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Photoelectrochemical reactors for the solar decontamination of water

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Abstract

Large photoelectrochemical reactors of various sizes, made of cylindrical photoanodes surrounding the counter electrode compartment, have been placed inside the glass tubes of either compound parabolic (CPC) or parabolic trough collectors (PTC, Helioman). Model pollutants have been destroyed at various solar light concentrations. Their oxidation rates have been found to be up to 1000-times higher than the values obtained with TiO_2 slurries. Separation of charges is much better when the photogenerated electrons are collected through an electrochemical bias and, moreover, the continuous measurement of photocurrents makes it possible to directly monitor the efficiency of the whole system and thereby improve it. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Compound parabolic collector; Parabolic trough collector; Water decontamination; Sun; UV radiation

1. Introduction

Since titanium dioxide, which is so far the photocatalyst most used to reduce water and air pollution, is a wide band gap semiconductor (E ca. 3.2 eV), only light below 400 nm is absorbed and capable of forming the e^-/h^+ pairs necessary for heterogeneous photocatalytic decontamination. It is, therefore, evident that especially in solar applications in which only less than 5% of the solar energy reaching the surface of the earth can be used, it is crucial to avoid any loss of the solar radiation needed for the photoexcitation of TiO_2. This means that the whole system, including light collectors, reactor materials, pollutant solutions and even the dispersion state of the photocatalyst itself, has to be carefully tested and optimised. If we consider the photoexcitation step, for instance, there is a big difference between a layer of fixed TiO_2 continuously illuminated and a TiO_2 slurry in which each particle may (or may not) enter the path of UV light for only a very short time. TiO_2 suspensions or thick layers of immobilised catalyst on the walls of glass tubes are opaque to the UV radiation. In both cases, the amount of suspended TiO_2 or the thickness of TiO_2 layers has to be carefully optimised, to avoid filtering and/or scattering of useful radiation by the photocatalyst itself. Such studies can be performed much faster by photoelectrochemical methods providing direct information on the various factors influencing the system, than by analysing the photooxidation products.

Several attempts at attaching titanium oxides to a variety of supports, such as glass tubes, fibreglass, woven mesh, etc. have been made [1,2], as the recovery of micron-sized particles from water decontaminated by a TiO_2 slurry may be an awkward process. Generally, the efficiency of the overall process decreases as the catalyst is immobilised because the illuminated surface area is smaller by several orders of magni-

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tude, and also because of the mass transfer limitations [3].

On the other hand, using TiO_2 suspensions for the oxidation of pollutants involves, in addition to costly, discontinuous treatments such as filtration and resuspension of the catalyst, and quite low quantum efficiency is obtained. Indeed, a high degree of recombination between photogenerated charge carriers occurs because each semiconducting particle behaves as a short circuited microelectrode under bandgap excitation and thus promotes oxidation and a reduction process on the same particle. By applying an external anodic bias to a thin TiO_2 layer deposited on a conducting substrate, the recombination between the photogenerated charge carriers can be suppressed and thus the quantum efficiency enhanced. If the photogenerated electrons can be kept away from the illuminated semiconductor/electrolyte interface, an increased number of holes are available, leading to a higher local concentration of $OH^\bullet$ radicals and thereby to more efficient degradation of organic contaminants. Furthermore, the accurate photocurrent values easily obtained during solar experiments performed under outdoor conditions are very useful for testing reactor materials and designs.

In previous work [4,5], two different kinds of single compartment reactors were adapted to a parabolic trough collector (PTC, Helioman [6]) and tested. The preliminary results obtained were used for the construction of the two-compartment reactor described here. In the present case, the counter electrode was placed inside an inner compartment surrounded by a cylindrical photoanode well adapted for the efficient collection of solar radiation. The inner compartment can contain the relatively high concentration of protons (1N or more) necessary to favour cathodic processes (such as hydrogen evolution) to occur at platinum sites of the counter electrode. Indeed, in such photoelectrochemical reactors, the collection of the electrons photogenerated by platinum counter electrodes can be efficiently performed in strong acidic solutions where hydrogen ions can be reduced to hydrogen gas. At the same time, even low concentrations of acids, bases or salts added to the working compartment as electrolytes, can be enough to ensure reasonable ionic conductivity and thus achieve the photoelectrochemical treatment of wastewater.

Moreover, if the cathodic reaction is very efficient, no external power is necessary: with the reactor working in the galvanic mode, pollutant decontamination can occur with simultaneous generation of hydrogen and/or electricity [7]. In principle, if pollutant decomposition can be achieved in such a galvanic photoelectrochemical reactor, the electricity produced as a photocurrent can compensate for the overall cost. And the same is valid for the hydrogen gas yielded at the platinum counter electrode with a 0.4% solar to chemical energy as described by Fujishima and Honda in their pioneering work [8]. However, the black platinum cathodes used by them are too expensive for practical applications. Therefore, we have tried to find cheaper electrode materials and to optimise reactor design for long cylindrical photoanodes able to collect efficiently the relatively low (1 sun) solar radiation provided by compound parabolic collectors (CPC's).

