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Solar photocatalysis for detoxification and disinfection of contaminated water: pilot plant studies

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Abstract

Photocatalytic processes in the presence of titanium dioxide provide an interesting route to destroy hazardous organic contaminants, being operational in the UV-A domain with a potential use of solar radiation. A preliminary evaluation of a photocatalytic process for water purification has been made to assess its effectiveness in reducing contaminant concentrations of drinking water standards. Studies reported in this paper also evaluate the performance of a low-cost compound parabolic concentrator (CPC) prototype built along this work and explore the feasibility of this concept as the basis for the solar photocatalytic oxidation facilities of water supplies. From our observations, a solar throughput value of 42 l/h m^2 for the low-cost CPC reactor tested at our facilities has been obtained. These calculations are based on the time required for the destruction of 500 μg/l of selected pesticides to maximum permitted levels (0.1 μg/l) and four-log inactivation of microorganisms. From the research performed, cost analyses have been made for a full-scale commercial system using the data available in this project. For a 500 m^2 facility, the estimated total costs for photocatalytic degradation is competitive with conventional technologies and estimated to be ca. 0.7 \$/m^3. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photocatalytic oxidation for water treatment applications refers to the heterogeneous oxidation reaction involving solid semiconductors surfaces. Titanium dioxide is a semiconductor that is particularly promising in this regard [1,2]. Extensive work have been done elsewhere on solar photocatalytic oxidation of organic compounds [3,4]. Therefore, recent research has shown that this technology might be effective in water disinfection [5,6,7].

A considerable amount of academic and research literature has been published on the photocatalytic oxidation of pesticides in water, but little operational data on the effectiveness of this technology for drinking-water treatment is available. Furthermore, to be competitive with other water-treatment technologies, such as AOP, GAC, etc. solar photocatalytic processes must meet the requirements of this particular application at a significant lower cost.

Although present cost for the solar water detoxification system is higher than that for conventional technologies, potentially greater cost reductions are being investigated. Testing of low and non-concentrating compound parabolic concentrator units at NREL [8]

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and PSA [9] have shown that these designs are very efficient for detoxification applications. Although the advantages of this system are clear [10], its cost may limit them in some practical applications for economic reasons. This paper summarises the work done through a joint research project aiming to develop an appropriate installation for the application of CPC technology which makes use of titanium dioxide catalytic photoreactions into detoxification of toxic materials and microorganisms in water. The work planned has covered the following stages:

- To study alternative one-sun reactor designs which will contribute heavily to achieve performance improvements and cost reductions of solar detoxification systems.
- To design and build a solar water-treatment plant of appropriate size for treating significant volumes.
- To carry out pilot-scale experiments in order to investigate the feasibility assessment of photocatalytic oxidation of selected pesticides (EPTC, butiphos and γ-lindane) and microorganisms (*Escherichia coli* and *Enterococcus faecalis)* according to EU regulations and World Health Organization (WHO) recommendations.
- To estimate the cost for a full-scale commercial system.

We have demonstrated through this work that CPC's technology can be practical if the reflector can be made at a cost much lower as compared to the cost of current one-sun design [11]. Since the ultimate goal was to provide products to be used commercially, it was decided to use only commercially available raw materials in this work which would allow a correct and immediate assessment of the cost of the advancement and also expedite market penetration.

2. Experimental

2.1. Chemicals

All chemicals were purchased through commercial organizations and were used without further purification. Thiocarbamate pesticides, such as EPTC (S-ethyl-N,N-dipropyl thiocarbamate), was supplied by North Hungarian Chemical Works, Sagrochem, and were 99% pure. Butiphos (S,S,S-tributyl-phosphorotrithioate) was supplied by DLR. High purity HPLC acetonitrile was obtained from Scharlau, S.A. The powdered semiconductor catalyst (P-25 TiO_2 Degussa) was used as supplied, without any pre-treatment.

The bacteria used in this study were obtained from the Spanish Type Culture Collection (*Escherichia coli* (CECT 471); *Enterococcus faecalis* (CECT 481)). Both, *E. coli* and *E. faecalis* were maintained on refrigerated nutrient agar slants before transfer to modified nutrient broth (*E. coli*) and brain heart infusion broth *(E. faecalis*) for overnight incubation at $37^\circ \pm 0.5^\circ C$. A second transfer was then made, and after 8–12 h cultures were harvested by centrifugation and resuspended on sterilised tap water for reactor inoculation.

