

# Comparative study of UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution

Igor T. Peternel, Natalija Koprivanac<sup>\*</sup>, Ana M. Lončarić Božić, Hrvoje M. Kušić

*Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, Zagreb 10000, Croatia*

Received 20 November 2006; received in revised form 23 February 2007; accepted 27 February 2007

Available online 3 March 2007

## Abstract

In this study advanced oxidation processes (AOPs), UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton, were applied in order to degrade C.I. Reactive Red 45 (RR45) dye in aqueous solution. The effects of key operating parameters, such as initial pH, catalyst and hydrogen peroxide dosage as well as the effect of initial dye concentration on decolorization and mineralization extents were studied. Primary objective was to determine the optimal conditions for each of the processes. The influence of added zeolite on the process efficiency was also studied. UV/vis spectrophotometric and total organic carbon (TOC) measurements were performed for determination of decolorization and mineralization extents. It has been found that photo-Fenton process was the most efficient with 74.2% TOC removal and complete color removal achieved after a 1 h treatment.

© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Reactive dye; UV radiation; AOPs; Mineralization; Color removal

## 1. Introduction

Organic synthetic dyes represent relatively large group of organic chemicals, which are present in practically all spheres of mankind daily life. Dyes are all around us, they make our world beautiful, but they also bring pollution and therefore the community has to be focused on possible environmental problems caused by dye industries. The manufacturing and the processing of dyes involve the handling and the production of many organic compounds that are toxic and hazardous to human health [1,2]. Recent studies indicated that approximately 12% of synthetic dyes are lost annually during manufacturing and processing operations [3]. Color removal from textile wastewater has also been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but often due to their visibility in recipient waters.

Reactive azo dyes are the largest group of organic dyes with –N=N– group as a chromophore in the molecular structure and represent more than a half of the global dye production specially because of their wide usage in dyeing industries due to the simple dyeing procedure [4]. These reactive dyes belong mostly to

the non-biodegradable and recalcitrant type of water pollutants, which make activated sludge treatment methods inadequate. A long residence time for microorganisms to degrade such a pollutant is required, because they are affected by organic pollutant toxicity. More intense physical/chemical conditions are needed in order to remove dyes from the wastewater [5]. Physical treatment of colored wastewater requires a post-treatment to remove newly secondary waste. The chemical oxidation of toxic and hazardous organic pollutants, which are frequently present in surface waters and wastewaters, is often carried out by using single oxidants such as ozone, hydrogen peroxide, potassium permanganate, chlorine, etc. Among chemical methods, advanced oxidation processes (AOPs) are a class of processes based on generation of hydroxyl radicals, highly reactive species, which promote the oxidation of hazardous organic compounds [6]. Therefore, AOPs represent a potential alternative method able to decolorize and to reduce recalcitrant colored wastewater load. In recent years, various AOPs, including application of technologies, such as ozonation, peroxone, non-thermal plasma, Fenton, photo-Fenton, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub>, UV/ZnO, for degradation of organic compounds in wastewater have been developed and described by many authors [7–10]. Degradation of organic pollutants by Fenton type processes could be significantly accelerated in the presence of UV irradiation, resulting with complete mineralization of organic

<sup>\*</sup> Corresponding author. Tel.: +385 1 4597 124; fax: +385 1 4597 143.  
E-mail address: [nkopri@marie.fkit.hr](mailto:nkopri@marie.fkit.hr) (N. Koprivanac).

pollutants [11]. The use of TiO<sub>2</sub> and ZnO as semiconductor photocatalysts for environmental clean-up has been of great interest due to their high efficiency, photochemical stability, non-toxic nature and low cost, especially when sunlight is used as the source of irradiation. Photocatalytic methods with TiO<sub>2</sub> and ZnO catalysts were successfully applied to the decomposition of many organic contaminants, i.e. including azo dyes [12–16].

The principal objective of this study was to investigate the application of UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton processes, for degradation of reactive azo dye C.I. Reactive Red 45. Synthetic zeolites are microporous crystalline materials with well-defined structure and strong ability to act as catalyst for chemical reaction which take place within the internal cavities [17,18]. Assumption has been made that NH<sub>4</sub>ZSM-5 could enhance overall efficiency of investigated AOPs. The effects of key operating parameters such as catalyst loading, pH and H<sub>2</sub>O<sub>2</sub> concentration as well as the influence of initial dye concentration on the decolorization and mineralization extents were also studied. The intention was to determine the optimal condition for each process including the possible effect of added solid particles on process efficiency.

## 2. Experimental

### 2.1. Chemicals

C.I. Reactive Red 45 (RR45) was purchased from Ciba-Geigy and used without any purification. The chemical structure of studied reactive dye is shown in Fig. 1. The commercially available photocatalysts; TiO<sub>2</sub> (anatase, Aldrich, 99.7% nanopowder, surface area 190–290 m<sup>2</sup>/g) and ZnO (Aldrich, nanopowder, surface area 15–25 m<sup>2</sup>/g) were used as received. All other used chemicals; hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), potassium hydroxide (KOH, p.a.), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 96%) and ferrous sulfates (FeSO<sub>4</sub>·7H<sub>2</sub>O, p.a.) were supplied by Kemika, Croatia. Zeolite NH<sub>4</sub>ZSM-5 was obtained from Zeolyst International, USA.

