

Catalyzed Photo-Fenton Oxidation for Removal of Some Direct Dyes From Their Aqueous Solutions

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Abstract

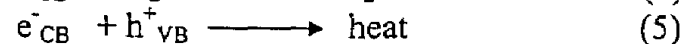
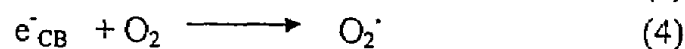
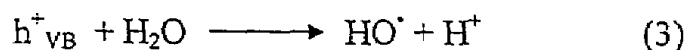
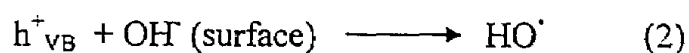
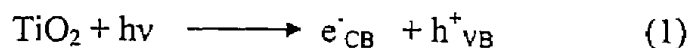
The effect of combining the photocatalytic processes using TiO_2 and the photo-Fenton reaction with ferrous sulfate as a source of Fe^{2+} was investigated in the color removal of a novel group of mono and disaryl azo dyestuffs that are based on the 1,2,4-benzothiadiazine 1,1-dioxide moiety. These processes utilize the very strong oxidizing power of hydroxyl radicals to oxidize organic compounds to harmless end products. Three dyes were used in this work. These dyes belong to direct dyes and they are resistant to biodegradation. The parameters studied were: titanium dioxide, ferrous sulfate and hydrogen peroxide concentrations; pH and reaction time. The decomposition of dyes was examined under visible light. The kinetics study of dyes degradation indicated that the process is first order. Experimental results revealed that, the first-order rate constants in case of using TiO_2 were higher than that in case of its absence by about 1.4 times. It was found that an increase of dyes photodegradation efficiency could be achieved when the photocatalytic process using TiO_2 is combined with photo-Fenton reaction. The maximum removal of color reached over 96% in case of using TiO_2 as a catalyst after a retention time ranging from 40-45 minutes.

Key words: Fenton's reaction, color removal, dyes, titanium dioxide.

1. Introduction

Textile dyes and other commercial colorants have become the focus of environmental remediation efforts because their natural biodegradability is made increasingly difficult owing to improve properties of dyestuffs [1-3]. Many dyes are highly water-soluble in order to meet the color requirement of deep dyeing. Consequently, traditional wastewater treatment methods such as flocculation, activated carbon adsorption, and biological treatment are increasingly ineffective. Advanced Oxidation Processes (AOPs) have been

intensively investigated over the last two decades for application in water and wastewater treatments. Among those processes, heterogeneous photocatalysis using TiO_2 and the photo-Fenton reaction have received great attention especially when solar irradiation is applied. Previous studies [1–14] showed that electron transfer between dyes and nanosized semiconductor particles occurs under visible and UV irradiation, and that dyes can be degraded to smaller organic substances and ultimately mineralized completely to water, carbon dioxide as well as other inorganic ions. Utilizing these processes to degrade colored organic pollutants, such as dyes, has important implications because they can make use of visible light or natural sunlight. Data reported recently in the literature on the photocatalyzed degradation of certain dyes by a heterogeneous photocatalytic process are not sufficient for industrial or for large scale pilot plant applications because several experimental parameters (e.g., light intensity, reactor geometry, pH, temperature, concentration & structure of reactant and concentration of TiO_2) have complex effects on the degradation reaction and thus also on treatment cost [15]. Heterogeneous photocatalysis through illumination of aqueous suspensions of TiO_2 offers an attractive advanced oxidation technology that is capable of purifying wastewater [16]. The photocatalyzed degradation of dyes has been reported for TiO_2 thin films [17] and in aqueous TiO_2 suspensions using simulated or natural sunlight [18–20]. As one of the AOPs, photocatalytic oxidation of toxic organic compounds by semiconductors is an emerging technology. Upon illumination by photons (solar radiation), electrons on the surface of the semiconductor are excited to the conduction band, and positive holes are formed in the valence band. The electrons and holes can either recombine and produce thermal energy, or interact with other molecules. The holes react with electron donors in the solution to produce powerful oxidizing free radicals such as hydroxyl radicals, which oxidize the organic on the surface. The holes can also oxidize the substrate by direct electron transfer, this can be summarized as follows [21]:



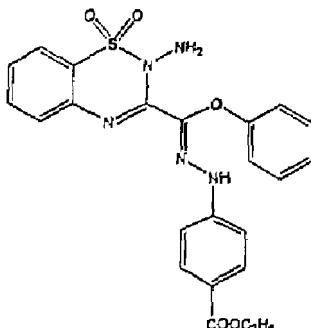
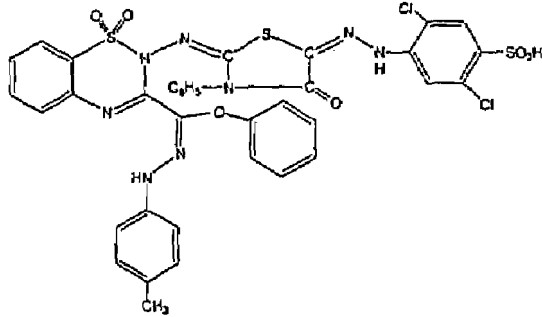
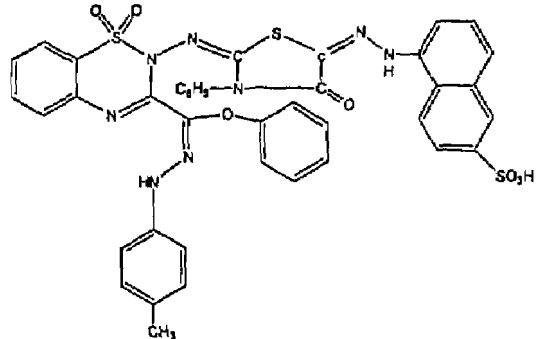
Where, $h\nu$ represents solar radiation, h^+_{VB} is valence bond hole, and e^-_{CB} is conduction band electrons. Generally, dyes resist photolytic degradation, therefore, the present work aims to examine the effect of combining the photocatalytic processes using TiO_2 as a catalyst and the photo-Fenton reaction with ferrous sulfate as a source of Fe^{2+} in the degradation of a novel group of direct dyes under visible light or natural sunlight.

2. Materials and methods

The three tested dyes (Table 1) were previously synthesized by Wali *et al.*, [22], and the solutions were prepared by dissolving the appropriate amount of each dye in distilled water at 75 mg/l. The pH solution was adjusted by adding H_2SO_4 or NaOH (El-Nasr Pharmaceutical Company) to attain the desired pH values. Hydrogen peroxide (Merck, 30% w/v); ferrous sulfate and titanium dioxide were obtained from Aldrich Chemical Company. All chemicals used of high purity grade. An aqueous solution (500 ml, 75 mg/l) of each dye was prepared in a one liter glass beaker. The initial pH of the solutions was adjusted prior to addition of TiO_2 , as necessitated by the experimental conditions. All reactions were performed in batch model using mechanical Jar test (Fig.1) and all experiments were conducted at room temperature (25 ± 2 °C) under visible light. In a series of glass beakers, aqueous solution of each dye was mixed with ferrous sulfate and hydrogen peroxide in different proportions. The whole beakers were firstly stirred for 1 minute at 200 r.p.m, after that stirring was continued for 15 minutes at a speed of 25-30 r.p.m and finally left for complete settling of solid materials. A 5 ml aliquot was sampled at various time intervals;

it was centrifuged prior to analyses, the remaining dye concentration was measured using a spectrophotometer (Galen kamp visi-spec SPR-590-010-W) .

Table 1: Chemical structure, color and maximum wavelength of the tested dyes.

Dye no.	Chemical structure	Color	Maximum wavelength
1	 <p>2-amino-3-[α-(<i>p</i>-4-Carbethoxyphenyl hydrazono)phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide</p>	Dark brown	410 nm
2	 <p>2-(4'-oxo-3'-phenyl-5'-2,5-Dichloro-4-sulphophenyl hydrazono-1',3'-thiazol-2'-ylimino)-3-[α-(<i>p</i>-tolylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide</p>	Red	540 nm
3	 <p>2-(4'-oxo-3'-phenyl-8-Sulphonaphthyl hydrazono-1',3'-thiazol-2'-ylimino)-3-[α-(<i>p</i>-tolylhydrazono)-phenoxymethyl]-1,2,4-benzothiadiazine 1,1-dioxide</p>	Navy blue	764 nm

3. Results and discussion

The first step was determining the optimum conditions for the best color removal of dyes from their aqueous solutions by Fenton process. These optimum conditions were determined from the experimental setup for dye (2) as an example for the tested dyes.

