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## PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE C.I. REACTIVE ORANGE 16 IN TiO<sub>2</sub> WATER SUSPENSION BY SIMULATED SOLAR LIGHT

The photodegradation of C.I. Reactive Orange 16 (RO16), commonly used as a textile dye, was investigated using TiO<sub>2</sub> as a catalyst and the sun lamp. The experiments showed that TiO<sub>2</sub> and simulated solar light are necessary for the effective photodegradation, although a low degradation/adsorption was observed when only the simulated solar light or TiO<sub>2</sub> was used. The effect of some parameters such as the initial concentration of the catalyst, the initial dye concentration, the initial Na<sub>2</sub>CO<sub>3</sub> and NaCl concentrations, pH, and the presence of H<sub>2</sub>O<sub>2</sub> on photodegradation of RO16 was examined. The photodegradation efficiency was highest at the catalyst concentration of 2.0 g/l. The degradation was faster in the acidic than in alkaline pH range. High adsorption of the dye was observed at low pH, while at high pH almost no adsorption was detected. A lower concentration of Na<sub>2</sub>CO<sub>3</sub> decreased the photodegradation of RO16, while a higher concentration increased the photodegradation. The presence of NaCl led to the inhibition of the photodegradation process. The low concentration of H<sub>2</sub>O<sub>2</sub> increased the RO16 photodegradation efficiency, while at higher concentration of H<sub>2</sub>O<sub>2</sub> inhibition was observed.

*Key words:* Textile dye, Reactive Orange 16, Titanium dioxide, Photodegradation.

Wastewaters from the textile industry contain a quantity of synthetic dyes, which are generally toxic and resistant to destruction by biological treatment methods. They are also resistant to destruction by physico-chemical methods, such as chemical precipitation and separation of pollutants, coagulation, elimination by adsorption etc [1,2]. These methods are non-destructive but only transfer the contamination from one phase to another, thus creating a new kind of pollution, which requires further treatment.

Among the new oxidation methods, also known as "advanced oxidation processes" (AOP), heterogeneous photocatalysis is an emerging destructive technology leading to the total mineralization of many organic pollutants [3-5].

Azo-dyes constitute a significant portion of synthetic dyes and probably have undesirable consequences in terms of surrounding ecosystems. The photodegradation of aqueous solutions of different azo-dyes have been reported [6-9]. C.I. Reactive Orange 16 (Figure 1) photodegradation was also studied [10, 11]. It was found that RO16 can be effectively degraded under the artificial and natural illumination using TiO<sub>2</sub> and ZnO as catalysts [10]. It was also established that the first step of the degradation is related to a cleavage of the azo bond of the molecule and the naphthalene ring, which led to further

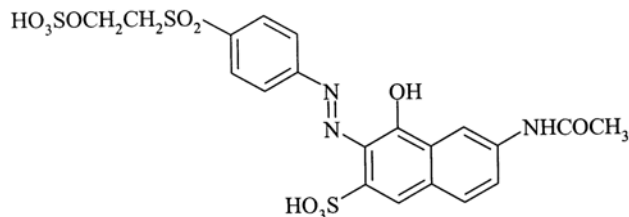


Figure 1. The structure of C.I. Reactive Orange 16.

degradation until a complete mineralization. GC/MS analysis showed that three degradation products were detected during the photooxidation process, namely 6-acetylamino-3-aminonaphthalene-2-sulfonic acid, N-(3,4-bishydroxymethylphenyl)-acetamide and phthalic acid [11].

The aim of the present study is to investigate the influence of various parameters on photocatalytic decomposition of RO16 dye, in the presence of TiO<sub>2</sub> irradiated by the simulated solar light. The effect of parameters such as the initial concentration of catalyst (0.4-2.4 g/l), the initial dye concentration (30-50 mg/l), the initial Na<sub>2</sub>CO<sub>3</sub> (0-2 % w/v) and NaCl concentration (0-2 % w/v) and pH was studied. In addition, the effect of H<sub>2</sub>O<sub>2</sub> was investigated (0-612.6 mmol/l).

