INVESTIGATION OF THE EFFECT OF OPERATIONAL PARAMETERS AND SNO₂-COUPLING ON THE PHOTOCATALYTIC ACTIVITY OF TiO₂

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ABSTRACT

The effect of different operational parameters in UV/TiO₂ process, such as initial dye concentration (20-50 mg l⁻¹), light intensity (8-45 W m⁻²), pH (2.83-10.22), hydrogen peroxide concentration (100-500 mg l⁻¹), temperature (21-45 °C) and photocatalyst concentration (150-900 mg l⁻¹) were investigated on the decolorization of Acid Yellow 23 as a model compound from monoazo textile dyes. The apparent first-order rate constants (k_{ap}) were evaluated which confirms pseudo first-order kinetics. k_{ap} increased with the enhancement of pH, light intensity and temperature. A desired concentration found for hydrogen peroxide (400 mg l⁻¹) and photocatalyst concentration (750 mg l⁻¹). The SnO₂ photocatalyst was not as effective as TiO₂ but had the same desired concentration (750 mg l⁻¹). Then TiO₂+SnO₂ suspensions (375+375 mg l⁻¹) as photocatalysts were employed for decolorization at different solution thicknesses. The results showed that the coupled particles were not much different from single TiO₂ system at the solution thickness of 4.5 cm in a batch reactor. But the coupled system was more effective when the solution thickness was reduced to 2.5 cm. Over 90% of decolorization occurs at the solution thickness of 1.1 cm after 30 min of irradiation while 90% decolorization takes place at the solution thickness of 4.5 cm after 100 min of irradiation.

1. INTRODUCTION

Dyestuff industries are the major source of the release of dyes into the environment and among these dyes, azo dyes which contain one or more azo bonds (-N=N-) in association with one or more aromatic systems which may also carry sulfonic acid groups, are main pollutants in dye wastewaters. They are considered highly toxic and known to be carcinogenic and hence the application of these dyes should be precisely controlled and the effluents should be treated before being released into the environment (Changes and Durrant, 2001).

Several methods such as adsorption on activated carbon, coagulation have been employed to decolorize the effluents but these treatments transfer dyes from solution to solid phase causing a secondary problem and thus further treatments are required. Ozone and hypochlorite oxidation are not desirable because of high operation and equipment cost and also secondary pollution from residual chlorine (Malik and Saha, 2003). Photocatalytic oxidation is an alternative for the complete degradation of azo dyes and it has proved to be a promising technique (Behnajady et al., 2006). Heterogeneous photocatalysis involving TiO₂ semiconductor has been quite effective in decolorization and mineralization of many organic molecules in aqueous media (Turchi and Ollis, 1989; Ollis and Al-Ekabi, 1993). TiO₂ is very active, chemically stable under illumination and has a great capacity for oxidation in aqueous solution. TiO₂ has been used to investigate the photodegradation of various organic pollutants and the results have revealed a very promising application of this semiconductor on photodecomposition of organic pollutants (Bacsa and Kiwi, 1998; Khodja et al., 2001). Under irradiation of semiconductor, conduction band electrons and valence band holes would be easily created. These electrons and holes along with hydroxyl ions and

dissolved oxygen will cause redox reactions on the surface of the semiconductor resulting in oxidation of organic pollutants. It is obvious that recombination of photogenerated holes and electrons in semiconductor reduces the photocatalytic activity In order to increase the photocatalytic efficiency of semiconductors an interparticle electron transfer process (IPET) by coupling two semiconductors with different redox energy levels to enhance charge separation for the corresponding conduction and valence bands has been suggested (Serpone et al., 1984). By this technique electrons are transferred from photoactivated semiconductor irreversibly to non-photoactivated semiconductor and holes travel in opposite direction (i.e. from non-photoactivated to phtoactivated semiconductor) and as a consequence the efficiency of photocatalyic reactions could be enhanced (Vinodgopal et al., 1995).

