



UVA and solar light assisted photoelectrocatalytic degradation of AO7 dye in water using spray deposited TiO₂ thin films

P.S. Shinde^{a,b}, P.S. Patil^b, P.N. Bhosale^c, A. Brüger^d, G. Nauer^e, M. Neumann-Spallart^f, C.H. Bhosale^{a,*}

^a Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, Maharashtra, India

^b Thin Film Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, Maharashtra, India

^c Department of Chemistry, Shivaji University, Kolhapur 416004, Maharashtra, India

^d Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Wien, Austria

^e Echem – Kompetenzzentrum für angewandte Elektrochemie GmbH, Viktor-Kaplan-Straße 2, A-2700 Wr. Neustadt, Austria

^f Groupe d'Étude de la Matière Condensée, C.N.R.S., 1 Place Aristide Briand, 92195 Meudon CEDEX, France

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ABSTRACT

The degradation of the azo-dye acid orange 7 (AO7) was performed in a photoelectrochemical reactor module consisting of up to nine photoelectrochemical cells equipped with TiO₂ electrodes deposited on transparent conducting substrates. These electrodes were illuminated from the backside by UVA broadband light or sunlight. Electrical bias was applied for efficient separation of photogenerated charge carriers.

Solutions of AO7 (≤ 1 mM) in dilute supporting electrolyte (10 mM HClO₄ or Na₂SO₄) were recirculated through the reactor(s) at a fixed flow rate of 12.2 l h⁻¹ (mean flow velocity of 4.24 cm s⁻¹). AO7 disappeared following first-order kinetics. During solar irradiation, using a total electrode area of 576 cm², and 1.5 V bias with respect to a stainless steel counter electrode, a decay rate constant normalized to unit volume, k' , of 0.23 cm³ s⁻¹ was found under a photocurrent of 0.1 A. Concentrations could be decreased to the micromolar range within 1 h.

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1. Introduction

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water. Over one billion people are exposed to unsafe drinking water due to poor source water quality and lack of adequate water treatment, a problem expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich. The problem is particularly significant in developing countries and in arid areas where water sources are scarce. This is a continually growing problem due to rising population and increasing demands for source waters. Moreover, with rapid industrialization, many pollutants such as various dyes, sulphates and toxic compounds are dumped into the water.

Waste water from textile processing plants is highly coloured and difficult to decolourize. Azo-dyes form the largest group among the synthetic colourants (60–70%) [1]. Their chromophoric system consists of azo groups ($-N=N-$) in association with aromatic

systems and auxochromes ($-OH$, $-NH_2$, etc.). It was estimated that more than 50,000 tons of dyes are discharged from dyeing and colouration industries every year [2,3]. Since azo dyes are intentionally designed to resist degradation, it is very difficult to degrade them by conventional wastewater treatment methods. In addition, the toxicity, mutagenicity and carcinogenicity of azo-dye degradation byproducts are of great environmental concern [4].

Chemical disinfection options such as chlorine and iodine treatment, ozonation, flocculation and filtering require additives and are also not cost-effective. Physical treatment such as boiling, distillation, reverse osmosis and UV irradiation require considerable energy input. One alternative drinking water treatment method that has been proposed is solar photocatalytic purification, a process that could be utilized in countries that receive abundant sunlight. Wide bandgap semiconducting transition metal oxide photocatalysts have been shown to decompose organic compounds, bacteria and other impurities present in water [5]. The most prominent, widely studied photocatalyst is TiO₂.

Upon irradiation of a semiconductor with photons of energy higher than the bandgap, charge carriers are generated. Those which are not lost by recombination can carry out electron transfer reactions at the interface between the semiconductor and a liquid containing an oxidizable or a reducible species. In the case of an n-type oxide semiconductor, valence band holes (h^+) lead (either

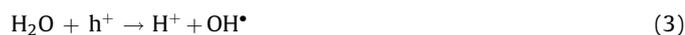
* Corresponding author. Tel.: +91 231 2609435; fax: +91 231 2691533.

E-mail addresses: pravinshindephysics@gmail.com (P.S. Shinde),

psp_phy@unishivaji.ac.in (P.S. Patil), mns@cnrs-belleveuve.fr (M. Neumann-Spallart),

chb_phy@unishivaji.ac.in (C.H. Bhosale).

directly, Eq. (5), or via OH^{\bullet} radicals, Eq. (6) [6,7]) to the oxidation of the solute (D), while conduction band electrons (e^{-}) lead to reduction of dissolved oxygen, if present, forming superoxide radical anions, $^{\bullet}\text{O}_2^{-}$. For TiO_2 under irradiation with light of wavelengths below 400 nm (UV light), the main steps of the reaction sequence are:



$^{\bullet}\text{O}_2^{-}$ and OH^{\bullet} radicals, if not participating in the degradation process, finally lead to the formation of water and oxygen, respectively (a full account of the occurring reactions is given in ref. [6]). Recombination of photogenerated positive holes and electrons inside the semiconductor (Eq. (2)) is responsible for a rather low quantum yield of the photocatalytic degradation. A way of increasing electron–hole separation and consequently enhancing quantum yield is the application of electrical bias, which is possible when the photocatalyst is deposited on an electrically conducting substrate [8–14]. Here, the working point of the photoelectrochemical reaction can be shifted to the potential range where photon flux limited (plateau) currents flow. Fig. 1 shows the schematics of such a system [11]. Due to backside illumination (through the transparent conducting substrate), direct photolysis is avoided and even strongly coloured solutions can be treated, as actinic light is encountering the semiconducting layer first. Electrons are drawn away from the interface, and reaction (4) occurs at the counter electrode instead. Oxygen is available in sufficient quantity as a depolarizer for the counter electrode, firstly due to rapid recirculation of the solution through a reservoir in contact with air and, secondly, due to water oxidation by reaction steps initiated by valence band holes (follow-up reactions of OH^{\bullet} radicals not consumed in reaction (6)).

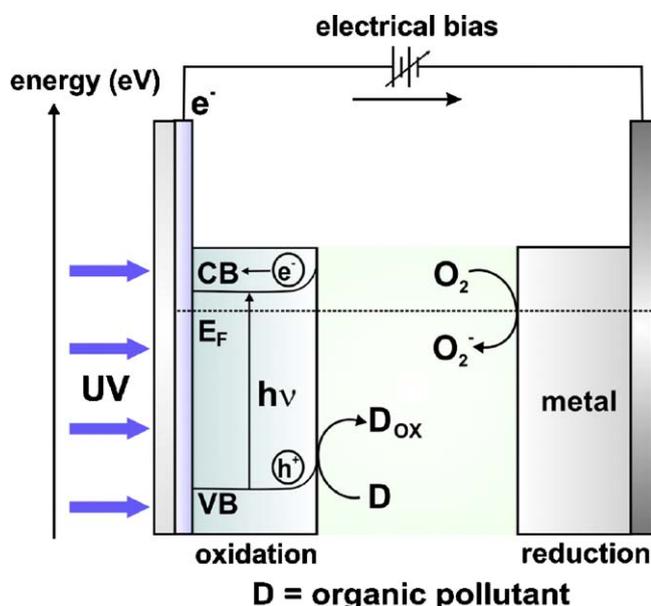


Fig. 1. Schematics of photoelectrochemical degradation process using an immobilized semiconductor layer on a transparent, conducting substrate.

As to the organic molecules which can be oxidized in this way, azo-dyes are of special interest, as mentioned above. Different methods have been explored for the removal of azo-dyes from solution. Bourikas et al. investigated the adsorption of a textile azo-dye, acid orange 7 (AO7), on the surface of TiO_2 in aqueous suspensions in the range of 0.1–1 mM at pH values between 2 and 10 [15]. Liu et al. studied degradation of AO7 quite differently, using a Fe/granular activated carbon system in the presence of ultrasound [16]. Singh et al. reported more than 90% dye decolorization of two monoazo dyes, monoacid orange 6 (AO6) and AO7, and their partial degradation in a sequential fixed-film anaerobic batch reactor (SFABR) using bacteria [17]. Fernandes et al. studied the electrochemical degradation of AO7 on a boron doped diamond electrode (BDD) and obtained 98% and 77% colour and chemical oxygen demand (COD) removal, respectively [18]. AO7 photofading by a photocatalytic method using TiO_2 nanotubes was also reported [19].

In this paper, we report on photoelectrochemical degradation of organic compounds by TiO_2 , taking AO7 as a model compound. The main aspects studied are (i) the use of electrical bias, (ii) the use of large catalyst surfaces, and (iii) the possibility of using solar light: can this illumination source which is rather poor in content of high energy quanta (>3.2 eV) be used efficiently, leading to the conversion of large quantities of contaminated liquid and reduce the concentration of the contaminant down to small concentration within short time?

2. Experimental

2.1. Chemicals, solutions and electrodes

HClO_4 and Na_2SO_4 (Loba) of analytical grade were used as supporting electrolytes. The model pollutant AO7 (Tropaeoline, 4-(2-hydroxy-1-naphthylazo)benzenesulphonic acid sodium salt, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$, Fig. 2) was obtained from Aldrich and used without further purification. Double distilled water was used for the preparation of solutions. For some experiments tap water was used as electrolyte ($\sigma = 350 \mu\text{S cm}^{-1}$). Using aliquots withdrawn from the reaction mixture at intervals, the concentration of AO7 in degradation experiments was estimated from UV–vis absorption (extinction) at 480 nm, recorded with a 119 SYSTRONICS UV–vis spectrophotometer (for the measurement of full spectra) or a battery powered photometer (NANOCOLOR Model 400D, Machery-Nagel) for outdoor single wavelength measurements. Total organic carbon (TOC) measurements were carried out on aliquots after acidification with phosphoric acid and purging out IC (inorganic carbon, CO_2) by catalytic combustion, using a Shimadzu autosampling TOC analyzer employing a non-dispersive infra-red detector.