### EXPERIMENTAL

#### Reagents

The hydrogen peroxide solution (30 %), hydrochloric acid, sodium chloride, sodium carbonate and sodium hydroxide (all p.a.) were obtained commercially. The photocatalyst employed was commercial TiO<sub>2</sub> obtained

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from Degussa as a gift (Aeroxide TiO<sub>2</sub> P25). According to the manufacturer's specifications, P25 has an elementary particle size of 30 nm, a BET specific surface area of 50 m<sup>2</sup>/g and its crystalline mode is 80% anatase and 20% rutile. The textile dye, C.I. Reactive Orange 16, was obtained from Bezema as a gift (commercial name Bezaktiv Orange V-3R) and used without further purification. Deionised water was obtained from a Millipore Waters Milli Q purification unit.

### Procedures

Irradiation was performed in an open thermostated flask (100 ml volume) with the sun lamp Osram ULTRA-VITALUX<sup>®</sup> 300 W (mix of lights; UV-A: UV-B=13.6:3 according to the manufacturer's specifications) placed 40 cm away from the surface of the dye solution.

The photodegradation of RO16 was studied by preparing a solution containing a known concentration of dye and the amount of TiO<sub>2</sub>. In a typical experiment, 50 ml of this solution was used. Agitation was then applied (500 rpm) to maintain the suspension homogenous. The flask was agitated in dark for 60 min and the sun lamp was switched on. Alternatively, the sun lamp was switched on immediately after the agitation began. After an appropriate time of irradiation the suspension was sampled. The concentration of the dye was determined by UV-vis spectrophotometer (Shimadzu 1700 UV-vis spectrophotometer) at  $\lambda_{\max}$ =493 nm after centrifugation of a sample. pH of samples was adjusted by adding NaOH and HCl and measured using pH meter (PHM93 reference pH meter, Radiometer Copenhagen, Denmark).

## RESULTS AND DISCUSSION

### The effect of different reaction conditions

These experiments were conducted under different conditions: under the simulated solar light in the absence of TiO<sub>2</sub>, in the dark with TiO<sub>2</sub> and under the simulated solar light in the presence of TiO<sub>2</sub>. The results obtained are presented in Figure 2. In the first experiment, in the presence of the simulated solar light only, no significant photodegradation effect was observed (about 3 %). In the second experiment, when TiO<sub>2</sub> was used, in the absence of the simulated solar light, the dye concentration initially falls to 85 %, as a result of adsorption. With time, the dye concentration increased due to desorption. In the third experiment, when the simulated solar light and TiO<sub>2</sub> were applied, a rapid degradation was observed. This suggests that the system was working in a pure photocatalytic regime.

Figure 3 shows the changes in the absorption spectra of RO16 solution in water during the photocatalytic degradation at different irradiation times. The RO16 textile dye shows four bands, out of which three bands are in the UV region and one band is in the

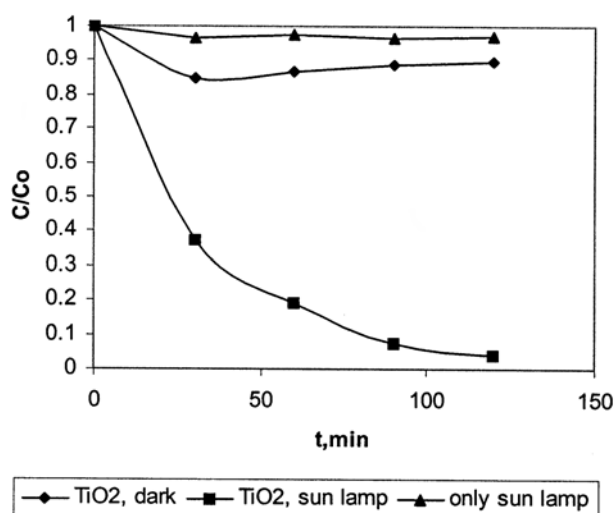


Figure 2. The effect of different experimental conditions on photodegradation of RO16 (initial dye concentration: 50 mg/l, initial concentration of TiO<sub>2</sub>: 2 g/l).