For example a solution of phenol was irradiated in presence of TiO_2 which was sensitized by CdS at $\lambda > 406$ nm through IPET while at the same conditions TiO_2 alone had no effect on the removal of phenol. The photodecomposition of 2-cholorophenol with TiO_2 and CdS/TiO_2 suspensions was compared and it was shown that the apparent rate constants and adsorption constants of 2-cholorophenol on CdS/TiO_2 system were 2 and 1.5 times higher than those on TiO_2 (Serpone et al., 1995). In the case of TiO_2 and SnO_2 a photoelectron generated on TiO_2 can be injected into the non-active SnO_2 conduction band while the photohole may remain on TiO_2 and also both semiconductors may be activated and transfer electrons from TiO_2 to SnO_2 and holes from SnO_2 to TiO_2 simultaneously (Kuo and Lin, 2004).
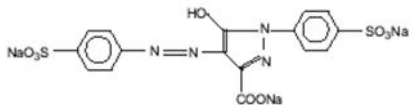
The present work has investigated the decolorization of AY23 as a model compound using TiO_2 and SnO_2 in a coupled form and a comparison has been made using TiO_2 alone at different operational conditions. Also the effect of solution thickness in the removal rate has been studied.

2.   EXPERIMENTAL
2.1 Materials
C.I. Acid yellow 23 (AY23), a mono azo anionic dye was purchased from ACROS organics (USA). Its chemical structure and other characteristics are given in Table 1.

Table 1. Structure and characteristics of C.I. Acid Yellow 23.

Strructure	
Other name	Tartrazine
CI number	19140
λ_{max} (nm)	428
M_W (g mol^{-1})	543.385

Titanium dioxide was Degussa P-25 and it was approximately 80% anatase and 20% rutile. It had a BET surface area of 50 m^2 g^{-1} and average particle diameter of 21 nm containing 99.5% TiO_2. SnO_2 was purchased from fulka (Switzerland). Hydrogen peroxide (30% w/w), HCl (37%), NaOH (99%), $NaHCO_3$ (99%), Na_2CO_3 (99%) and NaCl (99%) were products of Merck (Germany). Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment.

2.2. Photoreactor and Procedures
All experiments were carried out in a batch photoreactor with a radiation source of a UV lamp (30 W, UV-C, λ_{max}=254 nm, manufactured by Philips, Holland), which was situated above a Pyrex 200 ml reactor. The intensity of the light on the surface of the solution was measured by Lux-UV-IR meter (Leybold Co., Germany). In each experiment desired volume of the dye solution with distinct concentration was used and in 10 min time intervals, 2 ml of sample was withdrawn and analysed by a UV-vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, UK) then returned back into the reactor. In order to determine the solution thickness, desired volume of solution was poured into the reactor and the height of solution was measured and to maintain exact light intensities, the distance between UV lamp and surface of the solution was adjusted. The temperature was controlled by a heater (IKA RG-KT/C, Germany) and initial pH was monitored using HCl and NaOH and measured

by a pH meter (METTLER TOLEDOO MP 220, UK). The absorbance of the dye solution at different experiments was measured at 428 nm. Calibration plot based on Beer-Lambert's law was established by relating absorbance to the concentration and the molar absorption coefficient was calculated as 21631 M^{-1} cm^{-1}. Coupled semiconductor system was prepared using appropriate amount of each semiconductor as slurry by mixing them for one hour.

2.3. HPLC analysis
High performance liquid chromatograms were recorded on an HPLC (Perkin-Elmer series 200). A Spheri-5 RP-18 column with dimensions of 220×4.6 mm, 5 mm particle size and UV-vis detector with wavelength set at 254 nm were used. The eluent A consisted of 50% MeOH + 50% H_2O v/v and eluent B was 90% acetonitrile and 10% H_2O v/v, the flow rate was 0.9 ml min^{-1}.

