Studying of Photodegradation of Prepared Azo-dyes by TiO$_2$

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Abstract

The work consists of two parts . The first deals with the preparation of some mono azo dyes : 4- phenyl azo – α – fluoro phenol (BAFP) , 4 – phenyl azo – α – chloro benzoic acid(BACB) , 4- phenyl azo – α – methyl phenol (BAMP) . The prepared compounds have been identified by FT-IR ,and UV-Visible absorption spectroscopy .

The second part consists of photodegradation of the azo compounds mentioned above at lab temperature in presence and absence of titanium dioxide (anatase) as suspension by exposure of aqueous solution of dyes using light from a 150 w lamp with wavelength 350-800 nm. Generally it has been found that the rates of photodegradation of three dyes were higher in presence of TiO$_2$ suspention .

In this paper some physicochemical properties of the dyes , such as the electron – donor or electron – withdrawing character of dyes have been employed to asses their photodegradability.The results of photodegradation of all dyes illustrate that the rate of the degradation process depends on the conc. Of TiO$_2$, and physicochemical properties of the dyes .

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Introduction

In the present work we prepared three azo – dyes , which are different in the electronegativity of their substituents in the aromatic ring . Generally , many studies show clearly that the efficiency of a photocatalytic for the degradation of organic and inorganic compounds is strongly dependent on their chemical nature of the dye [1-4].TiO_2 catalyst can not absorb visible light and only makes use of 3-5 % of the solar beam that can reach the earth necessitating the utilization of an ultraviolet light source . It is necessary to develop a photo catalytic system which can be applied under visible and / or solar light irradiation [5,6] .TiO_2 photocatalyst initiates upon absorbing UV photons with generation conduction band (CB) electron and valence band (VB) holes within the particle .The hydroxyl radicals in particular , generated through the reaction of VB holes account for the strong oxidizing power of the TiO_2 photocatalytic system .

Although TiO_2 has been widely used as a photocatalyst , the bandgap excitation of TiO_2 proceeds only in the presence of UV light (λ < 388 nm) . Sensitized TiO_2 by ruthenium-based complexes or various dyes [7-11] has been extensively investigated in order to extend the spectral response into the visible region .The dye/TiO_2/visible light system where the system serves as both a sensitizer and a substrate to be degraded could develop into a viable technology for treating dye-polluted wastewaters .

Experimental.

Materials

All reagents were from commercial sources and were used without further purification. Hydrochloric acid , 2-amino benzoic acid , o-chloro phenol , o- fluoro phenol , o- methyl phenol 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 22035 nm [12]   . Synthesis .

All dyes were prepared by general coupling reaction method using equimolar quantities[12] , the dyes products were filtrated and washed with cold distilled water for several times and purified by chromatography on a silica column (pentane/EtOAc 3:3:1) and then recrystallised from EtOH/H_2O to yield 4-(2-benzoic acid azo)-2-fluoro phenol (BAFP) as yellow-orange crystals ,m.p.199-202 º C ,UV-Vis λmax (350) nm ; 4-(2-benzoic acid azo) -2-

288

chloro phenol(BACB)   as brownish – orange crystals 185-188 º C ; UV – Vis λmax (357 nm)   ; 4-(2- benzoic acid azo)-2-methel phenol (BAMP)   as yellow crystals , m.p. 155-159 º C ;UV-Vis λmax (384 nm) . Fig.1, shows the scheme structural formula of dyes . Photodegradation experiments .

The   photocatalytic   experiments were   performed   by   irradiating   the aqueous solution of dyes by using 50 ml Pyrex cell. The radiation source was a OSRAM lamp , the emitted spectrum between 350- 800 nm . Sample for kinetic study were taken from reactor by syringe   through   the   reaction   .The

solution were magnetically stirred during irradiation .The quantity of degraded dye was estimated in the λmax of dye using shemadzu UV spectrophotometer . Spectroscopic measurements .

