# Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide

E. Bizani [a], K. Fytianos [a,*], I. Poulios [b], V. Tsiridis [c]

[a] *Aristotle University of Thessaloniki, Department of Chemistry, Environmental Pollution Control Laboratory, GR-541 24 Thessaloniki, Greece*
[b] *Laboratory of Physical Chemistry, Chemistry Department, Aristotle University of Thessaloniki, Greece*
[c] *Chemical Process Engineering Laboratory, Department of Chemical Engineering, Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute, Greece*

## Abstract

In this study, the photocatalytic degradation of two commercial azo dyes in the presence of $TiO_2$ suspensions as photocatalyst has been investigated. The degradation of the dyes follows a pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. Under the certain experimental conditions, in the presence of $TiO_2$ P-25 decolorization is achieved within 100 min of illumination, while in the presence of $TiO_2$ Hombikat UV-100 complete color disappearance is accomplished in less than 50 min of light exposure. The influence of various parameters, such as the type and mass of the catalyst, the initial concentration of the dye, etc. on the degradation process was examined. The mineralization of organic carbon was also evaluated by measuring the dissolved organic carbon (DOC) of the dye solutions. Moreover, the toxic properties of the dye solutions treated by photocatalysis were examined by the use of a Microtox bioassay (*Vibrio fischeri*). Finally, experiments using real textile wastewater were also carried out, in order to examine the effectiveness of the method to a more complex substrate.
© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Photocatalysis; Azo dyes; Titanium dioxide; Toxicity

## 1. Introduction

The textile industry consumes considerable amounts of water during the dyeing and finishing operations [1]. Considering both volume discharged and effluent composition, the wastewater generated by the textile industry is rated as one of the most polluting among all industrial sectors. Given the great variety of fibers, dyes, process aids and finishing products in use, the textile industry generates wastewaters of great chemical complexity, diversity and volume. During the last few years, new and tighter regulations coupled with increased enforcement concerning wastewater discharges have been established in many countries [2]. In order to cope with these new restrictions and due to ineffectiveness of conventional biological treatment methods in decolorization and degradation of textile wastewater [2], the research interest was placed on establishing alternative, simple, low-cost technologies for the on-site treatment of wastewaters.

Dye molecules consist of a chromagen and there are about 12 classes of chromagenic groups, the most common of which is the azo type that makes up 60–70% of all textile dyestuffs produced. Another classification of dyes is based on their mode of application to textiles and distinguishes acid, reactive, metal complex, disperse, direct, vat, mordant, basic and sulfur dyes. Research is focused on reactive dyes because they represent an increasing market share, a large fraction of the applied reactive dye is wasted due to dye hydrolysis in the alkaline dyebath, and finally, conventional wastewater treatment plants have low removal efficiency for reactive and other anionic soluble dyes [2]. The degree of stability of reactive azo dyes under aerobic conditions is proportional to the structural complexity of the molecule and only few azo dyes can be degraded aerobically. In order to overcome this problem, azo dyes can be degraded under anaerobic conditions to give potentially hazardous and carcinogenic aromatic amines, which are not further metabolized anaerobically, but are successively degraded under aerobic conditions [2,5].

Up to the present, dye removal methods include chemical, oxidative or most commonly active sludge biochemical processes. Adsorption and chemical coagulation do not result in

---

* Corresponding author. Tel.: +30 2310 997873; fax: +30 2310 997873.
*E-mail address:* fyti@chem.auth.gr (K. Fytianos).

dye degradation and create an ongoing waste disposal problem. The chemical oxidation treatments are usually effective towards the destruction of chromophoric structures of dyes. In this way the water coloration is removed, but often a complete mineralization is not achieved. Chlorination and ozonisation cause decolorization by means of chemical reactions. The by-products of chlorination are chlorinated organics that may be more toxic than the dye itself [3,4]. Problems with using ozone include its instability and its hazardous nature due to strong and non-selective oxidizing power. Therefore, a post-treatment destruction unit must be used to prevent unreacted ozone from escaping into the atmosphere. Moreover, since dyes are intentionally designed to resist degradation, activated sludge systems do not achieve significant dye degradation, as already mentioned. So it is obvious that one single treatment cannot eliminate all contaminants in wastewater and the optimal combination of various treatment processes is today's challenge [3–6].

Heterogeneous photocatalysis is an advanced oxidation process (AOP), which can be successfully used to oxidize many organic pollutants present in aqueous systems. AOPs are all characterized by the same chemical feature: production of radicals ($^\bullet$OH) through a multistep process, although different reaction systems are used. These radicals show little selectivity of attack and are able to oxidize various organic pollutants due to their high oxidative capacity (reduction potential of HO$^\bullet$ $E_o = 2.8$ V) [7]. Photocatalytic degradation involves the use of certain semiconductors as catalysts for the production of the above-mentioned radicals and has proven to be an effective method for mineralizing commercial dyes without having any of the certain drawbacks mentioned above. Experimental observations indicate almost complete oxidation of most of the organic compounds to $CO_2$, $H_2O$ and inorganic anions via photocatalytic processes. The use of titanium dioxide ($TiO_2$) as a catalyst for the photo-oxidation of organic compounds has received much interest because $TiO_2$ is plentiful, inexpensive, powerful and environmentally friendly.

The photocatalytic oxidation of dyes is generally monitored by measuring the decolorization rate, the organic content reduction and the by-products obtained at the different photocatalytic stages. However, the qualitative and quantitative analysis of all individual by-products is very often incomplete, due to technical or financial limitations. Additionally, the generation of by-products that may be more toxic than the parent compounds and phenomena, such as bioavailability, synergistic or antagonistic effects, make toxicity testing of the photocatalytic process essential [8,9]. The Microtox test is amongst the most widely used bioassays for an integrated evaluation of the effectiveness of the photocatalytic process in terms of pollutant decomposition [10,11].

In the present paper, the photocatalytic degradation of two commercial textile dyes in aqueous solutions using two different types of $TiO_2$ as catalysts has been examined. The main objectives of the study were (i) to estimate the kinetics of the dye disappearance; (ii) to examine the influence of various parameters, such as the type and mass of the catalyst, the initial concentration of the dye, etc.; (iii) to evaluate the degree of mineralization and (iv) to examine the toxic properties of the initial dyes as well as of the photocatalytic products. The same treatment procedure was followed for the treatment of real wastewater obtained from a textile industry in order to study the effectiveness of the process to a more complex substrate.

