KINETIC STUDY OF PHOTODEGRADATION OF Azo DYES WITH TiO_2 UNDER VISIBLE LIGHT

Hassan A. Habeeb and Abbas A. A. Kadhum
Department of Chemistry, College of Education, Al-Qadisiya University.

Abstract

In this work, two mono azo dyes : 4-(2- benzoic acid azo)-m-amino phenol (BAMAP), and 4-(2-benzoic acid azo)-P-amino phenol (BAPAP)have been synthesized and identified by FT-IR spectroscopy. UV-Visible absorption spectra were recorded and some physical and chemical properties have been listed.

The photodegradation of dyes was investigated by using the light of tungsten lamp in presence and absence of titanium dioxide (anatase). It has been found that the increasing of TiO_2 mass caused an increasing in photodegradation of two dyes until the optimum mass (2gm/l) was reached. Also, the results indicate, that the basic media give more photodegradation rate than acidic medium, moreover ,the effect of temperatures in the range (298–323K) on degraded dye was studied ,and the activation energy of photodegradation processes was calculated from Arrhenius plot which equal 35.82KJ.mol^{-1}for BAMAP and 32.11KJ.mol^{-1}for BAPAP.The results showed the photoreaction is 1st order ,with decomposition constant equal 2.362×10^{-4}min^{-1}for BAMAP and 2.826×10^{-4} min^{-1}for BAPAP at 298k and neutral medium.

Generally, it has been found that the rate of photodegradation of BAPAP is more than BAMAP, and the decolonization rate of the two dyes was higher in presence of TiO_2 suspension.

Keywords: Titanium dioxide, Photocatalysis , Photodegradation of dyes, Visible light.

Introduction

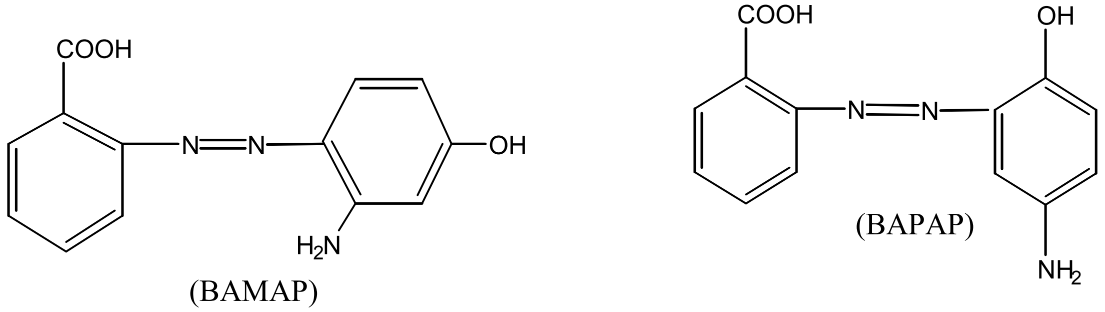
The presence of azo dyes and other water contaminations in dye bath effluents and existing of those in waste water treatment stations, indicate that these chemicals resist the natural biological degradation and other environmental conditions, for this reason ,the azo dyes and other water contaminations have a high atention in recent years.(1–5). The semiconductor TiO2 can generate highly degrading hydroxyl radical under exposing to UV illumination, as the mechanism (6) below showes: Titanium dioxide has important uses in heterogeneous catalysis as a result of its stability toward heat and photo corrosion. The rate of photooxidation depends on important factors such as : quantity of TiO2, concentration of adsorbate, pH, size of TiO2 particles, temperature, light intensity, and TiO2 type.

Generally, the heterogeneous means photocatalytic processes using semiconductors (TiO2 , ZnO , …..) are considered suitable to the degradation of water contaminants. The thin films of semiconductors witnessed a high expansion in recent years as a new process to color removal of dyes and other compounds in water (7-9). The application of illuminated semiconductors for the remediation of contaminants has been used successfully for a wide variety of compounds (10-14) such as alkenes, aliphatic alcohols, aliphatic carboxylic acids, and dyes.

$TiO_2 + h\upsilon \rightarrow TiO_2 \ (e^- / h^+)$
$TiO_2 (h^+) + H_2O_{ads} \rightarrow TiO_2 + {}^-OH_{ads} + H^{\cdot}$
$TiO_2 (h^+) + {}^-OH_{ads} \rightarrow TiO_2 + OH_{ads}$
e^- : electron , h^+ : hole , ads : adsorption
Oxygen can trap the electron and generates the hydroxyl radical:
$TiO_2 (e^-) + O_{2\,ads} \rightarrow O_{2ads} + TiO_2$
$O_{2ads} + H^+ \rightarrow HO_2$
$O_{2ads} + HO_2 \rightarrow OH + O_2 + H_2O_2$
$2HO_2 \rightarrow H_2O_2 + O_2$
$O_2 + H_2O \rightarrow OH + HO_2$

Semiconductor photocatalysis with a primary focus on TiO_2 as a durable photocatalyst have been applied to a varity of problems of environmental interest, in addition to water and air purification. It has been shown very useful for the destruction of microorganisms such as bacteria (15), viruses (16), inactivation of cancer cell (17 ,18), odor control (19), photosplitting of water to produce hydrogen gas (20-23), fixation of nitrogen (24), and for the clean up of oil spills (25 -27)

The aim of the present work is to evaluate the efficiency of applying photocatalysis to degrade organic contaminants in water such as dyes. Synthesized azo dyes: 4-(2-benzoic acid azo)-m-amino phenol (BAMAP) and 4-(2-benzoic acid azo)-P-amino phenol (BAMAP) were used as a model compound because it was possible to use UV-visible spectroscopy to monitor the degradation under different conditions: such as azo dyes concentration, pH, TiO_2 concentration. Scheme (1) shows the structural formula of synthesized dyes.