FT-IR spectra of prepared dyes were   recorded   on   Shimadzu   FT-IR 84005   spectrophotometer   using   KBr disk in the range 400-4000 cm^{-1}.UV – Visible absorption spectra for aqueous solution of dyes (1x 10 $^{-4}$ M)were obtained   by   shemadzu   UV-Visible1650pcspectrophotometer.   .
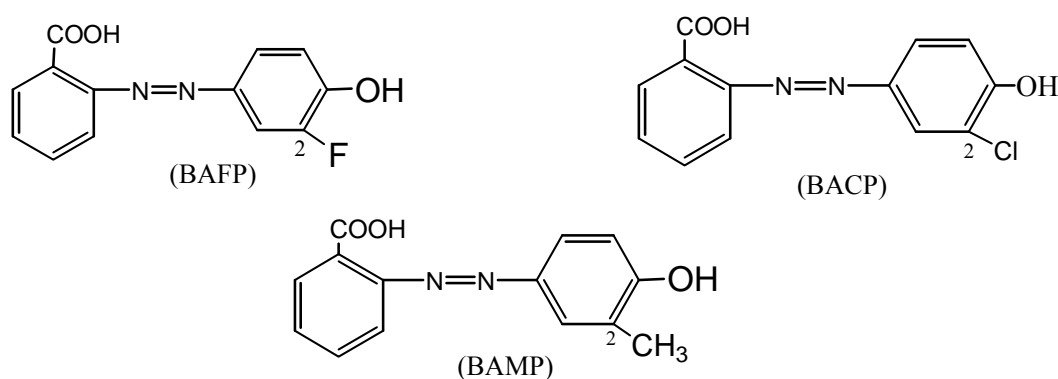

Fig . 1. Chemical structure for azo dyes .

Results and discussion

Direct photolysis essay .

for 6 h of irradiation , no direct photodegradation was observed for the three dyes because the molar absorptivities are very low at the radiation wavelength range used . Consequently , there is no place to a possible photoalteration process of the molecules . Thus , degradation of these dyes is exclusively due to photoactivation of the TiO_2 catalyst .

Photo assisted catalyse via TiO_2 .

Effect of TiO_2 concentration

To optimize the concentration of TiO_2 needed for the highest degradation rate the following quantities were used starting from 0.1 to $5.0 gl^{-1}$ depending on the nature of the compounds [14,15] .The most efficient TiO_2 concentration is not the same for all compounds .Above 2.5 g l^{-1} of TiO_2 the initial rate of dyes oxidation is negatively affected by the progressive increase of TiO_2 . This observation may be due to the aggregation of TiO_2 particles at high concentration , causing a decrease in the number of surface active sites . Several authors [16-18] related this observation to the light scattering and consequent reduction in light penetration through the solution induced by lightproof suspended catalyst . According to Fig. 2, shows a plot of the initial reaction rate (R_0) as a function of the catalyst concentration for the three dyes .It can be observed that the initial degradation rate increases proportionally toTiO_2 concentration .The degradation rate appears at TiO_2 concentration of around 2.0 g l^{-1} in the case of BAMP and BAFP , and at values of around 2.5 g l^{-1} in the case of BACP .To study the Photodegradation rates of different compounds have to be compared using the same optimal TiO_2 concentration for each substrate .For this reason , according to Fig. 2, a TiO_2 concentration of 2.0 g l^{-1} was used in this study .
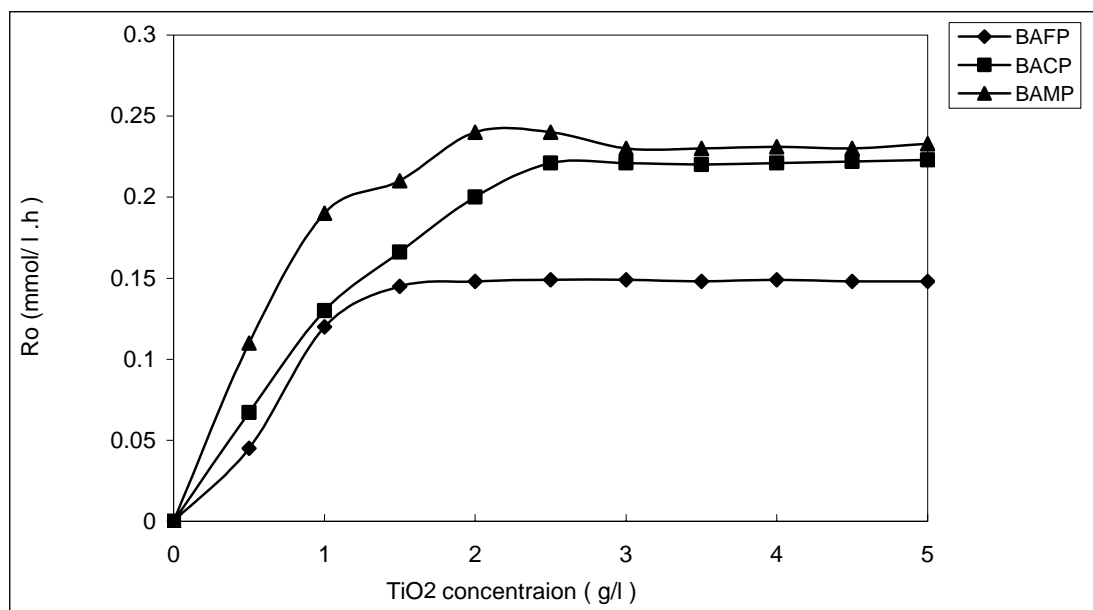
Fig. 2. Effect of TiO$_2$ concentration on the initial degradation rates of dyes .

