

## ADSORPTION AND PHOTODEGRADATION OF PROCION YELLOW H-EXL DYES IN TEXTILE WASTEWATER OVER TiO<sub>2</sub> SUSPENSION

M. A. Barakat \*

Central Metallurgical R& D Institute, P.O. Box 87 Helwan 11421, Cairo, Egypt

\* Currently at Faculty of Meteorology and Environment,  
King Abdulaziz University (KAU)

P.O. Box 80202 Jeddah 21589, Saudi Arabia

E-mail: [mabarakat@gmail.com](mailto:mabarakat@gmail.com)

### ABSTRACT

Removal of a commercial dye (Procion yellow H-EXL) in both synthetic and real wastewater from textile industry over TiO<sub>2</sub> suspension has been investigated. The study included both adsorption process (over TiO<sub>2</sub>) and photocatalytic degradation process in the presence of UV illumination (UV/TiO<sub>2</sub>). The processes were carried out in aqueous solutions containing the dyes in the presence of titanium dioxide, TiO<sub>2</sub>, (Degussa P-25) upon UV irradiation of 100 Watt. The photocatalytic process used the photogenerated holes (at the surface of TiO<sub>2</sub>) and hydroxyl radicals (at the solution bulk) as oxidizing species for the dyes. Different parameters affecting the adsorption and photocatalytic degradation processes such as solution pH, initial dyes concentration, and TiO<sub>2</sub> dosages were investigated. Results obtained revealed that various dyes concentration loads were removed at optimum solution pH = 5 with TiO<sub>2</sub> dosage of 1 g/L. The dyes removal % is inversely proportional to its concentration, the lower the dyes concentration, the higher the efficiency of dyes removal. The efficiency values of both adsorption and photocatalytic degradation processes reached maximum values of 46.4 and 100 %, respectively, with dyes concentration of 10 mg/L. The photocatalytic degradation of the investigated dyes exhibited pseudo first-order kinetics according to the Langmuir-Hinshelwood's heterogeneous catalytic model.

**Keywords:** Textile wastewater, Reactive dyes, adsorption, Photocatalytic degradation, UV/TiO<sub>2</sub>

### 1. INTRODUCTION

Textile dyeing is a significant consumer of water and producer of contaminated aqueous waste streams. Over 700,000 t of approximately 10,000 types of dyes and pigments are produced annually worldwide. From this amount, about 20% are discharged as industrial effluents during the textile dyeing and finishing processes without previous treatment (Carneiro et al. 2007). Reactive dyes, including azo dyes, are extensively used in the last few years due to their superior performance, but they are environmentally extremely hazardous because of the toxicity that many of them exhibit. They are representing a class of organic pollutants which are proven to be

potentially carcinogenic (Baranowska et al. 2002; Garcia-Montano et al. 2006). The traditional treatment technologies applied in dye wastewaters treatment, such as coagulation/flocculation, membrane separation or activated carbon adsorption, only do a phase transfer of the pollutant (Vandevivere et al. 1998). Most azo dyes are not biodegradable by aerobic treatment processes (Pagga et al. 1986), but they can be decolorized by anaerobic treatment (Brown et al. 1987; Carliell et al. 1995; Chinwetkitvanich et al. 2000). This treatment results in the cleavage of the nitrogen double bond, and the resulting fragments, which of aromatic amines, are proven carcinogens (Baughman et al. 1994). Therefore, it is necessary to find an effective treatment technology that leads to complete destruction of the dye molecules. Among these treatments, advanced oxidation processes (AOPs) are powerful alternative to conventional treatment methods for such wastewater decontamination (Andreozzi et al. 1999; Munter et al. 2001; Tarr et al. 2003; Parsons et al. 2004). Most of those works were focused on treatment with Fenton, photo-Fenton (UV/Fenton) or photo-Fenton-like reactions (Kang et al. 2000; Feng et al. 2003; Neyens et al. 2003; Swaminathan et al. 2003; Lucas et al. 2006; Sanja et al. 2008), UV + H<sub>2</sub>O<sub>2</sub> (or O<sub>3</sub>) (Arslan et al. 1999; Karadimas et al. 2003; Arslan et al. 2002), photocatalysis (UV + TiO<sub>2</sub> or other semiconductor particles) (Arslan et al. 2000; Tanaka et al. 2000; Poulis et al. 2003; Rao et al. 2003; Danfeng et al. 2004; Dong et al. 2007; Wu et al. 2008). These treatments are based on the in situ generation of highly reactive hydroxyl radicals (HO•). These radicals are high oxidant species; they attack the most of organic molecules. They are also characterized by low selectivity of attack which is useful characteristic for an oxidant used in wastewater treatment. In the last decade, most attention has been given to TiO<sub>2</sub> due to its high photocatalytic activity, low cost, non-toxicity and high stability in aqueous solution (Hermann et al. 1999). The photocatalytic degradation of azo dyes has been investigated on various TiO<sub>2</sub> nanoparticles as suspension (Akyol et al. 2008; Baran et al. 2008) or immobilized (Mahmoodi et al. 2009), TiO<sub>2</sub>/ZnO (Franco et al. 2009), WO<sub>3</sub>- / TiO<sub>2</sub> activated carbon (Sun et al. 2009), Au-TiO<sub>2</sub> (Kumar et al. 2008), and Co doped TiO<sub>2</sub>- SiO<sub>2</sub> (Li et al. 2008). In this study, a synthetic wastewater containing a commercial reactive dyes, Procion yellow H-EXL, was used to investigate a clean and safe removal of the dyes from solutions using ultraviolet-irradiated TiO<sub>2</sub> suspension. The influence of different parameters study affecting the photocatalytic degradation process and reaction pathways have been investigated. A real wastewater sample containing the Procion yellow H-EXL dyes from textile industry has been treated at the optimum conditions of the study.

