



TREATMENT OF ORGANIC COMPOUNDS (DYES) RESULTING FROM TISSUE INDUSTRIES

Ahmed Hassan Ali

Department of Chemical Engineering / College of Engineering / Al-Muthanna University
Al-Muthanna / Iraq

Email: dr.ahmedha@gmail.com ; Ph: 07802827535, 07830750424

ABSTRACT

Contaminants from dyes used in textile industries have become a major source of environmental pollution. 150 tons approximately of these pollutants are released daily from all over the world. The introduction of these dyes into the aquatic environment in addition to being contaminated is considered a non-aesthetic phenomenon and its presence in the aquatic environment is inappropriately need to be fully treated and removed. These dyes are resistant to atmospheric degradation under normal conditions and can also be transformed into dangerous and carcinogenic amino compounds. This paper includes the process of treatment of the dyes used in the textile industries, which are produced with the industrial waste water for textile industries. In the present paper, the degradation of dyestuffs under UV light with TiO₂ photocatalysts. There are many parameters have been tested like (concentration, pH, initial dyestuff concentration, COD reduction and kinetic behavior).

The results shows the optimum conditions for totally treatment are (photocatalyst concentration is 1.20 g/l; pH = 5 and initial dyestuff is 30 ppm). The photodegradation efficiency the initial concentration of the dye was 98 % for Initial dye concentrations (30) mg / L were used for this study. The COD reduction (95%) during the treatment process under optimal conditions was measured from the concentration of the catalyst and the acidic function.

1. INTRODUCTION

Photocatalytic processes to degrade organic pollutants in water by utilizing catalyst have been the subject of research recently. Semiconductor oxides such as ZnO and TiO₂ have been recognized to be preferable materials for photocatalytic processes, due to their high photosensitivity, non-toxic nature, low cost and chemical stability. The semiconductor or photocatalysis is initiated by the surface trapping of photo-generated electrons (e⁻) and holes (h⁺), which induces inter facial electron-transfer reactions with adsorbed substrates. However, because of the wide band gap of ZnO and TiO₂ [1-3]. Among various semiconductor oxides, TiO₂ proves to be the most suitable material because of its many desirable properties, such as strong oxidizing power, high photo- and thermal-stability, low price, facile synthesis and the low toxicity of titanium. However, the photocatalytic efficiency of pure TiO₂ needs to be improved to meet

industrial requirements[4-6]. Eosin yellowish was considered one of the most important dyes because of it is emotional-state lifetime which was very short and was constant to visible in addition give a useful investigation for the oxidation and reduction of photo reactions [7]. For the oxidation reaction about photo of Eosin yellowish in a slurry reactors and TiO₂ immobilized reactors, most studies had been made [8,9]. The experimental data of previous studies would give a good information in estimating the execution of a fluidized bed photocatalytic reactor in a three-phase. In the present paper, the photocatalytic degradation of eosin yellowish dye in aquatic solutions using two different photocatalysts has been tested. The major aims of the study were effect of catalyst concentration, effect of pH, effect of initial concentration of the dye and studies kinetic of reaction.

2. EXPERIMENTAL WORK

2.1. Materials

In present work commercial TiO₂ powder were gained from Merck Co. (Germany), eosin yellowish dye was taken up from Merck (Germany) and was applied without further purification. Distilled water was used for a preparation of different solutions.

2.2. Instruments

Photochemical degradation was carried out in specially designed insulation walled reaction containers (volume 500 ml) under UV light Constant stirring of the solution was covered by using magnetic stirrers. The temperature was kept constant during the reaction time by spreading the water in the photocatalytic reactor vessel.

2.3. Irradiation experiments

For 200 ml of the dye solution, photocatalyst was added and a suspension was an exhibit to irradiation. Experiments were carried out under UV light. The aqueous suspension was magnetically stirred over the experiment. At different time periods, an aliquot was taken out with the help of a syringe and then filtered through Millipore syringe filter of 0.45 μm.

2.4 Absorption measurements

The absorption spectrum was recorded using double beam UV-1800 (Shmadzo spectrophotometer) compared with distilled water as a reference liquid and the percentage rate of degradation was noticed in terms of change in intensity at λ_{max} of the dyes during irradiation time. The degradation efficiency (%) has been calculated as:

$$\% \text{ Degradation} = ((\text{Abs}_0 - \text{Abs}_t) / \text{Abs}_0) * 100$$

Where:-

% Degradation is a percentage of dye disappearance.

Abs 0 is initial absorption of dye (at time = 0 min.)

Abs t is absorption of dye (at time = t min.)