Effect of initial dyes concentration.

Different dyes concentrations were used ranging from 5 x 10^{-4} to 5 x 10^{-3} M and 2.0 g l^{-1} of TiO$_2$ at (pH=7.2) as a function of time .It was found that the best degradation was obtained with 0.0029 M (Fig. 3,4,and 5) .The degradation efficiency increased with decreasing concentration of dyes .It seems that degradation reaches a saturation limit at high concentration of the reactant .
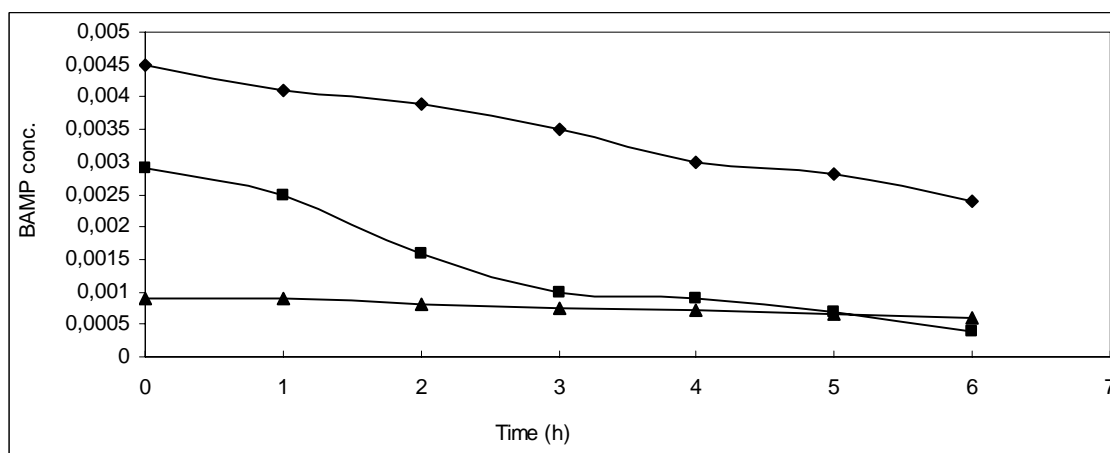
Fig. 3. Photodegradation of BAMP as a function of time in presence of 2.0 g L^{-1} of TiO$_2$ for various initial concentration of BAMP .
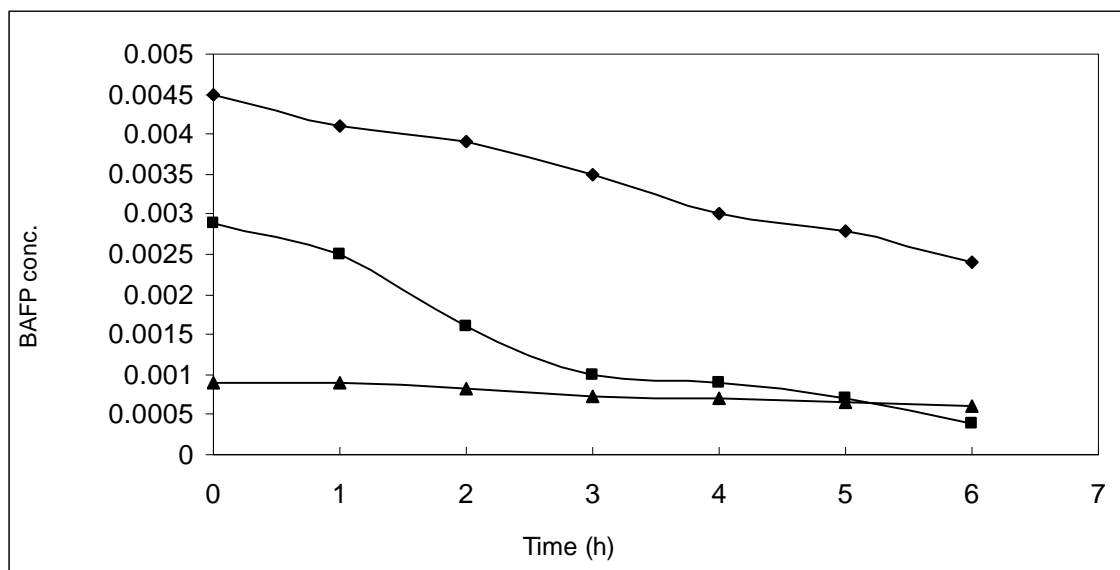
Fig. 4. Photodegradation of BAFP as a function of time in presence of 2.0 g L^{-1} of TiO$_2$ for various initial concentration of BAFP.
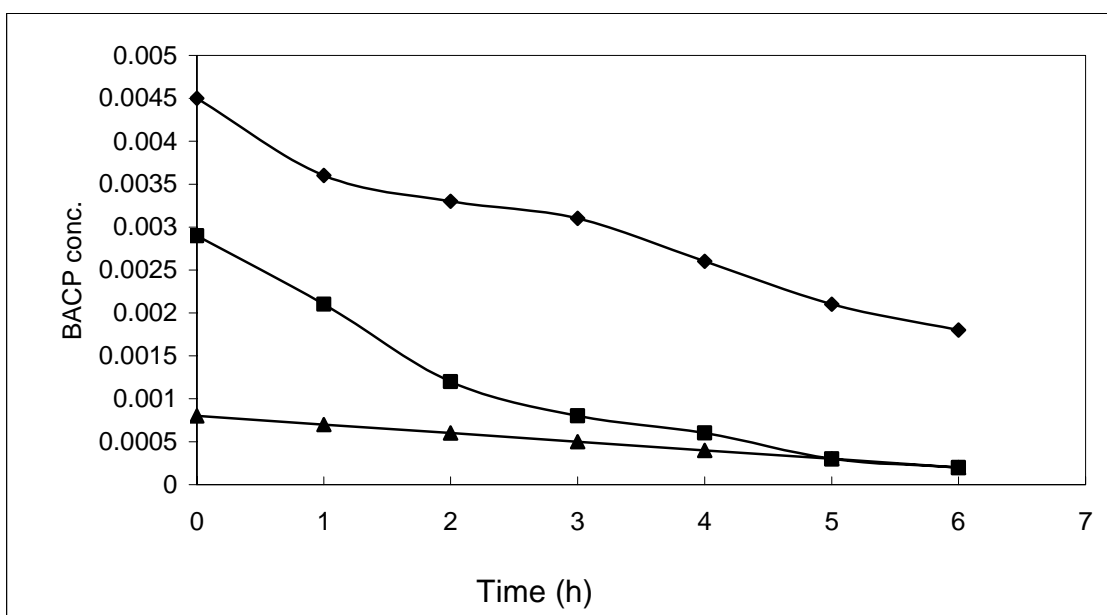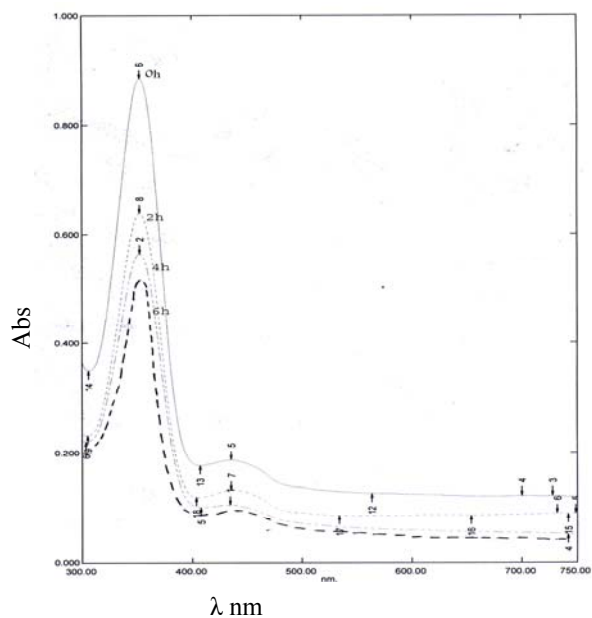