## 2. EXPERIMENTS

### 2.1. Materials

Titanium dioxide, TiO<sub>2</sub> (Degussa P-25), used in this work was obtained from Degussa Company, New Jersey, USA. This photocatalyst is a mixture of two phases, 80% anatase- 20% rutile, and has BET surface area of 50 m<sup>2</sup>.g<sup>-1</sup> (Konstantinou et al. 2004). Stock solutions of TiO<sub>2</sub> (10 g/L) were prepared; shaken for 24 hours and left for at

least three days for hydration. The TiO<sub>2</sub> suspension was shaken at least 30 minutes every time before use. The used azo dyes sample is a commercial reactive dyes, Procion yellow H-EXL, was manufactured by Dye Star Co., Germany. The dyes and a real wastewater sample (30 liter), containing the Procion yellow H-EXL dyes from textile industry, were provided from Rotex Co. for dyeing, printing and finishing of textiles, 10<sup>th</sup> Ramadan City, Egypt. Solutions of 1 M of sodium hydroxide (NaOH) and 1M HCl were used to adjust the pH. All chemicals were of chemically pure grade. The light source was a water-cooled 100 W high-pressure mercury lamp (Hanovia 608A36, ACE Glass, Vineland, NJ), the spectral irradiance for the UV lamp (260 W/m<sup>2</sup>) ranges from 228 to 420 nm at a distance of one m from the light source according to information provided by the manufacturer.

## 2.2. Methods

Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 2 L capacity (of 12-cm inside diameter and 20-cm height and a reflective interior surface). A 100-Watts mercury lamp was placed in a quartz tube (with 5 cm diameter) whose one end was tightly sealed by a Teflon stopper. The lamp and the tube were then immersed in the photoreactor cell (with a light path of 3.5 cm). To the reactor, it was added 1L of a solution containing appropriate amounts of the reactants (10-100 mg/L dyes), and 1 g/L TiO<sub>2</sub> solution with bi-distilled water. Compressed air was purged into the solution by bubbling compressed air from the bottom to maintain an aerobic conditions, and also using a magnetic stirrer to keep the whole solution chemically uniform. The pH values of the solutions were adjusted by adding of NaOH (1 M) and HCl (1 M) using an Orion Model 801A pH meter. After addition of TiO<sub>2</sub> to the dye, solution was allowed to equilibrate in dark for 30 minute before the lamp was turned on. Solutions were radiated by UV light for given time intervals then sampled for the analysis of residual concentrations of the dyes. A 10-mL sample was taken before illumination and every 30 minutes until 180 minutes of illumination. Solid TiO<sub>2</sub> was removed from solutions by centrifuge the dispersion and subsequent filtrating through 0.2 μm syringe filters (Gelman Acrodic syringe filter with 25 mm diameter, and Nylon membrane of 0.2 μm pore size, PN4436T, Pall Gelman Laboratory, Ann Arbor, Michigan). The filtrates were collected for analysis of any remaining dyes concentration.

## 2.3. Measurements

Dyes concentration in solutions were analyzed by UV-Visible Spectrophotometer, model JASCO V-570. The spectra measurement for the dyes concentration of 100 mg/L was identified to determine the absorbance and maximum fitted wavelength  $\lambda_{\max}$  before dyes concentration analysis.

### 3. RESULTS AND DISCUSSION

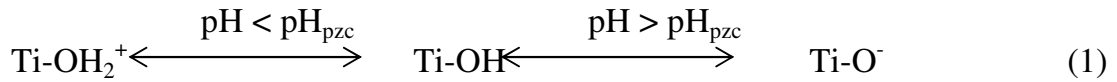
The characterizations and measured absorbance at the maximum fitted wavelength  $\lambda_{\max}$  of the used Procion yellow H-EXL dyes (100 mg/L) are given in Table 1.

**Table 1: The characterizations and measured absorbance at  $\lambda_{\max}$  for the Procion yellow H-EXL dyes (of 100 mg/L concentration)**