(BAMAP)

(BAPAP)

Scheme (1) : Structural formula for synthesized azo dyes.

Experimental

A. Materials :

All chemicals obtained in this work were used without further purification: p-amino phenol, m-amino phenol, 2-aminobenzoic acid, sodium nitrite, hydrochloric acid, and ethanol were supplied by BDH ,Titanium dioxide (TiO_2) Degussa–P25 mainly anatase 70 % with surface area of 55 m^2 / g and mean size of 22-35 nm (28) .NaOH and HCl were supplied by Riedel De haen.

B-Preparation of dyes:

The two dyes were synthesized by coupling reaction using equimolar amounts from 2-aminobenzoic acid and coupling compounds (p-Amino phenol and m-Amino phenol) .To 25 ml of mixture of distilled water and sulphuric acid (96%)1:1, 0.025 mol of 2-aminobenzoic acid was added, and the mixture was stirred at temperature below (5°C) for one hour. To this mixture an aqueous solution (10ml) of coupling compound (0.025mol) was added, and the mixture was stirred at room temperature overnight. The dye product was isolated by filtration through a 0.22 μm Millipore filter paper, and washed with cold distilled water for several times and recrystallized from ethanol, then dried at 80 °C for three hours and weighed. The purity of dyes was checked using thin layer chromatography and the eluent (acetic acid: ethanol: water) (2:4:4) respectively. R_f values of dyes were measured and silica gel was supported on glass plate. The physical and chemical data of two dyes are given in Table (1).

C-Spectroscopic Measurements:

UV- visible spectra of aqueous solutions of synthesized dyes were recorded by Shimadzu UV-Visible 1650PC spectrophotometer. FT-IR spectra were recorded on Shimadzu FT-IR 8400S spectrophotometer using KBr disk in the range400-4000cm^{-1}.

D-Photodegradation processes:

The photodegradation of dyes was performed by irradiating the aqueous solution of certain dye in 50 ml quartz cell with light of high pressure mercury lamp 200 W lamps (HPML) in the presence of TiO_2 suspension and stirring the suspension continuously. The temperature of suspension was maintained by using regulator water bath .Samples for kinetic study were taken from reactor by syringe through the reaction. The quantity of undegraded dye was estimated in the λ_{max} of dye using after remove the TiO_2 by filtration. The pH of suspension was controlled by using NaOH and HCl. Some experiments were performed without TiO_2 to investigate the effect of later on efficiency of photodegradation process.

Result and Discussion

The scope of the present work is the searching for the available and suitable processes to minimizing the environmental hazardous of spilling effluents of azo dyes baths. The synthesized dyes in this work have a good molar absorbance coefficient in the uv-visible region as Table (1). In direct photolysis (without TiO_2), 90 min of irradiation, no direct photodegradation was observed for two dyes because the molar absorptivities are very low at the radiation wavelength range used. Consequently, there is no place to a possible photo alteration process of the molecules. Thus, degradation of these dyes is exclusively due to photoactivation of the TiO_2 catalyst. Figs. (1) and (2) show that the absorption of the visible band at λmax of all dyes decreased with the time (0,15,30,60 and 90 min), this trend suggests that the dyes start to degrade with time. Also, Figs. (3) and (4) clearly show the existence of N=N stretching frequency of two dyes which appear at $1450cm^{-1}$for BAPAP and $1445cm^{-1}$ at for BAMAP which indicating that the reactions between 2-aminobenzoic acid and two coupling components are take place. Also, from these data, we can say that the synthesized two azo dyes have good acceptable spectral properties to be used as a photosensitizers.

Table (1)
Some physical, chemical and spectroscopic properties of synthesized dyes.

Dye	*M.Wt g/mol*	*color*	*Yield%*	*R_f*	*M_p °C*	*λ_{max} nm*	*€ $l.\ mol^{-1}.cm^{-1}$*	*$N=N,cm^{-1}$*
BAPAP	572	orange	65	0.85	171	310	4350	1450
BAMAP	572	brownish	72	0.72	197	327	5115	1445

The kinetic study of photodegradation of dyes in TiO_2 suspensions under visible light has often been modeled to the Differential method , data from this method allowed the assessment of decolourisation as a first-order kinetic relationship as Fig.(5), with decomposition constant equal $2.362x10^{-4}s^{-1}$ for BAMAP and $2.826x10^{-4}s^{-1}$ for BAPAP. Fig. (6) shows the influence of TiO_2 mass on photodegradation of two azo dyes. It is clear that the rates in the absence of TiO_2 are equal to zero in comparison with the existence of TiO_2 particles as a result of the adsorbed molecules of colored dye on to TiO_2 surface. The optimum quantity of photocatalyst is 2g/L, so this concentration was fixed in all followed experiments. It is clear that the TiO_2 is an important factor in photodegradation process which are due to the adsorbing of dyes over TiO_2 particles and the photodegradation is driven by injecting of an electron from excited state of dye into the conduction band of TiO_2 particles which leads to the oxidation of dye molecules, also the electron of conduction band caused by moving the electrons from valence band and these electron may be used to drive another photoreactions of dye molecules in different routs. The result of photodegradation of two dyes illustrate that the rate of degradation process depends on concentration of TiO_2. Figs. (7) and (8) show the depletion of concentration as a function variation of pH medium. From those figures and Fig.(9), it is clear that the rate of photodegradation of two dyes increases as the pH value increases and reaches the maximum rate at pH of 8, and may be the efficiency is increased if the pH increases more than pH of 8. The effect of temperature in the range (298-323K) was investigated, which indicates the positive effect of increasing temperature of two dyes as Fig.(10) clarifies. The activation energy of photodegradation processes was concluded from Arrhenius plot which equal 35.82KJ.mol^{-1} for BAMAP and 32.11KJ.mol^{-1} for BAPAP. The dye concentration is an essential factor in this process. The decreasing of concentration enhances the photodegradation rate. Fig.(11) presents that this realation is not too linearity.