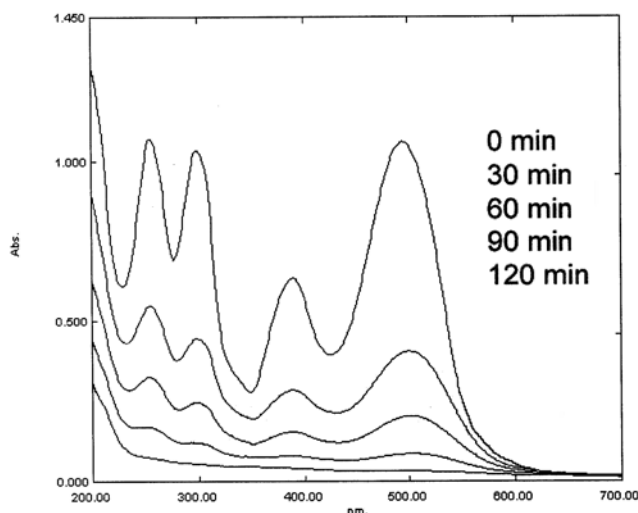


Figure 3. UV-vis spectra changes of RO16 (50 mg/l) in aqueous TiO<sub>2</sub> dispersion (TiO<sub>2</sub> concentration: 2 g/l) irradiated with the sun lamp.

visible region, with a maximum absorption at 493 nm. The decrease of absorption peaks indicates a rapid degradation of RO16 dye. A complete decolourization was observed after 2 hours of irradiation.

### The effect of the catalyst amount

All experiments were firstly carried out in the dark for 60 min, and then immediately irradiated by the sun lamp. The degradation curves (normalized concentration (C/Co, where C is concentration of RO16 and Co is the initial concentration of RO16) vs. time) shown in Figure 4, represent the effect of the amount of TiO<sub>2</sub> on the RO16 photodegradation. The photodegradation increased with the increased concentration of the photocatalyst, reached the highest value at 2.0 g/l and then decreased.

This may be due to the enhancement of light reflectance by the catalyst particles and the decrease in light penetration [3, 4]. It is also possible that, at higher TiO<sub>2</sub> concentration, all TiO<sub>2</sub> particles are not equally exposed to the sun lamp irradiation.

When all dye molecules are adsorbed on TiO<sub>2</sub>, the addition of higher quantities of TiO<sub>2</sub> has no effect on the photodegradation efficiency [4]. The photodegradation efficiency (X) is given by

$$X = (C_{eq} - C)/C_{eq} \tag{1}$$

where C<sub>eq</sub> is equilibrium concentration (at zero irradiation time) of RO16 in mg/l, C is concentration of RO16 at irradiation time t in mg/l. Figure 5 shows the effect of the amount of TiO<sub>2</sub> on the photodegradation efficiency of RO16 at irradiation time of 1.5 h. One can see that the highest photodegradation efficiency was achieved with the catalyst concentration of 2.0 g/l.

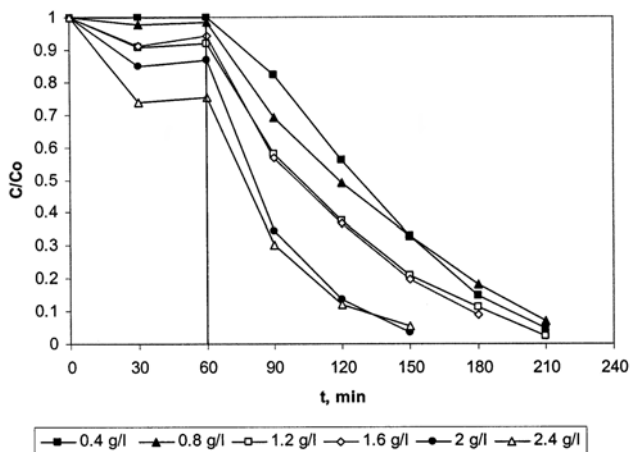


Figure 4. The effect of the initial concentration of TiO<sub>2</sub> on photodegradation of RO16 (dye concentration: 50 mg/l).