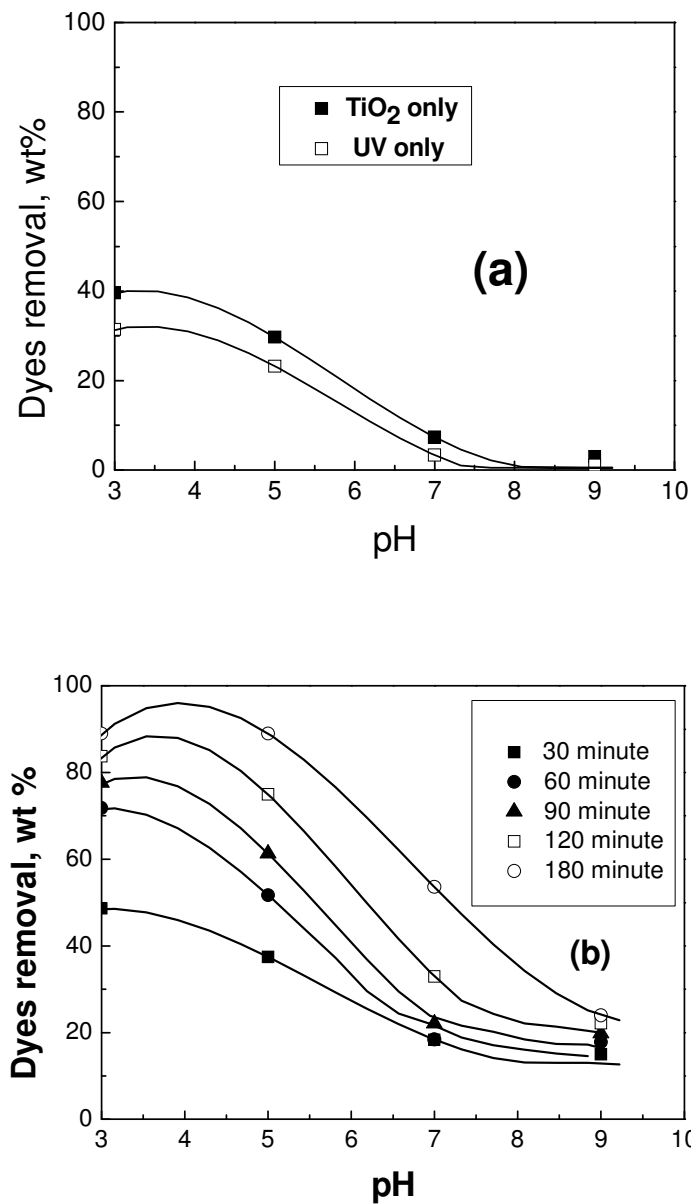
Reactive group	$\lambda_{\max 1}$	Absorbance <sub>1</sub>	$\lambda_{\max 2}$	Absorbance <sub>2</sub>
Aminochlorotriazine	294	1.69	414	1.5

Two peaks were identified for absorbance; the 1<sup>st</sup> peak (at  $\lambda_{\max 1}$  of 294 nm) was sharp, while the 2<sup>nd</sup> peak (at  $\lambda_{\max 2}$  of 414 nm) was broad. Thus all samples analysis were carried out at  $\lambda_{\max 1}$  of 294 nm.

The effect of pH on the dyes removal process is shown in Figure 1. The process was performed with TiO<sub>2</sub> (adsorption), UV individual (photolysis) for 180 minutes (Figure 1-a), and UV/TiO<sub>2</sub> (photocatalysis) at different time intervals (Figure 1-b). Solutions of 1 M of sodium hydroxide (NaOH) and 1M HCl were used to adjust and maintain the pH levels. Dyes solutions of 50 mg/L concentration in the presence of 1g/L TiO<sub>2</sub> were used. It can be seen that the process is strongly depended on the solution pH in the three mentioned cases. The process was favored at acidic pH values, while it decreases with raising the pH values. The optimum pH value for the dyes removal was 3. By utilizing TiO<sub>2</sub> or UV light individual, the dyes were adsorbed on the TiO<sub>2</sub> catalyst surface or degraded by photolysis with UV. Dyes removal efficiency values of 39.6 and 31.4 % were achieved at solution pH value of 3 for both of the adsorption and photolysis processes, respectively. The dyes removal was sharply decreased in the neutral and alkaline solutions. The dyes removal with the photolysis process is mainly due to generation of hydroxyl radicals through UV illumination. However the removal efficiency of that process was low due to the absence of oxidizing agent (such as ozone or H<sub>2</sub>O<sub>2</sub>). On the other hand, in the presence of UV light with the catalyst, the increase in the adsorption of dyes caused the increase in their photodegradation rate. The efficiency of the photocatalytic degradation process increased with lowering the solution pH and increasing the illumination time. A maximum photocatalytic degradation efficiency value of 89 % was achieved at both solution pH values of 3 and 5. A further increase in the solution pH (> 5) resulted in decreasing both the dye adsorption and its photocatalytic efficiency. The strong effect of the solution pH on the dyes removal (adsorption or photocatalytic degradation) from solutions can be explained as follows; hydrous solids, such as TiO<sub>2</sub>, are weak Bronsted solid acids, upon hydration, surface hydroxyl groups (TiOH) are formed. These groups can undergo proton association or dissociation reactions; thereby bring about surface charge which is pH-dependent. From the zeta potential data of the P-25 TiO<sub>2</sub> catalyst, its equilibrium point value (pH<sub>pzc</sub>) is 6.26 ± 0.05. Thus its surface charge should be positively polarized at pH lower than the pH<sub>pzc</sub> according to equation (1) (Baran et al. 2008).



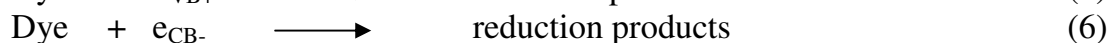
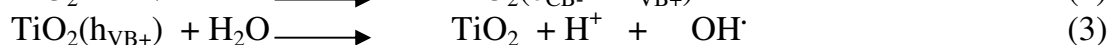
where  $\text{Ti-OH}_2^+$ ,  $\text{Ti-OH}$ ,  $\text{Ti-O}^-$  are positively, neutral and negative surface hydroxyl groups, respectively. On the other hand, the reactive group in the used Procion yellow H-EXL dye is aminochlorotriazine. At acidic solutions, the dye is strongly adsorbed on the photocatalyst due to formation of a H-bond between the proton from the catalyst and lone pair of electron on the amino group of the dye. Thus in the earlier oxidation stages of the dyes by the UV illumination, the rate of photodegradation process is achieved quickly, on comparing with that in neutral or alkaline solution pH.