### 2.2. Experimental procedure

All experiments were carried out in a batch waterjacketed photoreactor with the total capacity of 0.8 L. The irradiation source was a mercury lamp 125 W (UV-C, 254 nm), UVP-Ultra Violet Products, Cambridge, UK, which was placed in the inner quartz tube of the reactor as it was described elsewhere [11,19–21]. The incident UV-light flux at 254 nm,  $7.36 \times 10^{-6}$  Einstein s<sup>-1</sup>, was calculated on the basis of hydrogen peroxide actinometry measurements [22]. All experiments

were performed using initial dye concentration 80 mg/L, with exception of those related to the effect of initial dye concentration, where RR45 concentrations ranged from 20 to 120 mg/L. All model solutions were prepared by using deionised water with conductivity less than 1 μS/cm. The total solution volume for all applied experiments was 0.5 L. Duration of each experiment was 1 h. The initial pH values of model solutions were adjusted at desired level with the addition of KOH and H<sub>2</sub>SO<sub>4</sub> before the irradiation and not controlled during the course of the reaction. Minimum quantity of H<sub>2</sub>SO<sub>4</sub>, KOH, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an additional agent was added in order to minimize changes in the total volume of reaction mixture. The experiments were conducted by adjusting one parameter, while others were held constant. Mixing of model solution was provided by both the magnetic stirring bar and the peristaltic pump at a flow rate 0.1 L/min at temperature of 25 (±0.2) °C. Samples were taken periodically from the reactor (0, 15, 30, 45, and 60 min), centrifuged in order to remove solid particles and thereafter immediately analyzed. In the experiments with the addition of zeolites, 1 g/L of NH<sub>4</sub>ZSM-5 was added. All experiments were repeated three times and averages are reported.

### 2.3. Analytical methods

The initial and final pH values were measured by handy-lab pH/LF portable pH/conductivity-meter, Schott Instruments GmbH, Mainz, Germany. Decolorization of RR45 model solution was monitored at λ<sub>max</sub> = 520 nm by a Perkin-Elmer Lambda EZ 201 spectrophotometer. Mineralization extents of RR45 were determined on the basis of total organic carbon content (TOC) measurements, performed by Total Organic Carbon analyzer; Shimadzu TOC-V<sub>CPN</sub>, Japan.

## 3. Results and discussion

According to the literature and our previous investigations [6,11,19,20,23–26], the oxidation power of chemical, photochemical and photocatalytic AOPs is influenced by several operating parameters: catalysts loading, oxidant concentration, pH, treatment time, temperature, source and power of irradiation, reactor configuration, etc. Therefore, it is necessary to find optimal process parameters through the laboratory treatability tests. Thus, in this paper series of experiments were conducted in order to establish optimal values of changeable parameters: catalysts loading and pH for both photocatalytic processes, as well as pH and initial H<sub>2</sub>O<sub>2</sub> concentrations for photo-Fenton process.

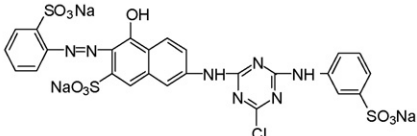
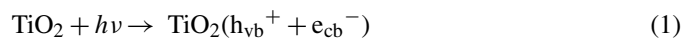
| Dye  | Name                 | Structure  | λ <sub>max</sub> (nm) |
|------|----------------------|--|-----------------------|
| RR45 | C.I. Reactive Red 45 |  | 520                   |

Fig. 1. Molecular structure of C.I. Reactive Red 45 (RR45) azo reactive dye.

Preliminary experiments where RR45 model solution was irradiated by UV light, partial decolorization, 30.3%, and negligible mineralization, 3.0% of TOC removal, were obtained. Further experiments were conducted in the dark due to the investigation of color removal by simple adsorption on TiO<sub>2</sub> and ZnO photocatalysts, and it was found no color removal after 60 min treatment.

### 3.1. UV/TiO<sub>2</sub> process

With the purpose to improve photochemical process of RR45 decolorization and mineralization TiO<sub>2</sub> as catalyst was added. As in all AOPs, generated OH radicals are considered to be the main oxidative species in UV/TiO<sub>2</sub> process (Eqs. (1)–(5)) [12]:



Series of experiments were conducted in order to optimize initial pH and TiO<sub>2</sub> dosage as predominant factors influencing decolorization and mineralization rates of organic compounds by UV/TiO<sub>2</sub> process. The pH value of RR45 model solution was 5 and the first set of experiments was conducted by changing TiO<sub>2</sub> dosage from 0.0 to 2.0 g/L without further pH adjustments. Results are presented in Fig. 2. It can be seen that the efficiency of photodegradation increases with an increase in catalyst dosage up to 0.5 g/L TiO<sub>2</sub>, and then starts to decrease. Thus, the highest RR45 model solution degradation, meaning 59.0% color and 23.0% TOC removal, was observed with 0.5 g/L of TiO<sub>2</sub>. Lower dye degradation in the cases with TiO<sub>2</sub> dosages below 0.5 g/L could be explained by the fact that catalyst surface and absorption of UV irradiation by the catalyst are the limiting factors. The increase in the amount of catalyst increased the num-

ber of active sites on the photocatalytic surface, which in turn, increased the number of hydroxyl and superoxide radicals. Also, after reaching the optimal level of photocatalyst, further increasing of photocatalyst dosage does not increase color removal. According to Daneshvar et al. [27], when all dye molecules are adsorbed on the TiO<sub>2</sub>, the addition of higher quantities of TiO<sub>2</sub> would have no effect on further process efficiency. Moreover, above the optimal loading of photocatalyst, increase in turbidity of the solution reduces the light transmission through the dye solution negatively influencing degradation of organic pollutants present in wastewater [15], which is very obvious in our case at the catalyst dosage over 0.5 g/L (Fig. 2).

Due to the amphoteric behavior of most semiconductor oxides, an important parameter governing the rate of reaction taking place on semiconductor particle surface is the pH of the dispersions since it influences the surface-charge properties of the photocatalysts. Therefore, the reactivity of UV/TiO<sub>2</sub> process also depends on pH value of the medium. The experiments were conducted in order to investigate the effect of pH in the range 2–12 on the process efficiency at established optimal TiO<sub>2</sub> dosage (0.5 g/L). Results are presented in Fig. 3. As it can be seen, strong acid conditions favor dye degradation by UV/TiO<sub>2</sub> process. Thus, the highest decolorization and mineralization extents were obtained at pH 3, with 71.0% color and 30.1% TOC removal, respectively. Increase of pH value to 5–12 resulted with gradual decrease of decolorization and mineralization efficiency, with the lowest color removal of 51.3% and TOC removal of 14.8% obtained at pH 12. According to the zero point charge of TiO<sub>2</sub> (pH around 7) its surface is presumably positively charged in acidic and negatively in basic medium. When the organic dye as a contaminant contains negatively charged sulfonate groups in the structure, acidic solution favors adsorption of the dye onto TiO<sub>2</sub> surface, thus increasing degradation efficiency of photocatalytic process [28,29]. That could be a plausible explanation for relatively low decolorization and mineralization extents of RR45 at pH > 3, obtained in this study.