Our objective is to design and build practical photoelectrochemical reactors, having photoanodes with a large surface area and improved on the basis of photocurrent values which can be measured during the decontamination process performed under outdoor conditions [4,5]. For such practical applications, the investment and maintenance costs are much lower for CPC's than for parabolic trough collectors [9]. We have therefore built a new type of photoelectrochemical reactor, in which the photoanode has a cylindrical form well adapted to the efficient collection of relatively low solar radiation such as provided by CPC's.

2. Experimental

2.1. Electrodes

Pt/SnO_2 counter electrodes have been prepared by coating several sheets (300 mm × 25 mm; or 300 mm × 12 mm) of conductive glass with a solution of 0.001 M H_2PtCl_6 in i-propanol. After drying for 6 h and firing at 400°C for 30 min, Pt/SnO_2 behaves as a platinum electrode with a large active area. The electrical conductivity of the SnO_2 layer has also been improved by depositing Ag layers (1–5 μm thick) on the edge of the conducting glass. Ti/TiO_2 photoanodes have been prepared from large cylindrical (95 cm × 5 cm or 220 × 10 cm) and 0.125 mm thick

Ti metal foils (1.4 cm or 2.8 cm diameter), cleaned with solvents (acetone, ethanol) and immersed during 20 min in a hot, aqueous solution of 50% HCl. A thin (100 nm) TiO_2 film was deposited on these cylindrical Ti sheets by dipping them into a methanol colloidal suspension containing 30 g/l of TiO_2 particles 20 nm in size [10]. After drying overnight at room temperature, these photoanodes were progressively heated to 450°C and baked for 30 min. The thickness of the TiO_2 films was measured by profilometry (Tencor Instr.) and found to be around 100 nm, while their morphology was examined by atomic force microscopy (AFM) in tapping mode. The average size of the TiO_2 particles has, thus, been estimated to be around 27 nm.

The photoelectrochemical properties of thin TiO_2 films deposited on various substrates (Ti, Au, SnO_2) were previously studied [11] on small (2.5 cm × 2.5 cm) electrodes in a three-electrode cell filled with 0.1 M NaOH in which a Pt counter electrode and the Luggin capillary of a calomel reference electrode were also immersed. The illumination of TiO_2 with a 1 W/m^2 Xenon lamp result in photocurrents which have been measured at various potentials by using a PAR scanning potentiostat Model 362 and a Kipp and Zonnen X/Y recorder. Typical photocurrent dependencies were recorded under chopped light and their characteristics (plateau photocurrents and onset potentials) were further used to evaluate the quality of TiO_2 thin films [10]. On the basis of such information obtained under laboratory conditions, large photoanodes were prepared for use in outdoor experiments under solar illumination. A calomel reference electrode (SCE) was used in the solar experiments but in the followings all potentials are given versus the hydrogen electrode (RHE).

2.2. Photoreactor design

Two kinds of photoelectrochemical reactors, one having one compartment, the other two, were erected with large Ti/TiO_2 photoanodes as working electrodes and Pt/SnO_2 sheets as counter electrodes. In the single-compartment photoreactor (Fig. 1a), a 220 cm × 4 cm, 4 mm thick-sheet of commercial glass, used as the substrate of the transparent Pt/SnO_2 counter electrode, was placed 5 mm above the Ti/TiO_2 photoanode in the same compartment. This photoreactor, having an internal volume of 440 cm^3, was introduced into the Helioman Pyrex tube (5.6 cm diameter), well positioned, glued to special glass devices and with the electrical connections of reference, counter and working electrodes established, as previously described [4,5].

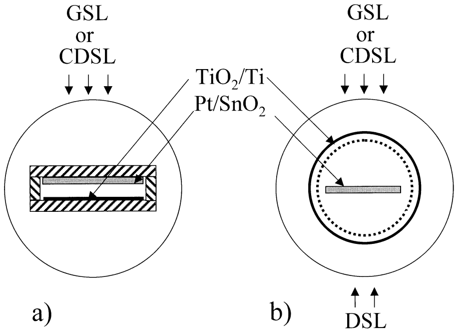

Fig. 1. Schematic cross section of: (a) a one-compartment reactor; (b) a two-compartments reactor. Global solar light, GSL; concentrated solar light, CDSL.

In the second type of photoelectrochemical reactor (Fig. 1b), the inner compartment was connected by several glass frits of fine porosity (4) previously filled with an ionic conductive polymer (Nafion). The inner compartments, surrounded by cylindrical photoanodes 220 cm or 95 cm long, were placed in the glass tubes adapted either to a Helioman module (Fig. 1b and Fig. 2a) or to coupled parabolic collectors (Fig. 2b).