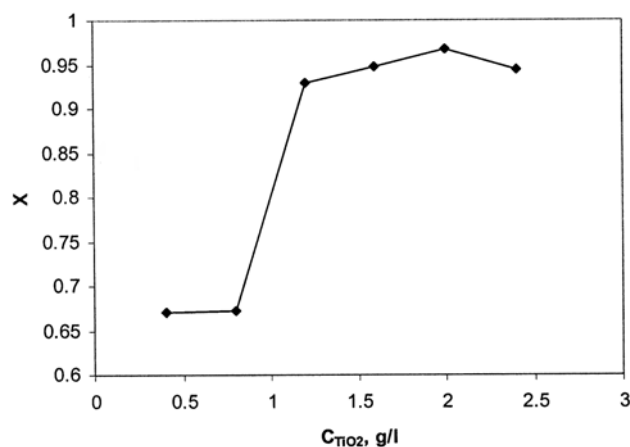


Figure 5. The effect of the concentration of TiO<sub>2</sub> on photodegradation efficiency of RO16 at irradiation time of 1.5 h (concentration of dye 50 mg/l).

The kinetics of photodegradation rate of most dyes [9,10,12] can be well described using a pseudo-first kinetic order, which is given by the following equations:

$$\ln (C_{eq}/C) = k \cdot t \tag{2}$$

$$C = C_{eq}e^{-k \cdot t} \tag{3}$$

where C<sub>eq</sub>, C and t are as given above, k is a pseudo-first order constant. For the reactions with the pseudo-first order, the half time of the reaction can be calculated using:

$$t_{1/2} = \ln 2/k \tag{4}$$

Using the given equations it is possible to calculate the pseudo-first order constant and the half time of the reaction, when different amounts of catalyst were used. The obtained data are presented in Table 1. It can be observed that the highest reaction rate was obtained with the catalyst concentration of 2.0 g/l. Further increase in the catalyst concentration leads to a decrease of the reaction rate. These results are in agreement with the published results on photodegradation of RO16 [10], where RO16 was irradiated using four parallel 15 W blacklight blue fluorescent tubes, with the maximum emission at 370 nm. The authors also found out that the TiO<sub>2</sub> concentration of 2.0 g/l was optimal for the photodegradation of RO16.

Table 1. The effect of the amount of TiO<sub>2</sub> on the RO16 photodegradation rate constant and half times of the reaction.

Concentration of TiO <sub>2</sub> g/l	k 10 <sup>-2</sup> min <sup>-1</sup>	R	t <sub>1/2</sub> min
0.4	1.69	0.942	41.01
0.8	1.51	0.976	45.90
1.2	2.89	0.997	23.98
1.6	3.12	0.995	22.21
2.0	3.64	0.994	19.04
2.4	3.38	0.981	20.50

**The effect of the initial dye concentration**

In addition, the effect of the initial dye concentration on photodegradation was studied and the results obtained are presented in Figure 6. The conclusion is that the increase in the initial dye concentration leads to a decrease in photodegradation of RO16. With the increase of dye concentration greater number of dye molecules are adsorbed on the surface of TiO<sub>2</sub>, which contributes to the inhibition effect of the reaction of dye molecules with holes, or hydroxyl radicals, due to the lack of any direct contact between them. The increased dye concentration also promotes the light adsorption by the dye molecules, and hence the photons cannot reach the photocatalyst surface causing the decrease of the photodegradation efficiency [4].