The anatase TiO_2 electrodes used in this study were deposited by spray pyrolysis onto large area ($10 \text{ cm} \times 10 \text{ cm} \times 0.125 \text{ cm}$) conducting glass plates (spray deposited fluorine doped tin oxide on glass, FTO, with sheet resistance of 10–20 Ω). Preparation and structural, optical and photoelectrochemical characterization of the TiO_2 electrodes have been reported elsewhere [20] and an optimized thickness of around 600 nm was chosen.

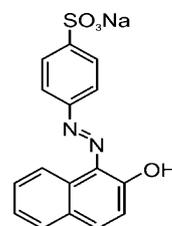


Fig. 2. Structure of the azo-dye acid orange 7 (AO7).

2.2. Light sources

Broadband ultraviolet light (UVA region, center wavelength 365 nm [20]) was supplied by a 20 W blacklight lamp (Conrad). Alternatively, solar light was used: irradiations at location 16°40'37"N 74°15'18"E were started around midday in February.

2.3. Photoelectrochemical measurements

Electrochemical measurements (current–potential curves) were carried out with an AMEL 2059 potentiostat, Italy. In degradation experiments, electrical bias to the cells was either provided by this potentiostat, or by a 1.5 V alkaline battery, or by an array of 3 silicon photovoltaic cells connected in series (providing an open circuit voltage of >1.5 V and a short circuit current of typically 0.2 A under full sun at midday).

The photodegradation module (Fig. 3) could be equipped with up to 9 individual photoelectrochemical cells. In an individual cell, a TiO₂ electrode coated on a conducting glass substrate was used as photoanode and a stainless steel plate at a distance of 0.1 cm, facing the photoanode, acted as cathode. The surface area of these electrodes in contact with the electrolyte was 64 cm² (identical to the illuminated area). The term “bias” is used for the voltage applied between the two electrodes. Backside irradiation (through the transparent conducting substrate) was used, employing either the UVA broadband lamp, placed behind the photoelectrode, or solar light using manual inclination and azimuth tracking.

A fixed amount of electrolyte, the major part of it being contained in an external reservoir, was recirculated through the cell(s) with a constant flow rate of 12.2 l h⁻¹ (corresponding to a mean flow velocity of 4.24 cm s⁻¹ across the photoelectrode) using a Gilson MINIPLUS peristaltic pump, France, and silicon tubing.

3. Results and discussion

We previously reported the degradation of oxalic acid under electrical bias on TiO₂ electrodes in reactors operated in single flow-through mode, using backside illumination [20]. The extent of degradation was shown to be significantly enhanced when the flow rate was reduced to very small values. However, although very small concentrations in the effluent can be obtained in this way, the overall efficiency is low, since it is limited by mass

transport. Therefore, to overcome this limitation, we now used high flow rate in combination with recirculation.

The very low levels of contaminant (1 mM and below as used in this study) would result in very low solution conductivity ($\sigma \leq 173 \mu\text{S cm}^{-1}$ for 10 mM AO7) leading to high series resistance, and in turn to high iR drop to be compensated by application of higher bias voltages, if plateau current conditions (see below) are to be maintained. Therefore, a small quantity of supporting electrolyte was added (10 mM) to help overcome the series resistance of the electrochemical cell to some extent and maintain a constant ionic strength, easing the interpretation of results. HClO₄ was chosen as supporting electrolyte and buffer, as AO7 interacts more efficiently with the surface of TiO₂ (adsorbs better) under slightly acidic conditions [15]. A current–voltage curve of a 64 cm² TiO₂ electrode in 1 mM AO7/10 mM HClO₄ using a steel counter electrode at a distance of 1 mm is shown in Fig. 4. When comparing these data with data of an experiment made with a 1 cm × 1 cm electrode of the same type under potentiostatic control in a concentrated electrolyte as shown in the inset, it can be seen that the current plateau is reached at around 0.6 V positive of the photocurrent onset in the strong electrolyte, but more than 1.5 V is needed to attain the plateau in the dilute electrolyte for the large electrode, due to electrolyte resistance (iR drop). The iR drop, however, was kept small by using a very small distance between the two electrodes. This is essential for work with electrolytes of low conductivity, especially contaminated drinking water. In order to show that even purification of drinking water is possible using the here presented arrangement, experiments were also performed with AO7 in tap water as electrolyte ($\sigma = 350 \mu\text{S cm}^{-1}$). The degradation rates found were somewhat lower than those obtained in experiments run with 10 mM Na₂SO₄ (see below).