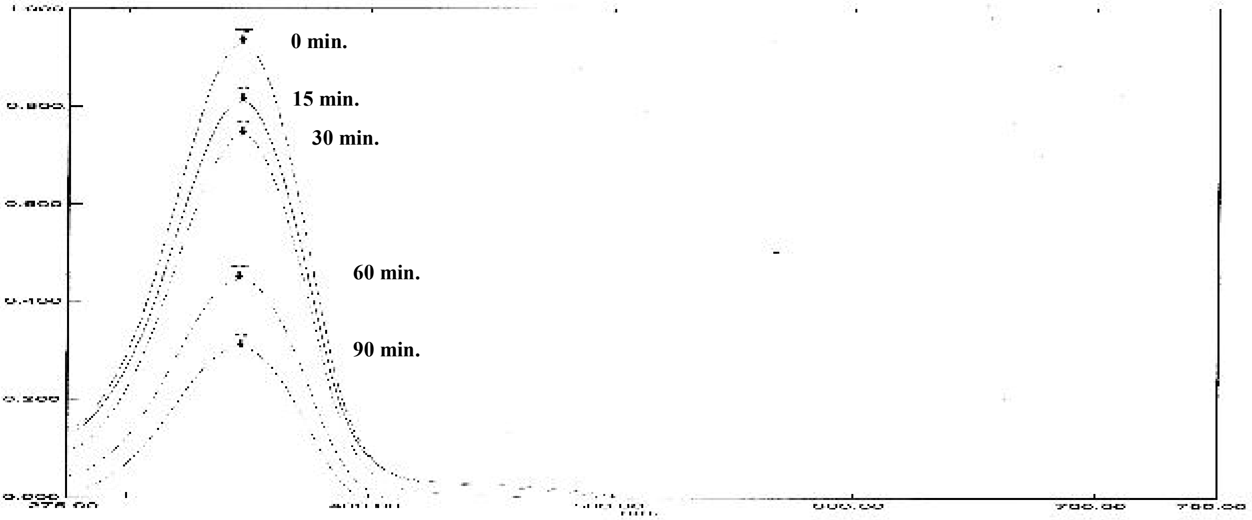


Fig. (1) : Absorption spectra for irradiated of BAPAP dye at different time .

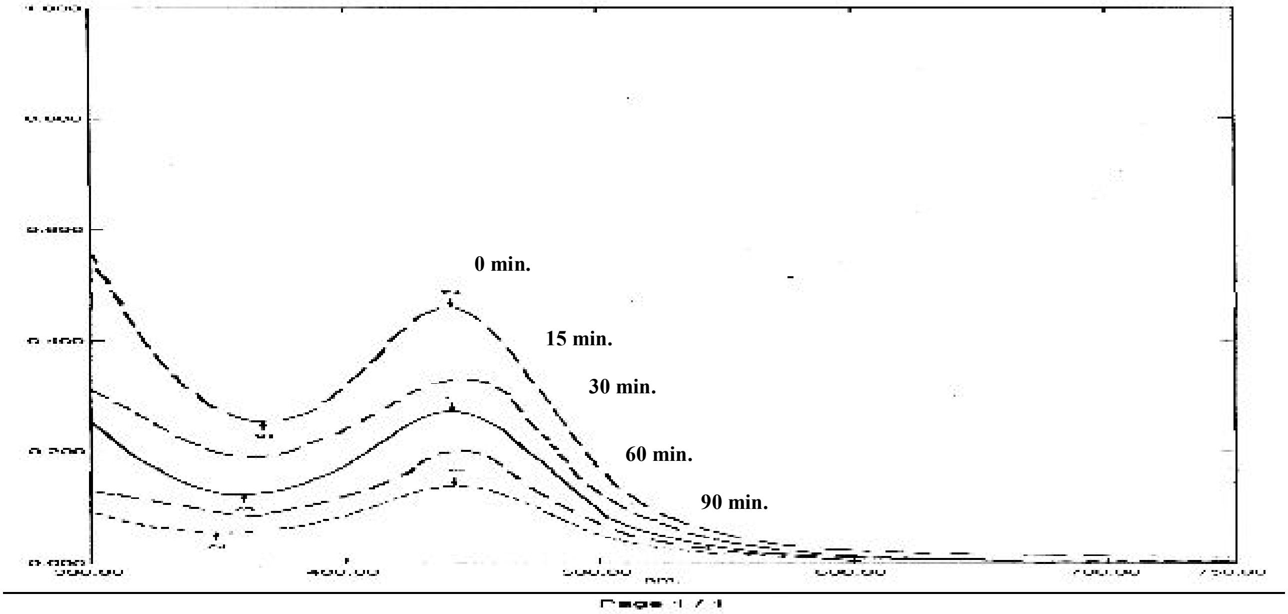


Fig. (2) : Absorption spectra for irradiated of BAMAP dye at different time .