If the design of the two-compartment photoreactor recently conceived (Fig. 1b) is compared with the single compartment photoreactor (Fig. 1a) previously tested in a Helioman module [4,5], it may be seen that the cylindrical photoanodes are well adapted to collecting global solar radiation (GSL). Moreover, this design (Fig. 1b) avoids any filtering effect due to the ‘transparent’ counter-electrodes or their supporting glass sheets, which may lead to a decrease up to 15% (or 35%, respectively) of the photocurrent. By contrast, electrochemical efficiency is not optimal when the counter electrode is inside the inner compartment (Fig. 1b) because the photoanode is not facing the counter-electrode at a short distance (5 mm) as required by an ideal electrochemical design (Fig. 1a).

In the case of the two-compartment photoelectrochemical reactor, the counter-electrode that is surrounded by the photoanode does not have to be transparent as was necessary for the first photoelec-

Fig. 2. Photoelectrochemical reactors in operation: (a) left, Helioman module, (b) right, CPCs.

trochemical reactor adapted to the Helioman module (Fig. 1a). Moreover, the counter-electrode can be placed inside an inner compartment in which the electrolyte can be different from the electrolyte used in the anode (working) compartment. Therefore, only low concentrations of acids, bases or salts can be added to the waste water to be treated.

In both types of reactors, whether adapted to CPC's or a Helioman module, the inner compartment was filled with 1 N H_2SO_4. Dark current and the photocurrent values were measured before organic pollutants were put in the working compartment filled with 0.01 N H_2SO_4, at several potentials ranging from 0 to 1.8 V/(RHE). In the Helioman module, photocurrents were measured under concentrated solar light (CDSL) obtained by sun-tracking in addition to global solar light (GSL). The photocurrents observed for the two-compartment reactor under CDSL irradiation provided by the Helioman collector are noticeably greater than those previously obtained with one-compartment reactors (Fig. 3). The values recorded under GSL radiation provided by CPC's are only 30% lower despite a smaller photoanode surface, which is 0.095 m^2 instead of 0.22 m^2 and this proves the efficiency of CPC collectors.

2.3. Chemicals

The catalyst used in slurry experiments was titanium dioxide (Degussa P-25), since it is the most widely used in photocatalytic decontamination. The water used in experiments comes from the PSA Desalination Plant and has an equivalent laboratory quality (Type III–IV ASTM), with a TOC content of a little over (<0.5 mg/l). The phenol and 4-chlorophenol were purchased from Merck. Agrevo S.A. (Alcácer, Spain) supplied Pyrimethanil technical grade (98.2% purity). The rest of the reactives used were sulphuric acid (synthesis grade) and sodium hydroxide (synthesis grade).

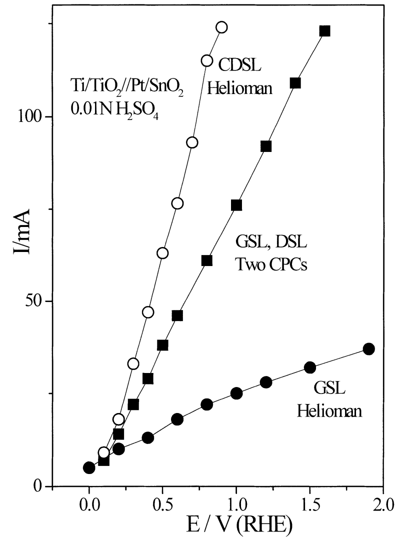

Fig. 3. Photocurrent-potential dependencies recorded for reactors with CPC's (■) or Helioman (●, ○).

3. Results and discussion

No photocurrent decrease was observed during the short half-hour measurements performed with three-electrode devices when low concentrations (20–30 mg/l) of model pollutants such as 4Cl-phenol, phenol or pyrimethanil were put in the working compartment.

3.1. Parabolic trough collectors (PTC, Helioman)

One-day experiments were performed with the reactor mounted on a Helioman module (Fig. 4) by a two-electrode device in which the counter-electrode also served as the reference electrode. The photoanode was polarised either at 1.4 V/(RHE) or at 0.8 V/(RHE), depending on whether 0.01 N H_2SO_4 or 0.05 M NaOH was put in the working compartment. A total volume of 180 l was circulated at a flow rate of 700 l/h and 0.7 bars. In all cases, a continuous decrease in the concentration of the organic compound was observed for the polarised Ti/TiO_2 photoanodes illuminated under the concentrated direct solar light (CDSL) provided by the Helioman module. During the illumination time (10 min) plotted in Fig. 4a, 900 mg of 4Cl-phenol was photooxidized. The geometrical surface of the photoanode is 0.22 m^2 and thus the photooxidation rate/time surface is 409 mg/min m^2. In the experiments with TiO_2 slurry (0.2 g/l), a total volume of 247 l was used and eight Pyrex tubes irradiated under CDSL [12]. The active surface of Degussa-P25 TiO_2 is 55 m^2/g and thus the photooxidation rate/time surface is 0.477 mg/min m^2, i.e., 857-times smaller than in the case of the polarised photoanode.