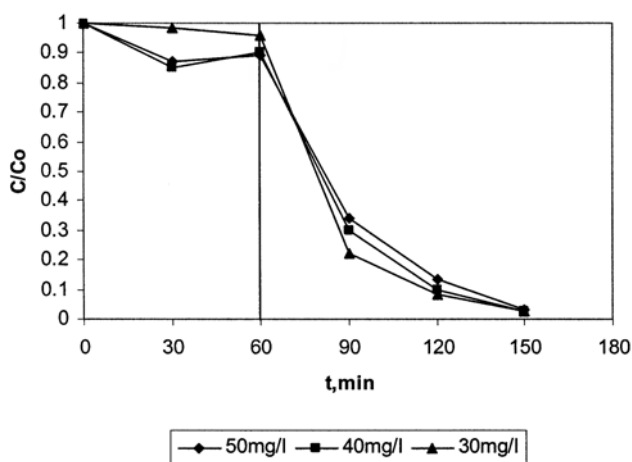


Figure 6. The effect of the initial dye concentration on photodegradation of RO16 (the initial  $\text{TiO}_2$  concentration: 2 g/l).

It is also possible to calculate the pseudo-first order constant and the half time of the reaction, when different initial dye concentrations are used by using equations 2 and 4. The results given in Table 2 show that the increase in the initial dye concentration (equilibrium concentration) leads to a lower photodegradation rate.

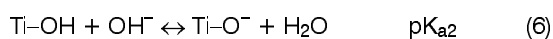
Table 2. The effect of the initial dye concentration on the RO16 photodegradation rate constant and half times of the reaction.

Initial dye concentration ( $C_{eq}$ , mg/l)	$k \cdot 10^{-2}$ , $\text{min}^{-1}$	$R$	$t_{1/2}$ , min
28.70	4.21	0.995	16.46
36.00	4.01	0.998	17.28
44.62	3.64	0.981	19.04

### The effect of pH

It is known that pH value has an influence on the photodegradation of some organic compounds in photocatalytic processes [13,14]. Photodegradation of RO16 was studied at five different pH values (1.45, 2.8, 6.0, 8.8 and 10.8). The third value is pH of a pure dye solution in deionised water.

It is also known that pH of the solution influences the adsorption of the dye molecules [15]. The change in adsorption can be explained by the intrinsic amphoteric behavior of suspended  $\text{TiO}_2$  and the acidic nature of the dye. It is known that metal oxide particles suspended in water behave similar to diprotic acids. For  $\text{TiO}_2$ , hydroxyl groups undergo the following acid-base equilibria:



where  $\text{TiOH}$  represents the titanol surface group and  $pK_{a1}$ ,  $pK_{a2}$  are the negative logs of the acidity constants for the first (Eq. (5)) and second (Eq. (6)) acid dissociation,

respectively. For Degussa P25,  $pK_{a1} = 4.5$  and  $pK_{a2} = 8.0$ , which yield a pH of zero point of charge equal to  $pH_{zpc} = 6.25$  [16]. On this basis, it is reasonable to expect that adsorption on  $\text{TiO}_2$  will depend on the electrical charge of the dye and the photocatalyst surface. RO16 has negatively charged sulfonic groups and it is expected that, at low pH, attractive forces between the  $\text{TiO}_2$  surface and the dye will favor adsorption. At high pH, the  $\text{TiO}_2$  surface is negatively charged and repulsive forces will lead to the decreased adsorption. At pH values close to the  $pH_{zpc}$ , the adsorption is expected to take intermediate values. The dependence of the adsorption capacity of  $\text{TiO}_2$  towards RO16 on the pH of the solution can be observed in Figure 7. The experimental data are in agreement with the explanation given above, since the pH of the solution affects the electrical properties of the  $\text{TiO}_2$  surface.