**Figure 1. The effect of solution pH on the H-EXL dyes removal**

a) with  $\text{TiO}_2$  or UV individual    b) with UV/  $\text{TiO}_2$  at different time intervals  
 $\text{TiO}_2$  dosage = 1g/L, dyes concentration = 50 mg/L

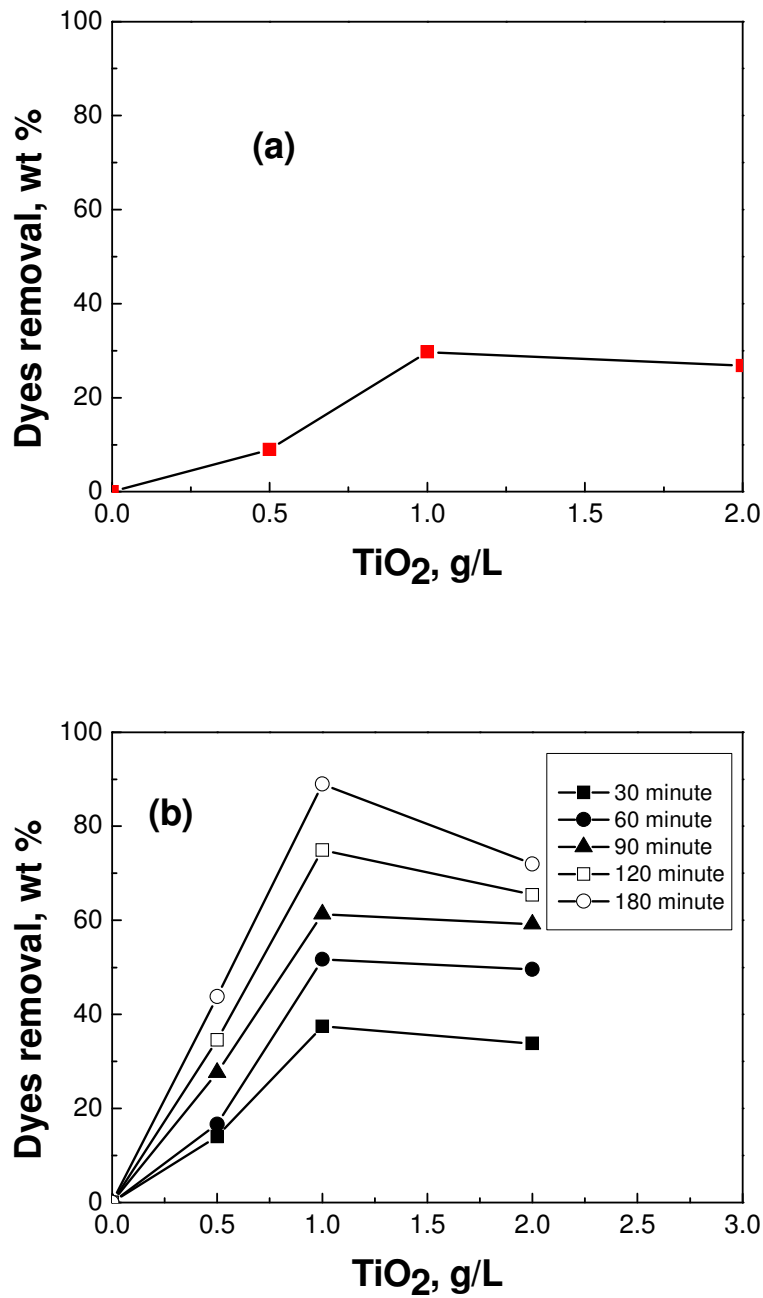
Konstantinou and Albanis (Konstantinou et al. 2004) summarized the photocatalytic degradation mechanism of dye in UV/TiO<sub>2</sub> as follows:



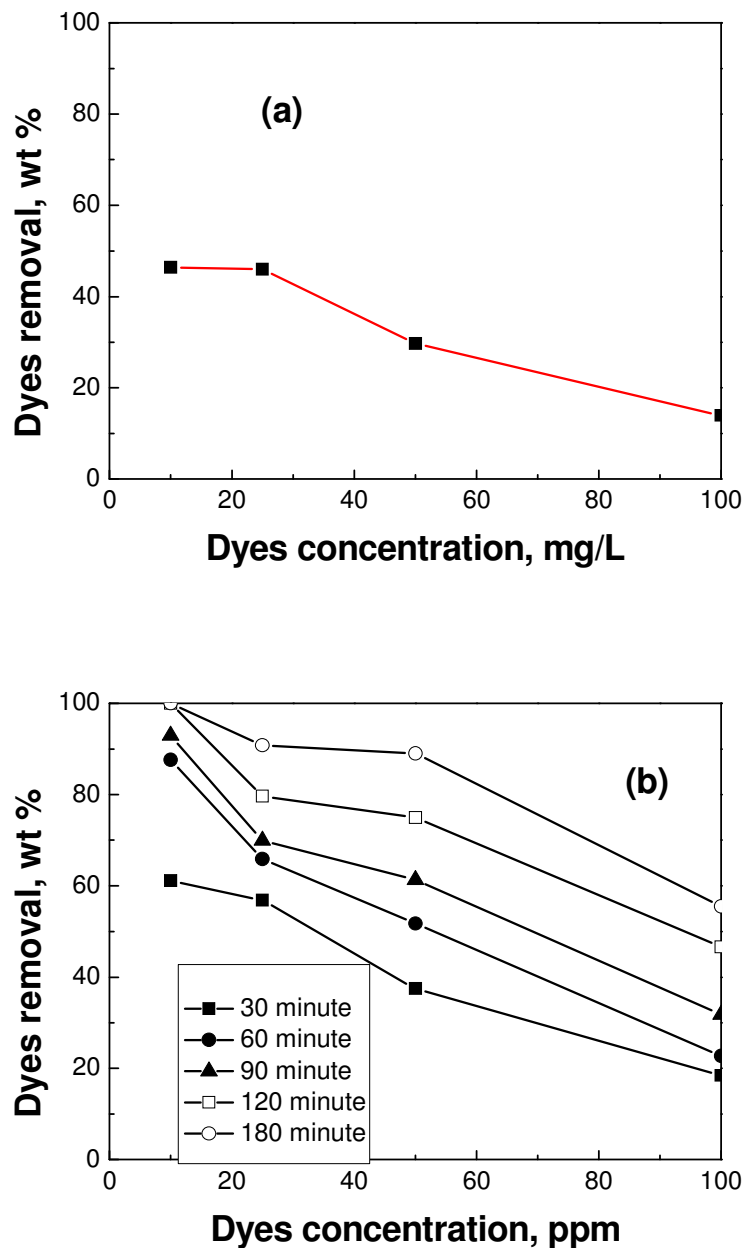
The trapped holes may be regarded as surface-bound hydroxyl radicals. The bound radicals can also diffuse away from the surface toward the solution bulk and exist transiently as free OH (Rajeshwar et al. 2008). This mechanism suggests that hydroxyl radicals and photogenerated holes ( $h_{\text{VB}^+}$ ) are the primary oxidizing species for the adsorbed or free dye molecules (Tryba et al. 2009), while photogenerated electrons ( $e_{\text{CB}^-}$ ) are the reducing species, in the UV/TiO<sub>2</sub> system.

