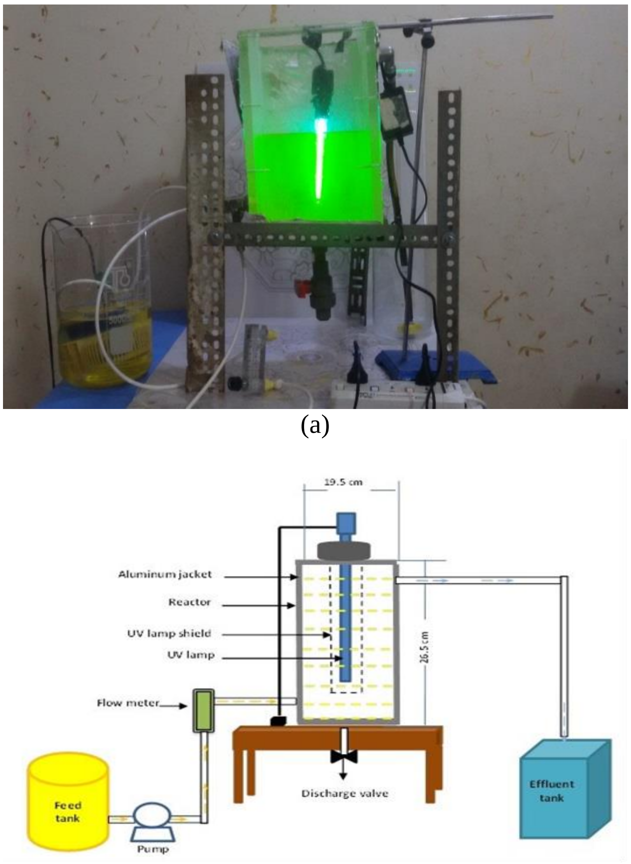
2.3 Experimental Work and Analysis

The continuous experiments procedure include a preparation of 6 L of aqueous solution with a desired concentration of R- yellow dye at (pH= 7, H_2O_2= 400 mg/l, and TiO_2 =25 mg/l) which obtained from previous batch experiments .H_2O_2 in addition to TiO_2 has been added to the aqueous solution, then the solution was pumped from storage tank at the desired flow rate which is controlled by flow meter. The solution enters the rectangular Pyrex glass reactor that had 10 L in volume with (19.5 × 19.5 × 26.5) cm^3 dimensions, from the bottom of tank and discharge as an overflow to another tank for treated water. The polluted water enters the tank from the bottom moves upward, until the discharging from the reactor leading to the full exposure of layers to the UV lamp. Fig. **3** illustrates the photograph and the sketch of a continuous reactor.

After each experiment, a sample was taken and analyzed by using (ADVANCED MICROPROCESSOR UV-VIS SPECTROPHOTOMETER SINGLE BEAM LI-295) to measure the concentration of R-yellow dye at 420 nm. The removal efficiency (%) was obtained from following equation:

$$\text{The removal efficiency} = (C_o-C)/C_o*100 \qquad (1)$$

Where: C_o = the initial concentration of dye in the aqueous solution (mg/l); C = the concentration (mg/l) after treatment.



(a)

(b)

Fig. 3. a, photograph of continuous reactor, b, Schematic diagram of the reactor

3- Results and Discussion

3.1. Influence of Initial Dye Concentration

The effect of different initial R-yellow concentration (20, 50, 75 and 100)mg/l on the removal efficiency was studied at flow rate (5 l/h) and their results were plotted in Fig. **4**. The results showed that the removal efficiency of dye dropped with increasing dye concentration from 93.25% to 67.18% for (20 – 100 mg/l) of dye concentration.

However, significant change in decolourization percentage was noticed beyond 20 mg/l. High decolorization may be at low concentrations because there are multiple active sites on the catalyst surface rather than the number of degrading dye molecules. [14], while increasing the concentration comes to saturation point and then excess dye is found in the reaction mixture.

On the other hand, a decrease in decontamination in higher concentration of dye molecules didn't allow enough light to penetrate through it to reach the catalyst surface (shadow effect). So the best initial concentration was 20 mg/l. This is in agreement with the finding of [15].

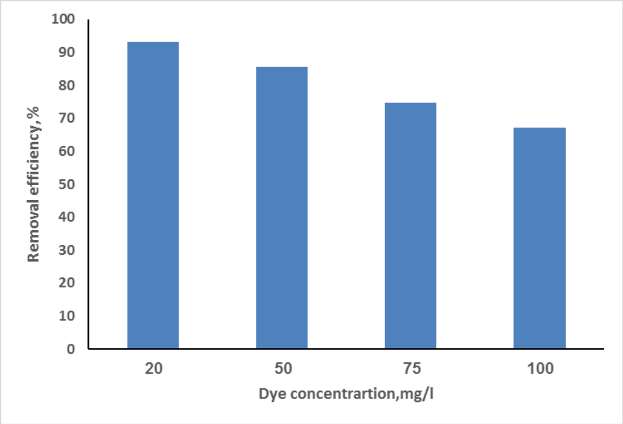


Fig. 4. Effect of initial dye concentration on the decolorization of R-yellow dye, pH= 7 [H_2O_2] = 400mg/l,[dye] = 20 mg/l, [TiO_2] = 25 mg/l