A dilute solution of AO7 shows absorption peaks at 485, 415 (sh), 310 and 254 nm (Fig. 5). The extinction at the location of the first of these peaks was taken as a measure for the concentration of AO7. During the course of the degradation experiments, the concentration of AO7 decreases due to decomposition (photoelectrochemical oxidation, Fig. 5). Blank experiments (no light, or no bias (Fig. 6), or absence of TiO₂ (use of uncoated FTO/glass substrate) confirmed negligible or imperceptible degradation.

First, degradation of AO7 was studied under broadband UVA illumination. The intensity of this light source was chosen such that similar photocurrents as produced with sunlight (see below) would be obtained. A dilute solution of AO7 in 10 mM HClO₄ (0.1 l) was recirculated through one electrochemical cell. The photocurrent at a

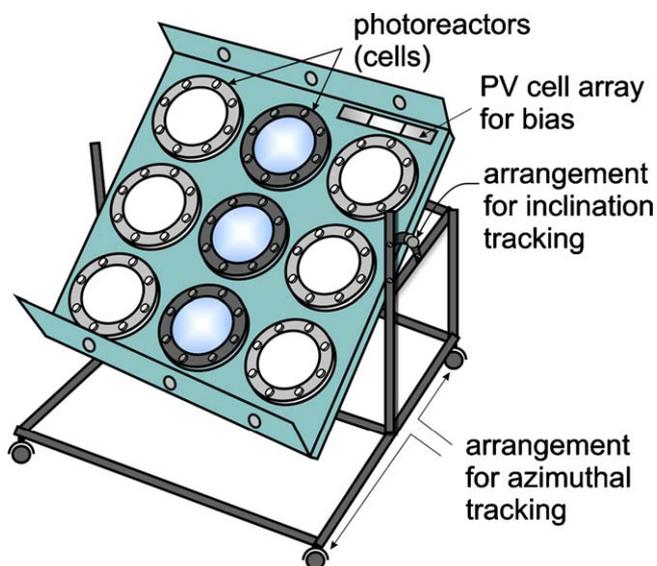


Fig. 3. Schematics of a photoelectrochemical detoxification module containing nine electrochemical cells.

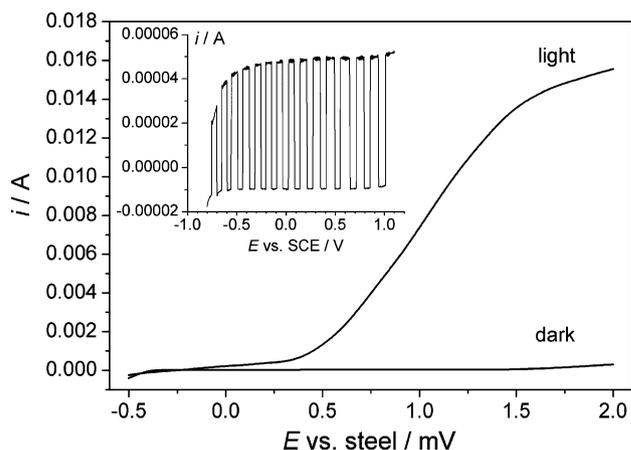


Fig. 4. Dark current and light current for a TiO₂ electrode (64 cm²) under UVA illumination for 1 mM AO7 in 10 mM HClO₄ as a function of applied voltage with respect to a steel counter electrode of equal size at a distance of 1 mm with a flow rate of 12.2 l h⁻¹. Inset: i - E curves of a 1 cm² electrode in strong electrolyte (0.1 M NaOH) under slow, rectangularly chopped monochromatic light (365 nm).

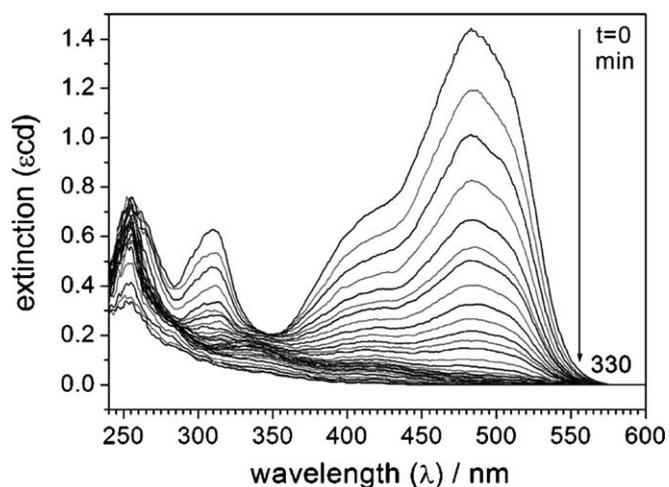


Fig. 5. Extinction spectra of collected samples of the electrolyte in the course of AO7 degradation under UVA illumination of a TiO₂ electrode. Initial concentration 1 mM AO7 in 10 mM HClO₄.