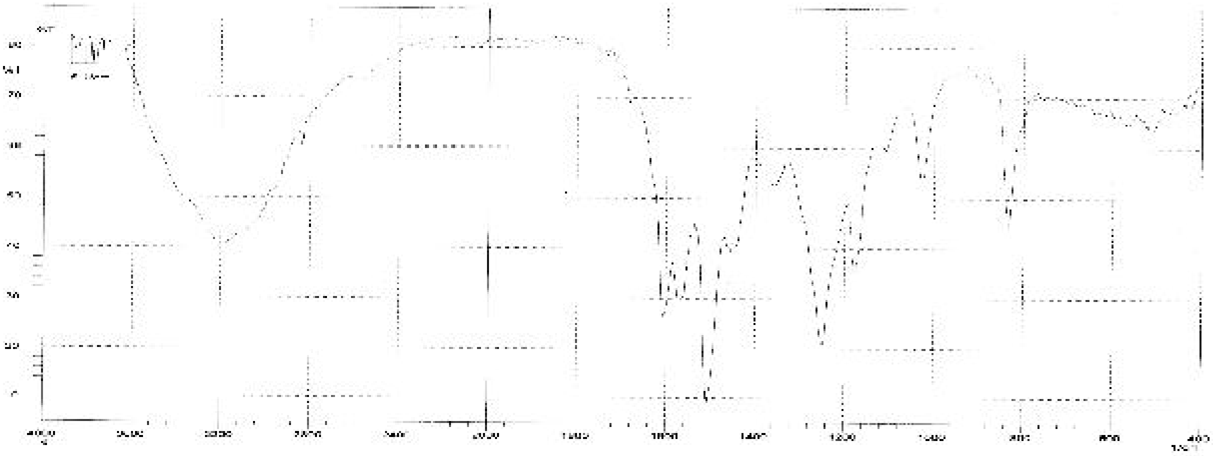


Fig. (3) : FTIR- spectrum for BAPAP .

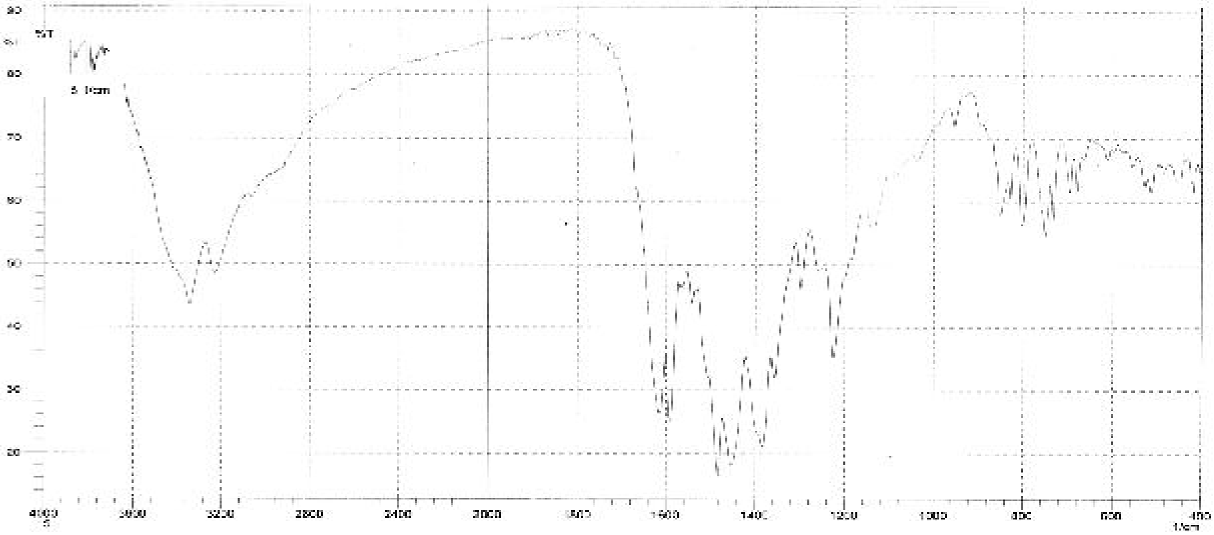


Fig. (4) : FTIR- spectrum for BAMAP.

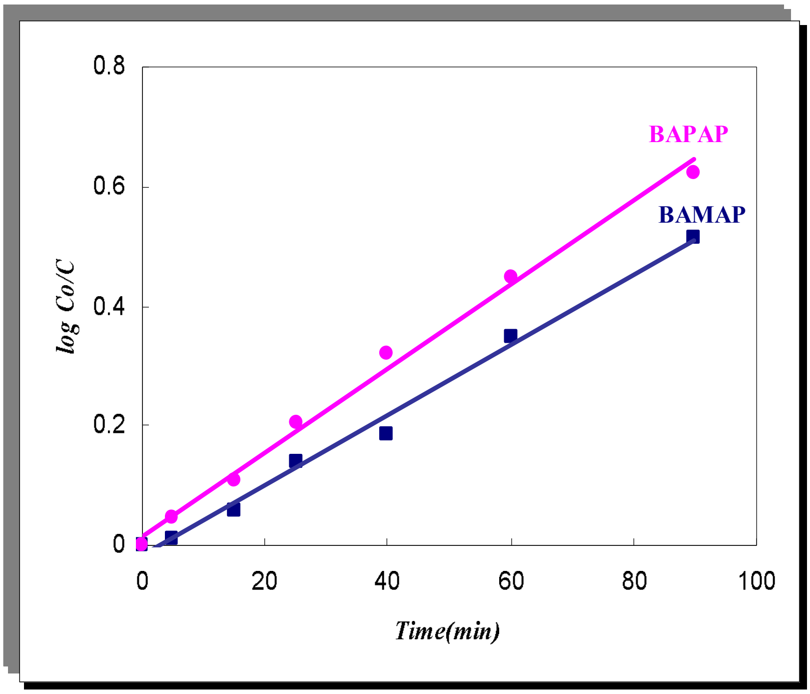


Fig. (5): Plot of first order kinetics of photodegradation for two dyes ($4x10^{-5}$mol/l) as a function to time at 298K,pH of 7, TiO_2 (2gm/l).