## 2. Experimental

### 2.1. Chemicals

The two commercial dyes used in this study were Cibacron Red FNR (dye 1) and Cibacron Yellow FN2R (dye 2), which are classified as reactive azo dyes and their chemical structures are protected by commercial patents. They were used as received from the textile industry, without further purification. Solutions were prepared by dissolving a defined quantity of these dyes in distilled water. Hydrogen peroxide (30%) was obtained from Panreac. $K_2S_2O_8$ was purchased from Merck. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area 56 m$^2$ g$^{-1}$) and titanium dioxide Hombikat UV-100 (anatase 100%, mean size 10 nm, surface area 250 m$^2$ g$^{-1}$ Schachtleben Chemie) were used as received. Colored wastewater was obtained from a textile industry located in Thessaloniki, Greece. It was taken right after the dyebath and before entering the activated sludge treatment system and it was stored at 4 °C in glass flasks and used without previous filtration.

### 2.2. Irradiation procedure

Irradiation experiments were carried out in a 1.5 L Pyrex UV reactor, wrapped in aluminum foil to increase reflection and equipped with a diving Philips HPK 125 W high-pressure mercury lamp, which provides maximum energy output at 365 nm with substantial radiation also at 435, 313, 253 and 404 nm. The lamp was jacked with a water-cooled Pyrex filter restricting the transmission of wavelengths below 290 nm, in order to simulate the wavelengths of the solar light reaching the earth's surface. The tap water cooling circuit maintained the temperature at 30–35 °C. The dye solutions of 1 L volume (50 mg L$^{-1}$, unless otherwise stated) with the appropriate amount of catalyst were magnetically stirred before and during the illumination. The solutions' pH, which was $7 \pm 0.2$, was not adjusted, with the exception of the experiments studying the influence of the initial pH. In order to investigate the influence of aeration, air was purged in the solution using an air pump and interposing a flask containing a NaOH solution.

Solutions with the desired concentration in dye and the load of $TiO_2$ were fed into the reactor and the suspensions were magnetically stirred. After 30 min of premixing in the dark, in order to achieve the maximum adsorption of the dye onto the semiconductor surface, the lamp was switched on to initiate the photocatalytic reaction. At regular time intervals samples of 10 mL were taken and filtered through a 0.45 μm Millipore syringe filter to remove $TiO_2$ particles.

## 2.3. Analytical procedures

The decolorization of dye solutions and of the wastewater was monitored spectrophotometrically with a Hitachi U-2000 spectrophotometer at their optimal analytical wavelength, respectively. In order to evaluate the extent of mineralization, dissolved organic carbon (DOC) measurements were carried out by a Shimadzu V-csh TOC analyzer.

The luminescent bacteria *Vibrio fischeri* was used for the examination of toxic properties of the samples collected at various times from the photodegradation process. The inhibition of the marine bacteria *V. fischeri* was measured by the Microtox test system (Microtox 500 Analyzer, SDI) within short exposure times of 5 and 15 min. Luminescent bacteria emit light as a by-product of their cellular respiration and metabolic processes. During direct contact with the target compounds, the reduction of the light emission indicates a decreased rate of respiration caused by the presence of toxic compounds. The bacteria were in freeze-dried form and activated prior to use by a reconstitution solution provided by SDI. *V. fischeri* is a marine organism and an adjustment of the osmotic pressure of the samples was applied, in order to obtain samples with 2% salinity, using a concentrated salt solution (22% NaCl). The experiments for the determination of the toxicity of the samples obtained from various stages of the photodegradation process were conducted using the 82% Microtox screening test protocol (sample concentration 82%) [12]. The pH value of the samples was adjusted to $7 \pm 1$, prior to the toxicity tests, by the addition of 0.1 N HCl or 0.1N NaOH solutions.
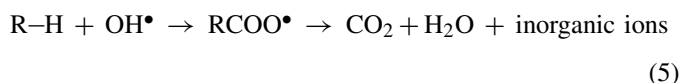
The lines connecting the data points in all the presented figures, except Fig. 3, are provided as a guide to the eye. Fig. 3 includes the best fit trend line corresponding to the data.

## 3. Results and discussion

### 3.1. Dye degradation and influence of TiO$_2$ type

The mechanism of the heterogeneous photocatalytic oxidation using semiconducting materials can be summarized as follows [8,13,14]: the illumination of the semiconductor with light energy ($hv$) greater than its bandgap energy ($E_g$) ($hv > E_g$), 3.2 eV for TiO$_2$, produces excited high-energy states of electron and hole pairs (e$^-$/h$^+$). Part of these photogenerated carriers recombine in the bulk of the semiconductor, while the rest migrate to the surface of particles, where the holes act as powerful oxidants and the electrons as powerful reductants and initiate a wide range of chemical redox reactions, which can lead to complete mineralization of the dyes. The photodegradation process at the semiconductor surface can be expressed as follows [8,13–15]:

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{1}$$

$$O_{2\,ads} + e^- \rightarrow O_2^{\bullet-}{}_{ads} \tag{2}$$

$$h^+ + H_2O_{ads} \rightarrow HO^\bullet + H^+ \tag{3}$$

$$h^+ + HO^-{}_{ads} \rightarrow HO^\bullet \tag{4}$$

$$R-H + OH^\bullet \rightarrow RCOO^\bullet \rightarrow CO_2 + H_2O + inorganic\ ions \tag{5}$$

The HO$^\bullet$ radicals formed on the illuminated semiconductor surface are extremely powerful oxidizing agents that non-selectively attack the adsorbed organic molecules or those close to the catalyst surface, thus, resulting to their mineralization.

In the case of dyes, due to their ability to absorb part of the visible light, another mechanism of degradation connected with visible light could occur as well. According to this mechanistic approach, the adsorbed onto the TiO$_2$ surface dye molecules form appropriate excited states due to visible illumination and then these excited states mainly transfer electrons to the conduction band of TiO$_2$ particles (Eq. (7)) [16–18]:

$$dye + hv \rightarrow dye^* \tag{6}$$

$$dye^* + TiO_2 \rightarrow dye^{\bullet+} + e^-(TiO_2) \tag{7}$$

In our case, due to the emission spectrum of the lamp and the properties of the studied substances, both mechanisms could occur simultaneously, but the process is controlled mainly by the mechanism initiated by the UV illumination. According to other researchers, UV-mechanism is prevalent and its contribution to the dye degradation is much more important than the visible light initiated mechanism [16,19].