Figure 2 (a & b) illustrates the effect of the TiO<sub>2</sub> catalyst dosage on the dyes removal from solution (at pH 5 with dye concentration of 50 mg/L) on both TiO<sub>2</sub> and upon illumination on the photocatalyst (UV/ TiO<sub>2</sub>), respectively. It can be seen that the extent of the dyes removal increased with TiO<sub>2</sub> dosage increasing to 1g/L. This is due to that the amount of dye adsorbed on the catalyst surface generally increases when increasing the TiO<sub>2</sub> loading. However, further increase of TiO<sub>2</sub> dosage decreased the degradation efficiency of the dyes. This can be explained as follows, the adsorption rate (on TiO<sub>2</sub>) and photodecomposition rates (upon UV/TiO<sub>2</sub>) of pollutants are influenced by the active site and the photo-absorption of the catalyst used. Adequate loading of the semiconductor increases the generation rate of electron/hole pairs for promoting the degradation of pollutants. However, addition of a high dose of the semiconductor decreases the light penetration by the photocatalyst suspension. Result of the TiO<sub>2</sub> dosage in this study was close to other previous works (Barakat et al. 2004, Rajeshwar et al. 2008, Wu et al. 2008, and Wu et al. 2009).

Figure 3 (a & b) illustrates the effect of dyes concentration on its removal rate from solution (at pH = 5 with 1g/L TiO<sub>2</sub>) on both TiO<sub>2</sub> and upon illumination on the photocatalyst, respectively. The limitation of surface sites for the reaction may control the dyes degradation. It is clear that, the dyes removal % is inversely proportional to its concentration, the lower the dyes concentration, the higher the efficiency of dyes removal. With TiO<sub>2</sub>, the dyes adsorption efficiency reached a maximum value of 46.4 % with dyes concentration of 10 mg/L, a further increase in the dyes concentration resulted in decrease in the adsorption efficiency to 13.9 % with dyes concentration of 100 mg/L. For the illuminated dyes samples, at a concentration of 10 mg/L, dyes can be totally degraded (complete oxidation) within 2-3 hours. Increasing the dyes concentration caused a decrease in the photodegradation efficiency value to 55.5 % with dyes concentration of 100 mg/L after 3 hours of illumination.



**Figure 2. Effect of the TiO<sub>2</sub> dosage on the H-EXL dyes removal**  
 a) with TiO<sub>2</sub>    b) with UV/ TiO<sub>2</sub> at different time intervals  
 dyes concentration = 50 mg/L, pH = 5



**Figure 3. Effect of H-EXL dyes concentration on its removal rate**

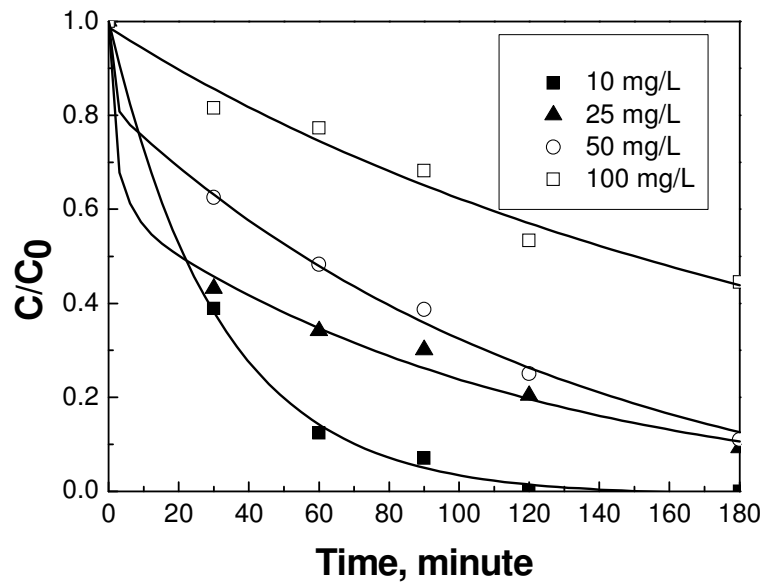
a) with TiO<sub>2</sub>    b) with UV/ TiO<sub>2</sub> at different time intervals