3. RESULTS AND DISCUSSION

3.1. The effect of initial dye concentration
The effect of initial dye concentration on the photocatalytic decolorization is an important factor of the study. Initial dye concentrations were changed in the range of 20-50 mg l^{-1}. The photodecolorization of AY23 at different initial concentrations in the presence of TiO_2 and UV light radiation is thought to be a pseudo first-order kinetics. The semi-logarithmic graphs of the concentration of ln ($[AY23]_o/[AY23]$) in the presence of TiO_2 vs. irradiation time (Fig. 1) yield straight lines indicating pseudo first-order reaction (Behnajady et al., 2008; Laoufi et al., 2008). The apparent first-order reaction rate constants (k_{ap}) were evaluated from experimental data using a linear regression. In all cases R^2 (correlation coefficient) values were higher than 0.99 which confirm the proposed kinetics for photodecolorization of AY23 in this process.
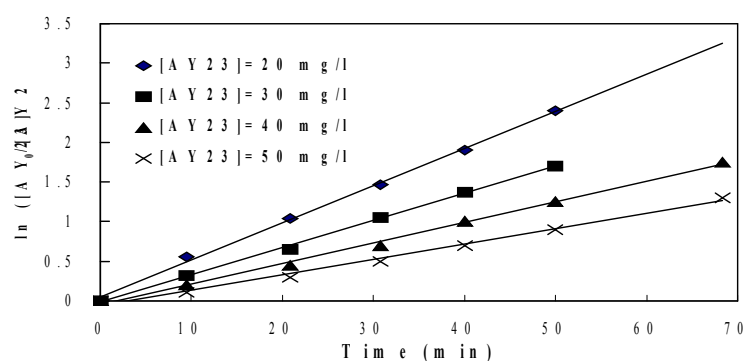

Figure 1. The effect of initial concentrations of AY23.
$[TiO_2]$ = 750 mg l^{-1}, I_o = 37 W m^{-2}, solution thickness = 4.5 cm, T = 21°C

Photodecolorization rate decreased as the concentration increases as shown in Fig. 2, because more organic substances are adsorbed on the surface of photocatalyst at high initial dye concentrations and generation of hydroxyl radicals will be reduced since there are fewer active sites left on the photocatalyst for adsorption of hydroxyl ions and the generation of hydroxyl radicals. Furthermore, as the dye concentration increases the interception of photons occurs before reaching the catalyst surface, therefore the absorption of photons by the catalyst decreases and consequently the decolorization percent is reduced (Daneshvar et al., 2004; Marandi et al., 2011).
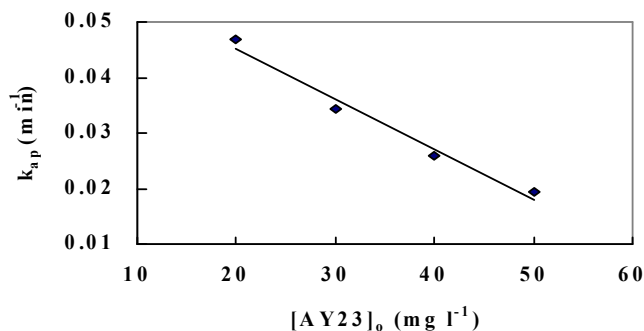
Figure 2. Relation between k_{ap} with initial concentrations of AY23.
$[TiO_2]$ = 750 mg l^{-1}, I_o = 37 W m^{-2}, solution thickness = 4.5 cm, T = 21°C.

3.2. The effect of light intensity

The influence of light intensity on the efficiency of decolorization was studied at four different light intensities, using dye concentration of 40 mg l^{-1} and TiO_2 catalyst loading of 750 mg l^{-1}. It is evident that the removal rate increases with increasing the light intensity as shown in Fig. 3.
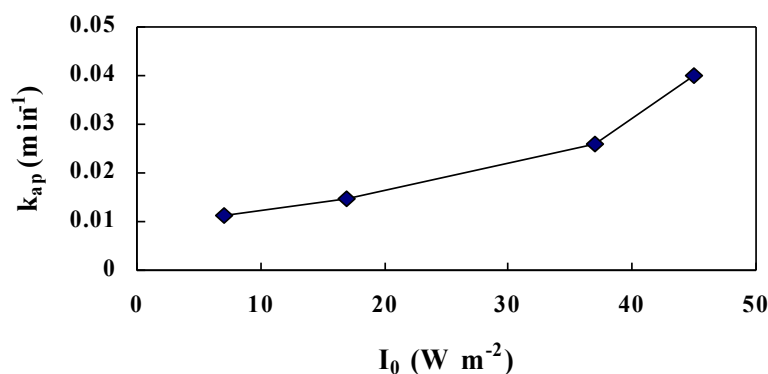

Figure 3. The effect of light intensit y on photodcolorization rate constant of AY23.
$[AY\ 23]_o$= 40 mg l^{-1}, $[TiO_2]$ =750 mg l^{-1}, solution thickness = 4.5 cm, T = 21°C.