Fig. 5. Photodegradation of BACP as a function of time in presence of 2.0 g L^{-1} of TiO$_2$ for various initial concentration of BACP .

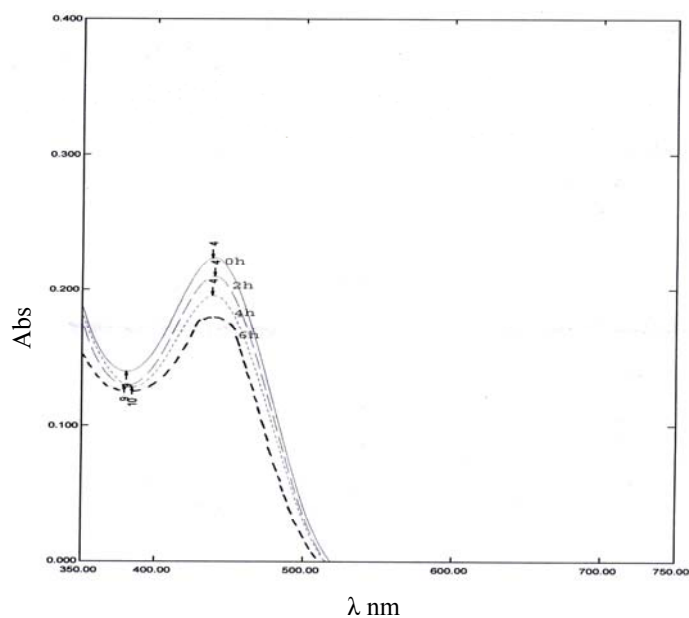Effect of time .

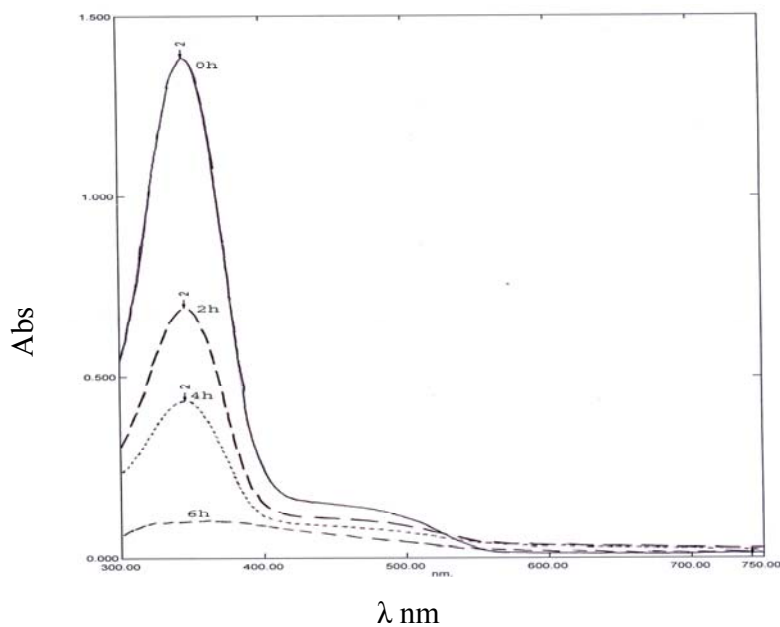   It is interesting to note from Fig. 6 , that the absorption of the visible band at λmax of all dyes decreased with the time (0,2,4,6 h) but with BAMP , it becomes greater . This trend suggests that the dyes start to degrade with time .