3.2. Influence of Flow Rate

The effect of different flow rate (5, 10 and 15) l/h on the removal efficiency of R-Yellow dye was studied and their results were presented in Fig. **5** , it can be seen from this figure that the maximum removal efficiency was (93.7%) at the flow rate 5 l/h . At high flow rate, the polluted wastewater was subjected to UV radiation in a short period of time that leads to decreases in the volume of provided energy for H_2O_2 to create additional hydroxyl radical [16]. An outcome given was that the rate of degradation of dye decreased with increasing the flow rate. This result was similar with the finding of [17].

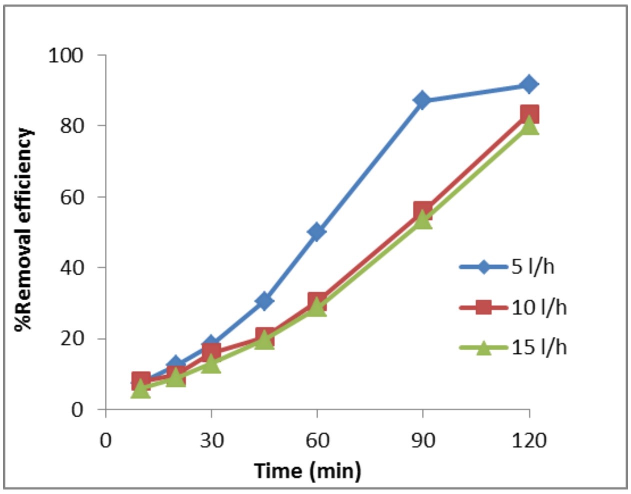


Fig. 5. Effect of Flow rate on the decolorization of yellow dye at pH= 7 [H_2O_2] = 400mg/l,[dye] = 20 mg/l, [TiO_2] = 25 mg/l

3.3. Effect Number of UV Lamp

Fig. **6** shows the effect of different number of UV lamp at different flow rate on the removal efficiency of R-yellow dye from aqueous solution while keeping other parameters constant from previous experiments; dye concentration=20 mg/l, H_2O_2=400 mg/l, TiO_2=25 mg/l, pH =7.

The results show that the removal efficiency decreased with increasing flow rate while it increased by increasing number of UV lamp as can be seen in Table **1** at 5 l/h flow rate .Increasing the number of UV lamps will supply more energy for generation of hydroxyl radical, furthermore the reaction time was decreased, which will be considered the best effect factor in decolorization and degradation of dye [18]. This result was similar with the finding of [19]

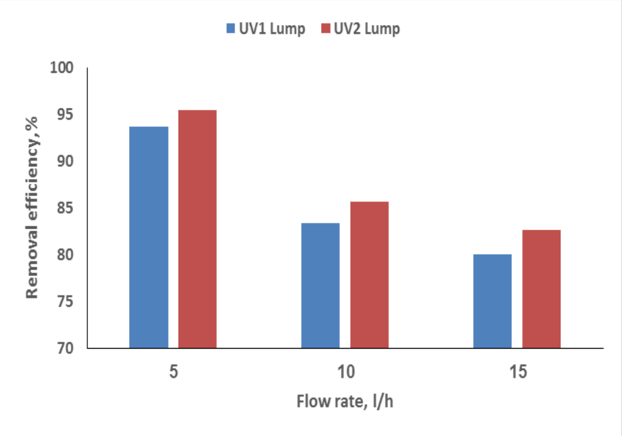


Fig. 6. Removal efficiency of R-yellow dye 20 mg/l with, one and two UV lamps, H_2O_2=400mg/l, TiO_2=25mg/l, pH=7 and Flow rate = 5 l/h

Table 1. Removal efficiency of R-yellow dye =20 mg/l by one UV and two UV, H_2O_2=400mg/L, TiO_2=25mg/L, pH=7and flow rate = 5 l/h in continuous system

Time	1 UV	2 UV
15	18.25	32.95
30	30.5	57.92
60	50	83.95
90	87.1	86.12
120	93.7	95.47

3.4. Effect of Irradiation Intensity

The influence of irradiation intensity (400 and 600) Mw/cm^2 of (6 and 11) w UV lamp, respectively on the removal efficiency was plotted in Figure (6).

It can be seen from this figure that the degradation rate increases with increasing in UV light intensity from 93.7% to 96.8% for 6 and 11 w, respectively. UV irradiation supports generate the photons required to enhance the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst, and as the energy of a photon is related to its wavelength, the overall energy input to a photocatalytic process turns out to be dependent on light intensity.