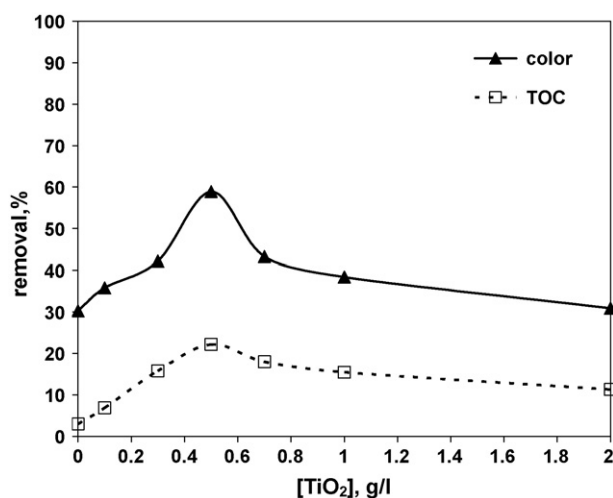


Fig. 2. Effect of TiO<sub>2</sub> dosage on color and TOC removal by UV/TiO<sub>2</sub> (pH 5, [RR45] = 80 mg/L).

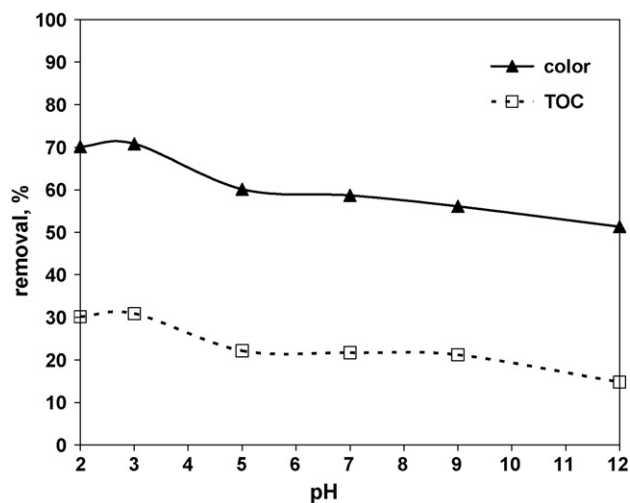


Fig. 3. Effect of initial pH on color and TOC removal by UV/TiO<sub>2</sub> ([TiO<sub>2</sub>] = 0.5 g/L, [RR45] = 80 mg/L).

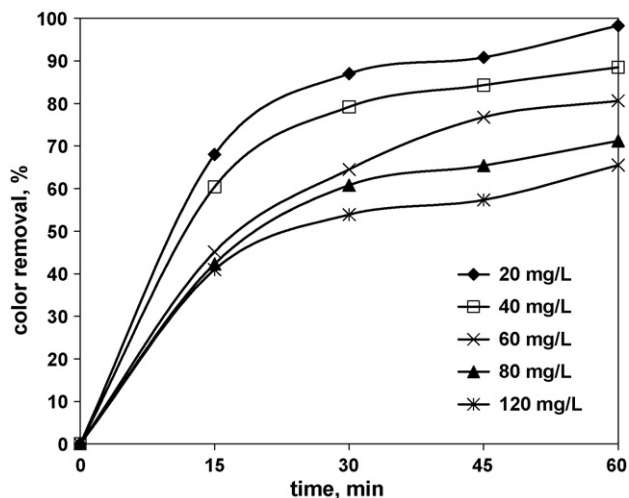
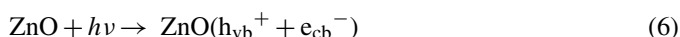


Fig. 4. Effect of initial dye concentration on decolorization rate by UV/TiO<sub>2</sub> (pH 3, [TiO<sub>2</sub>] = 0.5 g/L).

The pollutant concentration is also very important parameter in the wastewater treatment. The effect of various initial RR45 dye concentrations on photocatalytic decolorization by UV/TiO<sub>2</sub> process at above established optimal conditions (pH 3, [TiO<sub>2</sub>] = 0.5 g/L) has been investigated in the range of 20–120 mg/L and the results are presented in Fig. 4. It can be noticed that increase in the initial dye concentration from 20 to 120 mg/L resulted with a decrease in the initial rate of RR45 decolorization and consequently final color removal extents after a 1 h treatment ranged from 98.3% to 65.5%, respectively. Plausible explanation is given by Muruganandham and Swaminathan [30]. When the initial dye concentration increases, the amount of dye adsorbed on the catalytic surface also increases. This reduces the light absorption of the catalyst consequently lowering the catalytic activity. The increase in dye concentration decreases solution transparency, and consequently the path length of photon entering into the dye solution also decreases. At higher dye concentration, a significant amount of UV light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency.

### 3.2. UV/ZnO process

Degradation of organic pollutants present in wastewater can be also accomplished by photocatalytic process using ZnO as an alternative to TiO<sub>2</sub>. The pathway of OH radical generation is similar to that of UV/TiO<sub>2</sub>, thus can be described by Eqs. (6) and (2)–(5) [12]:



The advantage of ZnO in comparison to TiO<sub>2</sub> is that it absorbs over a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm. It is also suitable since its photodegradation mechanism has been proven to be similar to that of TiO<sub>2</sub> [27].

Similarly like for UV/TiO<sub>2</sub> process, the set of experiments was performed in order to determine the optimal catalyst dosage.

