



## Coupling of electrochemical and photocatalytic technologies for accelerating degradation of organic pollutants



Iosif Tantis<sup>a</sup>, Maria Antonopoulou<sup>b</sup>, Ioannis Konstantinou<sup>b</sup>, Panagiotis Lianos<sup>a,c,\*</sup>

<sup>a</sup> Department of Chemical Engineering, University of Patras, University Campus, GR-26504 Patras, Greece

<sup>b</sup> Department of Environmental and Natural Resources Management, University of Patras, GR-30100 Agrinio, Greece

<sup>c</sup> FORTH/ICE-HT, P.O. Box 1414, GR-26504 Patras, Greece

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### ABSTRACT

Acid orange 7 has been degraded in the presence of NaCl by coupling electrochemical treatment with purely photocatalytic degradation. First, electrochemical reduction broke the azo bond and the obtained fragments were then subjected to photocatalytic degradation. The coupling of the two processes accelerated the mineralization process. Electrochemical treatment was carried out at a moderate potential of  $-1\text{ V}$  vs Ag/AgCl and it was much faster in the presence of NaCl than in Na<sub>2</sub>SO<sub>4</sub>. The effects of salt and substrate concentrations were also studied. The degradation route was monitored by LC-MS and ion chromatography analysis. The transformation products at initial stages were 4-aminobenzene sulfonic acid and 1,4-naphthoquinone while at the end the nitrogen of the azo bond was fully mineralized to inorganic ions.

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### 1. Introduction

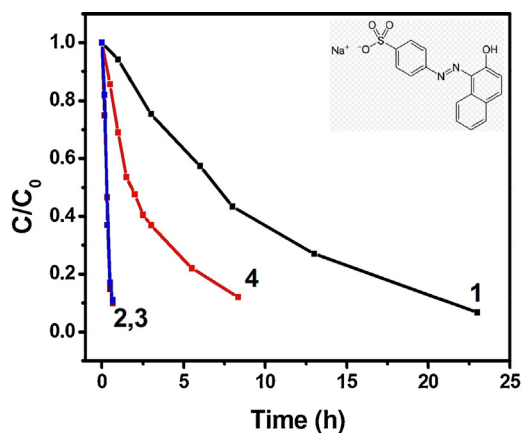
Photocatalytic degradation of organic dyes using semiconductor photocatalysts has attracted intensive scientific research, registering several thousands of publications during the last years [1–5]. As dyes are common water pollutants deriving from related industrial activity, their photocatalytic degradation is important for environmental remediation. Moreover, the simplicity regarding the monitoring of dye decolorization and photocatalysts efficiency by UV–vis spectrophotometry justifies its rising popularity.

However, the use of dyes for evaluating photocatalytic degradation has been frequently questioned [4]. The most important reason is the fact that decolorization does not mean mineralization but it is only a first stage of dye degradation, involving the chromophore moiety. Therefore, a crucial need for further monitoring of the degradation becomes evident. A second problem is faced when visible-light-responsive photocatalysts are studied, where organic dyes might interfere by their ability to sensitize photocatalyst [4]. A third reason is associated with the fact that parallel degradation routes could be significant, therefore the regime of the reaction is not fully photocatalytic. Nevertheless, there is a family of dyes, azo-dyes, like the presently studied acid

orange 7 (AO7, see Fig. 1 for chemical structure), which is one of the largest families of pollutants deriving from industrial activity and is frequently detected in contaminated waters [1,6–8]. The degradation route of such dyes demonstrates some common characteristics. Thus, the first step of their degradation pathway is breaching of the azo bond  $-\text{N}=\text{N}-$  [9–11]. In this respect, AO7 azo-dye has been selected as a model pollutant representative for the study of photo-assisted degradation procedures.

Photocatalytic degradation involves activation of a semiconductor photocatalyst by absorption of light and generation of active oxidants, capable of carrying out photocatalytic degradation. This procedure has been extensively studied in the past and it is reported in many works [1,12–17]. As it is well known, nanoparticulate titania is the standard choice of a photocatalyst both in powder form or supported on inert substrates and electrodes. Titania will be also used as photocatalyst in the present work. Photocatalytic processes however, suffer by some limitations such as the fast recombination of the reactive electron–hole pairs, the lack of absorption in the visible fraction of the solar light, etc. Therefore, it is necessary to find means to accelerate degradation rates and increase photocatalytic efficiency. This is the reason that in spite of the thousands of so far published works, this field is still raising interest in the search of more conclusive and satisfactory results. Photocatalytic degradation rate can be improved by photoelectrocatalytic procedures [18–20]. Application of electric bias facilitates photogenerated electron–hole separation preventing recombination and thus enhancing the

\* Corresponding author at: Department of Chemical Engineering, University of Patras, University Campus, GR-26504 Patras, Greece.  
E-mail address: [lianos@upatras.gr](mailto:lianos@upatras.gr) (P. Lianos).



