Photocatalytic Degradation of Reactive Yellow Dye in Wastewater using H_2O_2/TiO_2/UV Technique

Noor 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

In the present study, advanced oxidation treatment, the TiO_2 /UV/H_2O_2 process was applied to decolorisation of the reactive yellow dyes in aqueous solution. The UV radiation was carried out with a 6 W low-pressure mercury lamp. The rate of color removal was studied by measuring the absorbency at a characteristic wavelength. The effects of H2O2 dosage, dye initial concentration and pH on decolorisation kinetics in the batch photoreactor were investigated. The highest decolorisation rates were observed (98.8) at pH range between 3 and 7. The optimal levels of H_2O_2 needed for the process were examined. It appears that high levels of H_2O_2 could reduce decolorisation by scavenging the *OH. The color degradation rate decreases as the dye concentration increases. The rate coefficient (k=0.0319 min^{-1}) of degradation, follows the pseudo-first-order kinetics.

Keywords: Reactive Yellow dye; Titanium dioxide; Hydrogen peroxide; Advanced oxidation processes

1- Introduction

In recent years, the treatment of textile and dyeing wastewater coming from textile industries and other related industries has received the increasing attention because of the high yield, low biodegradability and the high toxicity of this wastewater. The artificial dyes are organic compounds with complex molecular structures and big molecular weights, which are using in chemical industries especially in the textile industry. Most of them are considered non –toxic, although some of them are not totally innocuous because they made of known carcinogens such as benzidine [1]. The pollution problem is different for the various types of fibers. Color is the first contaminant to be recognized in the wastewater and has to be removed before discharging into water bodies or on land. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects the aesthetic merit, water transparency and gas solubility in lakes, rivers and other water bodies [2]. Therefore, it is necessary to find an effective method of wastewater treatment in order to remove the color from textile effluents. There are different convention methods, such as chemical precipitation and separation of pollutants, electrocoagulation [3], elimination by adsorption on activated carbon etc., are currently used. One difficulty with these methods is that they are not destructive but only transfer the contamination from one phase to another, therefore a new and different kind of pollution is faced and further treatments are deemed necessary [4]–[7].

Advanced oxidative processes (AOPs) offer a possible solution to this problem. They allow the degradation of pollutants by highly oxidizing species, such as hydroxyl radicals, generated in the reaction medium. The most widely used techniques are Fenton and photo-Fenton reactions [8],[9], UV/H_2O_2, UV/O_3 and O_3 systems [10] and heterogeneous photocatalysis with metal oxides such as Ti and Zn [11].

Among AOPs, heterogeneous photocatalysis using TiO_2 as photocatalyst appears as the most emerging destructive technology [12]. The aim of the present work is to investigate the influence of various parameters on photocatalytic decomposition of an azo dye, called Reactive Yellow (RY) also to evaluate the degradation efficiency of simulated textile wastewater. The effect of the addition of H_2O_2 was also studied for enhancing of azo dye and the presence of unsupported suspended TiO_2 powder, which is irradiated by the UV-C light. Heterogeneous photocatalysis has been shown to be potentially advantageous as it may lead to the complete mineralization of pollutants to CO_2, water, and mineral acids [13].

2- Experimental

2.1. Materials

The commercial azo dye Reactive Yellow, (RY), Fig. **1**, obtained from AL-Hilla textile factory south of Baghdad, (Department of Dying and Printing).

TiO2-P25, powder supplied by Fluka (china) with 99% purity (molecular weight 79.87g/mol). The hydrogen peroxide (50% w/w) was obtained from Merck. The natural pH of the aqueous dye solution was 7. The experimental solutions were adjusted to the decided pH.
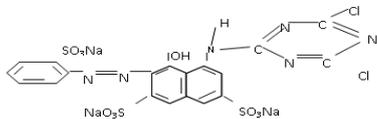

Fig. 1. Chemical Structure of reactive yellow [14], [15], [16]

2.2. Irradiation experiments

All photocatalytic and photochemical experiments were carried out in a batch mode laboratory-scale reactor. The reactor consisted of Pyrex glass cylinder 3 L volume with a magnetic stirrer and (MSH-300N, BOECO, Hamburg, Germany). UV radiation (254 nm) was generated from a UV lamp (TUV 6 W 4P-SE, Philips, Guildford, Surrey, England), which was fixed vertically at the top of the reactor. The lamp was totally immersed in the content of the cylindrical reactor.