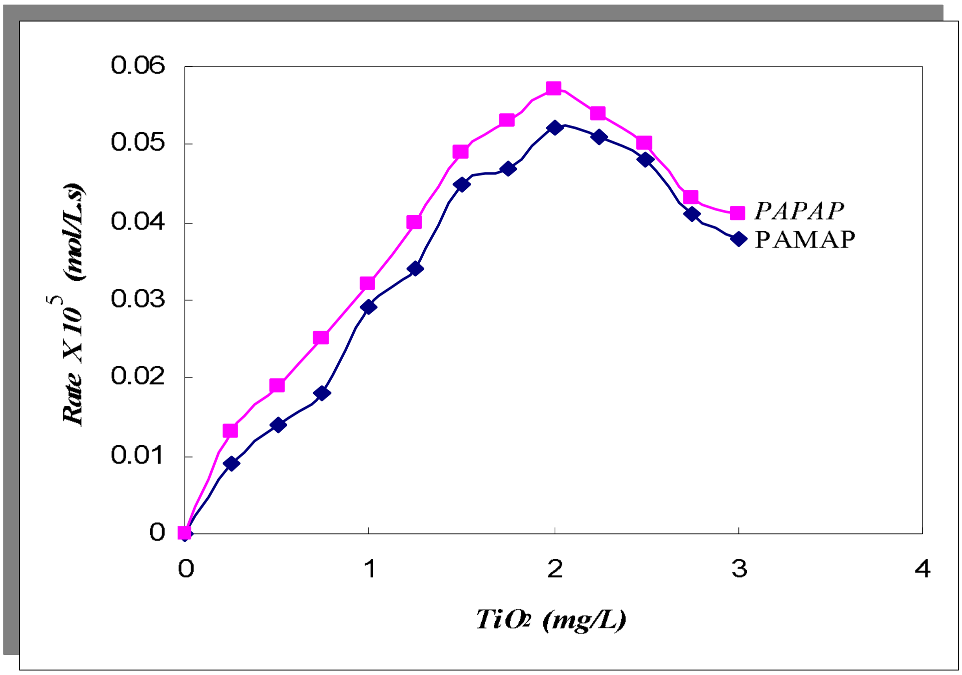


Fig. (6): Effect of TiO_2 concentration on the photodegradation rate of two dyes ($4x10^{-5}$mol/l), at 298K and pH of 7.

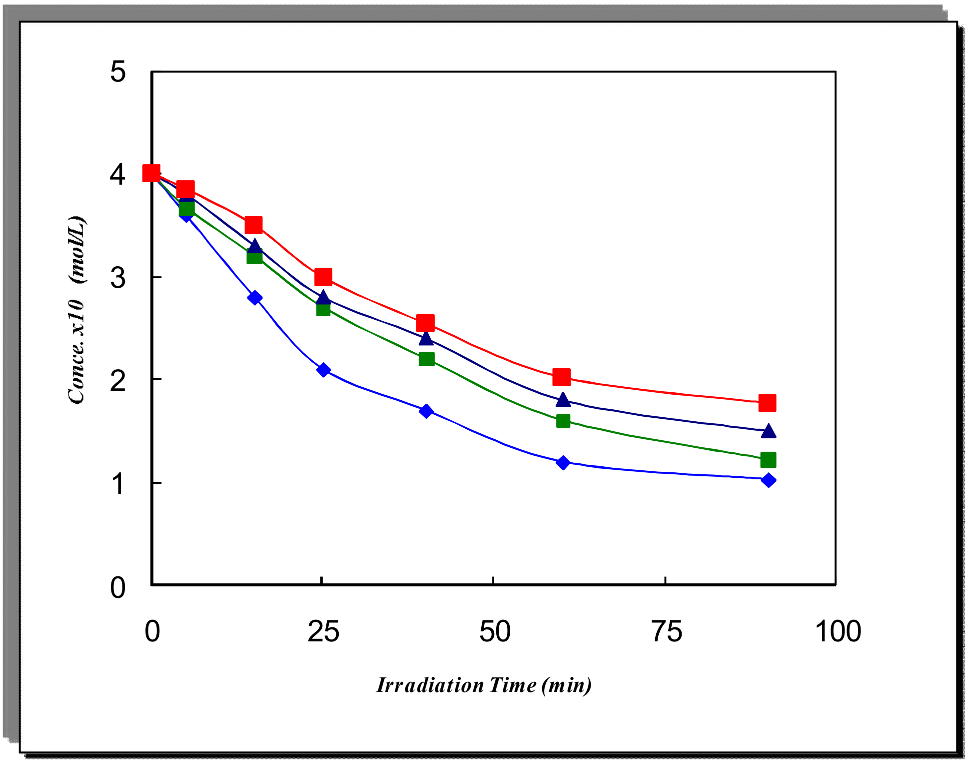


Fig.(7): Influence of pH medium over concentration gradient of BAMAP dye ($4x10^{-5}$mol/l), at 298K and TiO_2 (2gm/l).