In Fig. 4b, the decrease in concentration of 4Cl-phenol when the working compartment was filled with 0.05 M NaOH and the photoanode was polarised at 0.8 V/(RHE) may be seen. The value obtained for the photooxidation rate/time surface is 573 mg/min m^2, which is 1200-times higher than the value obtained for TiO_2 slurries. With the concentrated solar light provided by the Helioman (CDSL), in the case of TiO_2 slurries, a large number of electron-hole pairs are formed, but they recombine again quickly because the photogenerated electrons are not collected.

The photocurrent values recorded with the two-electrode device during prolonged 1-day degradation of 4Cl-phenol are only 5 mA instead of those initially obtained under CDSL with a three-electrode device (Fig. 3). Therefore, the whole system was cleaned, pure 0.1 N H_2SO_4 was introduced and the photoreactor was tested again. The photocurrent values recorded with the two-electrode device are much lower (Curve 3, Fig. 5) than those obtained with new (WE, CE) electrodes before putting any organic compound in (Fig. 3) and it was assumed that the counter electrode was damaged or deactivated due to poisoning of Pt sites. Indeed, with a new counter-electrode higher photocurrent values were measured both under GSL and CDSL (Curves 2 and 3, Fig. 5) with a two-electrode device than before (Curve 1, Fig. 5).

However, while the photocurrent values recorded under GSL are similar to those previously obtained with a three-electrode device (Fig. 3), the photocurrents measured under CDSL are 4- or 5-times smaller. Under concentrated (up to 10-times) direct solar light (CDSL), the counter electrode is not efficient enough to collect the photogenerated electrons and, therefore, the photoanode cannot reach its maximum photocurrent. Moreover, if 4Cl-phenol is again introduced into the photoreactor and the photoanode is polarised at 1.8 V/(RHE), the photocurrent values progressively increase, even if the UV radiation is lowered (Fig. 6). It is assumed that in a long-term experiment, the pho-

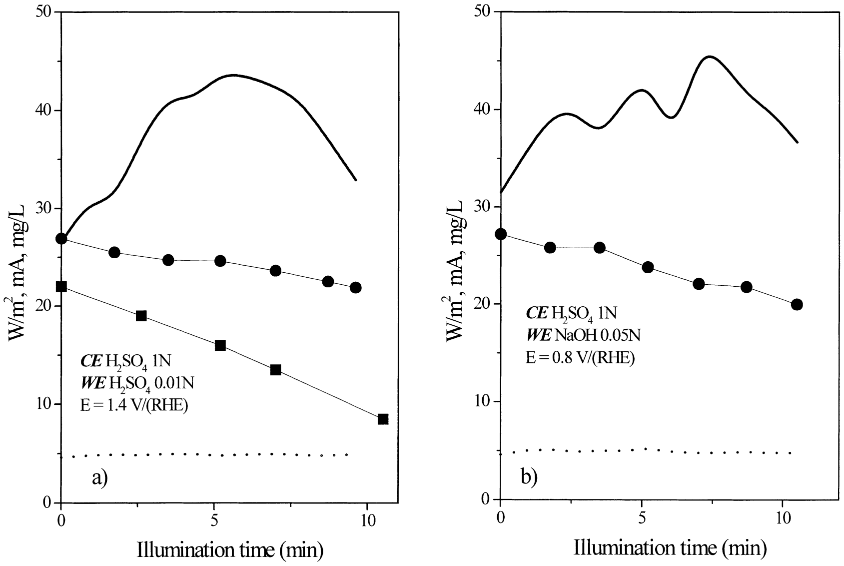

Fig. 4. Two-electrode experiments performed under CDSL with a Helioman collector: (a) 0.01 N H_2SO_4, (b) 0.05 M NaOH. Full curve: direct UV, W/m^2; dotted curve: photocurrent, mA; ●: 4Cl-phenol degradation in photoelectrochemical reactor; ■: 4Cl-phenol degradation in a TiO_2 slurry (0.2 g/l) photoreactor.

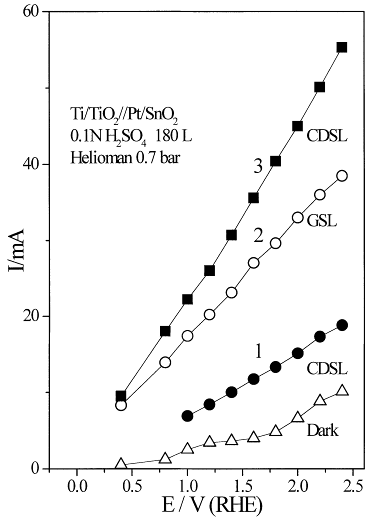

Fig. 5. Photocurrent-potential tests: (1) photoreactor after use with organics; (2,3) photoreactor with a new counter-electrode.

toanode, which was deactivated during the previous experiments with organics, progressively recovers its efficiency under CDSL with a high (1.8 V) anodic potential.