The photocatalytic decolorization of the two dye solutions in the presence of the two types of TiO$_2$ is presented in Fig. 1. It is clear that, under the certain experimental conditions, in the presence of TiO$_2$ P-25 the disappearance of the dyes is achieved within 100 min of illumination, while in the presence of TiO$_2$ Hombikat UV-100 complete disappearance is achieved in less
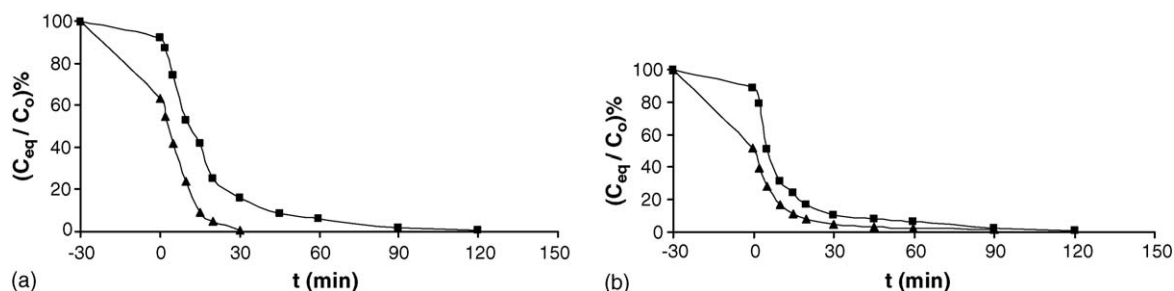


Fig. 1. Photodecolorization of dye 1 (a) and dye 2 (b) solutions (50 mg L$^{-1}$) as function of irradiation time in the presence of TiO$_2$ P-25 (1 g L$^{-1}$) (■) and TiO$_2$ UV-100 (1 g L$^{-1}$) (▲).
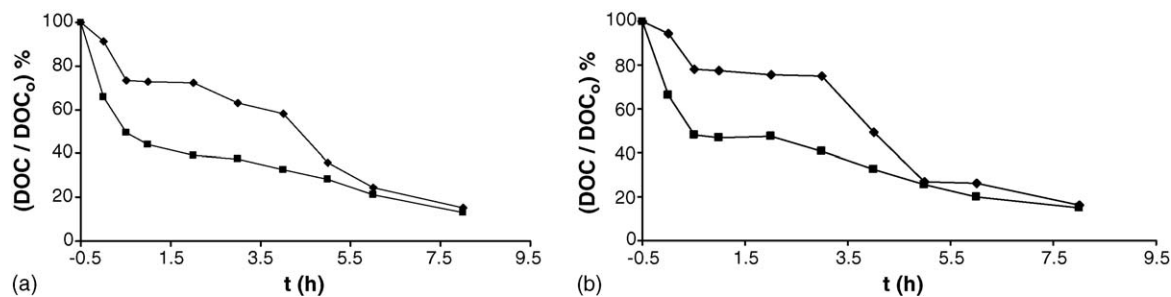
Fig. 2. DOC removal for dye 1 (a) and dye 2 (b) solutions (50 mg L$^{-1}$) vs. irradiation time in the presence of TiO$_2$ P-25 (1 g L$^{-1}$) ($\blacklozenge$) and TiO$_2$ UV-100 (1 g L$^{-1}$) ($\blacksquare$).

than 50 min of light exposure. The disappearance of the $\lambda_{max}$ absorption band of each dye (540 and 430 nm for dyes 1 and 2, respectively), which is measured spectrophotometrically, suggests that the chromophore responsible for the characteristic color of each dye breaks down during the process. Furthermore, the diagrams show that adsorption on the catalyst particles takes place at a different extent for each catalyst type.

In Fig. 2, the removal of DOC during a longer 8-h illumination period is presented showing that the mineralization of the dyes does not follow the decolorization of the solutions. In case of TiO$_2$ P-25 after 120 min of illumination the removal of DOC was 28% and 25% for dyes 1 and 2, respectively, and as far as TiO$_2$ Hombikat UV-100 is concerned, DOC removal reached 56% and 53% for dyes 1 and 2, respectively, after 60 min of illumination. At this time the decolorization of the corresponding dye solutions was complete, suggesting the presence of intermediates, which undergo further photocatalytic oxidation. As far as the two types of catalyst are concerned, they both lead to a similar extent of mineralization (almost 85% DOC removal), although TiO$_2$ Hombikat UV-100 achieves a faster degradation rate.

In general, TiO$_2$ Hombikat UV-100 appears to be more effective on dye oxidation than P-25. According to some researchers TiO$_2$ P-25 owes its high photoreactivity to a slow electron–hole recombination rate whereas the high photoreactivity of Hombikat UV-100 is attributed to a fast interfacial electron transfer rate [20–22]. Since Hombikat UV-100 is found to be more efficient in our case, it could be assumed that the rate-limiting step should be the electron transfer rate rather than the life time of the photogenerated electron–hole pairs. This fact also means that adsorption/desorption of both dyes to the semiconductor particles is relatively fast so that the recombination of the photogenerated electron–hole pairs is prevented by the reactions (2)–(4). Stronger adsorption on the surface of TiO$_2$ Hombikat UV-100, which can be attributed to its larger surface area, also helps in the faster decolorization.

Illumination of the dye solution in the absence of a catalyst showed that the photolytic decomposition of the dyes occurs at a much slower rate (almost 10% and 5% of dye removal after 5 h of illumination for dyes 1 and 2, respectively).

The effect of aeration of the semiconductor suspension was also studied. The decrease in dye concentration was evaluated when air is purged through the suspension and without the purging of air. It was obvious that an improvement in the rate of decolorization is achieved in the presence of air. This improvement seems to be more important at the end of the photocatalytic process, when the main part of the dissolved oxygen is consumed.

### 3.2. Kinetics

Since adsorption is considered critical in the heterogeneous photocatalytic oxidation process, the Langmuir–Hinshelwood model was used to describe the photo-oxidation kinetic of the dyes by a great number of researchers. Substrates have to be adsorbed on the TiO$_2$ surface to be effectively oxidized due to the fast recombination of electron–hole pair. In the Langmuir–Hinshelwood model the rate of reaction is proportional to the surface coverage $\Theta$ ($\Theta = KC_{eq}/(1 + KC_{eq})$). Therefore, the initial rate $r_0$ (mg L$^{-1}$ min$^{-1}$) of decolorization can be written as:

$$r_0 = -\frac{dC}{dt} = \frac{k_r K C_{eq}}{1 + K C_{eq}} \qquad (I)$$

where $k_r$ is the observed reaction rate constant; $K$, the constant for the adsorption of the organic substrate and $C_{eq}$, the equilibrium bulk solute concentration [23,24].

The expression (I) can be rearranged to the following linear form:

$$\frac{1}{r_0} = \frac{1}{k_r K C_{eq}} + \frac{1}{k_r} \qquad (II)$$

Experiments were carried out using various initial concentrations of dyes 1 and 2 (10–50 mg L$^{-1}$) for TiO$_2$ P-25 suspensions. The results depict the decrease in dye concentration during the dark adsorption-desorption equilibrium and the additional decrease caused by subsequent illumination of the pre-equilibrated suspensions. It is, therefore, clear that both dyes strongly adsorb on the TiO$_2$ particles and the extent of adsorption, under given pH values, depend on dye initial concentration and varies from about 10% to 90%. This is the reason why the equilibrium concentrations of the dyes are used, instead of the initial ones, in the kinetic study.