Similar experiments have used different catalyst concentration (0.25–1.25 g/l), to select the best concentration of catalyst TiO₂ at the same dye concentration of the solution (30 ppm)

3. RESULTS AND DISCUSSION

The effect of catalyst concentration on the degradation of Eosin yellowish dye solution (30 ppm) was investigated using commercial TiO₂ from 0.3 to 1.5 g/l keeping another parameters like (pH, temperature, and dye concentration) constant. The results in the Figure 1 showed that the degradation percentage increased with an increase in TiO₂ commercial concentration up to 1.2 g/l for TiO₂. This observation can be explained in terms of availability of active sites on the catalyst surface and the permeation of UV light into the suspension. The total active surface area increases with increasing catalyst dosage. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in solar light permeation as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Furthermore, at high catalyst loading, it is difficult to maintain the suspension homogenous due to particles agglomeration, which decreases the number of active sites [10-12].

The wastewater is produced at different pH, therefore, study of pH is very important on photodegradation of Eosin yellowish dye. Experiments have been done at different values of pH varying from 3 to 11 for 25 mg/L dye solution concentration and for the best of catalyst concentration (0.75) g/l of TiO₂. Figure 2 shows the percentage photodegradation of against values of pH. It is clearly increasing in pH up to 11 for TiO₂ because increasing in photodegradation activity [13]. The utilizing of TiO₂ as the catalyst is more appropriate at high pH values with the textile effluent. The interpretation of pH effects on the efficiency of the decolonization is a complex subject because many reactions can be occurs to dye degradation such as “hydroxyl radical reaction, direct oxidation by the positive hole and direct reduction by the electron in the conducting band”. The importance of each one depends upon the substrate nature and pH.

The photodegradation of Eosin yellowish was carried out by varying the initial concentration of the dye from 30–150 mg/l in order to determine the effect of initial dye concentration on the best catalyst type and dose (commercial TiO₂). As the concentration of the dye was increased, the percentage of degradation decreased indicating for either to increase the catalyst concentration or time span for the complete removal. Figure 3 depicts the time-dependent graphs of degradation of Eosin yellowish at different concentrations of dye solutions (30–150 mg/l). In the case of dye solutions of 30 mg/L and 150 mg/L, 100% and 78% degradation occurred within 120 and 300 minutes respectively and in case of 150 mg/l. The reason for this behavior was the path length of the photons entering the solution decreases in high dye concentration that means the photochemical reaction is decreased but the number of photons absorbed by catalyst is high at low initial dye concentration the number of photon absorption by the catalyst in lower [14-19].

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage reduction in COD was studied for dye samples (initial concentration-30 mg/L) under optimized conditions (catalysts dose 1.2 g/L, pH 5) as a function of irradiation time. It was observed that the percentage COD reduction lies 95% after 120 minute (Figure 4). The COD reduction is lesser than percentage decolorization which

may be due to the formation of smaller uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

Figure 5 shows the kinetic of the disappearance of Eosin yellowish dye for an initial concentration of 30 mg/l. The results show that the photocatalytic degradation of Eosin yellowish dye with commercial TiO_2 concentration 1 g/l can be described by the first order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time t ($y=0.0439X$). The semi-logarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.9743$ for commercial TiO_2 [20-22].

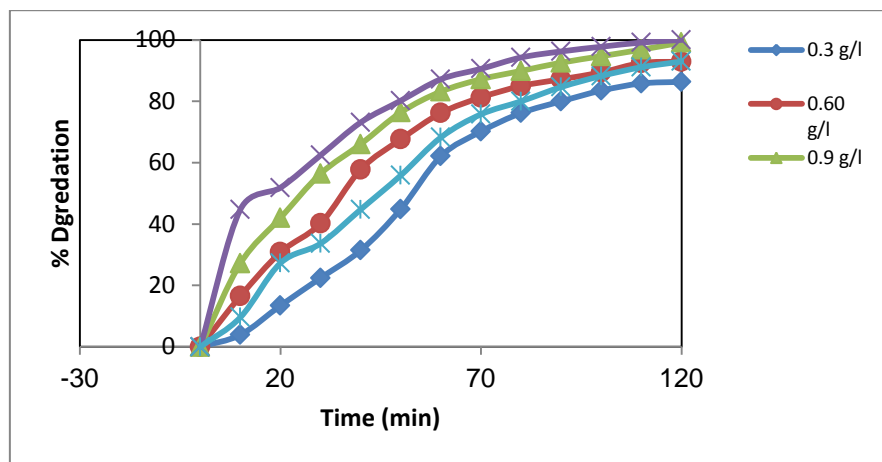


Figure 1: Effect the catalyst dose of TiO_2 on degradation of Eosin yellowish dye