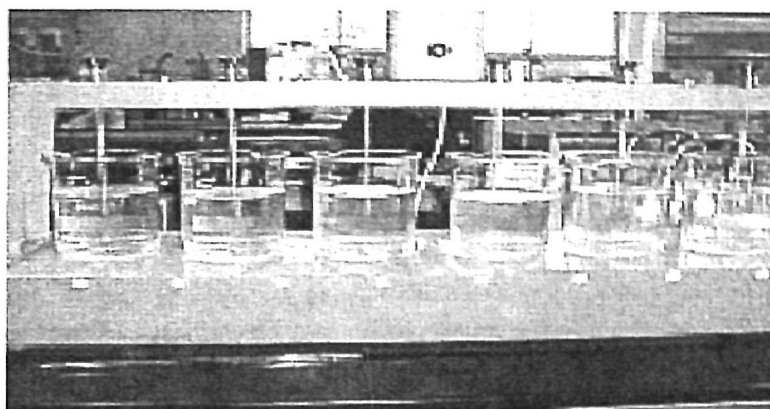


Fig. 1. Experimental Set-Up.

3.1. Effect of pH

Fenton's reaction is strongly affected by the pH value since it influences the generation of $\text{HO}\cdot$ radicals and thus the oxidation efficiency [11, 12]. Fig. (2) indicated that the remaining concentration was highly affected by the pH value. The optimum pH value for the maximum removal of the color of the tested dye was 3. Therefore, all the studied systems were firstly adjusted at pH 3. At pH values above 6 the degradation strongly decreases because, the ferrous catalyst is deactivated by the formation of ferric hydroxo complexes [13,23,24]. Also at higher pH values iron precipitates as hydroxide which reduces the transmission of light and in turn, deactivates the Fenton oxidation process.

3.2. Effect of hydrogen peroxide dose

Results obtained in Fig. (3) indicated that the color removal of dye from their aqueous solutions increases by increasing hydrogen peroxide doses. The effect

of hydrogen peroxide is not significantly effective at doses higher than 200 mg/l. Also it can be noticed from this figure that, the percent of removal was over 90 % at 200 mg/l hydrogen peroxide after retention time 70-80 minutes. At higher doses than 200 mg/l, there was a slight increase of dye removal. Generally, the removal rate of organic compounds increases as the dose of hydrogen peroxide increases until a critical value; after this critical value, the removal may decrease or not significantly increase as a result of so called scavenging effect. However, the excess of H_2O_2 will react with $HO\cdot$ radicals competing with the organic pollutants and consequently reducing the efficiency of the process, so that H_2O_2 should be added at an optimal concentration to achieve the best degradation.

3. 3. Effect of ferrous sulfate dose

The results shown in Fig. (4) indicated that the destruction of the tested dye in aqueous solutions increases by increasing ferrous sulfate dose, the effect of ferrous sulfate is not significantly effective at doses higher than 90 mg/l. It can be seen from this figure that, the percent of color removal was over 90 % after reaction time 70-80 minutes. The ferrous sulfate concentration recommended is around 90 mg/l., this will contribute to less formation of iron precipitate, one of the main disadvantage of Fenton process [25].

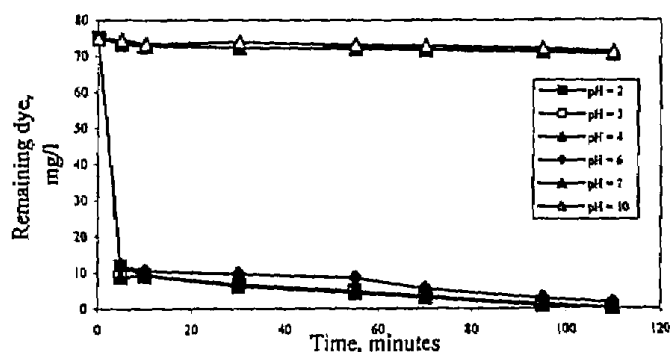


Fig.2: plot of remaining concentration of dye 2 at different pH values at 90 mg/l $FeSO_4$, 200 mg/l H_2O_2

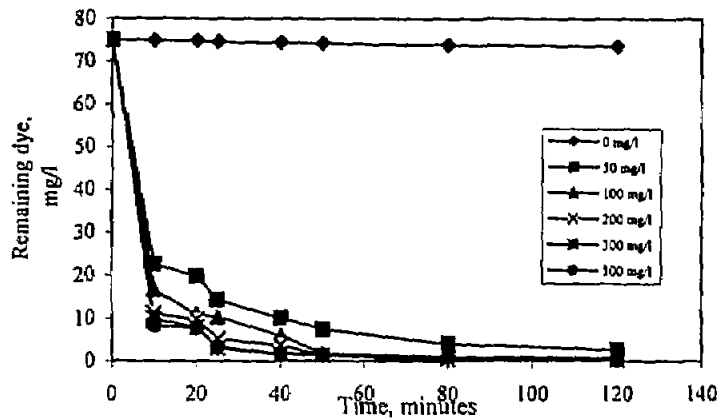


Fig.3: Plot of remaining concentration of dye 2 at different H₂O₂ doses at ferrous sulfate dose 90 mg/l and pH 3.