The $r_0$ values for dyes 1 and 2 were independently obtained from these curves, by the linear fit using only the experimental data obtained until 20% of dye removal was achieved, in order to minimize variations as a result of competitive effects of intermediates, pH changes, etc.
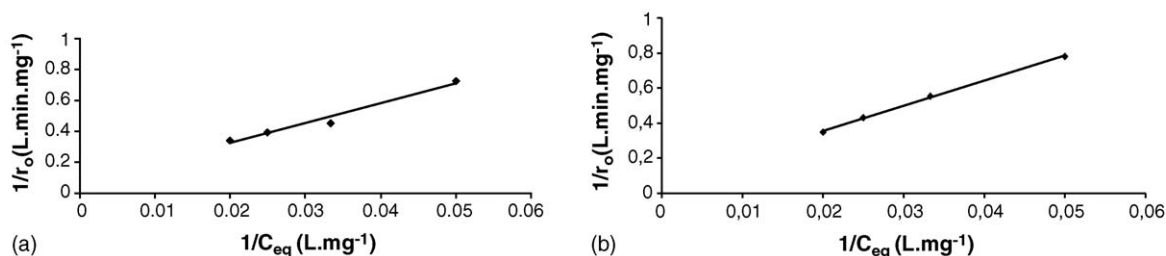
Fig. 3. Linearized reciprocal kinetic plot for the photocatalytic decolorization of dye 1 (a) and dye 2 (b) solutions in the presence of TiO$_2$ P-25 = 1 g L$^{-1}$.

Table 1
Constants of the Langmuir–Hinshelwood model

|       | $k_r$ (mg L$^{-1}$ min$^{-1}$) | $K$ (L mg$^{-1}$) |
|-------|--------------------------------|-------------------|
| Dye 1 | 15.1                           | 0.01              |
| Dye 2 | 14.4                           | 0.005             |

As indicated in Fig. 3, the plot of the reciprocal initial rate $r_0^{-1}$ as a function of the reciprocal initial concentration $C_{eq}^{-1}$ yields a straight line. In Table 1, the constants of the Langmuir–Hinshelwood model for dyes 1 and 2 are summarized, as they were evaluated according to the Eq. (II) from the slope of the straight line ($R^2 = 0.97$ for dye 1 and $R^2 = 0.99$ for dye 2) in the plots appeared in Fig. 3.

### 3.3. Effect of catalyst concentration

The influence of the catalyst concentration on the decolorization kinetics of the two dye solutions has been investigated using different concentrations of TiO$_2$ varying from 0.25 to 4 g L$^{-1}$ and the results are presented in Fig. 4(a) and (b). It is obvious that the rate increases with an increase of the concentration of catalyst up to a limit above which no improvement is obtained and the curves formed are reminiscent of a Langmuir type adsorption isotherm. A similar observation has been made by other authors, as well [15,25–28]. The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are, thus, adsorbed accelerating the process. The plateau, which is recorded after a certain amount of catalyst is added, may be a consequence of the fact that the reaction takes place on dye molecules adsorbed at the TiO$_2$ surface. When all the dye molecules are adsorbed on TiO$_2$ no improvement is achieved by adding more catalyst. The decrease in efficiency, which is observed in both figures, may be due to
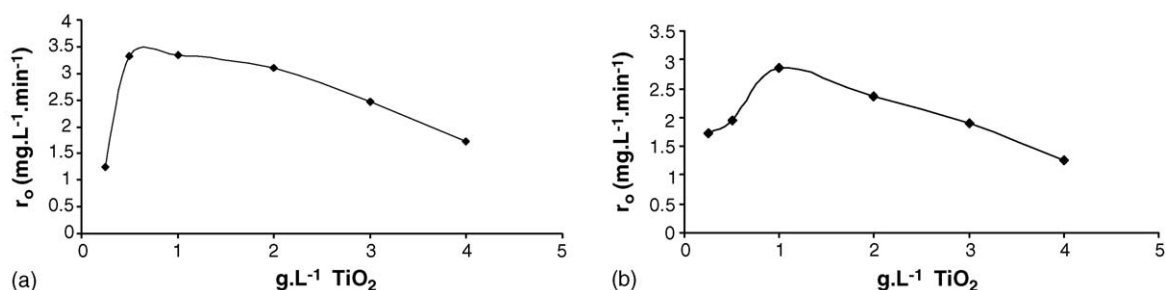
an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of TiO$_2$ particles [25]. Moreover, particle–particle interaction becomes significant as the amount of particles in solution increases, thus, reducing the site density for surface holes and electrons, because the rate of deactivation of activated molecules by collision with ground state titanium dioxide increases [26,27].

### 3.4. Influence of initial pH

The influence of the initial pH of the dye solution was studied as pH could be considered as one of the most important parameters that can affect the photo-oxidation process. In Fig. 5, the concentration decrease of the two dyes in three different pH values (acidic, neutral and alkaline) is presented. For altering pH in the acidic and in alkaline area HCl 2 M and NaOH 2 M solutions, respectively, have been used.

The effect of the solution pH on the degradation rate can be explained mainly by the modification of the electrical double layer of the solid–electrolyte interface, which consequently affects the sorption-desorption processes and the separation of the photogenerated electron–hole pairs in the surface of the semiconductor particles. In acidic suspensions, the adsorption of both dyes on the TiO$_2$ particles was significantly increased comparing to the extent of adsorption in neutral or alkaline suspensions. This is attributed to the fact that TiO$_2$ shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge for the used TiO$_2$ P-25 is pH $\approx$ 6 so below this value the surface of the particles is positively charged and above it is negatively charged. Because adsorption is favored in low pH (the extent of adsorption is almost four-fold for both dyes compared to the one at neutral pH values), it can be assumed that molecules of both dyes are negatively charged so an electrostatic attraction is developed.
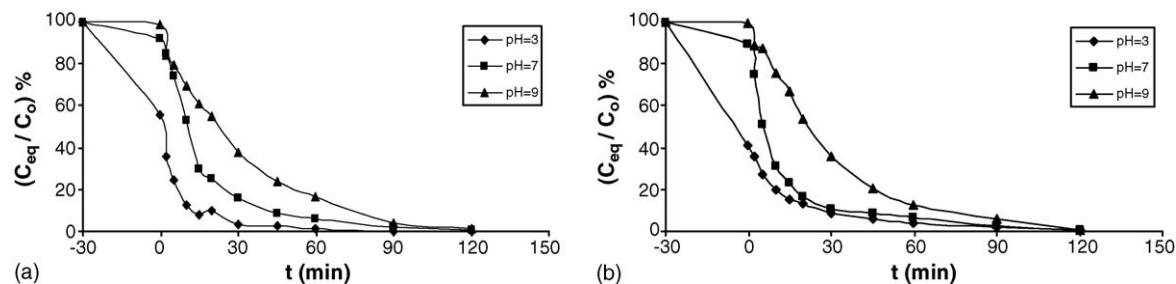


Fig. 4. Dependence of the initial rate $r_0$ of decolorization on the concentration of the catalyst for dye 1 (a) and dye 2 (b).