This is because of falling more radiation on catalyst surface per unit of time and hence generation of increasing number of electron-hole pairs and consequently producing more hydroxcyl radicals for decolorization process.

3.3. The effect of pH

Since the majority of semiconductor oxides display amphoteric behavior, pH of the dispersion is an important parameter governing the rate of reaction, which takes place on the surface of semiconductors. Furthermore, pH could easily influence the surface-charge properties of the photocatalysts. Experiments were carried out at different pHs from 2.83 to 10.22 using semiconductors individually and also in the coupled form. The results revealed that SnO_2 alone was not efficient and TiO_2 showed the same results as TiO_2+ SnO_2 at the above pHs. The rate of decolorization increased with increasing pH. The reason for this could be due to the dissolution of photocatalyst at acidic conditions and at higher pHs the existence of hydroxyl anions would facilitate photogeneration of hydroxyl radicals (Bekbolet and Balcioglu, 1996; Chakrabarti and Dutta, 2004; Zhao et al., 2004; Goncalves et al., 2005). The pH of the original solution was 5.5 and the solution thickness of 4.5 was employed.

3.4. The effect of hydrogen peroxide concentration

 Fig. 4 shows the removal percent of AY23 after 30 minutes of illumination at different H_2O_2 concentrations. Decolorization rate would be improved in the presence of hydrogen peroxide. The rate of photocatalytic decolorization of AY23 started to increase when hydrogen peroxide

concentration was increased but after reaching to a certain amount, increasing H_2O_2 concentration would decrease the reaction rate.

This dual effect of H_2O_2 can be explained by radical reaction mechanisms. The use of H_2O_2 could enhance the production of hydroxyl radicals, on the other hand addition of excess H_2O_2, would act as scavenger of hydroxyl radicals, forming much weaker peroxide radicals Bekbolet and Balcioglu, 1996; Zhao et al., 2004). Hence, high concentration of H_2O_2 inhibited the reaction rate of dye decolorization by competing with dye for available hydroxyl radicals. The role of different concentrations of H_2O_2 in the presence of single or coupled semiconductors was the same.
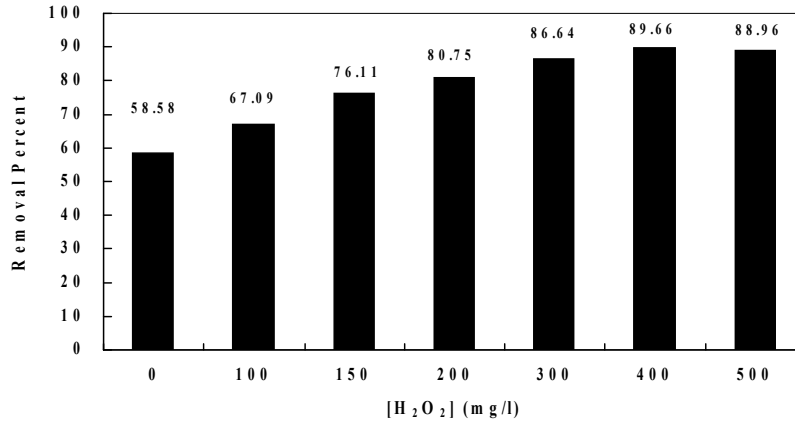

Figure 4. The effect of H_2O_2 concentration.
I_o = 37 W m^{-2}, [TiO$_2$] =750 mg l^{-1}[AY23]$_o$ = 40 mg l^{-1}, solution thickness = 4.5 cm, T = 21 °C.