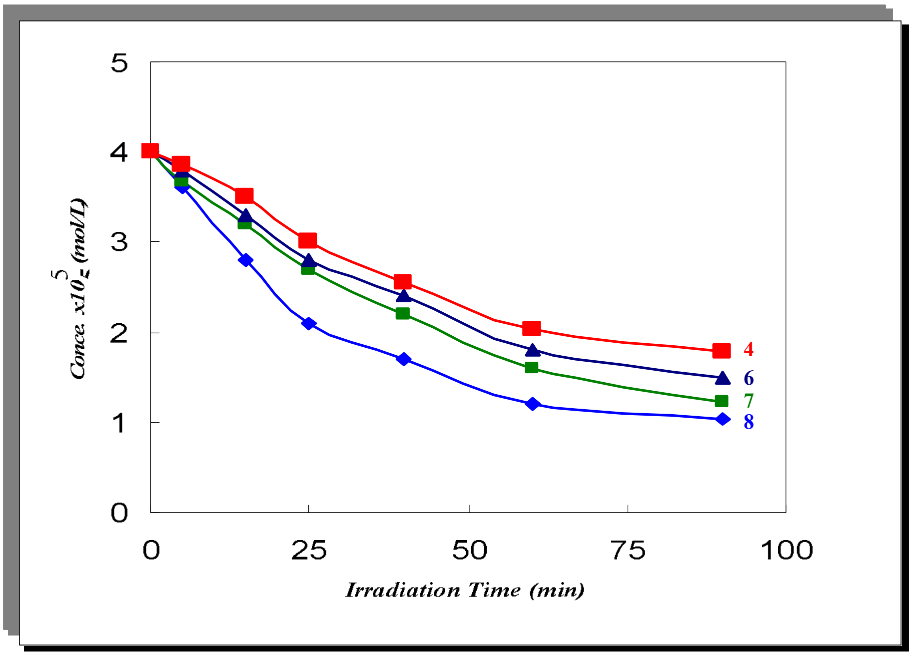


Fig. (8): Influence of pH medium over concentration gradient of BAPAP dye ($4x10^{-5}$mol/l), at 298K and TiO_2 (2gm/l).

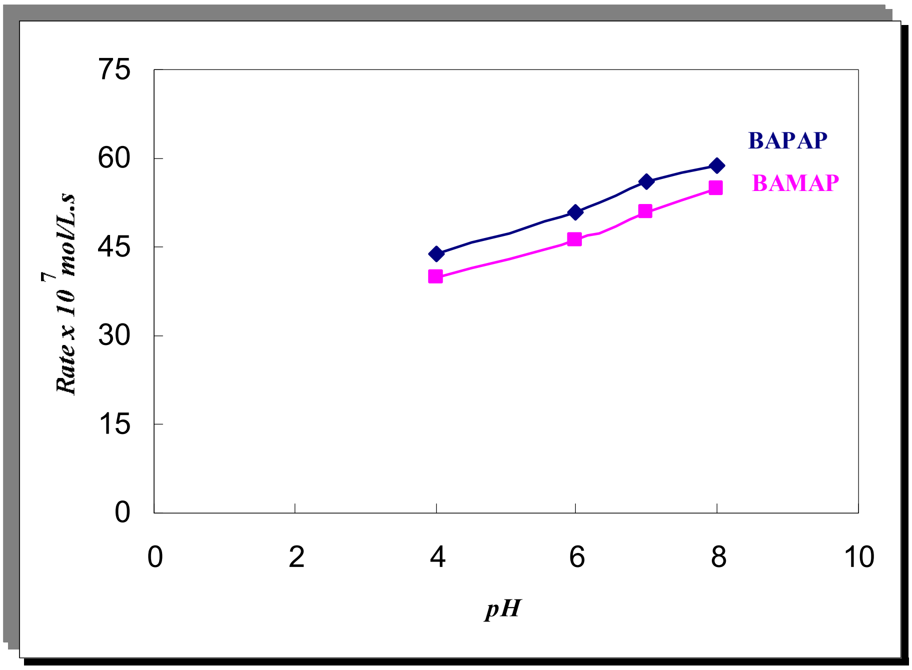


Fig.(9): Influence of pH medium over photodegradation rate of two dyes ($4x10^{-5}$mol/l), at 298K and TiO_2 (2gm/l).

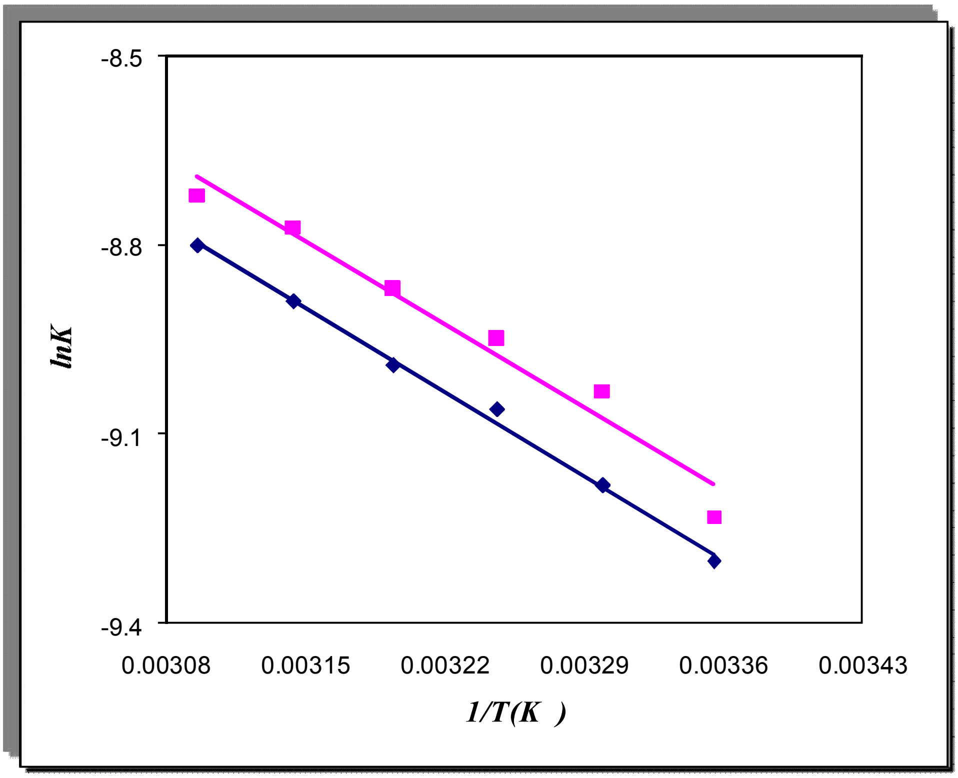


Fig.(10): Arrhenius plotting of photodegradation for two dyes (4x10^{-5}mol/l) as a function to time at pH of 7, TiO$_2$ (2gm/l).