The decrease in concentration in 4Cl-phenol shown in Fig. 6 is similar to that previously observed (Fig. 4) and the photooxidation rate/time surface is 477 mg/min m^2. This is 1000-times higher than the value obtained in a TiO_2 slurry, and the ratio is of the same order of magnitude as in earlier experiments (Fig. 4). No significant decrease in the photocurrent was observed during the test performed in pure 0.1 N H_2SO_4 at various potentials in a two-electrode device. Presumably, the deactivation of Ti/TiO_2 photoanodes, due to the presence of recalcitrant organics such as 4Cl-phenol occurs only with relatively low anodic potentials.

3.2. Compound parabolic collectors (CPC)

Since these collectors provide a noticeably lower (10-times) illumination ratio compared to Helioman modules, fewer electron/hole pairs should be produced. It is, therefore, of interest to compare the photooxidation rate/time surface ratios for photoanodes with Helioman or CPCs with those found for TiO_2 slurries under the same experimental conditions. The results obtained with two photoanodes having a total area of 0.095 m^2 are shown in Fig. 7 for the photooxidation of 4Cl-phenol in acidic and basic solutions at potentials of 1.4 V and 0.8 V/(RHE), respectively.

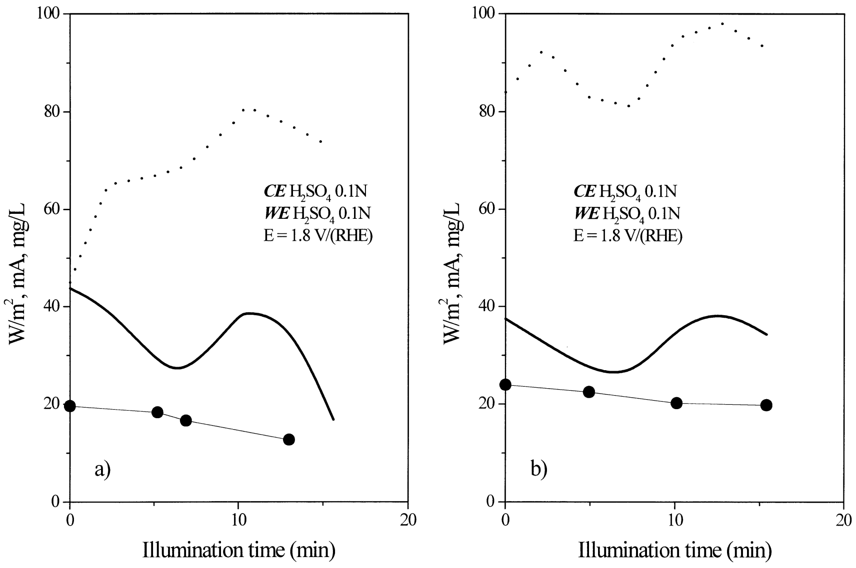

Fig. 6. One-day experiments performed with a Helioman module under CDSL for (a) 4Cl-phenol, and (b) phenol. The photoanode was held at 1.8 V/(RHE) versus the new counter-electrode.

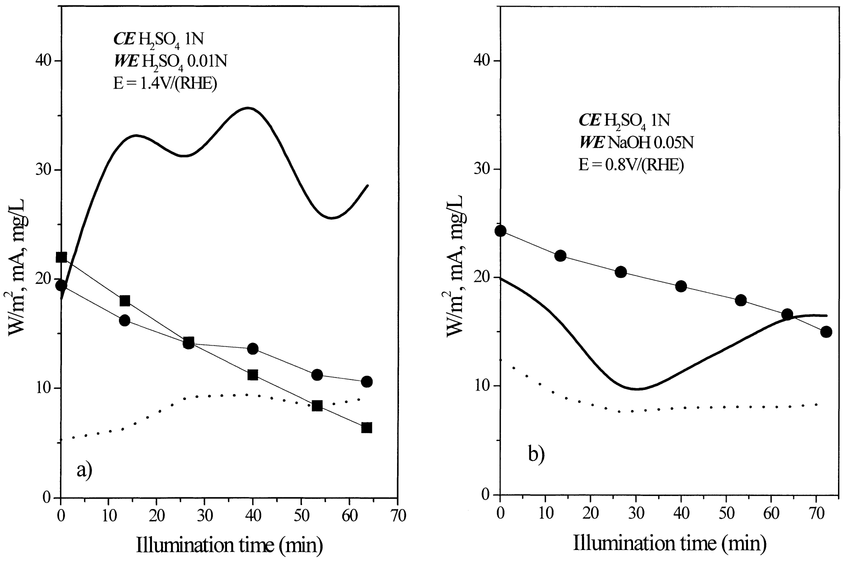

Fig. 7. Two-electrode experiments performed with CPC's in: (a) 0.01 N H_2SO_4 (b) 0.05 M NaOH. Full curve: direct UV, W/m^2; dotted curve: photocurrent, mA; ●: 4Cl-phenol degradation in photoelectrochemical reactor; ■: 4Cl-phenol degradation in a TiO_2 slurry (0.2 g/l) photoreactor.