3.5. The effect of temperature

In the process of dye photocatalysis temperature is an important factor. The photocatalytic decolorization rate of AY23 as a function of temperature was studied at 21 °C, 28 °C, 38 °C and 45 °C, using single and also coupled photocatalysts. Increasing temperature caused an increase in the removal rate. Because an increase in temperature helped the reaction to compete more efficiently with electron-hole recombination. The Arrhenius plots of ln k_{ap} versus 1/T for catalytic decolorization of AY23 in both UV/TiO$_2$ and UV/TiO$_2$+ SnO$_2$ have been shown in Figs. 5 and 6, respectively.
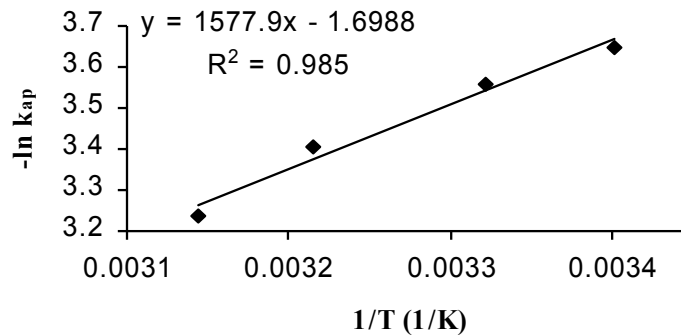

*Figure 5.*The effect of temperature on photodcolorization rate constant of AY23.
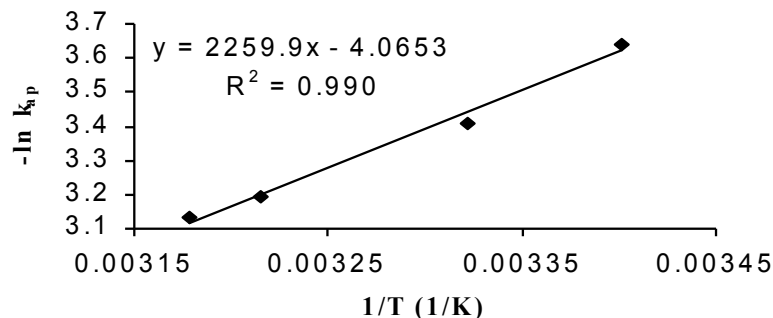I_o = 37 W m^{-2}, [TiO$_2$] =750 mg l^{-1}, [AY23]$_o$ = 40 mg l^{-1}, solution thickness = 4.5 cm

Figure 6. The effect of temperature on photodcolorization rate constant of AY23.
I_o = 37 W m^{-2}, [TiO_2] =375 mg l^{-1} + [SnO_2] =375 mg l^{-1}, [AY23] $_o$ = 40 mg l^{-1},
solution thickness = 4.5 cm

The activation energies for UV/TiO_2 and UV/TiO_2/SnO_2 processes were calculated to be 13.12 kJ mol^{-1} and 18.79 kJ mol^{-1}, respectively.

3.6. The effect of photocatalyst type and concentration

In order to find the proper quantity of catalyst for efficient removal of the dye, three series of experiments were carried out. First only TiO_2 was employed and then SnO_2 was used independently as shown in Fig 7. The desired amount of the above photocatalysts was found to be 750 mg l^{-1} for both of them. Therefore 375 mg l^{-1} of each catalyst was taken for coupled photocatalysts. It should be added that the effect of UV alone is negligible.
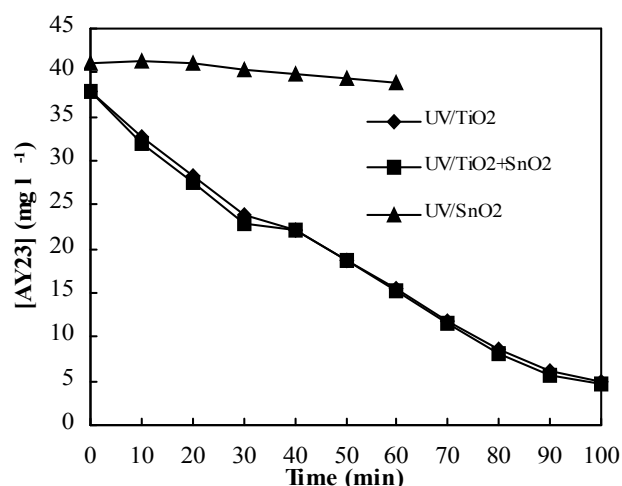