TiO<sub>2</sub> dosage = 1 g/L, pH = 5

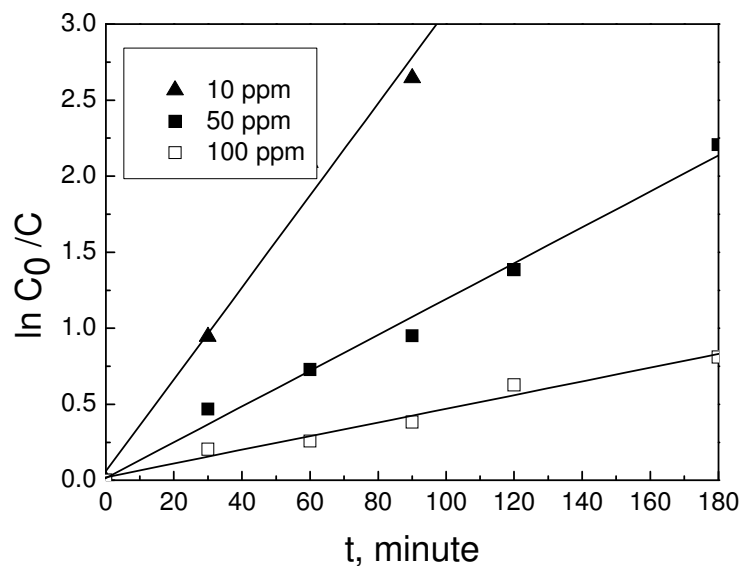
Figure 4 shows the dyes photodegradation rate ( $C/C_0$ ) with the illuminated time at a solution pH = 5. Here  $C_0$  and  $C$  are the initial and remaining dyes concentrations in the solution, respectively. It can be seen that, in all dyes concentrations, the time increases the reaction rate. However, the rate reached the highest value with lower dyes concentration. A Langmuir-Hinshelwood type of relationship can be used to describe the effect of dyes concentration on its degradation. The limitation of surface sites for the reaction may control the dyes decomposition. The results clearly



demonstrate that the photocatalytic oxidation process is promising at low concentrations of the pollutant. This is also true for heterogeneous catalytic systems where the reaction occurs at the interface between two phases. The reactivity of the reaction is generally high at low pollutants concentrations (Kumar et al. 2008). The rate of the reaction was calculated by plotting  $\ln C/C_0$ , at pH of 5, as a function of time, as shown in Figure 5. The plot gave different straight lines which confirmed that the degradation process follows a pseudo-first order reaction.



**Figure 4. Time variation of  $C/C_0$  ratio of the H-EXL dyes photodegradation**  
UV,  $TiO_2$  dosage = 1 g/L, pH = 5



**Figure 5. The reaction rate of the H-EXL dyes photodegradation**  
UV,  $TiO_2$  dosage = 1 g/L, pH = 5

## Treatment of the real textile wastewater sample

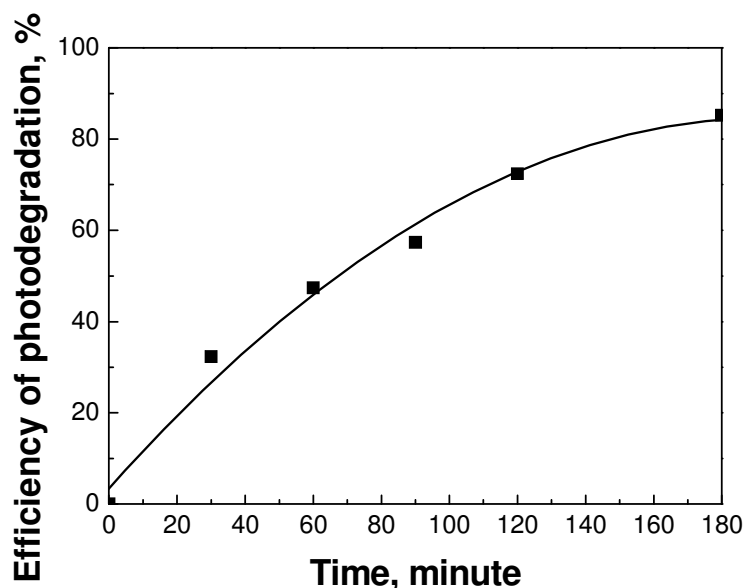
Table 2 illustrates the characterization of the real textile wastewater sample containing the Procion yellow H-EXL dyes. It can be seen that the pH of the real solution is very close to the proper pH of the degradation study. This can facilitate its degradation with a little adjustment for the solution pH. The sample was filtrated to separate the suspended particles.

**Table 2: Analysis of the textile wastewater sample (containing the Procion yellow H-EXL dyes)\***

Properties	Value
Solution pH	5.9
Solution color	Yellowish green
Total suspended solids, TSS	420 mg/L
Total dissolved substances	2640 mg/L
BOD	270 mg/L
COD	640 mg/L
Chloride	90 mg/L
Dye concentration	39 mg/L

\* The analysis data was provided by the Company. The sample contains some impurities and traces of other dyes which were not be analyzed

Figure 6 shows the efficiency of the H-EXL dyes photodegradation in the real textile wastewater sample. The real sample was preliminary treated by the same way that was applied for the synthetic samples. After addition of  $\text{TiO}_2$  to the dye, solution was allowed to equilibrate in dark for 30 minute before the lamp was turned on. The optimum conditions of the study (pH 5 with 1g/L  $\text{TiO}_2$ ) were applied on the real sample, concentration of the dyes in the sample was 39 mg/L. It can be seen that the dyes photodegradation increased with time reaching a maximum value of 85.2 % after 3 hours. This efficiency included both the adsorption and photodegradation processes. However, in comparing this results with that of the solution of pure dyes, it is concluded that the photodegradation rate of the real sample was a relatively lower than that of the pure sample. This can be attributed to the presence of some impurities and traces of other dyes which interfere with the H-EXL dyes.