A photooxidation rate/time surface of 7.3 mg/min m^2 was found after a total of 4.5 l of polluted water had been treated by the photoelectrochemical reactors. This must be compared to the photooxidation rate/time surface of 0.106 mg/min m^2 obtained for the abatement of 4Cl-phenol in a TiO_2 slurry (0.2 g/l) with a CPC loop (8.9 m^2 illuminated area) in 247 l. With the polarised photoanodes, the photooxidation

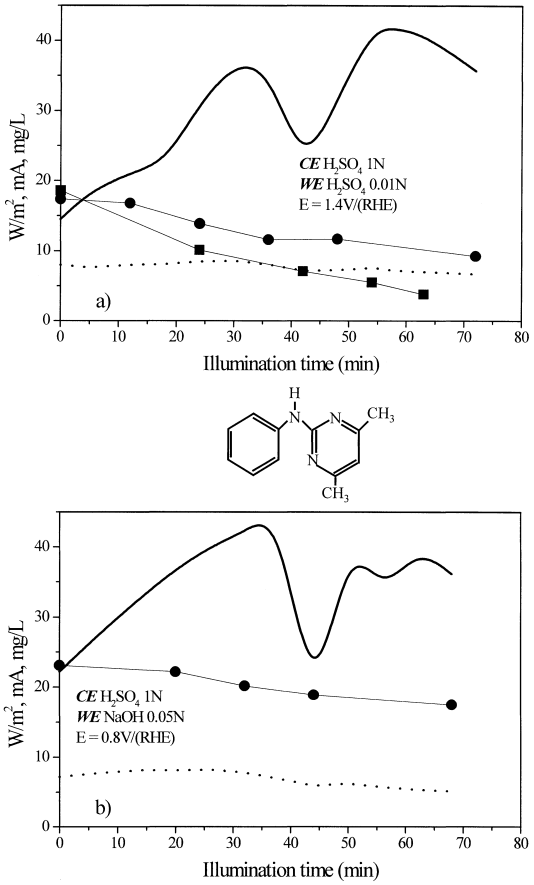

Fig. 8. Pyrimethanil degradation with CPC photoreactors filled with: (a) 0.01 N H_2SO_4 (b) 0.05 NaOH. Full curve: direct UV, W/m^2; dotted curve: photocurrent, mA; ●: pyrimethanil degradation in photoelectrochemical reactor; ■: pyrimethanil degradation in a TiO_2 slurry (0.2 g/l) photoreactor.

ratio is 69-times higher than with TiO_2 slurry, which is 12.7-times lower than the value obtained with a Helioman operating under tracking conditions. This result is in agreement with the solar light concentration ratio on the Helioman (up to 10 suns) and the CPCs (1 sun).

The decrease observed in a fungicide such as pyrimethanil (Fig. 8) is similar, whether 0.01 N H_2SO_4 or 0.05 M NaOH was introduced into the working compartment, while anodic potentials of 1.5 V/(RHE) and 0.8 V/(RHE), respectively, were employed. In the first case, the photooxidation rate/time surface is 6.21 mg/min m^2, i.e., 59-times higher than the value found for TiO_2 slurries.

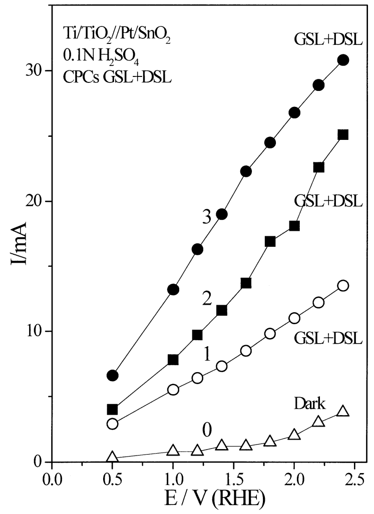

Fig. 9. Photoelectrochemical tests in dark (0) or under GSL + DSL for: (1) the photoreactor after use with pollutants; (2) the photoreactor with a new CE, (3) the photoreactor with a new CE and a reactivated (T) photoanode.

The photoreactors adapted to CPCs were tested after the experiments performed with 4Cl-phenol and pyrimethanil. The photocurrent values recorded for one of them with a two-electrode device by applying Various potentials (Curve 1, Fig. 9) are lower than in the case when a new counter-electrode is used (Curve 2, Fig. 9). Moreover, if the photoanode is heated at 400°C for 15 min, higher photocurrents are obtained (Curve 3, Fig. 10) as such thermal activation causes the removal of any organic compound adsorbed onto the TiO_2 layer. Nevertheless, photocurrent values measured for the photoreactor having a thermally reactivated photoanode (Curve 1, Fig. 10) are noticeably lower than those recorded for a new one (Curve 2, Fig. 10). The photocurrent values measured under flow conditions with a pair (old + new) of photoreactors are close to those resulting from the addition of photocurrents measured at the same potential for the old (Curve 1) and the new (Curve 2) photoreactor.