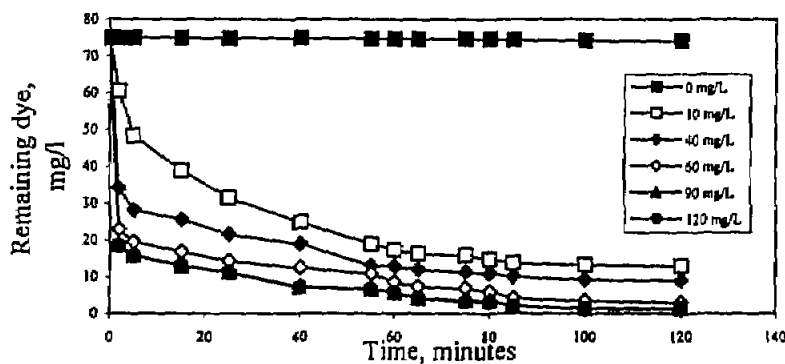


Fig. 4: plot of remaining concentration of dye 2 against time at different ferrous sulfate doses at pH 3 and 200 mg/l H₂O₂.

Results shown in Figures 2-4 indicated that, the optimum conditions for best color removal of dye (2) were 200 mg/l H₂O₂ 90 mg/l FeSO₄ at pH 3. Also it is clear that a reaction time ranging from 70 to 80 minutes was sufficient to verify the best color removal.

3.4. Addition of titanium dioxide

The main aim of this study was to examine the effect of presence of titanium dioxide as a catalyst on the color removal of dyes during the Fenton process. This

was achieved through using different doses of titanium dioxide at the determined optimum conditions for dye (3). Fig. 5 indicated that the remaining dye concentration decreases by increasing the dose of catalyst to certain limit up to 100 mg/l, after that the remaining concentration not affected by the catalyst.

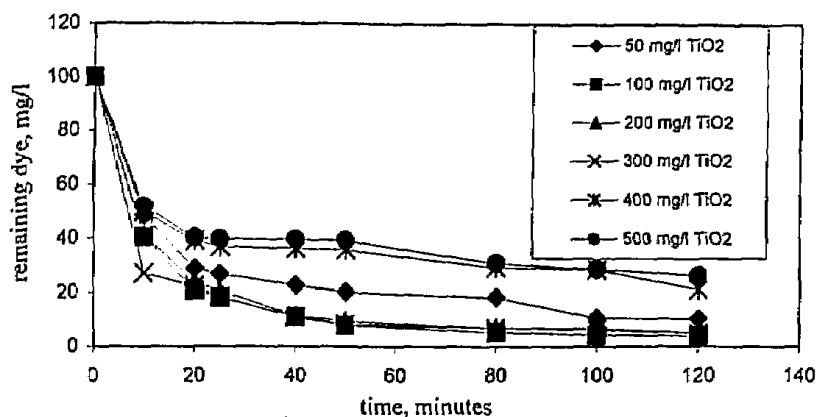


Fig.5: Plot of remaining dye concentration at different titanium dioxide concentration.

Two samples of aqueous solutions of the three dyes of concentration 100 mg/l were prepared, after that TiO₂ catalyst (100 mg/l) was added to one sample [90 mg/l FeSO₄, 200 mg/l H₂O₂ and pH = 3] while the other was subjected to treatment without the addition of the catalyst. It was observed that, the color removal efficiencies were increased in case of using catalyst and the process was faster as shown in figures 6-8.

The increase in color removal of dyes in the presence of TiO₂ may be attributed to illumination by photons (solar radiation) results in excitation of electrons on the surface of the semiconductor to the conduction band, and positive holes are formed in the valence band. The electrons and holes can interact with other electron donor's molecules in the solution to produce powerful oxidizing free radicals such as hydroxyl radicals, which oxidize the organic on the surface [21, 23 , 26]. This may explain the increase of degradation of dye or color removal in case of presence of TiO₂. From these figures, it clear that the sequence of color

removal for the three tested dyes were in the order, dye 1 > dye 2 > dye 3. This order of removal in accordance with the finding in the literature [21, 26], since monoazo dye (dye 1) is easily degrade than disazo dye (dyes 2 and 3).