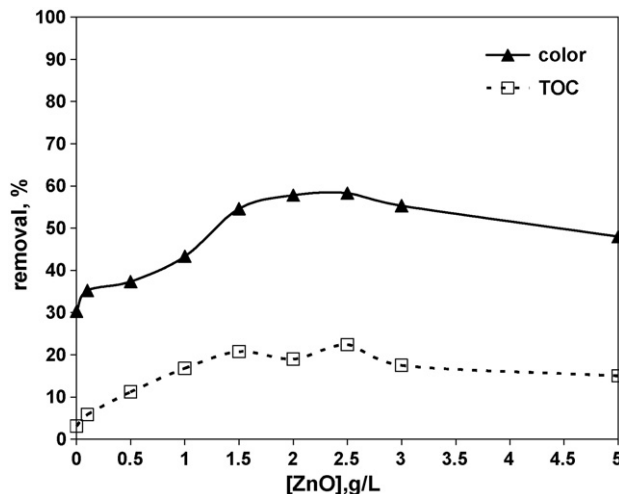


Fig. 5. Effect of ZnO dosage on color and TOC removal by UV/ZnO (pH 5, [RR45] = 80 mg/L).

Amount of added ZnO ranged from 0.0 to 5.0 g/L (Fig. 5), while pH was not adjusted. It can be seen that by increasing of initial ZnO dosage, decolorization and mineralization of RR45 also increased up to the achievement of certain optimal level. Maximal dye degradation, 58.3% color and 22.4% TOC removal, was obtained when 2.5 g/L of ZnO was added. Leveling off of the curve catalyst dosage versus removal demonstrated in Fig. 5 can be contributed to the same phenomena described for the addition of catalyst dosage over optimal in UV/TiO<sub>2</sub> process. Although similar final extents of decolorization and mineralization of RR45 were obtained by both UV/TiO<sub>2</sub> and UV/ZnO process (Figs. 2 and 5), it should be emphasized that five times higher dosage of ZnO than TiO<sub>2</sub> was required to reach the same maximal dye degradation extent, indicating lower catalytic activity of ZnO. Daneshvar et al. [27,28] reported similar observation in their study of photocatalytic degradation in an azo dye.

Further investigation was directed to determination of optimal pH for RR45 degradation by UV/ZnO process at above established optimal catalyst dosage, [ZnO] = 2.5 g/L. The effect of initial pH on photodegradation efficiency of RR45 solution was examined in the range of 3–11. It can be seen from Fig. 6 that the highest decolorization, 60.1%, and mineralization, 31.0%, extents by UV/ZnO process were obtained at pH 7. Since pH of zero point charge for ZnO is about 9, below that pH value active sites on positively charged catalyst surface are preferentially covered by dye molecules bearing sulfonate anions resulting with relatively high surface concentration of dye and low surface concentration of hydroxyl radicals. Inverse situation on surface occurs above pH 9 [31]. Surface reaction rate depends on both dye and hydroxyl radical concentration; hence, photocatalytic processes should be conducted at optimal pH determined from the extreme points of curve pH versus degradation, i.e. pH yielding with the highest color and TOC removal were obtained (Fig. 6). Advantage of UV/ZnO in comparison to UV/TiO<sub>2</sub> process is its performance at neutral pH, which is preferable from the operational and environmental point of view.

Like in the case of UV/TiO<sub>2</sub> process, the effect of initial dye concentration, in the range from 20 to 120 mg/L, at

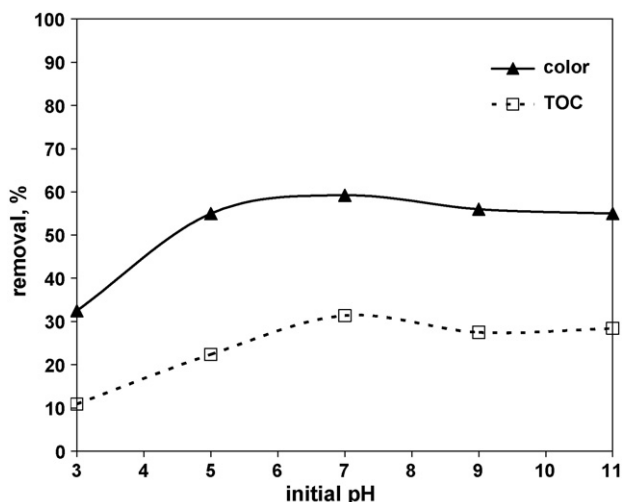


Fig. 6. Effect of initial pH on color and TOC removal by UV/ZnO ( $[\text{ZnO}] = 2.5 \text{ g/L}$ ,  $[\text{RR45}] = 80 \text{ mg/L}$ ).

above established optimal parameters (pH 7,  $[\text{ZnO}] = 2.5 \text{ g/L}$ ) for RR45 degradation by UV/ZnO process was investigated. It can be observed from Fig. 7 that percentage of color removal decreases with increasing initial dye concentration of model solution. Decolorization of model solution, RR45 20 mg/L, reached 99.3% by UV/ZnO process, which is similar to the result obtained by UV/TiO<sub>2</sub> process at same initial dye concentration (Fig. 4). Also, like in the case of UV/TiO<sub>2</sub> process, the initial rate of decolorization is decreasing with the increase of initial dye concentration. However, it should be emphasized that this effect is more pronounced in the case of UV/ZnO process and that final decolorization extents are correspondingly lower.

### 3.3. Photo-Fenton process

The next applied UV-based process for RR45 degradation in this study was UV enhanced Fenton process. Generally, Fenton type processes are proven to be rather efficient for degradation of

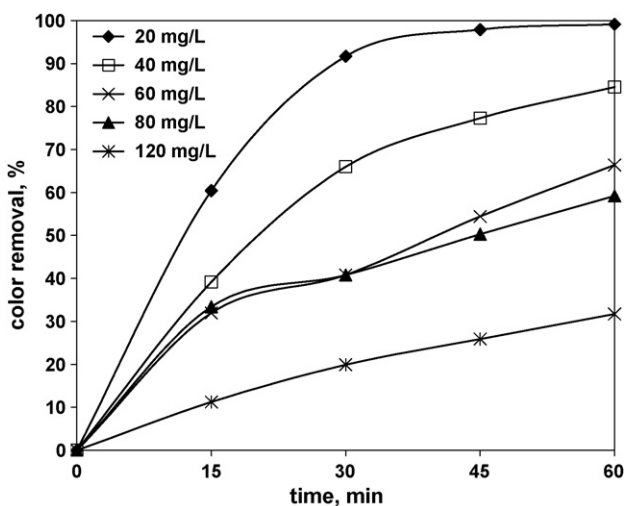
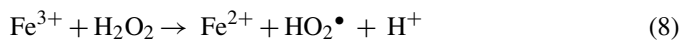
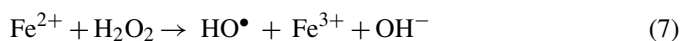