2.2. Analysis

High-performance liquid chromatography was used for EPTC degradation experiments. The liquid chromatography system consists of an isocratic LC pump (Perkin–Elmer LC 250) and was equipped with UV/visible detector (Perkin–Elmer LC-95).The reversed-phase column used was a 250×4.6 mm i.d. C_{18} column. The UV detection was carried out at 210 nm. The eluent was a 50×50 mixture of acetonitrile and water.

Capillary gas chromatography (Hewlett–Packard 5730 A) in combination with electron capture detector (ECD) was used for γ-lindane routine analysis. A 1.75×3-mm Type OV 17 (3%) column was used. The injector and detector were maintained at a temperature of 250°C using argon–methane as a carrier gas. The oven temperature was 200°C.

For butiphos analysis utilised gas chromatography (Perkin–Elmer) equipped with FID detector and OV-1 packed column and nitrogen as carrier gas. The injector and detector were maintained at 250°C. The oven temperature used for analysis was 200°C.

Samples were collected, filtered through 0.45-μm pore size regenerated cellulose filters and concentrated using a solid phase extraction C_{18} bond eluent cartridge (VARIAN) and a peristaltic pump (GILSON). The cartridge is dried and eluted with high-purity solvents, dichloromethane for lindane and butiphos and acetonitrile for EPTC. A total carbon analyser (Sievers

800) based on a patented detection technique which utilises a combination UV persulfate oxidation to form CO_2 and permeation/conductivity detection method was used for TOC measurements. The CO_2 sensor permits measurements of TOC at concentrations as low as 0.5 ppb.

Bacterial concentration in the inoculates was determined using calibration curves. Bacteria were enumerated using the membrane filtre technique. Media employed were m-FC Agar for *E. coli* and Slanetz & Bartley Agar for *E. faecalis*.

2.3. Experimental set-up

This prototype (4.5 m^2 area) consisted of twelve Pyrex tubes mounted in compound parabolic reflectors with the tubes running in the East–West line (Fig. 1). Considering the location and the duration of the test, the CPC aperture was tilted at a latitude so as to maximise the available solar irradiation. This prototype included the following components: Solar collector (Pyrex photoreactor tubes, aluminium reflective surface), flowmeter, pump, sensors (pH, O_2, T, UV radiation), pipes, fittings and tanks (PVC).

At the beginning of the test, a fresh batch of tap water was admitted into the storage vessel (150 l). Then, water was spiked with pesticides or inoculated with micro-organisms and titanium dioxide was added at the desired ratio. The catalyst loading in all kinetic runs was 0.05% weight fraction and for each analysis a fresh suspension of TiO_2 in water was prepared. The test solution was circulated through the photoreactor tubes (25 l) and then all instrumentation and controls necessary for the operation were connected. Data were expressed to represent exposure time, t_{exp}, which is defined as the amount of time each fluid element spent in the illuminated portion of the Pyrex photoreactor (1/6 total time). The system is operated at batch mode at flow rates sufficient to assure fully turbulent flow and avoiding the settlement of TiO_2 particles onto the tubes.

3. Results and discussion

A preliminary evaluation of a photocatalytic process for water purification has been conducted at pilot scale in Spain and Morocco, operating in the CPC pilot plant with pesticides or micro-organisms. The objective of batch experiments was to assess the effectiveness of photocatalytic processes in reducing contaminant concentrations to drinking water standards into a non-laboratory environment. Later research has demonstrated that the effects of water composition are probably the most significant process parameters with respect to field applications of solar photocatalytic reactions [12,13]. For example, it is well known that some natural water components, especially carbonate ions, can act as radical scavengers and effectively consume OH radicals. In this regard, tap water was used in all experiments in order to approximate our tests to field conditions. No attempt was made to control the pH of the influent water that generally exhibits a pH between 6 to 8. Water temperature generally increased up to 40°C along these experiments.

Solar detoxification and disinfection experiments were conducted in Bilbao, Spain (latitude 43°), and Rabat, Morocco (latitude 34°), with an average radiation ranged from 15–25 W/m^2 global UV (maximum of 35 W/m^2) and 20–35 W/m^2 global UV(maximum of 45 w/m^2), respectively.