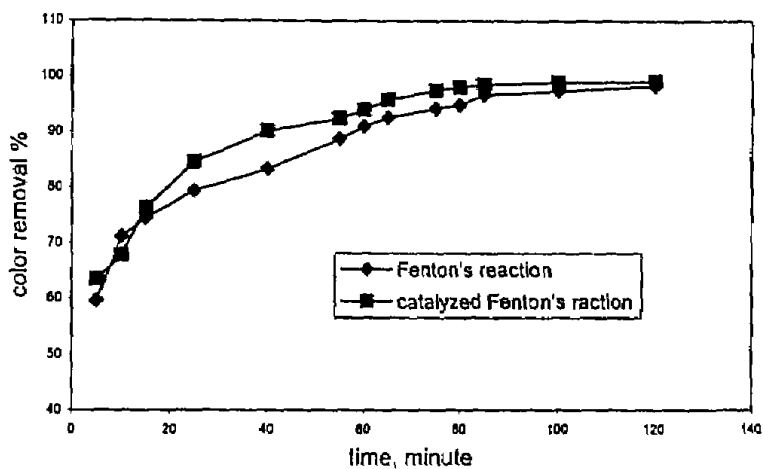


Fig. 6: Effect of TiO₂ on the removal of dye 1 (brown) at optimum conditions.

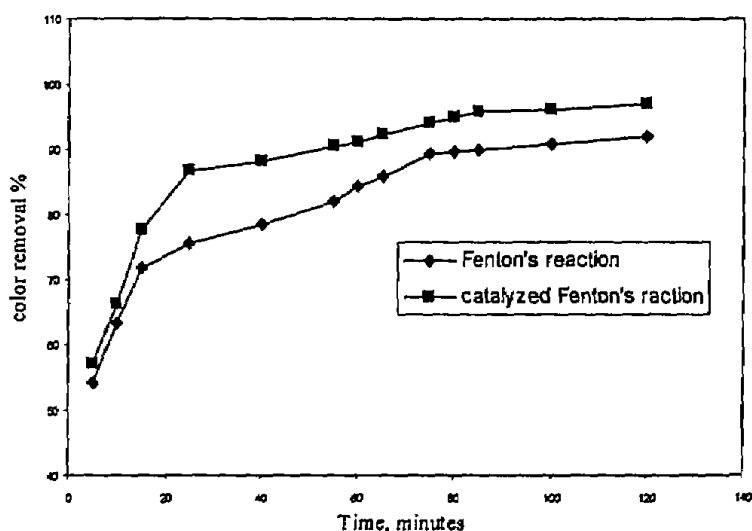


Fig.7: Effect of TiO₂ on the removal of dye 2 (red) at optimum conditions.

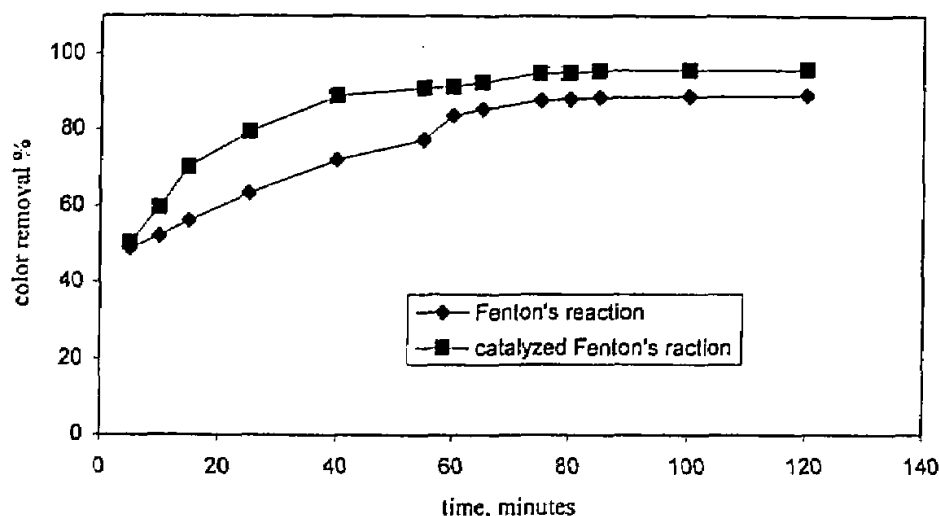


Fig.8: Effect of TiO₂ on the removal of dye 3 (navy blue) at optimum conditions.