BACP

BAFP

BAMP

Fig. 6. Absorption spectra for irradiated of dyes at different time.

Influence of physicochemical properties of dyes on their photodegradability.

The differences in photoreactivity discussed in the precedent section suggest that (R_0) is directly related to the electron-donor or electron-withdrawing character of the different substituents in the dyes aromatic ring , which can activate or deactivate the ring with respect to electrophilic attack of the $OH^.$ radical . This radical is very reactive in the oxidation of organic substances and is generated when the TiO_2 powder suspended in water , which is irradiated with near UV at $\lambda < 385$ nm [19-21] .To explain these results , only the effect of substituents in positions 2 , Fig.1, is taken into account since the substituent in other positions are similar in all cases .

4-(2- benzoic acid azo)-2- methyl phenol was the most reactive substance due to the presence of the CH_3 group which had a greater electron donor ability (inductive effect of the methyl group) [22] , which is benzene ring activating , and to the absence of halogen substituents Fig. 1, . The other dyes contain halogen atoms which are considered as deactivating.

Comparison of the photocatalytic degradation of the three dyes .

Fig. 7, shows the kinetics of disappearance, as a function of time, of illuminated dyes with an initial concentration 2.0 g l^{-1} of TiO_2 . The curves behave as an apparent first order process as confirmed by the linear transform shown in the figure .The total photodegradation of dyes was reached in approximately 1 h (BAMP) and 2 h for (BAFP) and (BACB).

The initial degradation rates (R_0) and the apparent first order rate constants (K_{app}) for the three dyes are presented in Table 1 .

Table 1, Initial degradation rates (R_0) and apparent first order rate constants (K_{app}) for the abatement of the three dyes .

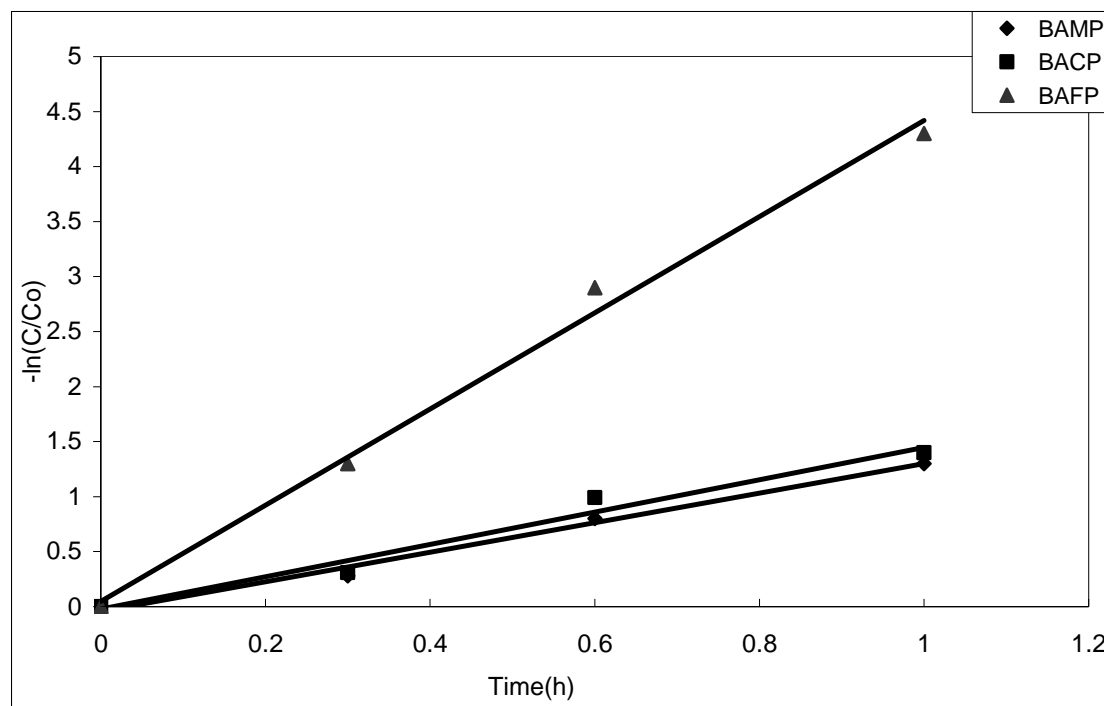| Dyes	R_0 (mmol l^{-1} h^{-1})	K_{app} (h^{-1})
BAFP	0.28	4.69
BACP	0.16	1.8
BAMP	0.12	1.41