Fig. 7. Effect of initial dye concentration on decolorization rate by UV/ZnO (pH 7,  $[\text{ZnO}] = 2.5 \text{ g/L}$ ).

various types of organic pollutants in colored wastewater. Those processes are considered as homogeneous catalytic processes due to the catalytic role of iron in Fenton reagent (Eqs. (7)–(9)) [11,32]:



Generated OH radicals play major role in degradation of organic pollutants. In photo-Fenton type processes, additional sources of OH radicals should be considered: through photolysis of H<sub>2</sub>O<sub>2</sub>, Eq. (10), and through reduction of Fe<sup>3+</sup> ions under UV light, Eq. (11) [23,24]:



The efficiency of Fenton type processes is influenced by several operating parameters. In this study effect of initial H<sub>2</sub>O<sub>2</sub> concentration, pH and initial dye concentration on the efficiency of photo-Fenton process was investigated, while concentration of ferrous salt was 0.5 mM, previously found to be optimal for degradation of RR45 by dark Fenton process [33].

Fig. 8 summarizes the relationship between RR45 dye degradation and the initial H<sub>2</sub>O<sub>2</sub> concentration in the photo-Fenton process in terms of decolorization and mineralization process efficiency. It can be observed that RR45 model solution decolorized completely with the addition of Fenton reagent. Thus, it can be concluded that Fenton reagent ratio does not influence the decolorization efficiency by photo-Fenton in investigated range  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:20\text{--}100$ . On the other hand, partial mineralization was obtained. The addition of H<sub>2</sub>O<sub>2</sub> from 10 to 30 mM increased mineralization extents from 53.1% to 74.2% of TOC removal. Further increase from 30 to 50 mM of the H<sub>2</sub>O<sub>2</sub> caused decrease of mineralization efficiency from 74.2% to 30.6%. Hence, the ratio of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:60$  was found to

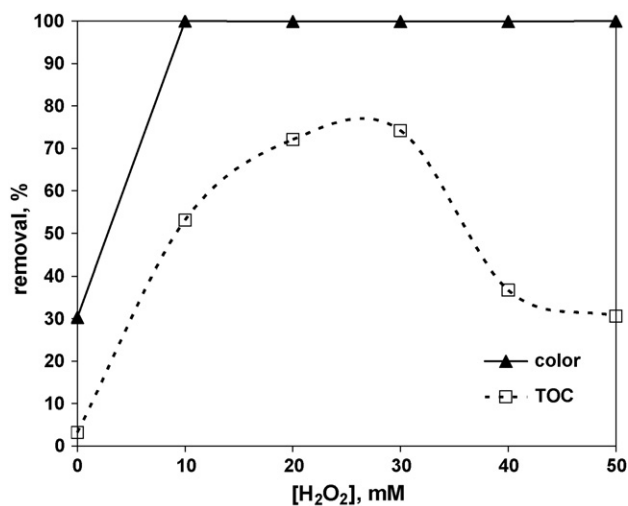
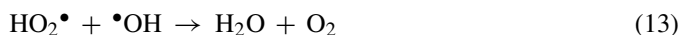
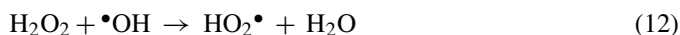


Fig. 8. Effect of initial H<sub>2</sub>O<sub>2</sub> dosage on color and TOC removal by photo-Fenton ( $[\text{Fe}^{2+}] = 0.5 \text{ mM}$ , pH 3,  $[\text{RR45}] = 80 \text{ mg/L}$ ).

be optimal at pH 3 and  $c(\text{Fe}^{2+}) = 0.5 \text{ mM}$ . The generation of OH radicals in photo-Fenton process is carried out through two main mechanisms, Fenton reaction (7) and photolysis of  $\text{H}_2\text{O}_2$  (10). In comparison to these two mechanisms the formation of OH radicals through reduction of  $\text{Fe}^{3+}$  ions (11) is considered negligible. According to our previous investigations of dark Fenton and UV/ $\text{H}_2\text{O}_2$  process [11,20,34] process efficiency, i.e. generation of OH radicals through reactions (7) and (8), respectively, is strongly influenced by the concentration of  $\text{H}_2\text{O}_2$ . Thus, in photo-Fenton process the concentration of  $\text{H}_2\text{O}_2$  is also limiting factor for degradation of organic pollutants in wastewater. Generally, by increasing  $\text{H}_2\text{O}_2$  concentration, the bulk concentration of OH radicals also results with higher process efficiency. However, after reaching an optimal value, further boost of  $\text{H}_2\text{O}_2$  concentration negatively influence process efficiency due to the pronounced behavior of  $\text{H}_2\text{O}_2$  as a radical scavenger (Eqs. (12) and (13)) [11,20,23,32]:



The equilibrium of ferrous/ferric ions and consequently generation of OH radicals are pH dependent. Therefore, pH is an important parameter influencing efficiency of Fenton type processes. In this study the effect of initial pH, in the range 2–6, on decolorization and mineralization of RR45 model solution by photo-Fenton process was investigated (Fig. 9). As it was expected, the complete decolorization was achieved in the complete investigated pH range at above established optimal  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  ratio. Rather high mineralization extents,  $\geq 50\%$ , were obtained, as presented in Fig. 9. The highest TOC removal, 74.2%, was achieved at pH 3. The same pH was found to be optimal in dark Fenton process [33], while optimal pH for UV/ $\text{H}_2\text{O}_2$  process was found to be 6 [21]. Therefore, it can be concluded that the predominate mechanism controlling photo-Fenton efficiency is generation of OH radicals through Fenton catalytic cycle. Decrease in process efficiency below pH 3 can be con-