The UV lamp was sheathed in a quartz sleeve for protection. The distance between the lamp and the reactor wall was fixed at 5 cm to ensure maximum light irradiation. The turbidity of the solution was measured using a turbidity meter (Hanna microprocessor, Padua, Italy). The initial pH of the solution was monitored using a pH meter (INOLAB 72, WTW Co., Weilheim, Germany).

2.3. Procedure and Analysis

The desired concentration of dye's stock (20, 50, 75 and 100 mg/L) was prepared and the pH was adjusted, before adding the reagents, by adding a dilute solution of HCl or NaOH to the reactor contents. TiO2 was added to the solution with (25, 50, 75 and 100 mg/L) and then the hydrogen peroxide (100, 250, 400 and 700 mg/L).

The solution was then subjected to stirring using a magnetic stirrer at 200 rpm for 120 min. The suspension was magnetically stirred in the dark for 16 min to attain primary adsorption equilibrium between dye and TiO_2. H_2O_2 was added after that. Then, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogenous.

Irradiation was carried out in the open-air condition. At specific time intervals, 10 ml of the sample was withdrawn and centrifuged at (3000 rpm for 15 min) to separate the catalyst. The concentration of dye in each sample was determined by a spectrophotometer (UV-Vis Spectrophotometer Perkin–Elmer 55 OSE) at λmax = 420 nm and a calibration curve Fig. **2** The percentage of decolorization was calculated as follows:

$$Decolorization \% = \frac{(C_o - C)}{C_o} \times 100\% \qquad (1)$$

Where: C_o = initial concentration of dye solution.
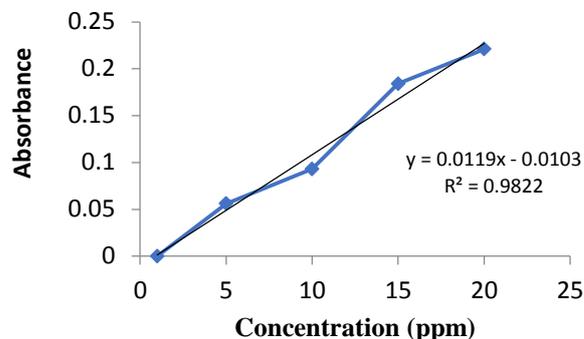C = final concentration of dye solution.
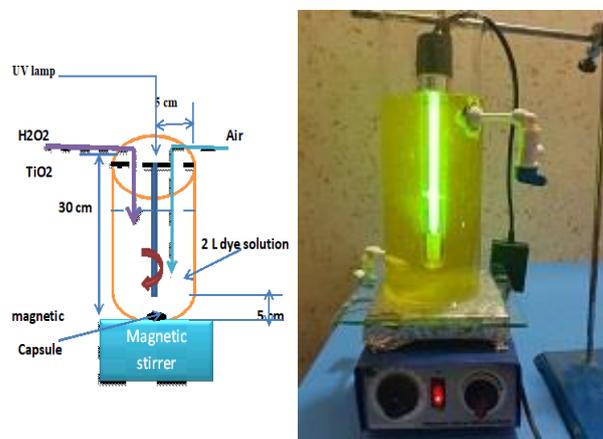

Fig. 2. Calibration curve in wavelength 420 nm

Fig. 3. Photograph and Schematic diagram of the batch reactor

3- Results and Discussion

3.1. Effect of Initial RY-14 Concentration

The effect of the initial concentration of RY -14 dye on the photocatalytic efficiency was investigated with concentrations ranging from 20 to 100 mg/l Fig. **4** at TiO_2=25 mg/l, H_2O_2 =400 mg/l and pH=7. From this figure, the sample was taken after 10 min from the experiment began; it was observed that the photodegradation conversion of RY-14 decreases with an increase in the initial concentration of RY. The presumed reason is that when the initial concentration of dye is increased, more and more dye molecules are adsorbed on the surface of TiO_2. A large amount of adsorbed dye is thought to have an inhibitive effect on the reaction of dye molecules with photogenerated holes or hydroxyl radicals, because of the lack of any direct contact between them. Once the concentration of dye is increased, it also causes the dye molecules to absorb light and the photons never reach the photocatalyst surface, thus the photodegradation efficiency decreases [17].
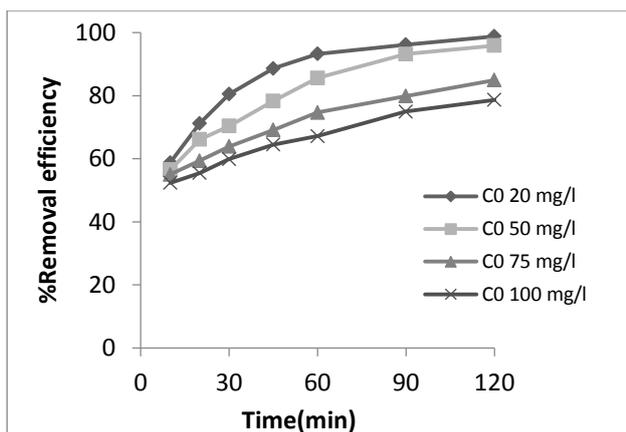
Fig. 4. Influence of initial RY dye concentration on dye degradation by the photocatalytic system at H_2O_2=400 mg/L, TiO_2 =25 mg/L and pH=7