However, the photocurrent values measured with a two-electrode device in which Pt/SnO_2 has been used as counter and reference electrode at the same time (Figs. 9 and 10), are noticeably lower than the photocurrents recorded with a three-electrode device (Fig. 3) in which the potential is set with regard to a reference electrode (SCE). This is due to the relatively

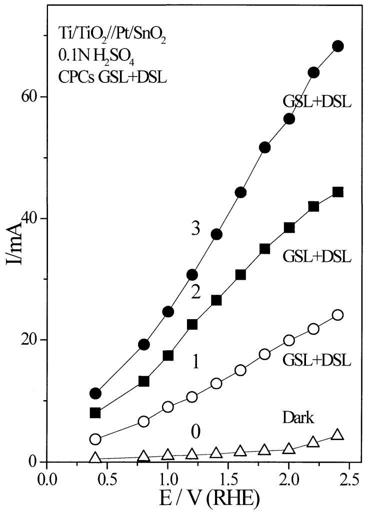

Fig. 10. I-E dependencies recorded under dark (0) or GSL + DSL for (1) the photoreactor with reactivated (T) photoanode, (2) the new photoreactor, (3) the coupled photoreactors.

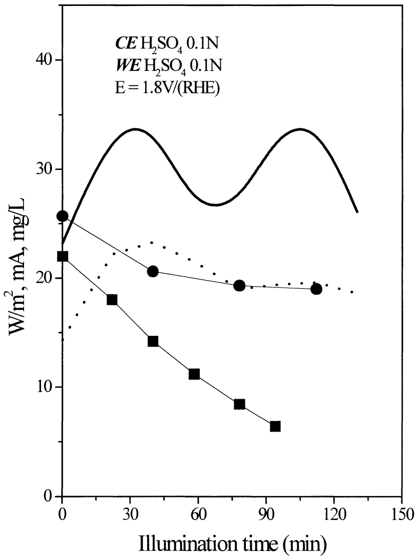

Fig. 11. Disappearance of 4Cl-phenol in coupled CPC photoreactors under GSL + DSL at 1.8 V/(RHE). Full curve: direct UV, W/m^2; dotted curve: photocurrent, mA; ●: 4Cl-phenol degradation in photoelectrochemical reactor; ■: 4Cl-phenol degradation in a TiO_2 slurry (0.2 g/l) photoreactor.

high resistivity of the SnO_2 conducting glass used as counter-electrode, and also to the poisoning of Pt sites needed for hydrogen evolution.

If the coupled photoreactors are polarised at 1.8 V/(RHE), the decrease in 4Cl-phenol in the working compartment filled with 0.1N H_2SO_4 remains relatively small (3.8 mg/min m^2) despite photocurrent values more than double (Fig. 11) those in the previous experiment (Fig. 7a). Moreover, the results obtained with the photoreactor adapted to a Helioman module, show that a higher photocurrent, such as shown in Fig. 6 compared to Fig. 4, does not lead to a faster decrease in 4Cl-phenol concentration, despite the higher number of OH$^\bullet$ radicals involved. One possible reason could be related to the slow water flow rate (700 l/h, Reynolds number = 3600, almost laminar flow) through the reactor due to its fragility. Under these conditions, low diffusion of reactives/products to/from the catalyst surface occurs and the reaction rate is not enhanced despite higher photocurrent values.

The amount of electricity involved in each experiment can be calculated as the product between the average photocurrent values (measured every hour with a digital multimeter) and the illumination time, usually 6 h, from 10 a.m. to 4 p.m. In the case of the photoreactor adapted to a Helioman module, the average photocurrent (5 mA) recorded during the photooxidation of 4Cl-phenol (Fig. 4a) was considerably lower than the values recorded (Fig. 6a) with a new counter-electrode. In the first experiment (Fig. 4a), 108 C were involved, i.e., 1.12 mM of electrons, an amount which is equivalent to that of the holes produced or to that of OH$^\bullet$ radicals. The total mineralization of 4Cl-phenol requires as much as 27 OH$^\bullet$ radicals for each molecule of pollutant [13], and thus for the total amount of organics (4.86 g) introduced in the photoreactor, 1.02 M of electrons are needed, or, in this case, only 1.12 mM of electrons are involved, i.e. 900-times less than needed for total mineralization. In the second experiment (Fig. 6a), the photocurrents recorded are higher and the amount of electricity involved (1512 C) too. In this case, 15.7 mM electrons are involved, i.e., 51-times less than the amount needed (800 mM electrons) for the total mineralization of the pollutant put (3.6 g) into the photoreactor. In these experiments with TiO_2 photoanodes adapted to Helioman modules, the degradation of 4Cl-phenol reached only the initial stages leading to organic intermediates. The situation is not very different for the photoreactors adapted to CPC's.