The degradation rate increases when more radiation falls on the catalyst surface, hence, more hydroxyl radicals are produced [20]. This was similar with the finding of [21]

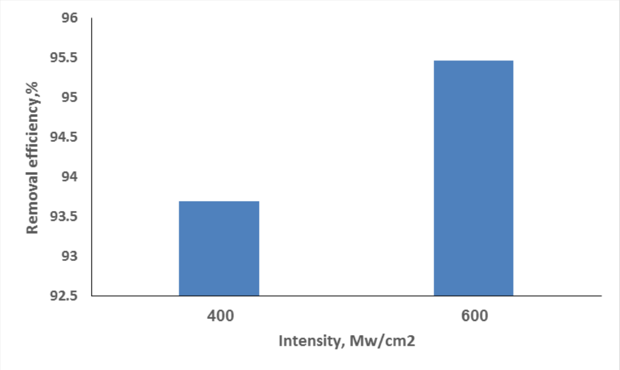


Fig. 7. Effect of intensity of UV at dye=20mg/l, H_2O_2=400 mg/l, TiO2=25 mg/l, pH=7, flow rates=5 l/h

3.5. Kinetic Studies on Photocatalytic Decolorization of Dyes

The experimental data for decolorization of the R-yellow can be fitted according to pseudo-first-order and pseudo-second-order. The linearized form of pseudo-first-order and second-order kinetic models can be given in equations (2) and (3): [22]

$$\frac{1}{C}-\frac{1}{C_o}=k_1t \qquad (2)$$

$$k.t=\ln(C_o/C) \qquad (3)$$

Where: *K*, K_1 are the pseudo-first- and pseudo-second-order rate constants in min^{-1} and L.mg^{-1} min^{-1} ,respectively, with respect to dye concentration; *t* is the irradiation time (in min); *C* is the dye concentration at time t; C_o : is the initial dye concentration؛

A plot of (ln *Co*/*C*), and (1/*C* -1\Co) versus time for each experiment lead to a straight line whose slope is *K* and *K*1 respectively. The regression analysis of the concentration versus reaction time indicated that the rate of decomposition of the compound could be described by first order kinetics, as shown in Table 2.

Table 2. Reaction rate constants in heterogeneous photocatalyst H_2O_2=400mg/L, dye=20mg/L, pH=7, TiO2=25 mg/L

Removal efficiency	First order K min^{-1}	R^2	Second order K_1 L.mg^{-1}.min^{-1}	R^2
98.8	0.0319	0.98	0.0328	0.8107
95.9	0.0229	0.9750	0.0037	0.9002
84.89	0.0134	0.9593	0.0005	0.9766
78.69	0.0093	0.9273	0.0002	0.9951

4- Conclusion

Reactive yellow dye removal using ($H_2O_2/TiO_2/UV$) process was examined. The results indicated that the $H_2O_2/TiO_2/UV$ methods can be effective for the removal of textile wastewater, with a flow rate of (5-15) l/h and reaction time ranging from (10 – 120) min. However, the increase in the flow rate led to a decrease in the rate of decolorization. Higher decolorization was required for a longer reaction time to generate a hydroxyl radical that could destroy the organic matter. Maximum removal efficiency (93.7%) was achieved at pH 7 and at 400 mg/l of H_2O_2, 25 mg/l of TiO_2, 120 min of 1UV at 400 w irradiation and low flow rate by 5 l/hr. It is also worth highlighting that the R-yellow Photo-degradation process appears to follow pseudo-first order kinetics, and that the rate constant is inversely proportional to the pollutant's initial concentration level.

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ازالة الصبغة التفاعلية الصفراء باستخدام المفاعل المستمر لعمليات الاكسدة المتقدمة

نور عبدالامير محمد[1], عبير الورد[1] و محمد سلمان[2]

[1]جامعة بغداد/كلية الهندسة/قسم الهندسة البيئية
[2]جامعة بغداد/مركز ابن سينا للتعليم الالكتروني

الخلاصة

تهدف هذه الدراسة الى استخدام مفاعل التحفيز الضوئي لازالة الصبغة الصفراء الفعالة من المحاليل المائية كما تضمنت التجربة استعمال مادة TiO_2 كمحفز ضوئي كما و تمت هذه العملية بدرجة حرارة الغرفة وبوجود مصباح للأشعة فوق البنفسجية (UV) تضمن البحث دراسة الآثار التآزرية لعوامل مثل معدل التدفق ، وعدد وكثافة مصابيح الأشعة فوق البنفسجية في مفاعل التحفيز الضوئي المستمر بثبات الدالة الحامضية عند ال7 وتركيز TiO_2 =(25 مجم / لتر) وتركيز بيروكسيد الهيمروجين H_2O_2 =400 ملغ / لتر.، تم التوصل الى ان الحد الاعلى لنسب الازالة عند60 دقيقة و باستخدام مصباحين من الأشعة فوق البنفسجية و تركيزالصبغة 20لتر وبمعدل تدفق 5 لتر / ساعة بلغت(95.4٪) ، كما بينت الدراسة وجود تطابق جيد بين النتائج العملية والنظرية المستحصله من موديل الامتزاز في تجارب الحركية عند استخدام موديل التفاعل الحركي الاول

الكلمات الدالة: الصبغة الصفراء التفاعلية, التحلل الضوئي, العامل المساعد غير المتجانس, معالجة مياه