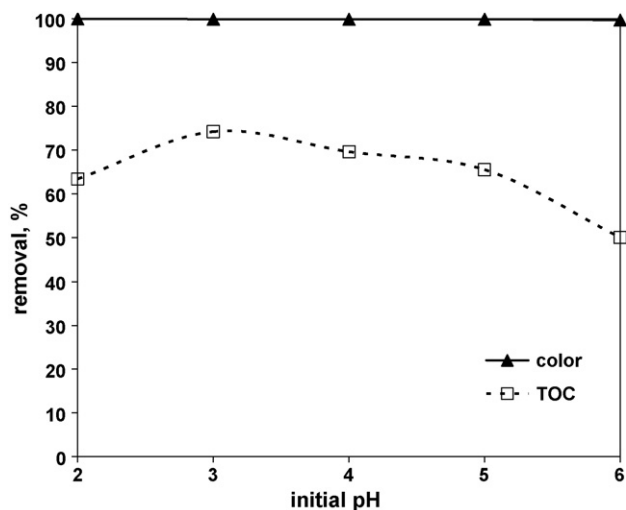


Fig. 9. Effect of initial pH on color and TOC removal by photo-Fenton ( $[\text{Fe}^{2+}] = 0.5 \text{ mM}$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:30$ ,  $[\text{RR45}] = 80 \text{ mg/L}$ ).

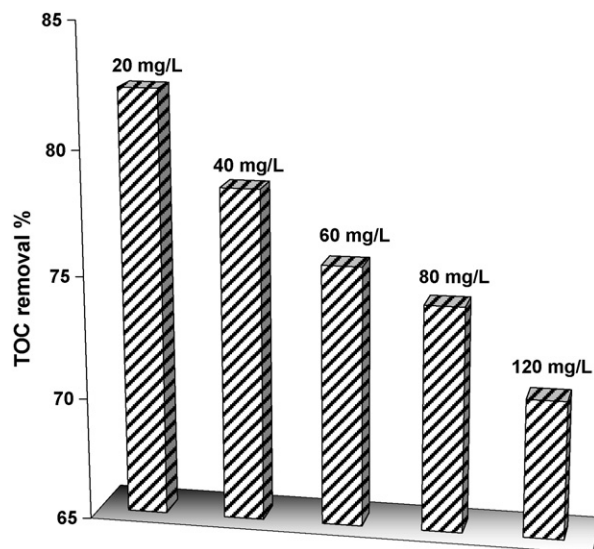


Fig. 10. Effect of initial dye concentration on final mineralization degree by photo-Fenton ( $[\text{Fe}^{2+}] = 0.5 \text{ mM}$ , pH 3,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:30$ ).

tributed to the enhanced stability of  $\text{H}_2\text{O}_2$  and reduced reactivity with ferrous ions. On the other hand, at higher pHs precipitated iron in a form of hydroxides is excluded from Fenton catalytic cycle [24,35].

Like in previous experiments of photocatalytic degradation of RR45 by UV/ $\text{TiO}_2$  and UV/ $\text{ZnO}$  processes, the effect of dye loading in model solution was investigated in the range of 20–120 mg/L. Results presenting final TOC removals after a 1 h treatment are summarized in Fig. 10. As it was expected, correspondingly higher mineralization extents were obtained by lowering initial dye concentration from 80 to 20 mg/L. The increment of initial dye contraction leads to lower TOC removal too. However, it should be emphasized that overall differences in TOC removal are rather small in investigated range of initial RR45 concentration (Fig. 10).

#### 3.4. Influence of zeolites

Due to the specific properties of synthetic zeolites and their ability to act as catalysts and/or adsorbents, the intention was to investigate whether ZSM-5 type of zeolite can act as a photocatalyst in UV/ZSM-5 process or cause a synergistic effect in a heterogeneous mixture with photocatalyst, which can contribute to the overall effectiveness of investigated UV-based AOPs. In Fig. 11, decolorization rates of RR45 by UV, UV/ $\text{NH}_4\text{ZSM-5}$ , UV/ $\text{TiO}_2$ , UV/ $\text{TiO}_2/\text{NH}_4\text{ZSM-5}$ , UV/ $\text{ZnO}$  and UV/ $\text{ZnO}/\text{NH}_4\text{ZSM-5}$  at earlier established optimal conditions for each of processes are compared. It can be seen that the addition of zeolite caused no significant changes in decolorization of RR45 during the time course. It should be emphasized that previous study showed that parent dye molecule cannot be adsorbed/penetrated onto/into  $\text{NH}_4\text{ZSM-5}$  [36]. From the comparison of results of RR45 decolorization present in Fig. 11, it can be seen that photocatalytic activity of  $\text{NH}_4\text{ZSM-5}$  zeolite is rather negligible, resulting with improvement in overall color removal up to 6% after a 1 h treatment.

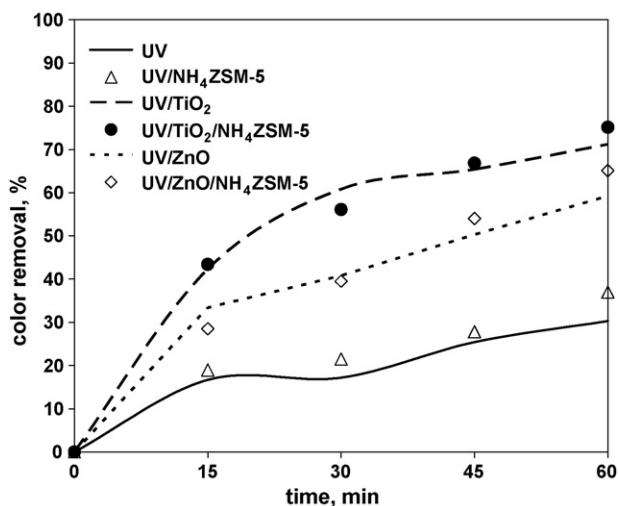


Fig. 11. Influence of NH<sub>4</sub>ZSM-5 zeolite on decolorization rate by UV, UV/TiO<sub>2</sub> and UV/ZnO processes at established optimal parameters ([RR45] = 80 mg/L).