3.2. Effect of The Amount Of Photocatalyst

The effect of the amount of TiO_2 on the RY removals was studied at a concentration (25,50,75 and 100) mg/l while keeping other parameters constant (C=20 mg/l, H_2O_2=400 mg/l, PH=7), and their results were plotted as shown in Fig. **5**. The photodegradation efficiency increases with an increase in the amount of photocatalyst reach the higher value of catalyst amount (25 mg/l) and then decreases. The most effective decomposition of RY was observed with 25mg/l of TiO_2. The reason of this observation is thought to be the fact that when all dye molecules are adsorbed on TiO_2, while the TiO_2 is exposed to UV light, the conduction band electrons (e−) and valence band holes (h+) are generated with light energy greater than its bandgap energy (Eg,3.2 eV), Eq. (2-5) .The photogenerated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the TiO_2 surface or dissolved in water, reducing it to superoxide radical anion $O_2^{\bullet-}$. The photogenerated holes can oxidize the organic molecule to form R^+ or react with OH^- or H_2O oxidizing them into $OH^{\bullet}$ radicals. Together with other high oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes, refers to Eq. (6-9). The addition of higher quantities of TiO_2 would have no effect on the degradation efficiency. Another cause for this is supposedly an increased opacity of the suspension works as a shading effect, brought about as a result of an excess of TiO_2 particles [18], [19].
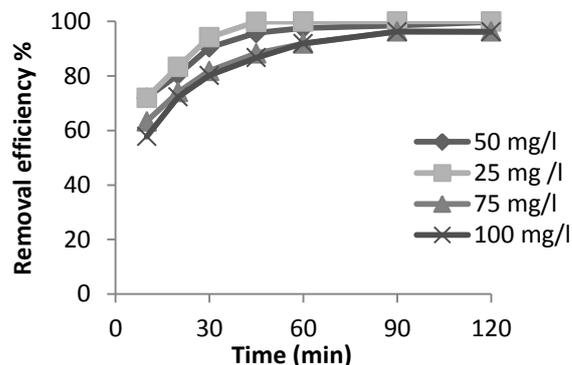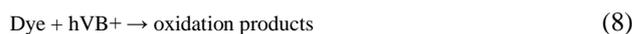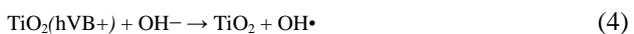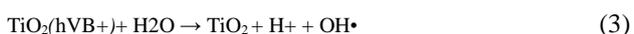
$$TiO_2 + hv(\lambda < 390\ nm) \rightarrow TiO_2(e−CB+ h+VB) \qquad (2)$$

$$TiO_2(hVB+)+ H2O \rightarrow TiO_2 + H+ + OH\bullet \qquad (3)$$

$$TiO_2(hVB+) + OH− \rightarrow TiO_2 + OH\bullet \qquad (4)$$

$$TiO_2(eCB−) + O_2 \rightarrow TiO_2 + O_2\bullet− \qquad (5)$$

$$O_2\bullet− + H+ \rightarrow HO_2\bullet \qquad (6)$$

$$Dye + OH\bullet \rightarrow degradation\ products \qquad (7)$$

$$Dye + hVB+ \rightarrow oxidation\ products \qquad (8)$$

$$Dye + eCB− \rightarrow reduction\ products \qquad (9)$$

Fig. 5. Effect of initial titanium dioxide (TiO_2) concentrations on dye degradation by the photocatalytic system at H_2O_2=400 mg/L, dye concentration 20 mg/L and pH=7

3.3. Effect of the Initial pH

In order to study the effect of the initial pH in the photocatalytic process, different values of pH (3, 5, 7,10and 11) were carried out at H_2O_2 = 400 mg/L, dye conc. = 20 mg/L, TiO_2 = 25 mg/L and there results shown in Fig. **6**, from this figure it can be noticed that the removal efficiency increases to reach a maximum of 98.85% at pH=7 because the difference between the degree of photodegradation of RY in acidic solution (pH=3 and neutral pH=7) was only 4%, the following experiments were carried out with neutral pH, this agrees with the previous study by [20].