Figure 7. Comparison of photocatalytic activity of TiO_2 , SnO_2 and SnO_2+ TiO_2
on decolorization of AY23.
[TiO_2] =750 mg l^{-1}, [SnO_2] =750 mg l^{-1}, [TiO_2] =375 mg l^{-1} + [SnO_2] =375 mg l^{-1}, I_o = 41 W m^{-2},
[AY23] $_o$ = 40 mg l^{-1}, solution thickness = 4.5 cm, T = 21°C

The increase in catalyst weight up to 750 mg l^{-1} increases the dye decolorization sharply which is due to an increase in the number of active sites and adsorbed dye molecules. Above this concentration, the decolorization starts to decrease which is attributed to the enhancement of light reflectance by the catalysts and decrease in light penetration into the solution (Muruganandham, 2006). As can be seen from Fig. 7, no enhancement of decolorization occurred when the photocatalysts were coupled, and SnO_2 did not play any important role in the process.

3.7. The effect of solution thickness

In previous section combination of photocatalysts did not improve decolorization rate as expected. But changing the solution thickness from 4.5 cm to 2.5 cm increased the removal percent using coupled photocatalysts instead of single ones as shown in Fig. 8.

Therefore different solution thicknesses were experimented and results revealed that, as the solution thickness was reduced, the removal percent of coupled system was increased. These results are shown in Fig. 9 and it can be seen that over 90% of decolorization occurs at 30 min at the solution thickness of 1.1 cm, while 90% decolorization at the solution thickness of 4.5 cm takes place after 100 min of illumination. It seems obvious that as solution thickness is reduced light easily penetrates and coupled system acts more efficiently because of producing more hydroxyl radicals.
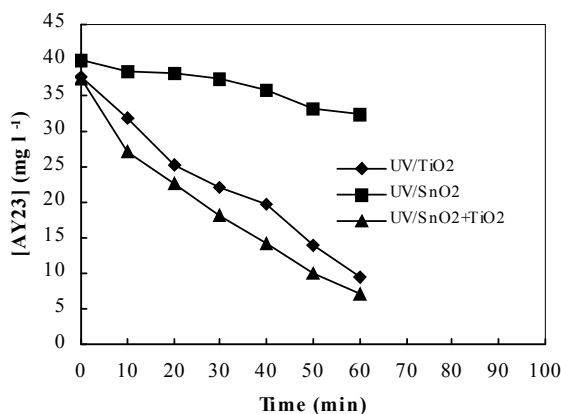

Figure 8. Comparison of photocatalytic activity of TiO$_2$, SnO$_2$ and SnO$_2$+TiO$_2$ on decolorization of AY23. [TiO$_2$] =750 mg l^{-1}, [SnO$_2$] =750 mg l^{-1}, [TiO$_2$] =375 mg l^{-1} + [SnO$_2$] =375 mg l^{-1}, I$_o$ = 41 W m^{-2}, [AY23]$_o$ = 40 mg l^{-1}, solution thickness = 2.5 cm, T = 21°C.
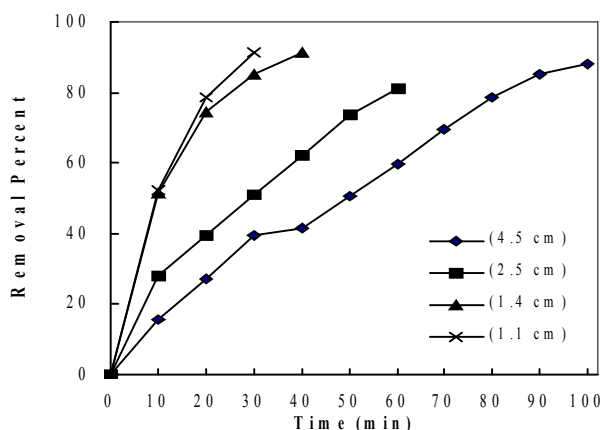

Figure 9. Effect of solution thickness on the photodecolorization activity of AY23.
[TiO$_2$] =375 mg l^{-1} + [SnO$_2$] =375 mg l^{-1}, I$_o$ = 41 W m^{-2}, [AY23]$_o$ = 40 mg l^{-1}, T = 21°C.