fixed bias voltage of 1.5 V vs. steel was recorded as a function of time and plotted in the upper part of Fig. 6. A steady photocurrent of 0.014 A was drawn (corresponding to a photocurrent density of 219 μA cm⁻²). In the lower part of Fig. 6, the variations in ln(*c*/*c*₀) as a function of illumination time are plotted. The linear section in this plot has a slope of $-k$. *k* can be taken as the apparent first order rate constant of the degradation reaction:

$$\ln\left(\frac{c}{c_0}\right) = -kt \quad (7)$$

where *c* is the concentration of AO7 remaining in the solution at time *t*, and *c*₀ is the initial concentration at *t* = 0. A rate constant, *k*, of $2.5 \times 10^{-4} \text{ s}^{-1}$ was determined from the data obtained in the experiment using UVA light. *k* corresponded to $k' = kV = 0.025 \text{ cm}^3 \text{ s}^{-1}$ considering the total volume (*V*) of the solution. (The rate constant in a batch reactor of given electrode size is inversely proportional to the volume.) Moreover, *k* is proportional to the area of the electrode if a sufficiently well collimated light

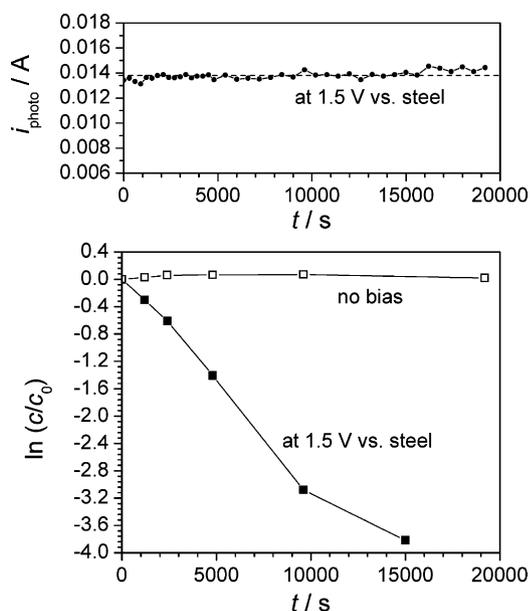


Fig. 6. Plot of photocurrent (upper part) as a function of degradation time for a single TiO₂ electrode under UVA illumination for 1 mM AO7 in 0.1 l of 10 mM HClO₄ with a flow rate of 12.2 l h⁻¹ and resulting AO7 degradation, ln(*c*/*c*₀) = *f*(*t*); bias 1.5 V vs. steel (lower part).

source is used, and to its intensity and therefore to the photocurrent. In order to abstract from these external parameters and to make comparison of experimental data obtained under various conditions possible, it is useful to define $k'' = k'/\text{electrode area (cm s}^{-1}\text{)}$ and $k''' = kVF/i_{\text{ph}} (\text{M}^{-1})$, where *F* is Faraday's constant (96,500 C mol⁻¹) and *i*_{ph} is the photocurrent. In this experiment, k'' was $3.9 \times 10^{-4} \text{ cm s}^{-1}$ and k''' was 172 M⁻¹. Within 250 min, 98% AO7 were degraded and 2% left.

Next, using the same TiO₂ electrode, a solution of identical composition was subjected to degradation under sunlight. Electrical bias (>1.5 V) to the photoelectrode was given through an array of photovoltaic cells. A photocurrent of 0.017 A was obtained under sunlight (photocurrent density of 234 μA cm⁻²). Considering the low content of UV light in sunlight at the surface of the earth, this is quite good (see spectral characterization of light sources in ref. [7]). Fig. 7 shows the course of the degradation experiment (ln(*c*/*c*₀) = *f*(*t*)). The decrease of the photocurrent in later stages of the experiment was due to the natural decrease in sunlight intensity in the afternoon. The initial values of the constants *k'*, *k''* and *k'''* were found to be 0.029 cm³ s⁻¹, $4.53 \times 10^{-4} \text{ cm s}^{-1}$ and 164.6 M⁻¹, respectively. In this experiment, it was possible to degrade with one TiO₂ electrode about 98% (2% AO7 left) in 15,000 s (250 min) under sunlight illumination.

In order to decrease the time necessary for degradation, in a following experiment, three photoelectrochemical cells were fitted to the module and connected in series as to liquid flow. The cells containing each a TiO₂ electrode synthesized under the same deposition conditions, were connected electrically in parallel and subjected to solar irradiation using again a solution of 1 mM AO7 in 10 mM HClO₄ (0.15 l). From the initial slope of a plot of ln(*c*/*c*₀) vs. *t*, *k'*, *k''* and *k'''* were found to be 0.12 cm³ s⁻¹, $6.25 \times 10^{-4} \text{ cm s}^{-1}$ and 289.5 M⁻¹, respectively. The higher value of *k'* was expected considering the enhanced photocurrent (0.04 A) obtained by the increased total electrode area (by combining the three cells electrically in parallel). *k''* and *k'''* were somewhat higher than expected. This can be attributed to an improvement of the photoelectrode surface by prolonged illumination and interfacial electron transfer. It was possible to degrade more than 93% (6.3% AO7 left) within 4800 s (80 min).