3.5. Kinetics of dyes degradation

In order to study the effect of TiO₂ addition on the photocatalytic treatment process, the values of the kinetic rate constant are calculated in presence and absence of TiO₂. The kinetic plots of $\ln C/C_0$ with time indicate that the process is first order as confirmed by the linear representations [21, 23], these plots are shown in figures 9-11 with correlation coefficient over 0.91. The evaluated data obtained from kinetic plots are listed in Table 2.

Table 2: First order rate constants for Fenton's reaction in presence and absence of TiO₂.

Dye no.	First order rate constants	
	Fenton's reaction (H ₂ O ₂ /FeSO ₄)	Photocatalytic Fenton's reaction (TiO ₂ /H ₂ O ₂ /FeSO ₄)
1	0.0273	0.0356
2	0.0153	0.0227
3	0.0163	0.0238

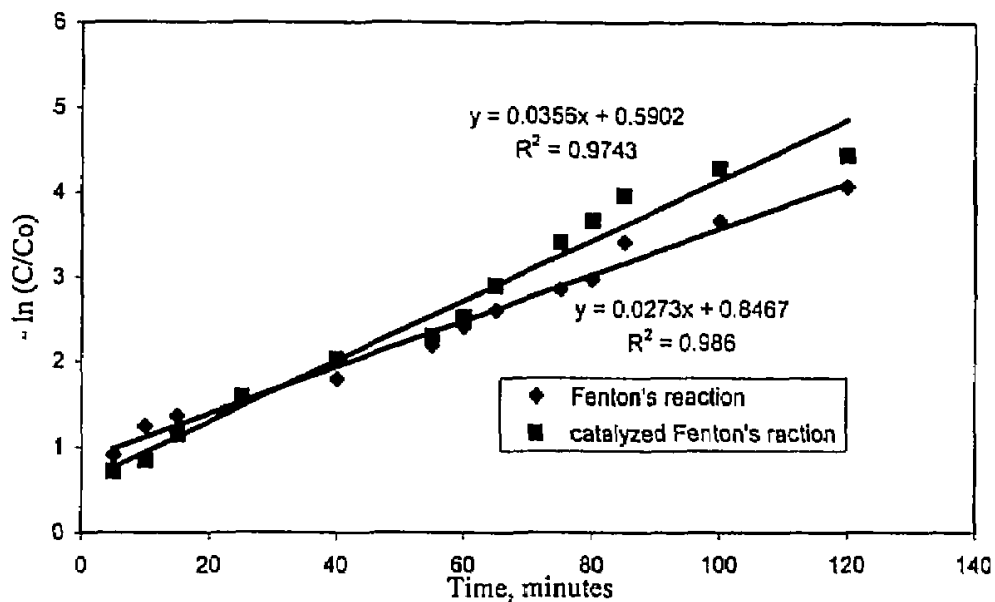


Fig.9: plot of first order rate constants for removal of dye 1 (brown) from aqueous solutions.

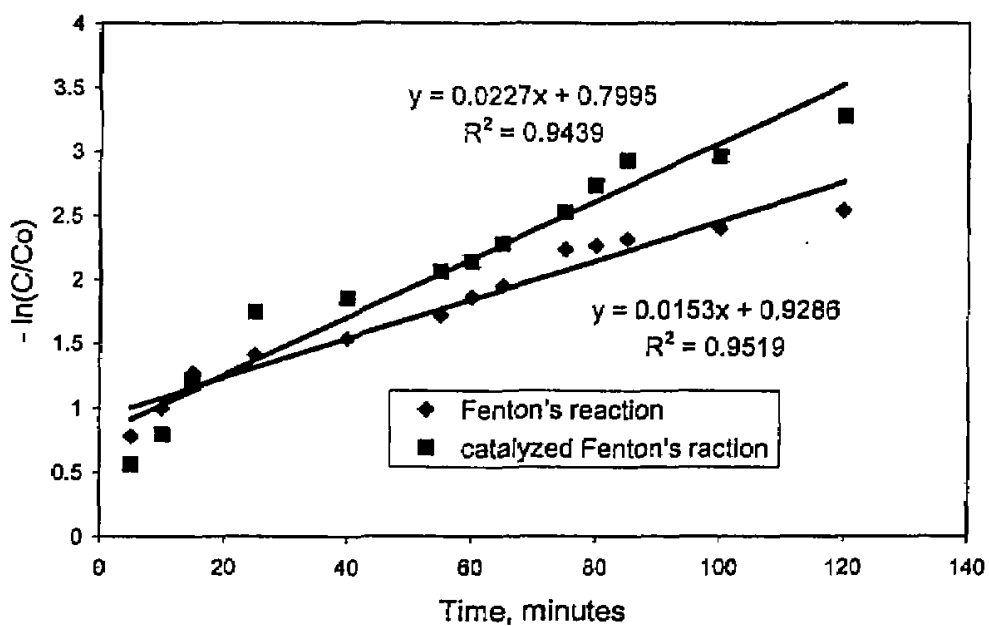


Fig.10: Plot of first order rate constants for removal of dye 2 (red) from aqueous solutions.