3.8. The spectral changes of AY23 during photocatalytic decolorization

The changes in absorption spectra of AY23 during UV/TiO$_2$+SnO$_2$ process at the solution thickness of 2.5 cm have been shown in Fig 10. The decrease of the absorption peaks at λ= 428 nm indicates a rapid decolorization of the dye molecules which could be related to oxidative attack to nitrogen double bond (-N=N-) of the azo dye (Behnajady et al., 2006). Detector of HPLC was adjusted at λ$_{max}$=254 nm and considerable decrease of absorption peak in this wavelength can be related to the elimination of aromatic rings and aromatic intermediates which are generated during the process (Fig. 11).
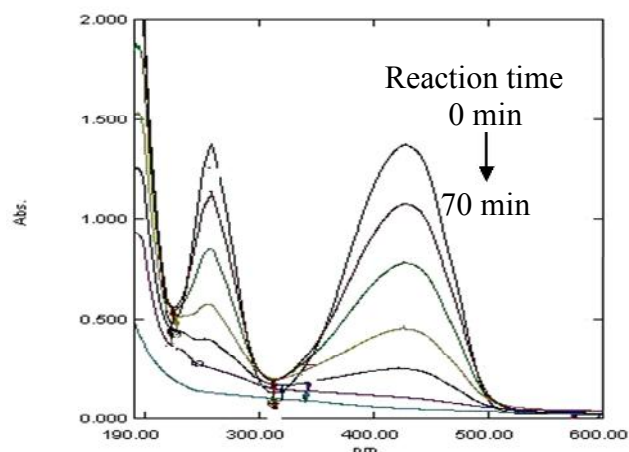
Figure 10. The UV-vis spectra of AY23 at the solution thickness of 2.5 cm during photodecolorization in 10 min time intervals. $[TiO_2]$ =375 mg l $^{-1}$ + $[SnO_2]$ =375 mg l $^{-1}$, I_o = 41 W m^{-2}, $[AY23]_o$ = 40 mg l $^{-1}$, T = 21°C.

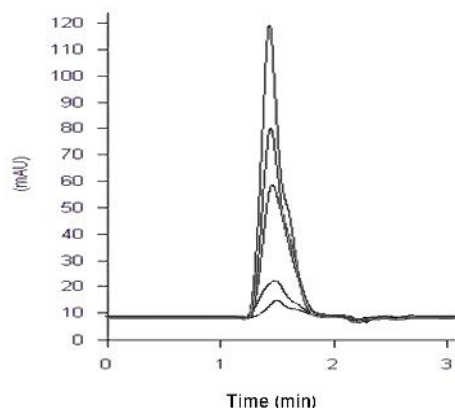*Figure 11.* The HPLC chromatograms of AY23 at the solution thickness of 2.5 cm during photodecolorization in 10 min time intervals. $[TiO_2]$ =375 mg l $^{-1}$ + $[SnO_2]$ =375 mg l $^{-1}$, I_o = 41 W m^{-2}, $[AY23]_o$ = 40 mg l $^{-1}$, T = 21°C.

4. CONCLUSIONS

The results obtained in present investigation demonstrate that coupled semiconductor system and single semiconductor does not differ from each other at the solution thickness of 4.5 cm. Therefore it appears that the solution thickness plays an important role in decolorization process since over 90% of decolorization occurs at the solution thickness of 1.1 cm. The apparent first-order rate constants (k_{ap}) were evaluated which confirms pseudo first-order kinetics. The findings also indicate that initial dye concentration, light intensity, H_2O_2 concentration, temperature, pH, and photocatalyst dosage would influence the removal rate and percent.

Acknowledgement

REFERENCES

Bacsa R.R. and Kiwi J. (1998), Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of p-coumaric acid, *Appl. Catal. B*, **16,** 19-29.

Behnajady M.A., Modirshahla N. and Hamzavi R. (2006), Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst, *J. Hazard. Mater.*, **133**, 226-232.