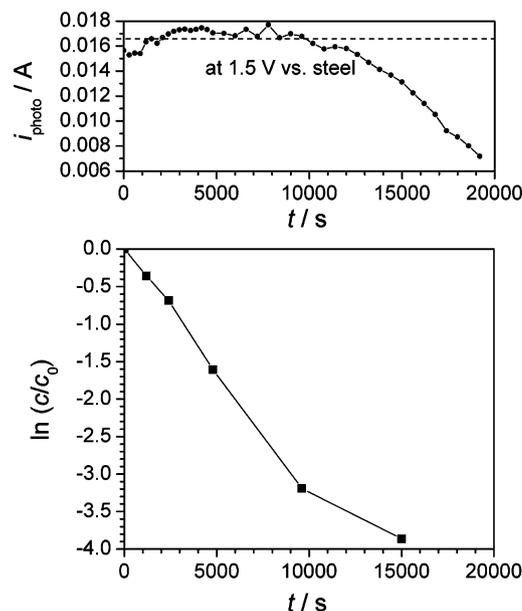


Fig. 7. Plot of photocurrent (upper part) as a function of time for a single TiO₂ electrode under solar illumination for 1 mM AO7 in 0.1 l of 10 mM HClO₄ with a flow rate of 12.2 l h⁻¹ and resulting AO7 degradation, ln(*c*/*c*₀) = *f*(*t*); bias 1.5 V vs. steel (lower part).

Also solutions with lower starting concentration were degraded. Using again three photoelectrochemical cells and solar illumination, 0.15 l of 0.1 mM AO7 in 10 mM HClO₄ was subjected to degradation. Fig. 8 shows the plot of photocurrent with degradation time. A large photocurrent of 0.045 A was observed which was almost constant throughout the experiment due to a perfectly cloudless sky. $\ln(c/c_0)$ is plotted as a function of illumination time in the lower part of Fig. 8. In this experiment it was possible to degrade 98.5% of the AO7 (1.5% left) within 80 min, corresponding to a decrease in concentration from 10^{-4} to 1.5×10^{-6} M.

Finally, nine photoelectrochemical reactors were used (576 cm² active area). For the degradation of 250 ml of 1 mM AO7 10 mM HClO₄ under sunlight and 1.5 V bias, k' was $0.23 \text{ cm}^3 \text{ s}^{-1}$, k'' was $3.99 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1}$ and k''' was 226 M^{-1} . The higher rate constant k' and the higher photocurrent (0.1 A) were due to the higher surface area, but somewhat smaller than expected due to varying properties of the nine individual electrodes.

3.1. Influence of electrolyte

The influence of pH of the supporting electrolyte on AO7 degradation has been noted previously [15]. In an early report the point of zero charge of TiO₂ is given as 5.8 [21], and for anatase, various similar values depending on preparation method were reported in ref. [22]. Below this pH, TiO₂ is positively charged, which seems to enhance interaction with AO7 and TiO₂, i.e. AO7 is adsorbed, leading to an increased probability of direct hole transfer, down to low concentrations. This should be directly reflected in the value of k''' . Degradation experiments were therefore performed with Na₂SO₄ as supporting electrolyte, at a pH of around 6. Under UVA illumination of a solution of 1 mM AO7 in 10 mM Na₂SO₄ a normalized decay constant, k''' of 30 M^{-1} was found, which is significantly lower than the value found for the acidic electrolyte (see Table 1). Although it would not be advisable to use an acid additive for drinking water purification, this possibility might be envisaged for industrial wastewater purification.

Table 1
Parameters and conditions for degradation of organic compounds by TiO₂ electrodes.