**Figure 6** The efficiency of the H-EXL dyes photodegradation in the real textile wastewater sample (pH = 5 with dyes concentration of 39 mg/L and 1g/L TiO<sub>2</sub>)

#### 4. CONCLUSIONS

A commercial reactive textile dyes, Procion yellow H-EXL was successively removed from solution by adsorption and photocatalytic degradation over TiO<sub>2</sub> suspension in both dark and in the presence of UV illumination, respectively. The removal of dyes was achieved at optimum solution pH 5 with TiO<sub>2</sub> dosage of 1 g/L. The dyes removal % is inversely proportional to its concentration, the lower the dyes concentration, the higher the efficiency of dyes removal. The dyes adsorption efficiency reached a maximum value of 46.4 % with dyes concentration of 10 mg/L, The efficiency values of the photocatalytic degradation processes were 100, 90.8, 89, and 55.5 % for the dyes concentration values of 10, 25, 50, and 100 mg/L. The kinetic model of Langmuir-Hinshelwood well describes the photoreactivity results. The photocatalytic degradation of the investigated dyes exhibited pseudo first-order kinetics. A real wastewater sample containing the Procion yellow H-EXL dyes from textile industry has been treated at the optimum conditions of the study. The photodegradation of the real sample reached a value of 85.2 % after 3 hours of irradiation. The photodegradation rate of the real sample was a relatively lower than that of the pure sample due to the presence of other dyes impurities.

#### REFERENCES

Akyol, A., Bayramoglu, M. (2008) The degradation of an azo dye in a batch slurry photocatalytic reactor, *Chemical Engineering and Processing*, 47, 2150–2156.

- Andreozzi, R., Caprio, V., Insola, A., Marotta, R. (1999) Advanced oxidation processes (AOPs) for water purification and recovery, *Catal. Today*, 53, 51–59.
- Arslan, I., Balcioglu I.A., Bahnemann, D.W. (2002) Advanced oxidation of a reactive dye bath effluent: comparison of  $O_3$ ,  $H_2O_2/UV-C$  and  $TiO_2/UV-A$  processes, *Water Res.*, 36, 1143–1154.
- Arslan, I., Balcioglu I.A., Tuhkanen, T. (1999) Advanced oxidation of synthetic dye house effluent by  $O_3$ ,  $H_2O_2/O_3$  and  $H_2O_2/UV$  processes, *Environ. Tech.*, 20 (9), 921–932.
- Arslan, I., Balcioglu, I.A., Bahnemann, D.W. (2000) Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel  $TiO_2$ -photocatalysts, *Appl. Catal. B: Environ.* 26, 193–206.
- Barakat, M.A., Chen, Y.T., Huang, C.P. (2004) Removal of toxic cyanide and Cu (II) ions from water by illuminated  $TiO_2$  catalyst. *Applied Catalysis B: Environmental*. 53, 13-20.
- Baran, W., Adamek, E., Makowski, A. (2008) The influence of selected parameters on the photocatalytic degradation of azo-dyes in the presence of  $TiO_2$  aqueous suspension, *Chemical Engineering Journal*. 145, 242–248.
- Baranowska, I., Pieszko, C., Rarog, D., Pielesz, A. J. (2002) *Environ. Sci. Health A* 37, 1841.
- Baughman, G.L., Weber, E.J. (1994) Transformation of dyes and related compounds in anoxic sediment: kinetics and products, *Environ. Sci. Technol.* 28, 267–276.
- Brown, D., Hamburger, B. (1987) The degradation of dyestuff: Part III: Investigation of their ultimate degradability, *Chemosphere* 16, 1539–1553.
- Carliell, C.M., Barclay, S.J., Naidoo, N., Buckley, C.A. (1995) Microbial decolorization of a reactive azo dye under anaerobic conditions, *Water SA*. 21(1), 61–69.
- Carneiro, P.A., Pupo Nogueira, R.F., Zanoni, M.V.B. (2007) Homogeneous photodegradation of C.I. Reactive Blue 4 using a photo-Fenton process under artificial and solar irradiation. *Dyes Pigments*, 74, 127–132.
- Chinwetkitvanich, S., Tuntoolvest, M., Panswad, T. (2000) Anaerobic decolorization of reactive dye bath effluent by a two-stage UASB system with Tapioca as a co-substrate, *Water Res.* 34(8), 2223–2232.
- Danfeng, L., Yihang, G., Changwen, H., Chunjie, J., Enbo, W. (2004) Preparation, characterization and photocatalytic property of the  $PW11O397-/TiO_2$  composite film towards azo-dye degradation, *J. Mol. Catal. A: Chem.* 207, 181–191.
- Dong, Y., Dong, W., Liu, C., Chen, Y., Hua, J. (2007) Photocatalytic decoloration of water-soluble azo dyes by reduction based on bisulfite-mediated borohydride, *Catalysis Today* 126, 456–462.
- Feng, J., Hu, X., Yue, P.L., Zhu, H.Y., Lu, G.Q. (2003) Degradation of azo-dye Orange II by photo-assisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst, *Ind. Eng. Chem. Res.* 42, 2058–2066.
- Franco, A., Neves, M.C., Ribeiro Carrott, M.M.L., Mendonc, M.H., Pereira, M.I., Monteiro, O.C. (2009) Photocatalytic decolorization of methylene blue in the presence of  $TiO_2/ZnS$  nanocomposites, *Journal of Hazardous Materials* 161, 545–550.