Indeed, in the experiment plotted in Fig. 7a, the amount of electricity involved (183.6 C) corresponds to 1.9 mM of photoproduced $OH^{\bullet}$ radicals, which is 9.7-times less than the amount needed (18.5 mM) for total mineralization of the 4Cl-phenol introduced into the photoreactor. In the second experiment plotted in Fig. 11, the amount of photoproduced $OH^{\bullet}$. radicals (4.48 mM) is six-times lower than the amount needed (27 mM) for total mineralization.

The decrease in concentration in 4Cl-phenol is similar in all the experiments examined above, but the amounts of photoproduced holes are different: presumably, when anodic potentials such as 1.8 V/(RHE) intermediates are more easily photooxidized. This may explain the increase in photocurrent values (Fig. 6) when the photoanode is illuminated with lower UV radiation, and why no photoanode deactivation or further decrease in photocurrent values was observed after the experiments plotted in Figs. 6 and 11.

4. Conclusions

Several photoanodes adapted either to PTC, Helioman, or to CPC's collectors have been tested used under outdoor conditions and it was found that a layer of TiO_2 photocatalyst deposited on a conducting substrate presents several advantages for the decontamination of water:

1. No separation of the photocatalyst from the decontaminated water is needed.
2. The photocurrent-potential dependencies measured either under global solar light (GSL) or concentrated direct solar light (CDSL) are very useful for rapid, simple evaluation of photoreactor performances. From the photocurrents measured continuously throughout the decontamination process, it is possible to obtain the amount of electricity involved and thus calculate the number of hydroxyl radicals to be entered in the mass balance. Such a possibility is very important for experiments performed under outdoor conditions where the intensity of solar radiation changes with time of day and local weather conditions, rendering the evaluation, and thus optimisation of the decontamination process, more difficult.
3. Better separation of charges occurs if photogenerated electrons are withdrawn by the application of a bias potential at the TiO_2/electrolyte interface, and this enhances the photooxidation of organic pollutants. The values of photooxidation rates/time surface measured with Ti/TiO_2 photoanodes are up to one thousand times higher than the values measured for TiO_2 slurries used under similar experimental conditions.

Among the various photoreactors tested, those having two compartments are of the most interest in practical applications such as water decontamination in solar plants. Indeed, the cylindrical photoanodes placed around an inner compartment are able to collect solar light at low concentration ratios, such as those provided by CPCs, efficiently. In addition, in the two-compartment photoreactors it is possible to include two different kinds of electrolytes at the same time: a strong acidic media in the inner compartment to favour cathodic hydrogen evolution, and in the working compartment, a second electrolyte with the pH adjusted to optimum efficiency for the photooxidation of organics.

However, several problems remain to be solved before the construction of photoelectrochemical reactors to be used in solar plants: porous conducting substrates with a large area have to be found for TiO_2 deposits and to test electrode materials such as Pt/Nb or reticulate vitreous carbon, which are more efficient than the conducting glass but also more expensive. Careful estimation of the investment needed for the construction of practical photoelectrochemical reactors, compared to the investment required for TiO_2 slurries from which the photocatalyst must be separated, is required. At the same time, more resistant reactors have to be designed to avoid mass transfer problems due to the low flow rates.

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References

[1] G.K.-C. Low, R.W. Matthews, Anal. Chim. Acta 231 (1990) 13.

[2] R.L. Pozzo, M.A. Baltanás, A.E. Cassano, Catal. Today 39 (1997) 219.

[3] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: Photocatalytic Treatment of Waters, CRC Press, Boca Raton, 1994.

[4] O. Enea, S. Malato, M. I. Maldonado, in: Martínez, D. (Ed.), Proceedings of the 1st Users Workshop on Training and Mobility of Researchers Programme at Plataforma Solar de Almería, CIEMAT, 1998, p. 13.

[5] O. Enea, J. Blanco, S. Malato, M.I. Maldonado, Proceedings of the 9th Solar Paces Symposium on Solar Thermal Concentrating Technologies, Font Romeu, France, 22–26 June 1998, 117.

[6] C. Minero, E. Pelizzetti, S. Malato, J. Blanco, Chemosphere 26 (1993) 2103.

[7] J.K.N. Mbindyo, M.F. Ahmadiand, J.F. Rusling, J. Electrochem. Soc. 144 (1997) 3153.

[8] A. Fujishima, K. Honda, Nature 238 (1972) 37.

[9] M. Romero, J. Blanco, B. Sánchez, A. Vidal, S. Malato, A. Cardona, E. García, Solar Energy, 1999, in press

[10] J. Moser, M. Gratzel, J. Am. Chem. Soc. 105 (1983) 6547.

[11] O. Enea, N. Vlachopoulos, ISE Ext. Abstr. 49 (1998) 216.

[12] C. Minero, E. Pelizzetti, S. Malato, J. Blanco, Solar Energy 56 (1996) 411.

[13] E. Brillas, R. Sauleda, J. Casado, J. Electrochem. Soc. 145 (1998) 759.