Due to the complete decolorization of RR45 obtained by photo-Fenton process, influence of zeolite on overall process efficiency was estimated on the basis of TOC removal (Fig. 12). It can be seen that with the addition of NH<sub>4</sub>ZSM-5, TOC removal was increased from 74.2% to 85.4%. Although demonstrated photocatalytic activity of zeolite in UV/NH<sub>4</sub>ZSM-5 is rather small (Fig. 11), it should not be ignored in photo-Fenton/NH<sub>4</sub>ZSM-5 process too. Besides photocatalytic effect, adsorption of organic dye by-products of appropriate size into NH<sub>4</sub>ZSM-5 zeolite should be taken into account. Namely, the findings of our previous study where scanned IR spectrograms of zeolites after the treatment with dark Fenton/NH<sub>4</sub>ZSM-5 process showed new peaks which corresponded to possible dye degradation by-products, indicating to the role of zeolites as adsorbents [34]. Furthermore, Kawai and Tsutsumi [37] reported that NH<sub>4</sub>ZSM-5 zeolite can adsorb phenol, and the same was confirmed in our previous study [38]. Generally, if phenol can

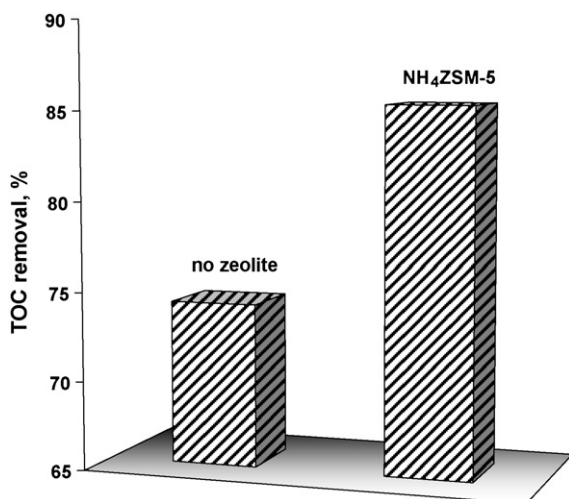


Fig. 12. Influence of NH<sub>4</sub>ZSM-5 zeolite on overall TOC removal by photo-Fenton process at established optimal parameters ([RR45] = 80 mg/L).

be adsorbed, it can be assumed that mono-substituted benzenes could also be removed from the aqueous solution by adsorption on/in NH<sub>4</sub>ZSM-5 zeolite. Furthermore, Feng et al. [39] proposed degradation mechanism of reactive dye with similar structure like RR45. They reported that after initial cleavage of azo bonds, in the bulk are remained mono- and di-substituted benzenes and naphtholes and triazine rings. Moreover, Styliadi et al. [40] detected phenol and other mono-substituted benzenes as by-products of azo dye degradation by OH radicals. Therefore, it can be concluded that both photocatalytic and adsorptive properties of NH<sub>4</sub>ZSM-5 contribute to the overall effectiveness of UV-based processes applied in the study.

#### 4. Conclusions

Applied UV-based AOPs, UV/TiO<sub>2</sub>, UV/ZnO and photo-Fenton, for degradation of RR45 were compared on the basis of decolorization and mineralization extents at established optimal parameters for each of processes. Complete decolorization of RR45 model solution was obtained only by photo-Fenton process throughout the complete range of all investigated parameters. Established optimal operating conditions of photocatalytic processes, UV/TiO<sub>2</sub> (pH 3, [TiO<sub>2</sub>] = 0.5 g/L) and UV/ZnO (pH 7, [ZnO] = 2.5 g/L), yielded with 71.0% and 60.1% of color removal, respectively. Similar mineralization extents, approximately 30% of TOC removal, were obtained by UV/TiO<sub>2</sub> and UV/ZnO processes. Significantly higher mineralization of RR45, 74.2% TOC removal, was achieved by photo-Fenton process, as it was expected. The poor photocatalytic activity of NH<sub>4</sub>ZSM-5 was demonstrated in all cases. Adsorptive properties of added zeolite have been taken into account in the case photo-Fenton process/NH<sub>4</sub>ZSM-5. The formation of smaller by-products of dye degradation and their adsorption into zeolite pores was assumed, thus contributing to the overall process efficiency.

#### Acknowledgement

The financial support from the Ministry of Education, Science, and Sport (Croatia) (project #0125–018) is gratefully acknowledged.

#### References

- [1] H. Zollinger, Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments, VCH Publishers, Weinheim, Germany, 1987.
- [2] F.P. Van der Zee, G. Lettinga, J. Field, Azo dye decolorisation by anaerobic granular sludge, Chemosphere 44 (2001) 1169–1176.
- [3] A. Reife, H.S. Freeman, Environmental Chemistry of Dyes and Pigments, John Wiley and Sons Inc., Canada, 1996.
- [4] C. Zhu, L. Wang, L. Kong, X. Yang, L. Wang, S. Zheng, F. Chen, F. MaiZhi, H. Zong, Photocatalytic degradation of AZO dyes by supported TiO<sub>2</sub> + UV in aqueous solution, Chemosphere 41 (2000) 303–309.
- [5] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigments 52 (2002) 69–78.
- [6] R. Gogate, B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