The results given in Figure 7 show(s) that there

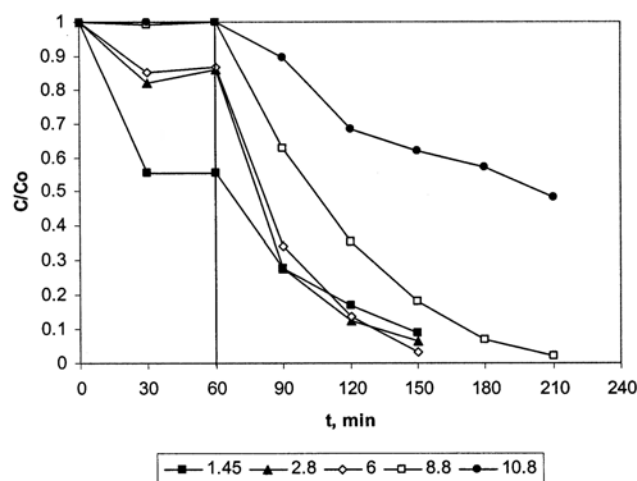


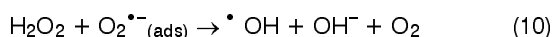
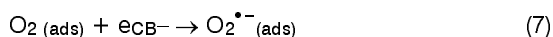
Figure 7. The effect of pH on photodegradation of RO16 (dye concentration: 50 mg/l, initial  $\text{TiO}_2$  concentration: 2 g/l).

was a strong dependence of the pH of the solution on the photodegradation of RO16. The degradation was faster in the acidic than in alkaline pH range. This probably has to do with the pH-dependence of the chemisorptive properties of  $\text{TiO}_2$ , as discussed above.

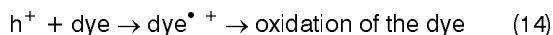
In the case of sulfonated dyes, a model has been proposed to account for the dramatic role played by pH in determining the critical step of the decomposition [17]. The description considers the charge status of both the target substrate and the catalyst surface by applying a simple electrostatic reasoning. Accordingly, the increase of bleaching recorded at acid pH was attributed to a strong dye adsorption on the catalyst, through the protonated  $-\text{SO}_3$  moiety. This favorable interaction would enhance the encounter probability of the nascent OH radicals with the organic dye. As opposed, at alkaline pH, the Coulombic repulsion arising between  $-\text{SO}_3$  and the negative oxide surface would make the dye access to the catalyst a diffusion-controlled

process. In this case, the OH radicals generated at the catalyst surface would attack the target molecule harder. The result, a slower decomposition, was measured.

The experimental results indicate that hole oxidation could be dominant in photodegradation of the dye in the acidic pH range [18]. On the other hand, OH radicals should be dominant in photodegradation in the alkaline pH range. The photodegradation by the OH radicals can be given by the following reactions [4, 6]:



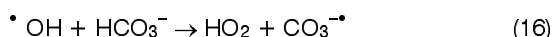
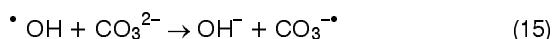
The role of holes can be depicted by:



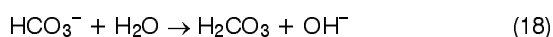
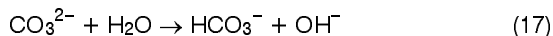
The results of the present work for RO16 are in good agreement with the model given in ref.[17] and are in agreement with the published results on photodegradation of RO16 [10] where it was found that the photodegradation is faster in the acidic than in alkaline pH range.

#### The effect of $\text{Na}_2\text{CO}_3$

Sodium carbonate is commonly used in textile processing. Therefore, the textile wastewaters contain a considerable amount of carbonate ions. We studied the effect of sodium carbonate using the concentration up to 2 % w/v. The obtained results are shown in Figure 8. No adsorption of the dye was observed in the presence of carbonate ions. Photodegradation in the presence of sodium carbonate (0.1 % w/v) was slower in comparison to the reaction without sodium carbonate. Contrary to expectations, the increase in carbonate concentration (1 and 2 % w/v) resulted in the increase in photodegradation even in comparison to the reaction without sodium carbonate. The decrease in the reaction in the presence of sodium carbonate is due to the hydroxyl scavenger property of carbonate ions [19]:



The increase in the reaction when the higher concentration of carbonate ions is present might be due to the formation of  $\text{OH}^-$  ions, which promotes the reaction [20]:



#### The effect of NaCl

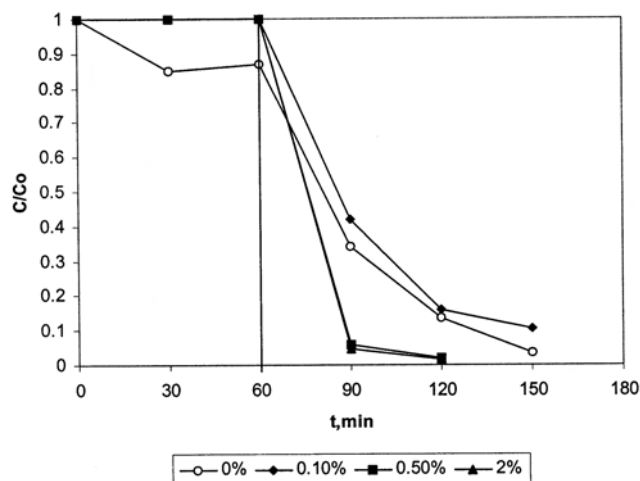


Figure 8. The effect of  $\text{Na}_2\text{CO}_3$  concentration on photodegradation of RO16 (dye concentration: 50 mg/l,  $\text{TiO}_2$  concentration: 2 g/l).

Chloride ion was employed to study the photodegradation of RO16. The influence of different concentrations of sodium chloride (0–2% w/v) on photodegradation of RO16 is given in Figure 9. The observed decrease of photodegradation of the dye in the presence of chloride ions is often explained by a competitive adsorption [9, 21] or by the hole scavenging properties of chloride ions [19, 21]:



While chlorine radicals are forming slowly, they are instantly converted into chloride anions. The surface site, normally available at the  $\text{TiO}_2$ /dye solution interface for the adsorption and the electron transfer from the dye to  $\text{TiO}_2$  conduction band, can be blocked by anions such as chloride, which are not oxidizable and are effective inhibitors for a detoxification process [19]. In such manner

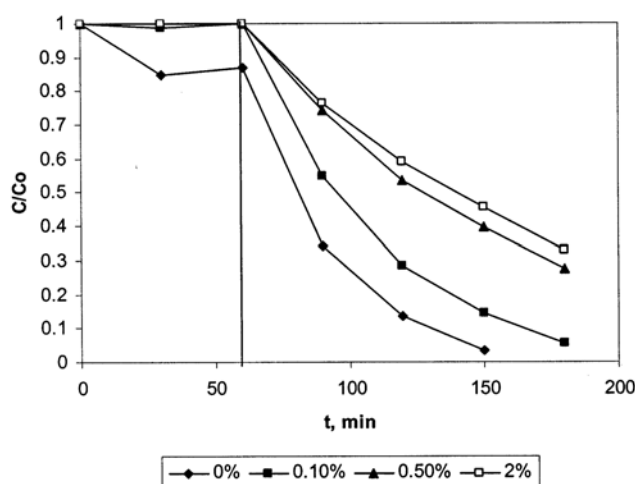
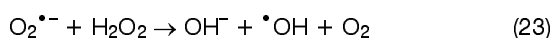
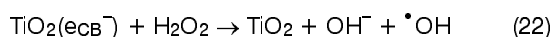


Figure 9. The effect of NaCl concentration on photodegradation of RO16 (dye concentration: 50 mg/l,  $\text{TiO}_2$  concentration: 2 g/l).

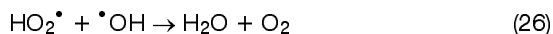
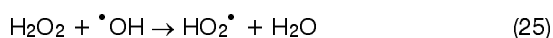
chloride anions inhibit the photodegradation by a competitive adsorption since a photosensitized degradation mechanism requires the adsorption of the dye on the semiconductor film and is very sensitive to the chemical composition of the surface [22].