3.1. Microbial results

Micro-organisms studied were classical bacterial indicators of faecal pollution (*Escherichia coli* and *Enterococcus faecalis*). Initial bacterial densities of *E. coli and E. faecalis*, in the reactor ranged from 10^2 to 10^4 cfu/ml, with most values falling around 10^3. These values are consistent with heavily contaminated raw water, according to Directive 75/440/EEC known as the “Surface water directive intended for abstraction of drinking water.”

The rate of destruction of micro-organisms is often postulated as a first-order chemical reaction (Chick’s law) [7] (Eq. (1)).

$$N_{\mathrm{t}} = N_0 \mathrm{e}^{-kt} \tag{1}$$

where N_{t} is the number of micro-organisms remaining at time t, N_0 the number of micro-organisms at time zero and k the rate constant characteristic of the type of micro-organisms, the UV intensity and the water quality aspects of system. Data have shown that inactivation rates of *E. coli and E. faecalis* followed the Chick law with r^2 values >0.9 using an exponen-

Fig. 1. Photograph of the CPC pilot plant.

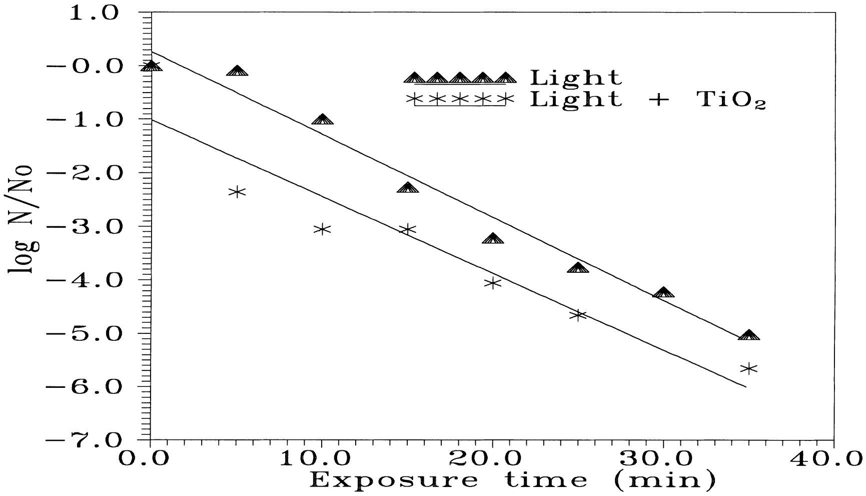

Fig. 2. Batch photocatalytic experiments with *E. coli*. Conditions: (∗) 0.05 % TiO_2; (▲) blank experiment. I = 25 W-UV global/m^2; pH ~7.8.

tial regression for all experiments. Least-squares fittings of the data resulted in $k = 0.25\,\mathrm{min}^{-1}$ for *E. coli*, a value 1.3 times higher than that of ca. $0.21\,\mathrm{min}^{-1}$ corresponding to inactivation of *S. faecalis*. Control experiments were run in parallel, and included water exposed to light with no titanium dioxide added. These tests have confirmed the effectiveness of germicidal action of sunlight which has long been recognised [14]. Water temperature variations up to 40°C do not play a significant role in bacterial inactivation [15]. Our results are plotted in Fig. 2 for *E. coli* and indicated that natural UV component of sunlight is able to destroy micro-organisms at a rate similar to that of illuminated TiO_2 particles. The rate constant ratio ($k_{\mathrm{with\,TiO_2}}/k_{\mathrm{without\,TiO_2}}$) was ≈1 for values falling around 10^3 cfu/ml, although it was dependent of the initial micro-organism concentration. In general, this ratio decreased when the initial concentration increased.

In spite of these results, it is important to note that photocatalytic oxidation is considered to be a preferred method than UV near disinfection, because it has been demonstrated that the OH radicals are able to destroy biological contaminants, with the oxidation of proteins, lipids or nucleic acids, thus resulting in inhibition of respiration or growth of the microorganisms [16].