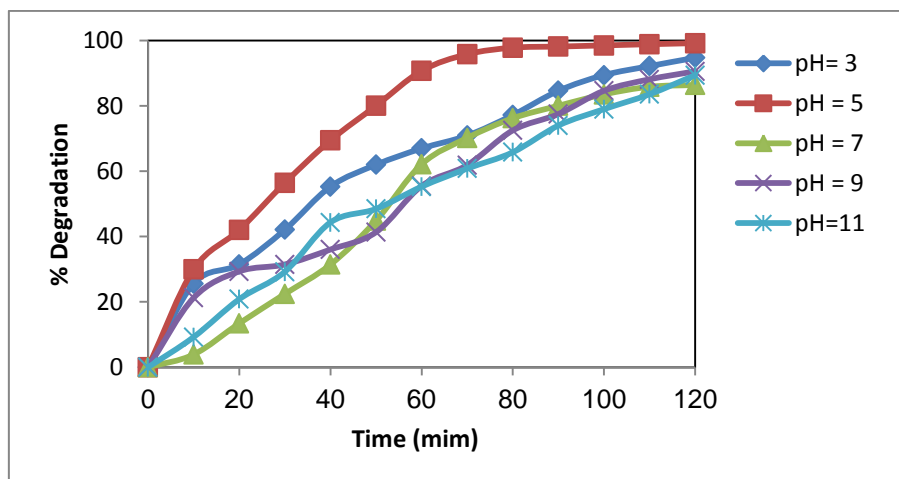


Figure 2: Effect the pH on degradation of Eosin yellowish dye

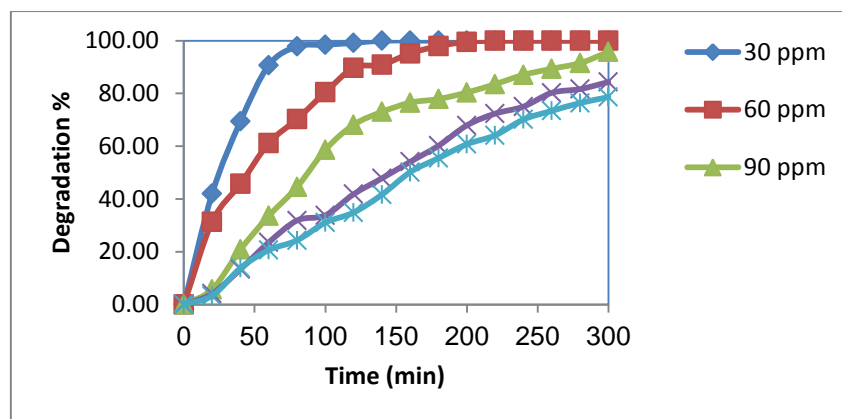


Figure 3: Effect the dye concentration on degradation of Eosin yellowish dye

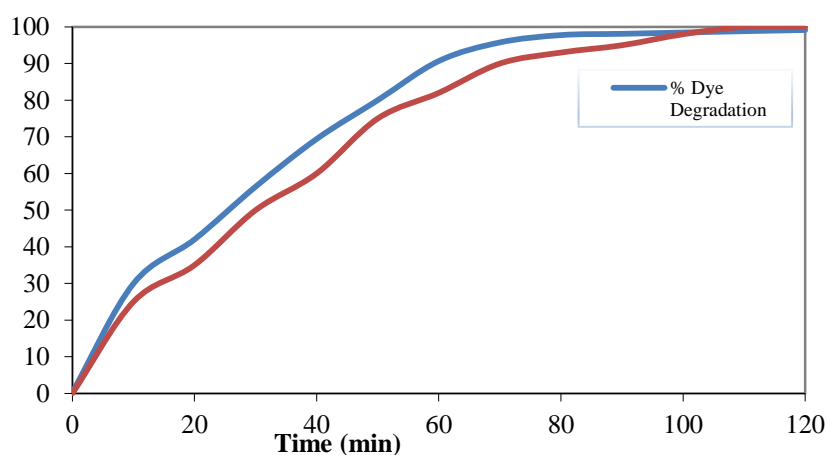


Figure 4: Comparison of percentage decolorization and percentage COD reduction for eosin yellowish dye