### The effect of H<sub>2</sub>O<sub>2</sub>

The reaction rate and, consequently, the photodegradation efficiency, can be increased by increasing the concentration of hydroxyl radicals because these species are widely considered to be promoters of the photocatalytic degradation [23–27]. This increase in the concentration of hydroxyl radical could be explained by the following reactions [23]:



In this paper hydrogen peroxide was used in the concentration up to 612.6 mmol/l. The results obtained are presented in Figure 10. The photodegradation efficiency of RO16 was highest at hydrogen peroxide concentration of 12.25 mmol/l. At higher hydrogen peroxide concentrations, an inhibition effect was observed. This could be explained by the fact that H<sub>2</sub>O<sub>2</sub> acts at higher concentrations as a  $\cdot\text{OH}$  scavenger [24,26,27]:



The results obtained are similar to the previously reported results of RO16 photodegradation [12] where the photocatalytic efficiency increases up to the optimum at around 2 mmol/l of H<sub>2</sub>O<sub>2</sub> and then decreases with the increase of H<sub>2</sub>O<sub>2</sub> concentration.

### CONCLUSION

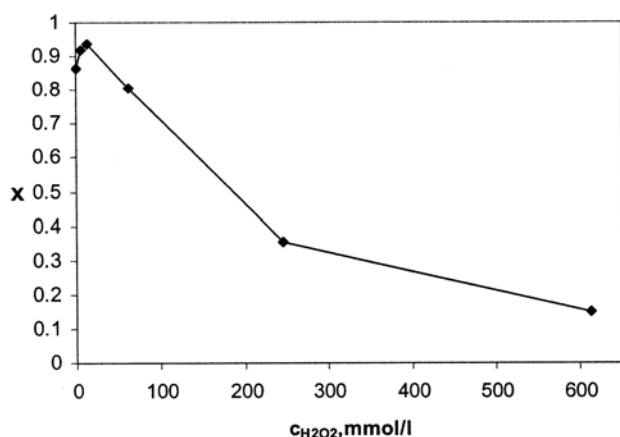


Figure 10. The effect of H<sub>2</sub>O<sub>2</sub> on photodegradation efficiency of RO16 after 60 min of irradiation (dye concentration: 50 mg/l, TiO<sub>2</sub> concentration: 2 g/l).

Photodegradation of C.I. Reactive Orange 16 has been studied using the simulated solar light and P-25 TiO<sub>2</sub>. The results obtained indicated that the photodegradation of RO16 was affected by the concentration of TiO<sub>2</sub>, the initial dye concentration and pH. The photodegradation increased with the increased concentration of the photocatalyst, reached the highest value at 2.0 g/l and then decreased. In the case of the initial dye concentration, the conclusion is that with the increase in the initial dye concentration there was a decrease in photodegradation of RO16. The degradation was faster in the acidic than in alkaline pH range. High adsorption of the dye was observed at low pH, while at high pH almost no adsorption was detected. Lower concentration of Na<sub>2</sub>CO<sub>3</sub> decreased the photodegradation of RO16, while higher concentration increased the photodegradation. The increase in the reaction at higher concentration of carbonate ions might be the result of the formation of OH<sup>-</sup> ions, which promote the reaction. The presence of NaCl led to the inhibition of the photodegradation process. The observed decrease of photodegradation of the dye in the presence of chloride ions could be explained by the competitive adsorption or by the hole scavenging properties of chloride ions. The low concentration of H<sub>2</sub>O<sub>2</sub> increased the RO16 photodegradation efficiency, while at higher concentration of H<sub>2</sub>O<sub>2</sub> inhibition was observed because H<sub>2</sub>O<sub>2</sub> acts at (the) higher concentrations as a  $\cdot\text{OH}$  scavenger.

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