3.2. Detoxification results

A pesticide concentration range from 20 to 500 μg/l was selected for pesticide tests. These values have been considered to represent a typical level of micropollutants in natural waters. A kinetic analysis of the photocatalytic degradation of pesticides has shown that for these low solute concentration a simple first-order kinetic model is sufficient in many instances (Eq. (2)), although photocatalysed reaction have been successfully described with a Langmuir–Hinshelwood equation [4,17].

$$c = c_0 \mathrm{e}^{-kt} \tag{2}$$

where c_0 is the initial concentration of pesticide, k the apparent first-order rate constant and t the reaction time. The first-order rate constants for the three selected pesticides were determined experimentally in the pilot plant. Least-squares fittings of the data resulted in values of k as 0.19, 0.18, 0.17 min^{-1} for EPTC, butiphos and γ-lindane, respectively, under the experimental conditions described in Fig. 3. Outside of the experimental errors, an interesting aspect of the kinetic data is that the observed disappearance rates for the different chemical compounds are very similar.

The generally accepted model for the oxidation of organics in illuminated TiO_2 suspensions, the Langmuir–Hinshelwood rate equation, assumed that at the surface of the particles the organic solute is adsorbed, then the organic react with the photoholes either directly or via an adsorbed hydroxyl radical intermediate. Although, there are a number of reports concerning the Langmuir–Hinshelwood model to describe the photocatalytic degradation of organic compounds, there are still some doubts concerning their use. Some studies have sought chemical evidence that the rate of photocatalytic oxidation does not correlate with the extent of adsorption, but depends on the physical properties of the photocatalyst, electron–hole recombination, trapping rates, etc. [18,19]. In this way, the similarity of disappearance rates for the different chemical compounds found in our tests could not be explained on the basis of an affinity of adsorption, because they are very different, but on a rate-limiting step consisting of hydroxyl radical formation [20]. Another potentially rate-limiting step might be pesticide mass transfer to the photoactivated surface. Such a circumstance would arise only at the parts per billion levels of this study.

Although the aim of this work was to evaluate the application of this photocatalytic oxidation technology for water purification according to EU regulations, some attempts were made to determine whether pesticides EPTC, lindane and butiphos were completely mineralised by measuring the final TOC. This method of analysis was used to demonstrate not only apparent destruction, but also complete degradation. It was observed that total mineralisation requires a much longer illumination time than the disappearance of the parent compound.

It was found that the illumination time to achieve total mineralisation was dependent of the selected pesticide, e.g. the degradation of lindane suggest a rapid mineralisation and absence of appreciable accumulated intermediates. For 500 μg/l, the photocatalytic treatment leads to a substantial 90% abatement of TOC and a 99.9% reduction in γ-lindane concentration. In contrast, the photocatalytic destruction of EPTC yielded higher amounts of intermediates prior to complete mineralisation. In that case, the photocatalytic process was able to decrease the TOC of about 70% when maximum permitted levels for EPTC were achieved (0.1 μg/l). A complete description of intermediates identified in the photocatalytic degradation of EPTC and γ-lindane are given in recent works [21,22].

Several researchers have demonstrated that these pesticides are converted to their inorganic forms under TiO_2 mediated photocatalytic oxidative conditions, e.g. inorganic species such as ${PO_4}^{-3}$, ${NO_3}^{-}$, ${NH_4}^{+}$, ${SO_4}^{2-}$, etc. have been identified in the literature as the final decomposition products for other N,P,S based organic compounds [23]. Blank experiments (light

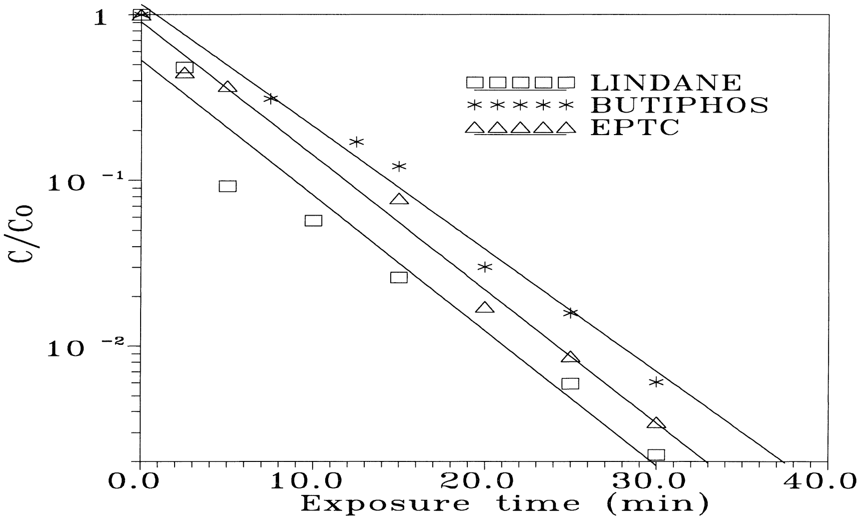

Fig. 3. Photocatalytic degradation of EPTC, butiphos and -lindane at the pilot plant. Conditions: [pesticide]$_0$ = 100 μg/l; 0.05% TiO_2; I = 35 w UV global/m^2; pH ∼7.3.

with no titanium dioxide) have confirmed that loss of the contaminants was only due to the photocatalytic process.