**Fig. 1.** Degradation of  $2 \times 10^{-5}$  M AO7 under various conditions: (1) pure photocatalytic degradation, monitored at 485 nm; (2) electrochemical reduction using Pt electrode, monitored at 485 nm; (3) electrochemical reduction using TiO<sub>2</sub>/FTO electrode, monitored at 485 nm; and (4) photocatalytic degradation after electrochemical reduction, monitored at 300 nm. In all cases, the aqueous AO7 solution contained 0.5 M NaCl. Insert: chemical structure of AO7.

performance of semiconductor photocatalyst. Degradation of organic pollutants may also be carried out by electrochemical processes in the absence of light [6,21–23]. Anodic oxidation, for example, is being studied for several decades [22–25]. Metal oxides or mixed metal oxide anodes have attracted interest because they demonstrate selectivity [22,24]. Electrochemical reduction of organic pollutants has also been employed to carry out degradation [26,27]. Electrochemical treatment, for example, results in breaching of the —N=N— bond in azo dyes [26,27].

Photoelectrocatalytic and, more generally, electrochemical treatment of organic pollutants can only be carried out in the presence of an electrolyte. It is then attractive to use a natural and abundant material for this purpose. Indeed, the focus of the present work is placed on NaCl, which makes the added electrolyte in most of the presently discussed experiments. It is then necessary to briefly introduce the role of Cl<sup>−</sup> on the degradation process, since these ions will be present in solution when such an electrolyte is added. Chlorine ions are oxidized in solution providing aqueous chlorine [23,28]:



which is hydrolyzed to give hypochlorous acid, HClO,



the latter being in equilibrium with ClO<sup>−</sup> ion



It is accepted [23] that Cl<sub>2, aq</sub>, HClO and ClO<sup>−</sup> species prevail at pH <3.0, 3.0–8.0 and >8.0, respectively. For this reason dye electrochemical degradation in the presence of Cl<sup>−</sup> is expected to be more effective in acidic rather than in alkaline media [23]. In the present work, NaCl solutions in the presence of AO7 attained pH values, which ranged between 6.5 and 7.0, therefore, it is expected that the presence of Cl<sup>−</sup> in the aqueous electrolyte may create upon oxidation active oxidant species among which, HClO may prevail. However, photocatalytic processes usually involve formation of hydroxyl radicals •OH, which are expected to react with Cl<sup>−</sup> and create •Cl radicals [23]



which will also take part to the degradation process as active oxidants.

By taking into account all the above knowledge, in the present work we have studied the degradation pathway of AO7 by following a combined electrochemical, photoelectrochemical and photocatalytic route in an effort to develop an efficient and reliable system for the degradation of this present dye and other similar water pollutants.

## 2. Experimental

### 2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. Commercial nanocrystalline titania Degussa P25 was used as photocatalyst and Millipore water was used in all experiments. SnO<sub>2</sub>:F transparent conductive electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

### 2.2. Description of the reactor

In this work, we used a photoelectrochemical cell made of Plexiglas, which could function, if necessary, in a 3-electrode configuration. The photoanode was made of an FTO glass on which a nanoparticulate titania film was deposited, as explained in the following subsection. The active area of the electrode was 2.5 cm × 2.5 cm = 6.25 cm<sup>2</sup>. This electrode played the role of reactor window. In 3-electrode configuration, the photoanode was used as working electrode. In some cases, a platinum foil was instead used as working electrode having the same active area (i.e., 2.5 cm × 2.5 cm = 6.25 cm<sup>2</sup>). An additional then glass plate of the same size as the titania/FTO photoanode electrode sealed the reactor on that side. A Pt foil of the same as above size was always used as counter electrode. A Ag/AgCl was used as reference electrode when necessary. The reactor was filled with 15 ml of aqueous NaCl or Na<sub>2</sub>SO<sub>4</sub> electrolyte at various concentrations ranging between 0.1 M and 1 M. In most cases, electrolyte concentration was 0.5 M. AO7 was dissolved, when necessary, in this electrolyte at various concentrations ranging between  $2 \times 10^{-5}$  M and  $6 \times 10^{-5}$  M. In most cases, dye concentration was  $2 \times 10^{-5}$  M. Illumination through reactor window, when necessary, was made by employing a 300 W Xenon lamp (Oriel-Newport), which provides to a rough approximation simulated solar light. The intensity of radiation at the position of the photocatalyst was 100 mW cm<sup>−2</sup>. Only an IR water filter was used to cut heat but since titania absorbs only UV light, obviously, the reactor functioned only by the UV portion of the Xe lamp radiation.

### 2.3. Deposition of the photocatalyst film

The following procedures were undertaken in order to deposit photocatalyst on the photoanode (working) electrode [18–20]. Nanocrystalline titania (nc-TiO<sub>2</sub>) film was deposited in two layers, a bottom compact layer and a top open structure. The bottom layer was synthesized by the sol–gel method while the top layer was deposited by using a paste made of Degussa P25 nanoparticles. A densely packed nanocrystalline titania layer was first deposited on a patterned FTO electrode, which was cleaned by sonication in acetone, isopropanol and ethanol: 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 ml ethanol. Then 3.4 ml glacial acetic acid and 1.8 ml of titanium tetraisopropoxide were added under vigorous stirring. After a few minutes stirring, the film was deposited by doctor blading a thin layer of the sol and then it was left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature ramp was 20°/min up to 550 °C and the sample was left for about 10 min at that temperature. The final compact film, was about 300–350 nm thick. On the top of this compact

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