Fig. 5. Plot of the photodecolorization of dye 1 (a) and dye 2 (b) solutions ($50\,\mathrm{mg\,L^{-1}}$) vs. irradiation time in three different initial pH values, in the presence of $TiO_2$ P-25 = $1\,\mathrm{g\,L^{-1}}$.

However, the strong adsorption leads to a major decrease of the active centers on the catalyst's surface, which means the absorption of the light quanta by the catalyst is decreased as well. This could be the reason why the initial rate of the decolorizarion is lower in acidic solutions. Moreover, it could be assumed that strong adsorption causes a multilayer of dye molecules around the catalyst particles and as a result these molecules are not in direct contact to the catalyst, so they do not participate in the photo-oxidation process. On the other hand, in alkaline solutions a decrease of the initial rate is also observed, reflecting the difficulty of the dye molecules to approach the catalyst surface. As a result, the optimum pH among those tested under these certain experimental conditions appears to be the neutral one. Similar observations have been made by other researchers for dyes and several other types of pollutants [24,28,29].

### 3.5. Influence of oxidants

The addition of other powerful oxidizing species, such as hydrogen peroxide ($H_2O_2$) and potassium peroxydisulfate ($K_2S_2O_8$) to $TiO_2$ suspensions is a well-known procedure and in many cases leads to an increase in the rate of photo-oxidation [5,15,23,24,28]. In our case, the photocatalytic degradation of the two dyes in the presence of $1\,\mathrm{g\,L^{-1}}$ $TiO_2$ P-25 for dyes 1 and 2 has been studied at different $H_2O_2$ concentrations and at a specific concentration of $K_2S_2O_8$. The reaction kinetics was similar to those observed without the oxidants. Since the influence of the above additives, and especially $H_2O_2$, has been in some cases controversial and appeared strongly dependent on substrate type and experimental conditions, their use must be carefully studied.

The $H_2O_2$ is considered to have a dual role during the process of photocatalytic degradation. It accepts an electron from the conduction band, and thus, promotes the charge separation and it also forms $OH^\bullet$ radicals.

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \tag{8}$$

$$H_2O_2 + O_2^- \rightarrow OH^- + OH^\bullet + O_2 \tag{9}$$
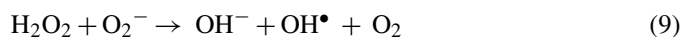
In the presence of excess $H_2O_2$, it may act as hole or $OH^\bullet$ scavenger or react with $TiO_2$ to form peroxocompounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of $H_2O_2$ for the maximum effect [28].

In Fig. 6, the initial photo-oxidation rates for dyes 1 and 2 versus the concentration of $H_2O_2$ are presented. It is obvious that small concentrations of the oxidant enhance the process. At high concentrations, the addition of hydrogen peroxide causes a decrease (Fig. 6) to the reaction rate because it can act as a hole or $OH^\bullet$ scavenger. The optimum concentration appears to be $100\,\mathrm{mg\,L^{-1}}$ $H_2O_2$ for both dyes tested, under the certain experimental conditions.

The influence of another oxidant, $K_2S_2O_8$, was also studied. This oxidant can act according to the following reaction:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \tag{10}$$
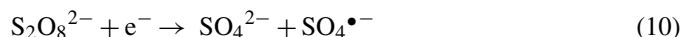
That means that $K_2S_2O_8$ also traps the photogenerated conduction band electron, preventing its recombination with the positive hole, and at the same time produces the sulfate radical, which is a very strong oxidizing agent (reduction potential, $E_o = 2.6\,\mathrm{V}$) that can also take part in the oxidation process of the
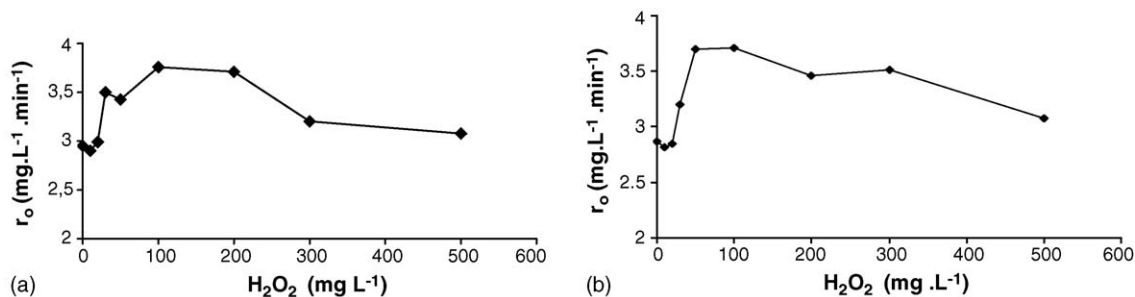


Fig. 6. Effect of the $H_2O_2$ concentration on the initial rate of the photocatalytic decolorization of dye 1 (a) and dye 2 (b) solutions ($50\,\mathrm{mg\,L^{-1}}$) in the presence of $1\,\mathrm{g\,L^{-1}}$ $TiO_2$.
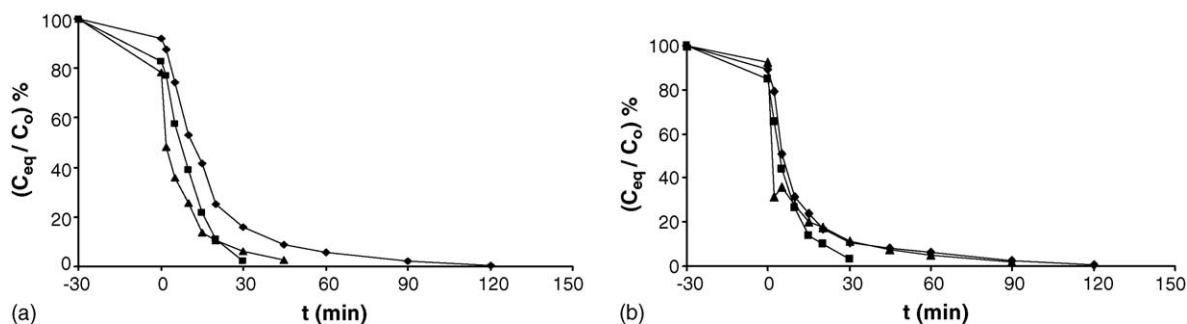
Fig. 7. Photodecolorization of dye 1 (a) and dye 2 (b) solutions in the presence of $1\,\mathrm{g\,L^{-1}}$ TiO$_2$ (◆), plus $3 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ H$_2$O$_2$ (■), or plus $3 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ K$_2$S$_2$O$_8$ (▲) vs. photocatalytic treatment time.

dye molecules. Because of reaction (11):

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^+ \qquad (11)$$

the addition of this oxidant causes a significant decrease of pH, which becomes $2.5 \pm 0.2$.