Solution	Light source	Bias or potential (V)	k (s ⁻¹)	$k' = kV$ (cm ³ s ⁻¹)	Active surface area (cm ²)	$k'' = k'/\text{area}$ (10 ⁻⁴ cm ³ s ⁻¹)	i_{ph} (A)	$k''' = kV/i_{\text{ph}}$ (M ⁻¹)	Remaining at the end of the experiment	Reference
100 ml 1 mM AO7 10 mM HClO ₄	UVA	1.5	0.000250	0.02500	64	3.906	0.0140	172.32	2.2% (250 min)	This work
100 ml 1 mM AO7 10 mM HClO ₄	Sun	1.5 (PV)	0.000290	0.02900	64	4.531	0.0170	164.62	2.1% (250 min)	This work
100 ml 1 mM AO7 10 mM Na ₂ SO ₄	UVA	1.5	0.000028	0.00280	64	0.438	0.0090	30.02	78.4% (320 min)	This work
150 ml 1 mM AO7 10 mM HClO ₄	Sun	1.5 (bat)	0.000800	0.12000	192	6.250	0.0400	289.50	6.3% (80 min)	This work
150 ml 0.1 mM AO7 10 mM HClO ₄	Sun	1.5 (bat)	0.001290	0.19350	192	10.078	0.0450	414.95	1.5% (80 min)	This work
150 ml 0.1 mM AO7 10 mM Na ₂ SO ₄	Sun	1.5 (PV)	0.000570	0.08550	192	4.453	0.0280	294.67	7.1% (80 min)	This work
250 ml 1 mM AO7 10 mM HClO ₄	Sun	1.5 (bat)	0.000920	0.23000	576	3.993	0.1000	221.91	–	This work
75 ml 0.054 mM aniline (pH 6.5)	365 nm ^a	0.5 vs. SCE	0.001083	0.08122	72	11.281	0.0400	195.96	–	[23]
15 ml 1 mM 4-CP 0.1 M Na ₂ SO ₄	365 nm ^b	0.6 vs. SCE	0.000031	0.00047	1	4.680	0.0003	150.54	–	[10]
15 ml 1 mM oxalic acid 0.1 M Na ₂ SO ₄	365 nm ^b	0.6 vs. SCE	0.000070	0.00105	1	10.500	0.0003	337.75	–	[10]
13 ml 1 mM 4-CP 0.4 M NaClO ₄	UV ^c	0.6 vs. SCE	0.000260	0.00341	3.8	8.967	0.0160	20.39	–	[24]

PV—photovoltaic cell array, bat—alkaline battery.

^a Centre wavelength.

^b Monochromatic.

^c 200 W XeHg-arc lamp.

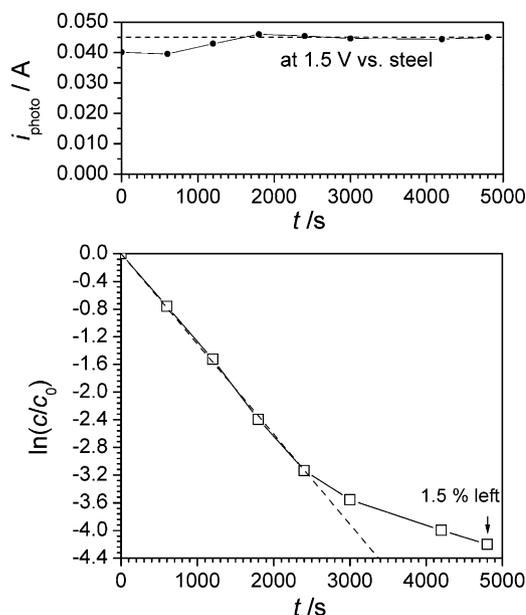


Fig. 8. AO7 degradation ($\ln(c/c_0) = f(t)$) under sunlight illumination using three TiO₂ electrodes in series (lower part). Initial concentration 0.1 mM AO7 in 10 mM HClO₄, total volume 0.15 l, flow rate 12.2 l h⁻¹; bias 1.5 V vs. steel. The upper part shows the plot of photocurrent as a function of time.

3.2. Extent of mineralization

The observed decay constants are indicative of the destruction of the main chromophore of AO7. This may serve some aesthetic purpose when coloured effluents from industries are considered. However, there is a large amount of organic substances (intermediary products) left when all of the main chromophore is destroyed. In Fig. 5 this can be seen when looking at the last few extinction vs. wavelength traces recorded towards the end of a degradation experiment (at 12,600, 14,400, 16,200, 18,000 and 19,800 s (330 min)). There is an absorption

peak left at 254 nm, belonging to the aromatic system. However, one can see that this system is degraded too, but much more slowly. Measurements of TOC at the beginning and at the end of degradation experiments show that the decay rate of the extinction at 254 nm, ext_{254} , and the TOC are directly correlated, with $d(\text{ext}_{254})/dt \approx d(\text{TOC})/dt$.

3.3. Rate constants

The various parameters and constants associated with AO7 degradation by TiO₂ electrode(s) under UVA and solar illumination in typical experiments are listed in Table 1. The rate constants k'' , which are normalized to unit area and solution volume are in the range of 4×10^{-4} to $10 \times 10^{-4} \text{ cm s}^{-1}$. They reflect properties of the light source, the IPCE (incident photon to current efficiency as a function of electrode potential) and the efficiency of photocatalyst/solute interaction and are useful for comparing results obtained with different electrode sizes (surface areas). In the case of sunlight, they can be compared directly with values obtained with other reactor geometries and experimental conditions carried out with this light source. k''' finally reflects the interaction of the photocatalyst (surface properties) and the solute alone, independent of light source. Only in the case of higher pH (supporting electrolyte 10 mM Na₂SO₄), a much lower value for k''' was obtained (30 M^{-1}), due to absence of adsorption of the dye molecule on the semiconductor.