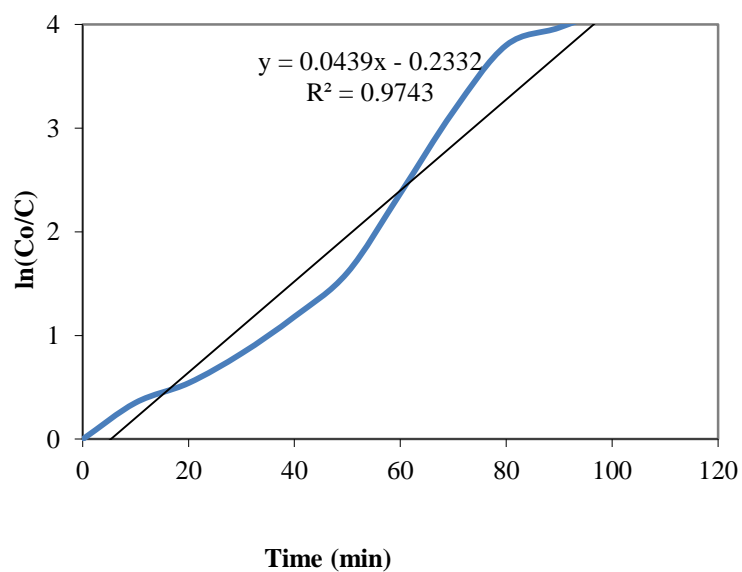


Figure 5: Kinetic study of the disappearance of Eosin yellowish dye

4. CONCLUSIONS

The photocatalytic degradation of aqueous solutions of Eosin yellowish dye has been examined with the use of a solar light-irradiated TiO₂ catalyst. It has been found that the process leads to decolorization and, eventually to complete mineralization of the dye solution. Evolution of intermediates and final products on photocatalyst surface and the solution has been monitored with a variety of techniques, which enable the identification of the reaction pathway, from adsorption of the dye molecule on the photocatalyst surface, to the formation of final products.. The photocatalytic degradation followed pseudo-first order kinetics.

REFERENCES

- [1] S.Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye : comparison of photocatalytic efficiency of ZnO and TiO₂, Sol. Energy Mater. Sol. Cells77 (2003)65–82.
- [2] E.Evgenidou, K.Fytianos, I.P. Ioulios, Semiconductor-sensitized photodegradation of dichlorvos in water using TiO₂ and ZnO as catalysts, Appl. Catal. B: Environ. 59 (2005) 81–89.
- [3] N. Daneshvar, S. Aber, M.S. Seyed Dorraji, A.R. Khataee, M.H. Rasoulifard, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light, Sep. Purif. Technol. 58 (2007) 91–98.
- [4] S. Papic, N. Koprivanac, A. Loncaric-Bozic, A. Metes, Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process, Dyes Pigm. 62 (2004) 291–298.
- [5] Ahmed Hassan Ali, Kansal, S.K., and Kapoor, S.. Photocatalytic decolorization of biebrich scarlet dye in aqueous phase using different nanophotocatalysts, Desalination, 259 (2010) 147-155.
- [6] Ahmed Hassan Ali, Kansal, S.K., Kapoor, S., and Bahnemann, D.W. (2011). Synthesis of flower like zinc oxide nanostructure and its application as a photocatalyst, Sep. Purif. Technol. 80 (2011) 125-130.
- [7] G. T. Brown ; J. R. Darwent. Photoreduction of Eosin yellowish sensitized by colloidal titanium dioxide. J. Chem. Soc. Faraday Trans. 1984a , (80), 1631–1643.
- [8] G. T. Brown ; J. R. Darwent. Eosin yellowish as a probe for photooxidation reactions of colloidal TiO₂. J. Phys.Chem. 1984b , (88), 4955–4959.
- [9] L.C. Chen. Effects of factors and interacted factors on the optimal decolorization process of Eosin yellowish by ozone. Wat. Res. 2000 (34), 974–982.
- [10] C. Zhu ; L. Wang ; L. Kong ; X. Yang ; L. Wang ; S. Zheng ; F. Chen ; F. Maizhi; H. Zong. Photocatalytic degradation of azo dyes by supported TiO₂ and UV in aqueous solution. Chemosphere. 2000 (41), 303–309.
- [11] S. K. Kansal ; Ahmed Hassan Ali ; S. Kapoor. Photocatalytic decolorization of biebrich scarlet dye in aqueous phase using different nanophotocatalysts. Desalination 2010 (259), 147–155