- [7] J. Prado, J. Arantegui, E. Chamarro, S. Esplugas, Degradation of 2,4-D by ozone and light, *Ozone: Sci. Eng.* 16 (1994) 235–254.
- [8] Y.S. Shen, Y. Ku, K.C. Lee, The effect of light absorbance on the decomposition of chlorophenols by UV radiation and UV/H<sub>2</sub>O<sub>2</sub> processes, *Water Res.* 29 (1995) 907–914.
- [9] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, *Chemosphere* 58 (2005) 1409–1414.
- [10] N. Koprivanac, H. Kušić, D. Vujević, I. Peternel, B.R. Locke, Influence of iron on degradation of organic dyes in corona, *J. Hazard. Mater.* 117 (2005) 113–119.
- [11] H. Kusic, N. Koprivanac, A. Loncaric Bozic, I. Selanec, Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study, *J. Hazard. Mater.* 136 (2006) 632–644.
- [12] P. Pichat, Photocatalytic degradation of pollutants in water and air: basic concepts and applications, in: M.A. Tarr (Ed.), *Chemical Degradation Methods for Wastes and Pollutants—Environmental and Industrial Applications*, Marcel Dekker Inc., New York, USA, 2003, pp. 77–121.
- [13] Z. Haoqiang, T. He, Photocatalytic degradation of acid azo dyes in aqueous TiO<sub>2</sub> suspension. Part I. The effect of substituents, *Dyes Pigments* 37 (1998) 231–239.
- [14] C. Hu, Y. Tang, J.C. Yu, P.K. Wong, Photocatalytic degradation of cationic blue X-GRL adsorbed on TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst., *Appl. Catal. B* 40 (2003) 131–140.
- [15] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO<sub>2</sub>, *Sol. Energy Mater. Sol. Cells* 77 (2003) 65–82.
- [16] C.G. Silva, J.L. Faria, Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation, *J. Photochem. Photobiol. A* 155 (2003) 133–143.
- [17] K. Smith, New developments in selective aromatic substitution with the help of solid catalysts, in: B.K. Hodnett, A.P. Kybett, J.H. Clark, K. Smith (Eds.), *Supported Reagents and Catalysts in Chemistry*, The Royal Society of Chemistry, Cambridge, 1998, pp. 31–37.
- [18] A.A.G. Tomlinson, *Modern Zeolites Structure and Function in Detergents and Petrochemicals*, Trans Tech Publications, Zurich, Switzerland, 1998.
- [19] H. Kusic, N. Koprivanac, L. Srsan, Azo dye degradation using Fenton type processes assisted by UV irradiation: a kinetic study, *J. Photochem. Photobiol. A* 181 (2006) 195–202.
- [20] H. Kusic, N. Koprivanac, A. Loncaric Bozic, Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies, *Chem. Eng. J.* 123 (2006) 127–137.
- [21] I. Peternel, N. Koprivanac, H. Kusic, UV-based processes for reactive azo dye mineralization, *Water Res.* 40 (2006) 525–532.
- [22] I. Nicole, J. De Laat, M. Dore, J.P. Duguet, C. Bonnel, Utilisation du rayonnement ultraviolet dans le traitement des eaux: mesure du flux photonique par actinometrie chimique au peroxyde d'hydrogene: Use of U.V. radiation in water treatment: measurement of photonic flux by hydrogen peroxide actinometry, *Water Res.* 24 (1990) 157–168.
- [23] F.J. Beltran, Ozone-UV radiation-hydrogen peroxide oxidation technologies, in: M.A. Tarr (Ed.), *Chemical Degradation Methods for Wastes and Pollutants—Environmental and Industrial Applications*, Marcel Dekker Inc., New York, USA, 2003, pp. 1–77.
- [24] M.A. Tarr, Fenton and modified Fenton methods for pollutant degradation, in: M.A. Tarr (Ed.), *Chemical Degradation Methods for Wastes and Pollutants—Environmental and Industrial applications*, Marcel Dekker Inc., New York, USA, 2003, pp. 165–200.
- [25] S. Papic, N. Koprivanac, A. Loncaric Bozic, D. Vujevic, S.K. Dragicevic, H. Kusic, I. Peternel, AOPs in azo dye wastewater treatment, *Water Environ. Res.* 78 (2006) 572–579.
- [26] <http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html>.
- [27] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO<sub>2</sub>, *J. Photochem. Photobiol. A* 162 (2004) 317–322.
- [28] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, *J. Photochem. Photobiol. A* 157 (2003) 111–116.
- [29] E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz, O. Erbatur, Comparison of several advanced oxidation processes for the decolorization of Reactive Red 120 azo dye in aqueous solution, *J. Hazard. Mater.* 109 (2004) 85–93.
- [30] M. Muruganandham, M. Swaminathan, TiO<sub>2</sub>–UV photocatalytic oxidation of Reactive Yellow 14: effect of operational parameters, *J. Hazard. Mater.* 135 (1–3) (2006) 78–86.
- [31] A. Akoyol, H.C. Yatmaz, M. Bayramoglu, Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions, *Appl. Catal. B* 54 (2004) 19–24.
- [32] R. Chen, J.J. Pignatello, Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds, *Environ. Sci. Technol.* 31 (1997) 2399–2406.
- [33] I. Peternel, N. Koprivanac, A. Loncaric Bozic, S. Papic, D. Vujevic, AOP; decolorization and mineralization of RR45, in: Presented at the 1st International Symposium on Environmental Management SEM2003, Zagreb, Croatia, 2003.
- [34] H. Kusic, A. Loncaric Bozic, N. Koprivanac, S. Papic, Fenton type processes for minimization of organic content in colored wastewaters. Part II. Combination with zeolites, *Dyes Pigments* 74 (2007) 388–395.
- [35] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and photo-Fenton processes, *Dyes Pigments* 73 (2007) 305–310.
- [36] I. Peternel, H. Kusic, N. Koprivanac, B.R. Locke, The roles of ozone and zeolite on reactive dye degradation in electrical discharge reactors, *Environ. Technol.* 27 (2006) 545–558.
- [37] T. Kawai, K. Tsutsumi, Adsorption characteristic of surfactants and phenol on modified zeolites from their aqueous solutions, *Colloid Polym. Sci.* 273 (1995) 787–792.
- [38] H. Kusic, N. Koprivanac, B.R. Locke, Decomposition of phenol by hybrid gas/liquid electrical discharge reactors with zeolite catalysts, *J. Hazard. Mater.* 125 (2005) 190–200.
- [39] W. Feng, D. Nansheng, H. Helin, Degradation mechanism of azo dye C.I. reactive red 2 by iron powder reduction and photooxidation in aqueous solutions, *Chemosphere* 41 (2000) 1233–1238.
- [40] M. Styliidi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO<sub>2</sub> suspensions, *Appl. Catal. B* 40 (2003) 271–286.