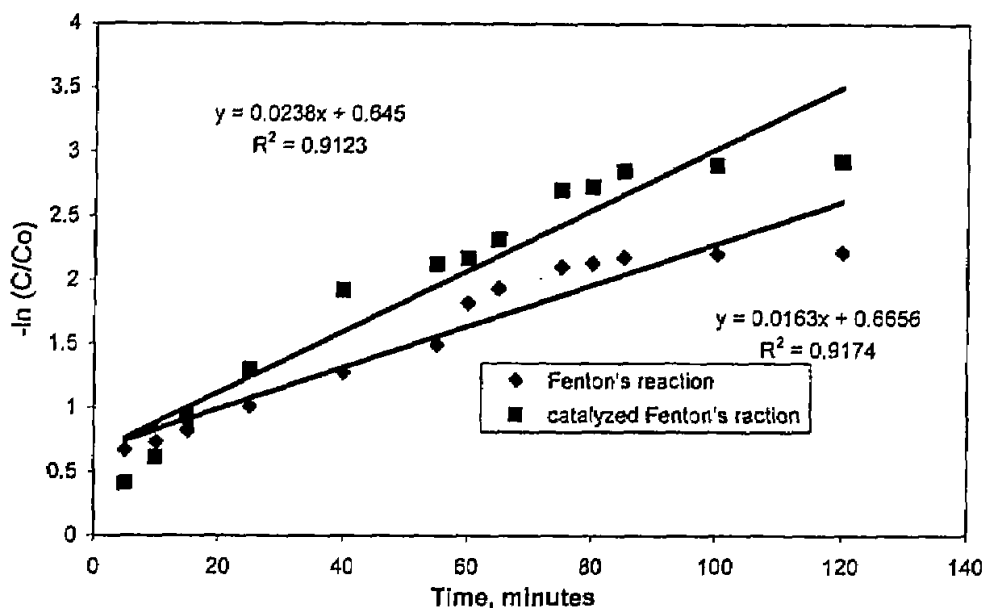


Fig.11: Plot of first order rate constants for removal of dye 3 (navy blue) from aqueous solutions.

Generally, the first order rate constant in case of using titanium dioxide is higher than that in case of its absence by 1.30, 1.48 and 1.46 times for dyes 1,2 and 3 respectively. The main effect of titanium dioxide is not only to increase the color removal of dyes but also to accelerate the process and reducing retention time by about 35 minutes.

4. Conclusions

The following conclusions can be withdrawn from this research:

1. Fenton's oxidation process successfully achieved good color removal efficiency of dyes (over 90%) at optimum conditions (pH=3, H₂O₂ dose=200 mg/l FeSO₄ dose=90 mg/l), while adding 100 mg/l of titanium dioxide at optimum conditions, the color removal efficiency increased to be over 96%.
2. The main effect of titanium dioxide is not only to increase the color removal of dyes but also to accelerate the process and reducing retention time by about 35 minutes.

3. Kinetic plots indicate that the process is first order as confirmed by the linear representations of results. The first order rate constant in case of using titanium dioxide is higher than that in case of its absence by 1.30, 1.48 and 1.46 times for dyes 1, 2 and 3 respectively.