In Fig. 7, the effect of the same concentration of the two oxidants on the dye photodegradation is presented. It is obvious that K$_2$S$_2$O$_8$ has a more positive effect on the reaction rate, at least at the beginning of the process, as far as both dyes are concerned, which may be attributed to the fact that the pH of the suspension turns to strongly acidic with the addition of K$_2$S$_2$O$_8$. This change of pH is favorable to the adsorption of the dye to the catalyst particles, as it has already been mentioned above. In the case of K$_2$S$_2$O$_8$ addition though, despite the decrease of pH, the mineralization rate is also positively influenced, probably because the oxidizing properties of the system prevail on the effect of pH reduction.

### 3.6. DOC removal–toxicity evolution

The complete decomposition to CO$_2$ via photocatalytic reactions is of great significance in water treatment because it is the unequivocal evidence of the total destruction of organic compounds in water. For this reason, the extent of mineralization of the two dyes was studied by measuring the dissolved organic carbon of the illuminated suspensions. However, the evaluation of mineralization is considered more complete when toxicity assessment of the treated water is also carried out. In case of dyes, where a considerable number of not easily determinable by-products could be formed during the degradation process, the toxicity evaluation of the solution in certain time intervals becomes of great importance [29]. The toxicity of the samples collected from different stages of the applied photocatalytic processes was evaluated using the Microtox test. Toxicity assays have been chosen to determine the toxicity of the solutions, because they are standardized and reliable. The results obtained after 15 min exposure time of the bacteria to the samples as well as the results of DOC measurements for both dyes are presented in Fig. 8.

It is obvious that decolorization of dye solutions is not followed by the same extent of mineralization. That means that the dye decomposes to smaller organic intermediates that are still present in the solution. Within a longer illumination period

though, a significant removal of DOC is accomplished (almost 85–90% DOC removal for both dyes was accomplished for 5-h illumination), which means that prolonged illumination can probably lead to complete mineralization. As far as the addition of oxidants is concerned, H$_2$O$_2$ seems to be more effective in mineralizing the dyes than K$_2$S$_2$O$_8$, although their effectiveness in decolorizing the solutions was the reverse. This is probably due to different degradation products formed when K$_2$S$_2$O$_8$ was used, as another oxidation agent is also present in the system according to the Eq. (10).

As shown in Fig. 8, the toxicity evolution of the applied photocatalytic processes depended on the oxidant used. As far as the initial toxicity values of both dye solutions are concerned, they varied between 45% and 60%. The lower initial toxicity values were observed when no oxidants were added, while the higher initial toxicity values were observed in the cases of the addition of H$_2$O$_2$. During the photocatalytic process, the higher toxicity values for dye 1 were obtained in the process with the addition of K$_2$S$_8$O$_8$ and for dye 2 in the process without the addition of oxidants, while the lower toxicity values were generally obtained for both dyes during the photocatalytic processes with the addition of H$_2$O$_2$. The intermediates produced during the photocatalytic degradation of the two dyes, without the addition of oxidants and with the addition of K$_2$S$_8$O$_8$, were in some time intervals more toxic than the parent compounds.

The variation of the toxicity results obtained could be attributed to the different photocatalytic products with different toxic properties that generated during the applied processes, as well as to synergistic or antagonistic joint effects between the generated products [11,30]. Moreover, even though effective decolorization and degradation of the two dyes occurred, the toxicity of the solutions was not significantly decreased during the photocatalytic process and in some time intervals the toxicity was increased.