This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to the strong adsorption of the latter on metal oxide support .

The interpretation of pH effects on the efficiency of dye photodegradation process is very difficult task because of its multiple roles, this is because three possible reaction mechanisms can contribute to dye degradation, (1) hydroxyl radical attack, (2) direct oxidation by the positive hole, and (3) direct reduction by the electron in the conducting band. The contribution of each one depends on the substrate nature and pH [21].

Moreover, the positive holes are considered as the major oxidation species at low pH which react with hydroxide ions forming hydroxyl radicals, thus the efficiency of the process is enhanced. With high pH, there is Columbia repulsion between the negatively charged surface of the catalyst and the hydroxide anions which prevent the formation of OH° and decrease the photocatalytic degradation [22].
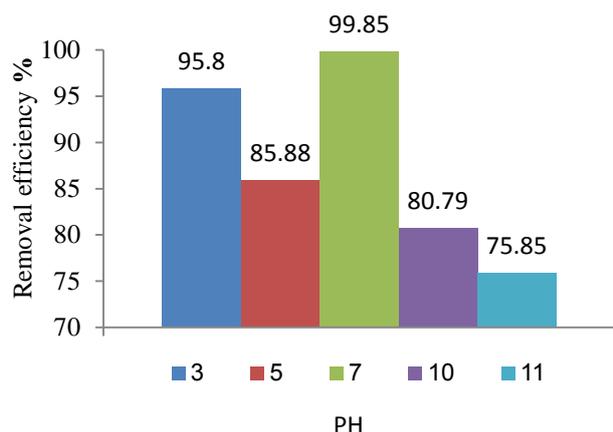
Fig. 6. Effect of pH on dye degradation by the photocatalytic system at H_2O_2=400 mg/L, dye concentration 20 mg/L and TiO_2=25mg/l

3.4. Effect of Addition of H_2O_2

The photocatalytic degradation of RY was a focus in this study at different hydrogen peroxide concentrations up to (400 mg/l), the results are given in Fig. **7**.

The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radicals.

At a low concentration of hydrogen peroxide, it inhibits the electron-hole recombination, according to Eqn. 10, and it could act as an alternative electron acceptor to oxygen Eqn11 because hydrogen peroxide is a better electron acceptor than molecular oxygen according to Eqn. 12 this agrees with the previous study by [23].

The degradation rate of RY increased with increasing H_2O_2 concentration up to 400 mg/l, but above this value there was a decrease in the degradation rate that could be due to by scavenging effect as •OH according to Eqns.13and14 it became predominant, this agree with a previous study [24].
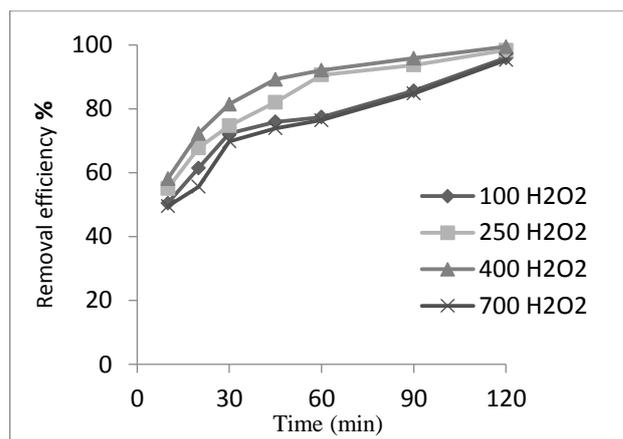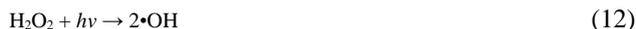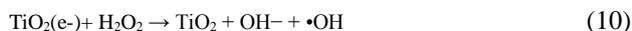
$$TiO_2(e\text{-})+ H_2O_2 \rightarrow TiO_2 + OH- + •OH \qquad (10)$$