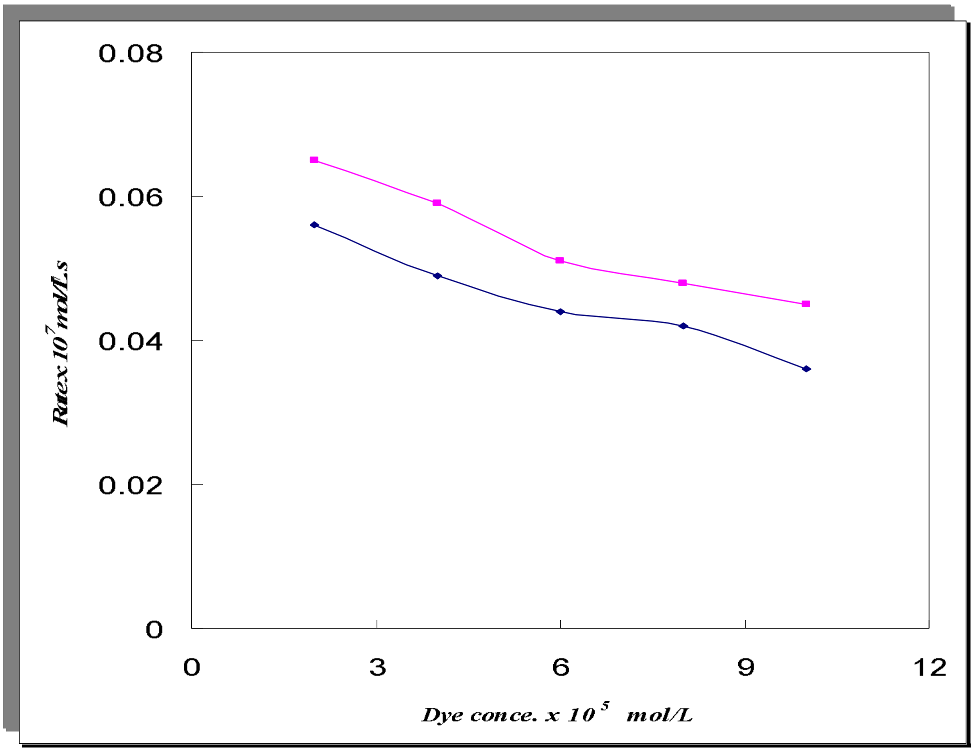


Fig.(11): Effect of dye concentration on photocatalytic degradation rate at 298K, pH of 7, TiO$_2$ (2gm/l).

References

[1] I. Hisz, A-Dombi , K. Mogyorosi, A. Farkas and I.Dekany, "Photodegradation of visible-light absorbing organic compounds in the presence of semiconductor catalysts", Applied catalysis B: Environmental , Vol. 10 , 2002, pp. 1214 .

[2] N. I. Stock, J. Peller, K. Vinodgopal and P. V. Kamat," Combinative sonolysis and photocatalysis for textile dye degradation "Environ. Sci. Technol., Vol. 4, No. 9, 2000, pp. 1747-50.

[3] K. Vinodgopal , J. Peller , O. Makogen , and P. V. Kamat ," Ultrasonic mineraliztion of reactive textile azo dye , Remazol Black B. " Water Res. , Vol. 32, No. 40 ,1998 , pp.3632-46 .

[4] S. Parra , J. Olivero and C. Pulgarin , "Relationships between physicochemical properties and photo reactivity of four biorecalcitrant phenyl urea herbicides in agueous TiO_2 suspension", Applied catalysis B: Environmental, Vol. 36 , 2002, pp. 75-85.

[5] P. V. Kamat , R, Huchn and R. Nicolaeseu, "A sense and shoot approach for photocatalytic degradation of organic contaminants in water"J. Phys. Chem., B, Vol. 106, 2002, pp. 788-94.

[6] H. A. Habeeb, N. A. A. ALRudha and F. A. Jabber ,"Utilization of sun light radiation to degradation of polluted green reactive textile dye by photocatalytic and chemical processes ", J. of AL-Qadisiya, pure Sciences, Vol. 11, No. 4, 2006, pp. 226-227 .

[7] M. R. Hoffman , S. T. Martin and W.Choi, "Enviromental applications of semiconductor photocatalytic", chem.. Rev., Vol. 95, 1995, pp. 95 , 69.

[8] I. Sopyan, M. Watanabe and S. Muvasawa, "Anefficient TiO_2 thin -film photocatalyst : photocatalytic properties in gas-phase acetaldehyde degradation , J. Photo. Chem. Photobilo. A. Chem.: Vol. 98, 1996 , pp. 69-70 .

[9] D. Chen. A. K. Ray ,"Photo catalytic kinetics of phenol and its derivatives over UV irradiated TiO_2 ", Appl. Catal. B: Environ. Vol. 23, 1999, pp.143.

[10] G. Mills and M. R. Hoffmann," photocatalytic degradation of pentachlorophenol on TiO_2 particles: Identification of intermediates and mechanism of reaction", Environ. Sci. Technol., Vol. 27, No. 8, 1993, pp. 1681-1689.

[11] C. Kormann ,D. W. Bahnemann and M. R. Hoffmann , "Photolysis of chloroform and other organic molecules in agueous TiO_2 suspensions "Environ. Sci. Technol., Vol. 25 , No. 3 , 1991 , pp.494-500.

[12] A. Chemeseddine and H. P. Boehm," A study of the primary step in the photochemical degradation of acetic acid and chloroacetic acid on a TiO_2 photocatalyst", J. Mol. Catal., Vol. 60, 1990, pp.295-311.

[13] J. C. Doliveira ,C. Minero ,C.Pelizzetti and E. Pichat ,"Photodegradation of dichlorophenols and trichlorophenols in TiO_2 agueous suspension", J. Photochem. Photobiol. A:Chem., Vol. 72, 1993, pp. 261-267.