- [12] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigation, *Appl. Catal. B: Environ.* 2004 (49), 1–14.
- [13] C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, Optimized photodegradation of reactive blue 19 on TiO₂ and ZnO suspensions, *Catal. Today*, 76 (2002) 235–246.
- [14] S. Rabindranathan, D.P. Suja, S. Yesodharan, Photocatalytic degradation of phosphamidon on semiconductor oxides, *J. Hazard. Mater. B.* 2003 (102) 217–229.
- [15] A.H.C. Chan, J.F. Porter, J.P. Barford and C.K. Chan, Effect of thermal treatment on the photocatalytic activity of TiO₂ coatings for photocatalytic oxidation of benzoic acid, *J. Mater. Res.* 2002 (17), 1758–1765.
- [16] M. Styliidi, D.I. Kondarides and X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions, *Appl. Catal. B: Environ.* 2003 (40) 271–286.
- [17] S. Sakthivel ; B. Neppolian ; M.V. Shankar ; B. Arabindoo. M. Palanichamy ; V. Murugesan. Solar photocatalytic degradation of azo dye comparison of photocatalytic efficiency of ZnO and TiO₂. *Sol. Energy Mater. Sol. C.* 2003 (77), 65-82.
- [18] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard. Mater.* 2004 (112) 269–278.
- [19] H. Wang, C. Xie, W. Zhang, S. Cai, Z. Cai, Z. Yang, Y. Gui, Comparison of dye degradation efficiency using ZnO powders with various size scales, *J. Hazard. Mater.* 2007 (141), 645–652.
- [20] R.J. Davis, J.L. Gainer, G.O. Neal, I.W. Wu, Photocatalytic decolorization of wastewater dyes, *Water Environ. Res.* 1994 (66) 50.
- [21] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, *J. Photochem. Photobiol. A: Chem.* 2003 (157) 111–116.
- [22] M.V. Shankar, S. Anandan, N. Venkatachalam, B. Arabindoo, V. Murugesan, Novel thin-film reactor for photocatalytic degradation of pesticides in aqueous solutions, *J. Chem. Technol. Biotechnol.* 2004 (79) 1258–1279.
- [23] S. Lathasree, R. Nageswara, B. Sivasankar, V. Sadasivam, K. Rengaraj, Heterogeneous photocatalytic mineralization of phenols in aqueous solutions, *J. Mol. Catal. A Chem.* 223 (2004) 101–105.
- [24] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂, *J. Photochem. Photobiol. A Chem.* 162 (2004) 317–322.

معالجة المركبات العضوية (الأصباغ) الناتجة من معامل الانسجة

احمد حسن علي

قسم الهندسة الكيماوية / كلية الهندسة / جامعة المنى

الملخص :

اصبحت الملوثات الناتجة عن الصبغات المستخدمة في الصناعات النسيجية مصدرا رئيسيا لتلوث البيئي. حيث ان ما يقارب ١٥٠ طن يطرح يوميا من هذه الملوثات في جميع أنحاء العالم. ان طرح هذه الأصباغ الى البيئة المائية بالإضافة لكونها ملوثة يعتبر ظاهرة غير جمالية ووجودها في البيئة المائية غير لائق يحتاج الى معالجة وازالة بصورة كاملة. ان هذه الصبغات تكون مقاومة للتحلل الهوائي تحت الظروف الاعتيادية كذلك يمكن أن تتحول إلى مركبات أمينية خطيرة ومسرطنة.

هذا البحث يتضمن عملية معالجة الصبغات المستخدمة في الانسجة والتي تطرح مع فضلات المياه الصناعية لمعامل الانسجة وقد استخدمت عملية الاكسدة الضوئية بوجود اوكسيد الزنك كعامل مساعد ضوئي. تم تحضير محلول مشابه الى محلول المياه الناتجة من معامل الانسجة وبعدها تم دراسة بعض العوامل المؤثرة على عملية المعالجة منها تأثير كمية العامل المساعد الضوئي المستخدم للمعالجة ، ودرجة pH والتركيز الابتدائي للصبغة في المحلول . لقد تم دراسة جميع العوامل المؤثرة على انحلال الصبغات والمواد العضوية الموجودة في المحلول بوجود الاشعة فوق البنفسجية بطول موجي (٣٦٥ نانوميتر). تم تحديد الظروف التي اعطت اقصى درجة انحلال للصبغة وكانت عند تركيز 120ملغم/لتر للعامل المساعد ودالة حامضية ٥ وكانت نسبة انحلال الصبغة تقريبا 95% في 120 دقيقة. بعد ذلك تم تثبيت تلك الظروف القياسية للعامل المساعد والدالة الحامضية وتغيير التركيز الابتدائي للصبغة وقد استخدمت التراكيز (30) ملغم/لتر لهذه الدراسة. تم قياس اختزال متطلب الاوكسجين الكيماوي (COD) الى (٩٥%) خلال عملية المعالجة وتحت الظروف المثلى من تركيز للعامل المساعد ودالة حامضية.