Table 1 also contains values from the literature. Whenever (not too often) the required details were given, k' , k'' and k''' were calculated. Unfortunately, literature data on the decomposition of dyes, especially azo-dyes, could not be processed, since direct photolysis contributed to a great extent to the decay curves, as front side illumination was used throughout. Moreover, this illumination mode led to substantial shielding of the electrodes from the light, as these dyes had high extinction coefficients in the wavelength region of TiO₂ absorption. The cited references therefore refer to studies of degradation of molecules absorbing light of wavelength shorter than that emitted by UVA lamps and the sun (aniline [23], 4-CP [10,24] and oxalic acid [10]). Cases where only degradation of the parent molecule is studied (by HPLC or light absorption) can in general not be directly compared to cases where total mineralization as measured by TOC or CO₂ formation is considered, since the initial step of breakdown and total mineralization occurs at different rates. In the case of aniline degradation [23], TiO₂ (rutile) obtained by thermal oxidation of Ti was used. Interestingly, the degradation rate constants were found to be of the same order as those found for anatase electrodes (usually anatase is thought to be a better electrocatalyst than rutile). Also in ref. [10] rutile turned out to be more active for degradation of 4-CP (data not shown in the table) while anatase yielded a better degradation of oxalic acid. The low value of k''' calculated from ref. [24] may be attributed to a surface of low activity due to the way of preparation (CVD).

Finally, the Faradaic efficiency, f , of the oxidation reaction of D being in competition with water oxidation may be calculated from the observed decay curves. f characterizes the efficiency of a photocatalyst in combination with a particular oxidizable solute molecule and is defined as

$$f = \frac{|dn/dt|}{d(Q/F)/dt} = \frac{|dn/dt|}{i/F} \quad (8)$$

where n is the number of moles of a species formed or consumed in an electrochemical reaction and Q is the charge passing the electrode. For the photoelectrochemical reaction considered here, $i = i_{\text{ph}}$, and f can be calculated for any point of the degradation

experiments by taking the tangent at time t of an n vs. t curve. For the linear sections of the decay curves from which k was calculated, Eq. (8) simplifies to

$$f = \frac{kVc}{i_{\text{ph}}/F} = k''' c \quad (9)$$

This is valid when $f \ll 1$, i.e. for very small concentrations of the solute, D [9]. The existence of a linear section as observed in the experiments follows from the assumption of simple competition kinetics [9]. From the values of k''' and the concentrations measured at the end of the experiments listed in Table 1, it can be seen that f becomes very small, i.e. at the end practically all charge carriers are consumed in water oxidation.

Efficient mass transport was maintained in the experiments reported in this work by using high flow velocity. Excessive flow velocities were avoided as they would lead to too high a pressure in the system. A maximum efficiency (best use of collected charge carriers) can be obtained when the reaction rate is solely controlled by photon flux and not by mass transport. Preliminary experiments in a specially designed electrochemical cell under very high flow velocities and low light intensity showed that the photon flux limited value of k''' lies around 1000 M^{-1} for the TiO₂ electrodes used in this study in combination with AO7 at low pH (10 mM HClO₄).

The electrodes used in this study have been exposed so far to illumination and bias for more than 80 h without showing any sign of deterioration.

4. Conclusions

A new way of degradation of organic compounds using a specially designed photoelectrochemical detoxification reactor module was investigated. The degradation of the azo-dye AO7 was demonstrated under broadband UVA and solar illumination of TiO₂ electrodes on transparent conducting substrates using electrical bias for suppressing bulk carrier recombination in the semiconductor. In the course of the reaction, the molecule AO7 in aqueous solution could almost completely be removed, as seen by the extinction of the main chromophore disappearing with first-order kinetics of 0.025 and 0.029 $\text{cm}^3 \text{ s}^{-1}$ under broadband UVA (center wavelength 365 nm) and solar illumination, respectively, using 64 cm^2 active catalyst surface area. The rate constant scales with surface area. Using three photoelectrochemical cells ($3 \times 64 \text{ cm}^2$), the rate constant was 0.12 $\text{cm}^3 \text{ s}^{-1}$. This translates into a decay rate constant normalized to unit area of $6.25 \times 10^{-4} \text{ cm s}^{-1}$ for solar illumination. Therefore, if 1 m^2 active area were used, a quantity of 1 l solution of AO7 could be degraded down to 1% content in about 12 min. Full mineralization occurs at about ten times lower rate, as the destruction of the aromatic system is a slow, rate limiting step. The photocurrent density is relatively low ($234 \mu\text{A cm}^{-2}$) under typical solar irradiation levels. Therefore, electrical bias can be conveniently supplied by a small photovoltaic array that does not increase the overall footprint of the device. The mechanical and chemical stability of this type of TiO₂ electrodes (prepared by spray pyrolysis) shows that photocatalysis under bias is a promising way of carrying out degradation reactions (water purification).

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