- Garcia-Montano, J., Ruiz, N.; Munoz, I., Domenech, X., Garcia-Hortal, J.A., Torrades, F., Peral, J. (2006) Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal. *J. Hazard. Mater. A* 138, 218–225.
- Hermann, J.M. 1999 Heterogeneous photocatalysis: fundamentals and applications, *Catal. Today* 53, 115–129.
- Kang, S., Liao, C., Po, S. (2000) Decolorization of textile wastewater by photo-Fenton oxidation technology, *Chemosphere* 41, 1287–1294.
- Karadimas, V., Spilios, D., Bontozoglou, V., Papapolymerou, G., Decolorization of Direct Blue and TRE Blue dyes, *Proc. 2nd Panhellenic Scientific Conference in Chem. Eng., Thessaloniki, May 27–29, 1999*, pp. 85–89.
- Konstantinou, I.K., Albanis, T.A. (2004) TiO<sub>2</sub>-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations - a review, *Applied Catalysis B: Environmental* 49, 1–14.
- Kumar, P.S.S., Sivakumar, R., Anandan, S., Madhavan, J., Maruthamuthu P., Ashokkumar, M. (2008) Photocatalytic degradation of Acid Red 88 using Au–TiO<sub>2</sub> nanoparticles in aqueous solutions, *Water Research* 42, 4878–4884.
- Li, J., Liu, S., He, Y., Wang, J. (2008) Adsorption and degradation of the cationic dyes over Co doped amorphous mesoporous titania–silica catalyst under UV and visible light irradiation, *Microporous and Mesoporous Materials* 115, 416–425.
- Lucas, M.S., Peres, J.A. (2006) Decolorization of the azo dye reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments* 71, 236–244.
- Mahmoodi, N.M., Arami, M. (2009) Degradation and toxicity reduction of textile wastewater using immobilized titania nanophotocatalysis, *Journal of Photochemistry and Photobiology B: Biology*. 94, 20–24.
- Munter, R. (2001) Advanced oxidation processes-current status and prospects, *Proc. Estonian Acad. Sci. Chem.* 50, 59–80.
- Neyens, E., Baeyns, J. (2003) A review of classic Fenton's peroxidation as an advanced oxidation treatment, *J. Haz. Mat.*: 98, 33–50.
- Pagga U., Brown, D. (1986) The degradation of dyestuffs: Part II: Behaviour of dyestuffs in aerobic biodegradation tests, *Chemosphere* 15(4), 479–491.
- Parsons, S. (2004) *Advanced oxidation processes for water and wastewater treatment*, IWA Publishing, London.
- Poulios, I., Panou, E., Mikropoulou, E., Kostopoulou, E. (2003) Degradation and decolorization of Eosin Y in the presence of semiconducting oxides, *Appl. Catal. B: Environ* 41, 345–355.
- Rajeshwar, K., Osugi, M.E., Chanmanee, W., Chenthamarakshan, C.R., Zaroni, M.V.B., Kajitvichyanukul, P., Krishnan-Ayer, R. (2008) Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 9, 15–36.
- Rao, K.V., Rachel, A., Subrahmanyam, M., Boule, P. (2003) Immobilization of TiO<sub>2</sub> on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants, *Appl. Catal. B: Environ.* 46, 77–85.
- Sanja, P., Dinko, V., Natalija, K., Danijel, S. (2008) Decolourization and mineralization of commercial reactive dyes by using homogeneous and

- heterogeneous Fenton and UV/Fenton processes, *Journal of Hazardous Materials* 140 (1-2), 325–332.
- Sun, J., Wang, Y., Sun, R., Dong, S. (2009) Photodegradation of azo dye Congo Red from aqueous solution by the  $\text{WO}_3\text{-TiO}_2$ / activated carbon (AC) photocatalyst under the UV irradiation, *Materials Chemistry and Physics* 115 (1), 303–308.
- Swaminathan, K., Sandhya, S., Carmalin Sophia, A., Pachhade, K., Subrahmanyam, Y.V. (2003) Decolorization and degradation of H-acid and other dyes using ferrous- $\text{H}_2\text{O}_2$  system, *Chemosphere* 50, 619–625.
- Tanaka, K., Padermpole, K., Hisanaga, T. (2000) Photocatalytic degradation of commercial azo dyes, *Water Res.* 34(1), 327–333.
- Tarr, M.A. (2003) *Chemical degradation methods for wastes and pollutants*, Marcel Dekker, New York.
- Tryba, B., Piszcz, M., Grzmil, B., Pattek-Janczyk, A., Morawski, A.W. (2009) Photodecomposition of dyes on Fe-C-TiO<sub>2</sub> photocatalysts under UV radiation supported by photo-Fenton process, *Journal of Hazardous Materials* 162, 111–119.
- Vandevivere, P.C., Bianchi, R., Verstraete, W. (1998) Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, *J. Chem. Technol. Biotechnol.* 72, 289–302.
- Wu, C.H., Chang, C.L., Kuo, C.Y. (2008) Decolorization of Procion Red MX-5B in electrocoagulation (EC), UV/TiO<sub>2</sub> and ozone-related systems, *Dyes and Pigments* 76, 187-194.
- Wu, R.J., Chen, C.C., Chen, M.H., Lu, C.S. (2009) Titanium dioxide-mediated heterogeneous photocatalytic degradation of terbufos: Parameter study and reaction pathways *Journal of Hazardous Materials* 162, 945–953.