$$•O^{-2}+ H_2O_2 \rightarrow OH- + •OH + O_2 \qquad (11)$$

$$H_2O_2 + hv \rightarrow 2•OH \qquad (12)$$

$$H_2O_2 + •OH \rightarrow HO_2• + H_2O \qquad (13)$$

$$HO_2• + •OH \rightarrow H_2O + O_2 \qquad (14)$$

Fig. 7. Effect of H_2O_2 addition on photodegradation efficiency of RY-14 [RY] = 20 mg/l, TiO2 = 25mg/l, pH=7

3.5. Reaction Rate Constant for Heterogeneous Photocatalyst

The experimental data for dye degradation 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 Eqn. (15) and (16) reported in [25].

$$\ln \frac{[c_0]}{[c]} = K \qquad (15)$$

$$\frac{1}{[c]} - \frac{1}{[c_0]} = Kt \qquad (16)$$

Where; Co is the initial concentration of dye and C is the concentration at irradiation time t, K and K1 are the pseudo-first- and pseudo-second-order rate constants in min^{-1} and $L.mg^{-1}.min^{-1}$, respectively , t is the irradiation time (in min). Plot of $\ln \frac{[c_0]}{[c]}$, and $\frac{1}{[c]} - \frac{1}{[C_0]}$ versus time for each experimental lead to a straight line whose slope are K and K_1, respectively [20]. The regression analysis of the concentration curves versus reaction time indicates that the decomposition rate of this compound could be described by 1st - order kinetics. The results are summarized in Table **1**.

Table 1. Reaction rate constants in heterogeneous photocatalyst

Heterogeneous photocatalyst ; H_2O_2=400mg/L , dye=20mg/L, pH=7 ,TiO_2=50mg/L				
Removal efficiency	First order $K \times 10^3 min^{-1}$	R^2	Second order $K1 \times 10^6 \ L.mg^{-1}.min^{-1}$	R^2
98.8	0.0319	0.98	0.0328	0.8107

4- Conclusion

$H_2O_2/TiO_2/$ UV was used to examine the performance of AOP for the degradation of RY dye wastewater. The reaction was influenced by the input concentration of H_2O_2, pH, the amount of TiO2 and the concentration of RY in the wastewater.

The addition of the proper amount of hydrogen peroxide could improve the photodegradation rate. However, at high concentrations, H_2O_2 would quench hydroxyl radicals. The reaction was found to be of a first-order throughout the systems. The removal efficiency for the system at best $H_2O_2/TiO_2/$ UV conditions and dosage (H_2O_2 = 400mg/L, pH=7, , TiO2=25mg/L) for 20mg/L load was found to be 98.8%.

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ازالة الصبغة الصفراء الفعالة من مياه الملوثة المحضرة باستخدام تقنيه الاكسدة المقدمة

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

[1]جامعة بغداد, كلية الهندسة, قسم الهندسة البيئية
[2]جامعة بغداد, مركز ابن سينا

الخلاصة

في هذه الدراسة تم استخدام الاشعة فوق البنفسجية لازالة الصبغة الصفراء الفعالة من مياه الصرف الصحي ذات الطول الموجي 420 نانوميتر بواسطة عملية الاكسدة المتقدمة (AOP) باستخدام عملية (TiO$_2$/UV/H2O2) .وتم دراسة تاثير المتغيرات الرقم الهيدروجيني للمحلول وتركيز بيروكسيد الهيدروجين (PH) وتركيز الصبغة الابتدائي و تركيز ثنائي اوكسيد التيتانيوم (TiO$_2$) في مفاعل ذو الدفعة الواحدة عند الزمن 120 min. ولوحظت أعلى معدلات إزالة اللون في نطاق الأس الهيدروجيني بين 3 و 7. وقد تم فحص المستويات المثلى من بيروكسيد اللازمة لهذه العملية. يبدو أن المستويات العالية من بيروكسيد الهيدروجين يمكن أن تقلل من إزالة اللون وكذلك عندما ينخفض مع زيادة تركيز الصبغة .كما اظهرت النتائج ان موديل التفاعل كان من الدرجة الاولى.

الكلمات الدالة: الصبغة الصفراء الفعالة, ثنائي اوكسيد التيتانيوم, بيروكسيد الهيدروجين, عملية الاكسدة المتقدمة