In addition, the toxic response in 15 min exposure time was not significantly greater than 5 min exposure time in almost all the photocatalytic processes. However, in the photocatalytic processes with the addition of K$_2$S$_8$O$_8$ the 15 min toxic response was considerably higher than 5 min toxic response. Although, there is no clear interpretation of which type of chemicals may affect the time-effect dependencies, generally the toxic response of *V. fischeri* is increased notably from 5 to 15 min due to the presence of inorganic metal ions [30]. In the applied photocatalytic
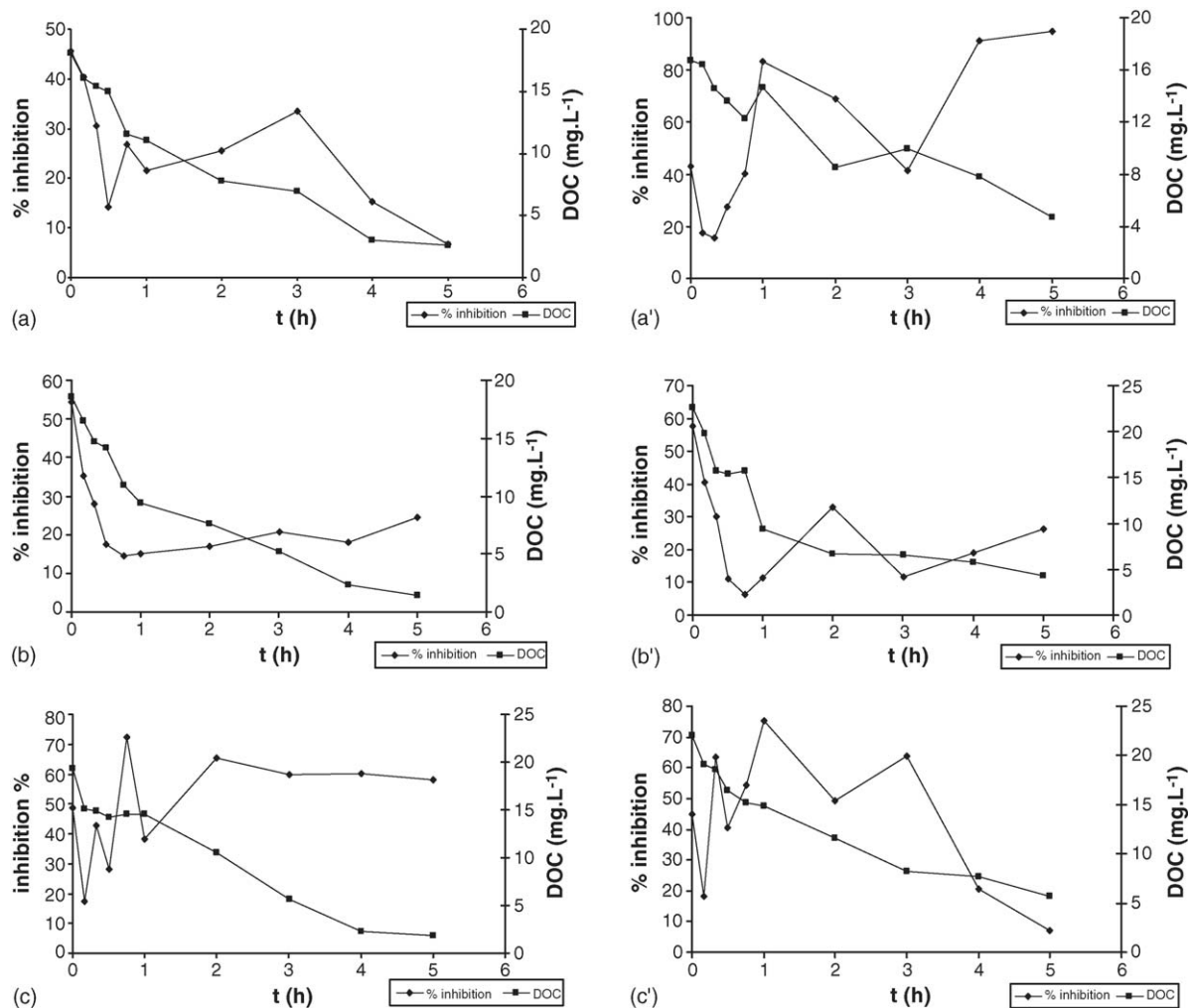
Fig. 8. Toxicity evolution and TOC removal in the presence of $1\,g\,L^{-1}\,TiO_2$ P-25, in the presence of $1\,g\,L^{-1}\,TiO_2$ P-25 $+ 3 \times 10^{-3}\,mol\,L^{-1}$ $H_2O_2$ and in the presence of $1\,g\,L^{-1}\,TiO_2$ P-25 $+ 3 \times 10^{-3}\,mol\,L^{-1}$ $K_2S_8O_8$ for dye 1 solutions (a, b and c, respectively) and for dye 2 solutions (a′, b′ and c′, respectively) vs. photocatalytic treatment time (initial dye concentration $50\,mg\,L^{-1}$).

processes there is no evidence indicating the presence of such toxic constituents, however, in the photocatalytic processes with the addition of $K_2S_8O_8$, the noticeable increase of the toxic response from 5 to 15 min that was observed, could be attributed to the generation of sulfur radicals that results in the change of oxidation mechanism and the pH decrease [5,13].

Combining the results obtained from the decolorization rate and DOC measurements with the corresponding toxicity values of the tested dyes, it can be concluded that the photocatalytic process by the addition of $H_2O_2$ is presented as the most efficient process. During this process and as far as both dyes are concerned, under the certain experimental conditions, a relatively sufficient degradation and detoxification capacity is achieved in a relatively short time, about 1 h, which suggests a photocatalytic process for 1 h for the optimization of the process.

### 3.7. Wastewater treatment

In order to investigate the effectiveness of semiconductor photocatalytic treatment, experiments using real textile wastew-

ater were carried out. The decolorization of the wastewater was measured to the wavelength of maximum absorbance of the wastewater which was $\lambda_{max} = 550\,nm$. The textile effluent was taken before entering the biological treatment and was used as received, without dilution. The initial DOC value of the wastewater was $330.5\,mg\,L^{-1}$, while its initial pH value $\approx 6.0$ and has slightly increased during the process. The results of decolorization and toxicity evolution for a 6-h treatment are presented in Fig. 9.

Complete decolorization of the wastewater was achieved within 6 h, but the detoxification of the wastewater was only partly achieved ($\approx 35\%$ for 6-h treatment). On the other hand, the DOC was also partly removed (initial DOC $330.5\,mg\,L^{-1}$, final DOC after 6-h treatment $235.3\,mg\,L^{-1}$, DOC removal 29%). The addition of oxidants did not produce significantly improved results, and in some time intervals it also generated more toxic degradation products, while the absorbance decrease and DOC removal was only slightly accelerated. It is obvious that prolonged irradiation is needed, in order to achieve total destruction of
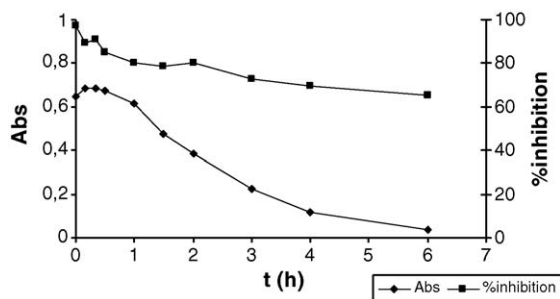
Fig. 9. Toxicity evolution (■) and absorbance decrease (♦) of textile wastewater in the presence of $1 \, g \, L^{-1}$ TiO$_2$ P-25 vs. photocatalytic treatment time.

the contaminants, thus, resulting in the high cost of the method.

However, when facing the problem of pollution the combination of methods could be the key to the total solution. AOPs in general have higher operating costs than those of a biological treatment. Their use as pre-treatment, though, for the enhancement of the biodegradability of wastewater containing recalcitrant contaminants, such as dyes could be suggested. In that way, the intermediate reaction products could be degraded by microorganisms in a biological post-treatment, thus, making the complete mineralization unnecessary. From the point of view of practical application of the heterogeneous photocatalysis, it should be noted that this method gives the opportunity of using the solar irradiation as well and it can be selected among the most popular solar technologies. Combining this fact with the effectiveness of the method and the ability to be teamed up with other conventional technologies, heterogeneous photocatalysis using TiO$_2$ could be considered as an alternative, promising method for the treatment of dye wastewaters [6,11].