[14] J. C. Doliveira ,C. AL-Sayyed and G. Pichat , " Photodegradation of -2- and -3-chlorophanols in TiO_2 agueous suspension". Environ. Sci. Technol., Vol. 24, 1990, pp. 990-996.

[15] J. C. Ireland , E. W. Rice and R. M. Clark, "Inactivation of escerichia coli by titanium dioxide photocatalytic reaction " Appl. Environ. Microbiol. ,Vol. 59 , No. 5 ,1993 , pp. 1668-1670.

[16] R. X. Cai , Y. Kubota and K. Fujishima, "Induction of cytotoxicity by photoexcited TiO_2 particles " , Cancer Res. , Vol. 52 , 1992 ,pp. 2346-2348.

[17] J. C. Sjogren ,R. A. Sierka ,"Inactivation of phage MS_2 by Iron-Aided Titanium Dioxide photocatalysis ", Appl. Environ. Microbiol .,Vol.60, 1994 ,pp.344-347.

[18] R. Cai ,K. Hashimoto and Y. Fujishima , "Interment of photocataltic killing of cancer cells using TiO_2 with the aid of superoxide dismutase ", Chem. Lett. , Vol. 55, 1992, pp.427- 430.

[19] K. Karakitsou and X. E. Verykiso , "Effect of altervalet cation doping on its performance as photocatalst for water cleavage " , Phys. Chem. , Vol. 97, 1993, pp. 1184 -1189 .

[20] Gratzel, M.," Artificial photosynthesis: Water cleavage into hydrogen and oxygen by visible light "Acc. Chem. Res., Vol. 14, 1981, pp. 376.

[21] D. Duong hong ,E. Borgarello and E. Gratzel ,"Dynamic of light –induced water cleavage in colloidal systems " J. Am. Chem. Soc.,Vol.103, 1981, pp. 4685.

[22] I.Arslan and A.I. Balcioglu" Degradation of remazol black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogeneous media", Coloration Technology, Vol. 117, No. 1, 2001, pp.38 - 42 .

[23] A.Bozzi , A. Lopez and G. Mascolo, "pharmaceuticals degradation by UV and UV/H_2O_2 treatments ", Water Supply, Vol. 2 , No. 2 , 2002 , pp. 19-26.

[24] A. Wold ," Photocatalytic properties of titanium dioxide (TiO_2) " , Chem. Mater. Vol. 5, 1993 ,pp. 280-283.

[25] M. Schiavello," Some working principle of heterogeneous photocatalysis by semiconductors", Electrochim. Acta., Vol. 38, 1993 , pp.11-14.

[26] M. Khan, D. Chatterjee, M. Krishnaratnam and M. Bala , "Photosensitized reduction of N_2 by $[Ru(bipy)_3]^{2+}$ adsorbed on the surface of $Pt/TiO_2/RuO_2$. semiconductor particulate system containing Ru(III)-EDTA complex and L-ascorbic acid" J. Mol. Catal. , Vol. 72, No. 1 , 1992 , pp.13- 18.

[27] H. Gerischer and A. Heller," Photocatalytic oxidation of organic molecules at titanium dioxide particles by sunlight in aerated water ", J. Electrchem. Soc. Vol. 139, No. 1, 1992, pp. 113-118.

[28] Kipling J. J., Adsorption from solution of Non-Electrolytes, Aecdemic press, London, P. 234 (1965).

[29] J.A.Abbas , K.H.Salih and H.H.Falah " Photocatalytic degradation of textile Dyeing Wastewater Using Titanium Dioxide and Zinc Oxide " E-Journal of Chemistry, Vol.5, No.2, 2008, pp. 219-223.

[30] Serpone, N., "Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis", Vol. 5, 1997, pp. 59.

الخلاصة

يتضمن البحث تحضير صبغتي ازو أحادية وهما 4-(2-حامض البنزويك ازو) بارا امينو فينول(PAPAP) و 4-(2- حامض البنزويك ازو) ميتا امينو فينول (PAMAP) . تم تشخيص الأصباغ المحضرة بوساطة مطيافية الأشعة تحت الحمراء. و سجلت كذلك أطياف الأشعة المرئية وفوق البنفسجية وتم دراسة بعض الخواص الفيزيائية والكيميائية .

وتضمن البحث كذلك دراسة التحطم الضوئي للأصباغ المحضرة بوساطة استخدام ضوء من مصباح مرئي بوجود وغياب عالق ثاني اوكسيد التيتانيوم (الانتيز) .وجد إن زيادة تركيز TiO_2 أدت إلى زيادة سرعة التحطم الضوئي لكلا الصبغتين لحين الوصول إلى التركيز الأمثل ل TiO_2 وهو 2غم/لتر . ودلت النتائج أيضا بان المحيط القاعدي قد حفز من سرعة التحطم الضوئي أكثر بالمقارنة مع المحيط ألحامضي .درس تأثير درجة الحرارة ضمن المدى 323- 298 كلفن حيث وجد آن درجات الحرارة العالية أدت إلى زيادة سرعة تحطم الصبغتين ووجد إن طاقة التنشيط كانت 35.82 كيلو جول/مول للصبغةPAMAP و 32.11 كيلو جول/مول للصبغةPAPAP للصبغة.دلت النتائج بان التفاعل الضوئي المحفز تبع حركيات من المرتبة الأولى ووجد أن ثابت سرعة التفكك $2.362 \times 10^{-4}\ min^{-1}$ للصبغة PAMAP و $2.826 \times 10^{-4}\ min^{-1}$ للصبغة PAPAP .

و بصورة عامة وجد بان سرعة التحطم الضوئي للصبغة BAPAP كانت أعلى من الصبغةBAMAP ، كذلك فان سرعة إزالة اللون لكلا الصبغتين كانت أعلى بوجود عالق TiO_2 .