References

1. Tianyong Z., Toshiyuki O., Akio A., Hisao H., Jincai Z. and Nick S.; *Journal of Photochemistry and Photobiology A: Chemistry* **140**, pp163–172 (2001).
2. Ganesh R., Boardman G.D. and Michelson D., *Water Res.* **28**, 1367 (1994).
3. Weber E.J. and Adams R.L., *Environ. Sci. Technol.* **29**, 113 (1995).
4. Glaze W. H., Kang J. W. and Chapin D. H., *ozone Sci. Eng.*, **9**, pp. 335-352, (1987).
5. Chen J., PhD Thesis, Dept. of Env. Tech. Of Wageningen Agricultural Univ., The Netherlands (1997).
6. Fenton H. J. H., *J. Chem. Soc.*, **65**, pp. 899-910 (1894), as cited in reference 5.
7. Kitis M., Adams C. D. and Daicger G. T., *Wat. Res.* , **33**(11), pp. 2561-2568 (1999).
8. Roppert C. and Bauer R., *Chemosphere*, **27**, pp. 1339-1347, (1993).
9. Venkatadri R. and Peters R. W., *Haz. Waste Haz. Mater.* **10**, pp. 107-149 (1993).
10. Pingatello J. J., *Environ. Sci. Technol.* , **26**, pp. 944-951 (1992).
11. Ilisz I. and Dombi A. , *Applied catalysis A: General*, **180**, pp. 35-45, (1999).
12. Ghaly M. Y., Hartel G., Mayer R. and Haseneder R., *waste management*, **21**, pp. 41-47 (2001).
13. Kange, Y. W. and Hwang , K. Y., *Wat. Res.* , **34**(10), pp. 2786-2790, (2000).
14. Nogueira R.F.P. and Jardim W.F., *J. Adv. Oxid. Technol.*, **4**(1), pp. 1-4 (1999).
15. Serpone N., Sauve G., Koch R., Tahiri H., Pichat P., Piccinini P., Pelizzetti E. and Hidaka H., *J. of Photochem. & Photobiol. A* **94**, 191 (1996).
16. Ollis D.F., Pelizzetti E., Serpone N., in: N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis - Fundamentals and Applications*, Wiley/ Interscience, New York, pp. 603–637 (1989).
17. Matthews R.W., *J. Chem. Soc. Faraday Trans.* **185**, 1291 (1989).
18. Reeves P., Ohlhausen R., Sloan D., Pamplin K. and Scoggins T., *Sol. Energy*, **48** 413 (1992).
19. Lakshmi S., Renganathan R and Fujita S, *J. Photochem. Photobiol. A* **88** 163 (1995).
20. Sopajaree K., Qasim S.A., Basak S. and Rajeshwar K., *J. Appl. Electrochem.*, **29**, 533 (1999).
21. Walter Z. T. and Huren A., *Chemosphere*, **31**(9), pp. 4171-4183 (1995).

- 22.Wali F. K. M. I., PhD Thesis, Faculty of Science (Damietta), Mansoura University, Egypt (2005).
- 23.Maha A. T., M. SC. Thesis, Faculty of Eng., El-Minia University, Egypt, (2005).
- 24.Bigda R., Chem. Eng. Progr., 91, pp. 62-66 (1995).
- 25.Daneshvar N. and Khataee,A.R., Journal of Environmental Science and Health Part A,41,pp.315-328 (2006).
- 26.Barbusinski K., Polish Journal of Environmental Studies , 14(3), pp.281-285 (2005).

استخدام تفاعل فنتون المنشط في أكسدة بعض الأصباغ المباشرة من محاليلها المائية

يستخدم هذا البحث إحدى الطرق المتقدمة للأكسدة لإزالة ألوان بعض الأصباغ المباشرة من محاليلها المائية باستخدام تفاعل فنتون في وجود أو عدم وجود ثاني أكسيد التيتانيوم. تم دراسة أنسب الظروف التي يمكن التوصل إليها والتي تعطي أفضل النتائج أثناء عملية إزالة هذه الأصباغ من محاليلها المائية. ولقد أثبتت الدراسة أن أفضل الظروف لإزالة هذه الأصباغ تكون عند رقم الأس الهيدروجيني 3 ، 200 ملجم /لتر من فوق أكسيد الهيدروجين ، 90 ملجم /لتر من كبريتات الحديدوز ، ويلزم زمن قدره يتراوح من 70 إلى 80 دقيقة لحدوث أفضل إزالة لألوان الأصباغ. تم تطبيق الظروف المثلى للعملية (والتى تم تحديدها مسبقاً) لإزالة ألوان هذه الأصباغ من محاليلها المائية في وجود وفي غياب ثاني أكسيد التيتانيوم. وأثبتت القياسات أنه تم بنجاح إزالة هذه الألوان بنسبة إزالة حوالي 90 % في حالة غياب ثاني أكسيد التيتانيوم في خلال مدة زمنية حوالي 70 دقيقة، بينما في حالة وجود ثاني أكسيد التيتانيوم ارتفعت نسبة إزالة اللون إلى أكثر من 96% في فترة زمنية أقل حوالي 30 - 40 دقيقة. بدراسة كيناتيكا التفاعل لإزالة ألوان الصباغات من محاليلها المائية وجد أنها من الدرجة الأولى وان ثوابت المعدل تكون أعلى في حالة أضافه لأكسيد التيتانيوم بحوالي 4 و 1 مرة تقريبا عنها في حالة عدم الإضافة.