## 4. Conclusions

The photocatalytic oxidation of two commercial dyes has been studied using two types of TiO$_2$ as catalysts. The results of the study could be summarized as follows: (i) Dye solutions were successfully decolorized using TiO$_2$ photocatalysis and titanium dioxide Hombikat UV-100 proved to be a more efficient photocatalyst than P-25. (ii) The photo-oxidation of both dyes followed first order kinetics, which fitted the Langmuir–Hinshelwood model. (iii) Parameters, such as concentration of the catalyst or initial pH value play an important role affecting the reaction rate. (iv) In the case of the addition of oxidants, such as hydrogen peroxide and potassium peroxidisulfate into illuminated TiO$_2$ suspensions, a synergistic effect was observed leading to an enhancement of the process. (v) The mineralization of the two dyes was determined by measuring the dissolved organic carbon of the dye solutions and by evaluating their toxicity. Although DOC was almost 80% removed after 5 h of illumination, the toxicity of the solutions is slightly decreased in the presence of the catalyst and the oxidants, but the intermediate degradation products seem to be more toxic than the initial compound. (vi) The application of the TiO$_2$ photocatalytic method to real wastewater proved to be efficient in decolorizing

the wastewater (complete decolorization within 6 h of illumination) and it achieved partial DOC and toxicity removal (29% DOC and 35% toxicity removal for a 6-h illumination period).

## References

[1] C. Galindo, P. Jacques, A. Kalt, Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74), J. Photochem. Photobiol. A: Chem. 141 (2001) 47–56.

[2] P.C. Vandevivere, R. Bianchi, W. Verstraete, Treatment and reuse of wastewater from textile wet-processing industry: review of emerging technologies, J. Chem. Technol. Biotechnol. 72 (1998) 289–302.

[3] K. Sopajaree, Photocatalytic oxidation of methylene blue by titanium dioxide in a photoreactor, in: Proceedings of the 6th Intrnetional Conference on Environmental Science and Technology, Pythagorion, Samos, Greece, 30/8–2/9/1999.

[4] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation, Water Res. 32 (1998) 2721–2727.

[5] V. Augugliaro, C. Baiocchi, A. Bianco Prevot, E. Garcia-Lopez, V. Loddo, S. Malato, G. Marci, L. Palmisano, M. Pazzi, E. Pramauro, Azodyes photocatalytic degradation in aqueous suspension of TiO$_2$ under solar irradiation, Chempsphere 49 (2002) 1223–1230.

[6] C. Hu, Y. Wang, Decolorization and biodegradability of photocatalytic treated azodyes and wool textile wastewater, Chemosphere 39 (1999) 2107–2115.

[7] S. Espulgas, J. Giménez, S. Contreras, E. Pascual, M. Rogríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[8] I.K. Konstantinou, T.A. Albanis, TiO$_2$-assisted photocatalytic degradation of azo-dyes in aqueous solution: kinetic and mechanistic investigations. A review, Appl. Catal. 49 (2004) 1–14.

[9] A. Kungolos, P. Samaras, A.M. Kipopoulou, A. Zoumboulis, G.P. Sakellaropoulos, Water Sci. Technol. 40 (1) (1999) 357.

[10] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Photocatalytic degradation and mineralizetion of bisphenol A by TiO$_2$ and platinized TiO$_2$, Appl. Catal. A: Gen. 261 (2004) 225–237.

[11] A.R. Fernandez-Alba, D. Hernando, A. Aguera, J. Caceres, S. Malato, Toxicity assays: a way for evaluating AOPs efficiency, Water Res. 36 (2002) 4255–4262.

[12] Microbics Corporation, Microtox Manual, A Toxicity Testing Handbook, vol. 1–5, Carlsbad, CA, USA, 1992.

[13] M. Hoffman, S. Martin, W. Choi, D. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

[14] J. Peral, X. Domenech, D. Ollis, Heterogeneous photocatalysis for purification, decontamination and decolorization of air, J. Chem. Technol. Biotechnol. 70 (1997) 117–140.

[15] I. Poulios, I. Aetopoulou, Photocatalytic degradation of the textile dye reactive orange 16 in the presence of TiO$_2$ suspensions, J. Chem. Technol. Biotechnol. 74 (1999) 349–357.

[16] C. Galindo, P. Jacques, A. Kalt, Photodegradation of the aminoazobenzene acid orange 52 by three advanced oxidation processes: UV/H$_2$O$_2$, UV/TiO$_2$ and VIS/TiO$_2$. Comparative mechanistic and kinetic investigations, J. Chem. Technol. Biotechnol. 130 (2000) 35–47.

[17] Y. Ma, J.-N. Yao, Photodegradation of Rhodamine B by TiO$_2$ thin films, J. Chem. Technol. Biotechnol. 116 (1998) 167–170.

[18] F. Chen, Y. Xie, J. Zhao, G. Lu, Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation, Chemosphere 44 (2000) 1159–1168.

[19] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, TiO$_2$-assisted photodegradation of dye pollutants. II. Adsorption and degradation kinetics of eosin in TiO$_2$ dispersions under visible light irradiation, Appl. Catal. B: Environ. 15 (1998) 147–156.

[20] M. Muneer, H.K. Singh, D. Bahnemann, Semiconductor-mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenylhydrazine, in aqueous suspension, Chemosphere 49 (2002) 193–203.

[21] M. Muneer, D. Bahnemann, Semiconductor-mediated photocatalysed degradation of two selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole, in aqueous suspension, Appl. Catal. B: Environ. 36 (2002) 95–111.

[22] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, Morphology of a $TiO_2$ photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases, J. Catal. 203 (2001) 82–86.

[23] W.Z. Tang, H. An, $UV/TiO_2$ photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 31 (1995) 4157–4170.

[24] I. Poulios, I. Tsachpinis, Photodegradation of the textile dye Reactive Black 5 in the presence of semiconducting oxides, J. Chem. Technol. Biotechnol. 74 (1999) 349–357.

[25] M.S.T. Goncalves, A.M.F. Oliveira-Campos, E.M.M.S. Pinto, P.M.S. Plasencia, M.J.M.S. Queiroz, Photochemical treatment of solutions of azo dyes containing $TiO_2$, Chemosphere 39 (1999) 781–786.

[26] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and $TiO_2$ assisted degradation of textile dye reactive blue 4, Chemosphere 46 (2002) 1173–1181.

[27] L.-C. Chen, T.-C. Chou, Photobleaching of methyl orange in titanium dioxide suspended in aqueous solution, J. Mol. Catal. 85 (1993) 201–214.

[28] I. Poulios, A. Avranas, E. Rekliti, A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Technol. Biotechnol. 75 (2000) 205–212.

[29] L.B. Reutergardh, M. Iangphasuk, Photocatalytic decolorization of reactive azo dye: a comparison between $TiO_2$ and CdS photocatalysis, Chemosphere 35 (1997) 585–596.

[30] V.A. Sakkas, I.M. Arabatzis, I.K. Konstantinou, A.D. Dimou, T.A. Albanis, P. Falaras, Metolachlor photocatalytic degradation using $TiO_2$ photocatalysts, Appl. Catal. B: Environ. 49 (2004) 195–205.