It is worth mentioning that pilot-scale experiments were performed with water of similar quality (ionic strength <500 μS/cm). Tests conducted along this work have shown that the presence of ions or molecules (Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $HCO_3{}^-$, etc.), frequently found in water, did not seem to affect the oxidation rates expected for laboratory data. This behaviour could be explained by the low mineralisation of tap water used. It was also reported that the presence of inorganic species, when a solid catalyst is employed, did not seem to affect the efficiency of removal of organic matter to the extent that it does with other advanced oxidation technologies, because the oxidation reaction occurs at or near the catalyst surface [24].

3.3. Cost analysis

The treatment capacity of the CPC pilot plant built along this work has been expressed in Table 1 in the form of solar throughput, defined as the volume of water treated per square meter of aperture area which is able to reduce initial contaminant concentrations to maximum permitted levels. These calculations are based on the time required for the destruction of 500 μg/l of selected pesticides to maximum permitted levels (0.1 μg/l) and the four-log inactivation of *E. faecalis* bacteria. In this case, we have assumed our results for yearly average conditions when the average global UV insolation is 25 W/m^2. Table 1 summarises the costs for a 500-m^2 solar water-treatment plant using the data available in this project. These estimates were based on 1997 construction cost indices, and total annualised costs were calculated by using an interest rate of 10% over a 15-year period. The treatment cost was estimated to be US$ 0.7 per m^3 and is competitive with conventional technologies. Most of the cost examples for drinking-water treatment are in the vicinity of US$ 1 per m^3 [25]. In Table 1 a key assumption in the extrapolation of available data was to consider that the ultrafiltration for TiO_2 slurries in a large-scale system is a viable alternative (assuming 10% losses).

4. Conclusions

Although present costs for the solar water detoxification system are higher than for conventional technologies, potentially greater cost reductions have been investigated. We have demonstrated through this work

Table 1
Treatment cost calculations with photocatalytic systems based on TiO_2

COMMON INPUT DATA	
Yearly working days	365
Availability factor	80%
Average of useful hours (sunny days)	12 h
Effective yearly operating hours	3500 h
UV global radiation (average at operating hours)	25 wUV/m^2
Total collector area (111 units × 4.5 m^2)	500 m^2
Total land area	2000 m^2
Cost of TiO_2	14.5 $/Kg
Solar collector cost	160 $\$/m^2$
Land cost	1.5 $\$/m^2$
COST ESTIMATION	
Treatment capacity	42 $l/h\,m^2$
Direct cost	
Total collector cost (500 m^2)	US$ 80 000
Piping and tanks	US$ 8500
Auxiliary equipment and controls	US$ 9100
Land and civil works	US$ 18 000
Ultrafiltration system and valves	US$ 62 000
Total direct	US$ 177 600
Indirect costs	
Contingencies (12%)	US$ 21 312
Spare parts (1%)	US$ 1776
Total capital required	US$ 200 688
Annual cost	
Capital (10% of TCR)	US$ 20 068
Consumables	US$ 21 047
O&M (5% of TCR)	US$ 10 034
Total annual cost	US$ 51 149
Treatment cost	US$ 0.7 per m^3

that CPC technology for solar detoxification and disinfection of contaminated water can be practical if the reflector can be made at a very low cost compared to the cost of current one-sun designs. Numerous designs and cost details remain to be worked out prior to the industrial use of this treatment concept, but it appears to represent a promising and potentially cost-saving alternative to current conventional methods for treating drinking water. From the research performed, cost analyses have been made for a full-scale commercial system using the data available in this project. For a 500 m^2 facility, the estimated total costs for photocatalytic degradation is competitive with conventional technologies and estimated to be about US$ 0.7 per m^3.

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