Behnajady M.A., Modirshahla N., Mirzamohammady M., Vahid B. and Behnajady B. (2008), Increasing photoactivity oftitanium dioxide immobilized on glass plate with optimization of heat attachment method parameters, *J. Hazard. Mater.*, **160**, 508-513.

Bekbolet M. and Balcioglu I. (1996), Photocatalytic degradation kinetics of humic acid in aqueous TiO$_2$ dispersions: The influence of hydrogen peroxide and bicarbonate ion, *Water Sci. Technol.*, **34,** 73-80.

Chakrabarti S. and Dutta B.K. (2004), Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *J. Hazard. Mater.*, **112**, 269-278.

Changes E.P. and Durrant L.R. (2001), Decolorization of azo dyes by phanerochaete chrysosporium and pleurotus sajorcaju, *Enzyme Microb. Technol.*, **29**, 473-477.

Daneshvar N., Rabbani M., Modirshahla N. and Behnajady M.A. (2004), Kinetic modeling of photocatalytic degradation of Acid Red 27 in UV/TiO$_2$ process, *J. Photochem. Photobiol. A*, **168**, 39-45.

Goncalves M.S.T., Pinto E.M.S., Nkeonye P. and Oliveira-Campos A.M.F. (2005), Degradation of C.I. Reactive Orange 4 and its simulated dyebath wastewater by heterogeneous photocatalysis, *Dyes Pigments*, **64**, 135-139.

Khodja A.A., Sehili T., Pilichowski J.F. and Boule P. (2001), Photocatalytic degradation of 2-phenylphenol on TiO$_2$ and ZnO in aqueous suspensions, *J. Photochem. Photobiol. A*, **141**, 231-239.

Kuo C.Y. and Lin H.Y. (2004), Effect of coupled semiconductor system treating aqueous 4-nitrophenol, *J. Environ. Sci. Health. A*, **39**, 2113-2127.

Laoufi N.A., Tassalit, D. and Bentaher, F. (2008), The degradation of phenol in water solution by TiO$_2$ photocatalysis in a helical reactor, *Global NEST J.*, **10**, 404-418.

Malik P.K. and Saha S.K. (2003), Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep. Purif. Technol.*, **31**, 241-250.

Marandi R., Khosravi M., Olya M.E., Vahid B. and Hatami M. (2011), Photocatalytic degradation of an azo dye using immobilised TiO$_2$ nanoparticles on polyester support: central composite design approach, *Micro Nano Lett.*, **6**, 958-963.

Muruganandham M., Shobana N. and Swaminath M. (2006), Optimization of solar photocatalytic degradation condintions of Reactive Yellow 14 azo dye in aqueous TiO$_2$, *J. Mol. Catal. A*, **246**, 154-161.

Ollis D.F. and Al-Ekabi H. (1993), Photocatalytic purification and treatment of water and air, Elsevier: Amsterdam.

Serpone N., Borgarello E. and Gratzel M. (1984), Visible light induced generation of hydrogen from H$_2$S in mixed semiconductor dispersions; improved efficiency through inter particle electron transfer, *J. Chem. Soc. Chem. Commun.,* **342**, 123-133.

Serpone N., Maruthamuthu P., Picat D., Pelizzetti E. and Hidaka H. (1995), Exploiting the inter particle electron transfer process in the photocatalyzed oxidation of phenol, 2-choloro phenol and pentacholorophenol: chemical evidence for electron and hole transferr between coupled semicoductors, *J. Photochem. Photobiol. A*, **85**, 247-255.

Turchi C.S. and Ollis D.F. (1989), Mixed reactant photocatalysis: Intermediates and mutual rate inhibition, *J. Catal.*, **119**, 483-496.

Vinodgopal K. and Prashant V.K. (1995), Enhanced rates of photocatalytic degradation of an azo dye using SnO$_2$/TiO$_2$ coupled semiconductor thin films, *Environ. Sci. Technol.*, **29**, 841-845.

Zhao H., Xu S., Zhoug J. and Bao X. (2004) Kinetic study on the photocatalytic degradation of pyridine in TiO$_2$ suspension systems, *Catal. Today*, **93-95,** 857-861.