Fig. 7. Photodegradation of dyes solution (0.0029 M) as a function of time in presence of TiO$_2$ (2.0 g l^{-1}) .

Conclusions

The photodegradation rate of the studied dyes is affected by the TiO$_2$ concentration . The photpdgradation order found for the three dyes (BAMP >> BACP ,BAFP) suggests that their photoreactivity is directly related to the donor or withdrawing effect induced by the different substituents on the aromatic ring.

References

1- J. He, J.Zhao , T. Shen , H. Hidaka ,and N. Serpone , *J. Phys. Chem. B* , 9027 , **101** , 1997 .

2- J. Hodak, C. Quinteros , M.I.Litter , and E.San Roman , *J.Chem. Soc.* , Faraday

   Trans . , 5081, **92** , 1996 .

3- E. San Roman , J. A.Navio , and M.I.Litter **, J. Adv. Oxid**. Technol. , 261 , **3** , 1998 .

4-D. Bockelmann , M. Lindner , and D. Bahnemann , in:E. Pelizetti (Ed.) , Fine Particles

Science and Technology , *NATO-ASI Series 3* , High Technology , 675 , **12** , 1996 .

5-K. Sayama , and H. Arakawa **,** *J. Chem. Soc*. , Faraday Trans . , 1647, **93** , 1997 .

6-A. Kudo , and M. Sekizawa , *Chem. Commun*. 1371 , 2000 .

7- A. Hagfeldt , and M. Gratzel , *Chem. Rev*. , 671 **, 93** , 1995 .

8- N. J. Cherepy , G. P. Smestad , m. Gratzel, and J.Z.Zhang , *J. Phys. Chem. B* ,9342 **,**

101 ,1997.

9- A. Kay, R. Hamphry-Baker , and M. Gratzel, *J. Phys. Chem*. , 952 **, 98** , 1994 .

10-B. Patrick , and P.V. Kamat , *J. Phys. Chem.*, 1423 , **96 ,** 1992 .

11-Y. Cho. , W.Chi , C.H.Lee , T.Hyeon , and H.I.Lee , *Environ. Sci. Technol*. , 966 ,

35 , 2001 .

12- I. Vogel , " A Text book of practical organic chemistry'' , 3rd ed. , Longmans , Green and

Co.Ltd.London ,   pp.622-623 , 1964 .

13- n. Serpone ,*EPA Newsletter* , 5 , **59 ,** 1997 .

14- J. Gimenez, and D. Curco, *M.A. Queral, Catal*. Today , 229, **54** , 1999 .

15- D. Chen , and A.K.Ray , *Appl. Catal. B:Environ* . ,143, **23** ,1999 .

16- J. Bandara, J. Kiwi, R. Humphry-Baker, C. Pulgarin**,** *J. Adv. Oxid. Technol*. , 162 ,

1 , 1996 .

17 – L. Le campion , and C. Giannotti , *J. Ouazzani, Chemosphere* , 1561**, 38** , 1999 .

18- Y. Inel , and   A.N. Okte, *J. Photochem . Photobiol. A:Chem*. , 175 ,**96** , 1996 .

19- S. Parra, V.Sarria, S. Malato, P. Peringer, and C. Pulgarin , *Appl.Catal. B:Environ*.,

153, **27** , 2000 .

20- P. F. Schwarz , and J . N. Turro , *J. Phys. Chem. B* , 7127 , **101** , 1997 .

21-M .R .Hoffmann , S .T . Martin , W . Choi , *Chem. Rev* . 69-96 , **95** , 1995 .

22- A . Bahl , B . S. Bahl , *Advanced organic chemistry* , sixth edition , 2004 .