

Water detoxification and disinfection using high solar concentration and homogeneous photocatalysts

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Abstract. The objectives of the research were to explore the use of concentrated sunlight combined with dissolved photocatalysts to improve water quality. Initial experiments with bromacil using organic-dye photosensitizers indicated that the reaction kinetics were enhanced by concentrated light. Other pesticides (EPTC, Tribufos, Atrazine and Lindane) were also tested in normal and concentrated sunlight. Organic dyes were effective in degrading some of these compounds but did not appear to be promising for complete mineralization. For most target compounds, the reaction rates were approximately proportional to the intensity of light. Iron compounds, especially in combination with hydrogen peroxide as the oxidizer, proved to be effective for degrading all the target pesticides. This system was also shown to mineralize phenol. Reaction rates were again approximately proportional to sunlight intensity. The photoefficiency of this reaction was in a range high enough to indicate that visible light, as well as UV, was participating in the photo-reactions. Preliminary disinfection tests have indicated that either organic dyes or iron compounds are effective. It is concluded from this work that solar irradiation with either organic dyes or the iron-peroxide system are a promising, possibly low cost, means of improving water quality.

Keywords. Solar detoxification; concentrated sunlight; water purification; photocatalysts.

1. Introduction

This program was undertaken to determine conditions for the photochemical destruction of organic contaminants and micro-organisms in water by means of solar irradiation, using dissolved organic dye catalysts. Several investigators have reported accelerated oxidation of organic materials dissolved in water by use of solar radiation in the presence of organic dye catalysts such as methylene blue. R Turnheim–Ashkenazi¹ demonstrated greatly enhanced oxidation of bromacil (a common pesticide) at solar concentrations of up to about 8000 suns. It was hoped to demonstrate in the present investigations that concentrating sunlight would be a general method of efficiently destroying organic compounds and micro-organisms.

However, after a variety of experiments, it became apparent that most compounds were mineralized to a limited degree or not at all by oxidation using organic-dye photosensitizers. The investigations were therefore broadened to include Fenton-type

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chemistry involving dissolved iron compounds and hydrogen peroxide oxidant.

The objectives of the research were the following:

- To find low-cost methods of destroying pesticides and other toxic organic chemicals in water using homogeneous catalysts combined with sunlight,
- to investigate destruction of micro-organisms by similar means, and
- to investigate the effect of high concentrations of sunlight.

2. Basic chemistry

2.1 Singlet oxygen photochemistry

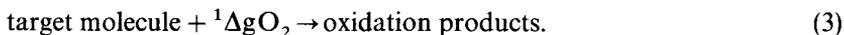
The overall reaction is an oxidation of the dissolved organic with dissolved O_2 as the oxidizing agent. The first step is absorption of a photon by the photosensitizer (dye) to reach an excited state



The excited sensitizer molecule is able to transfer its energy to a dissolved oxygen molecule to change it from the ground state ($^3\Sigma g O_2$) to the first excited state ($^1\Delta g$) which has a higher energy by 22.5 kcal mole⁻¹ and a lifetime of 1 to 10 msec in water

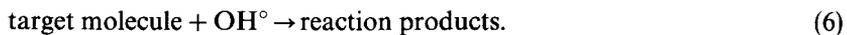
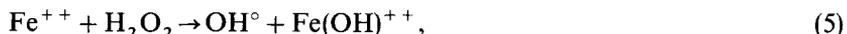
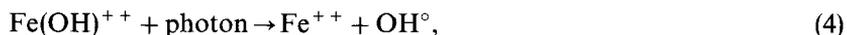


The singlet O_2 , ($^1\Delta g$) then is the oxidizing agent,



2.2 The Fenton reaction

This system is based on the capture of a photon by a ferric-hydroxyl complex with its conversion to a ferrous ion plus a hydroxyl radical. This reaction can be energized by photons from the ultra-violet into the violet and blue. The ferrous ion can be oxidized by molecular oxygen to restore the original ferric complex. However, a much faster reaction occurs with hydrogen peroxide as the oxidant, creating a second hydroxyl radical as follows,



Two OH° radicals are generated for each H_2O_2 , and for each photon absorbed. Two H_2O_2 are needed to oxidize one C atom to CO_2 .

3. Cost of solar detox of water

3.1 Background

The potential usefulness of solar detox is based on the effectiveness and cost of the process in comparison to alternatives. Research on solar detox has not reached a point where definitive comparisons can be made to conventional alternatives such as carbon absorption and/or incineration. However, there are sufficient data to establish the order of magnitude of the costs.

The main costs of solar detox are for (1) photons and (2) chemicals. We shall consider 3 detox alternatives here: (1) TiO_2 -catalyzed reactions that have been shown to oxidize (mineralize) or reduce most contaminants, (2) FeCl_3 -catalyzed reactions that have been shown to oxidize (mineralize) many contaminants, and (3) organic-dye catalyzed reactions that have been shown to oxidize some contaminants but have less capability for mineralization.

In the TiO_2 catalyzed reaction, photons in the ultraviolet are used, with 2 electrons made available for the process wherein each photon is absorbed in TiO_2 . In the FeCl_3 -catalyzed reaction, active photons extend from UV into the violet and blue, with again 2 electrons per photon if H_2O_2 or $\text{S}_2\text{O}_8^{2-}$ is the active oxidizer and if O_2 is the oxidizer, then the electron yield per photon is 1. For a methylene blue photocatalyst, photons near orange are used with 2 electrons per photon.

The oxidizers currently considered with their estimated costs are O_2 at \$50/tonne, H_2O_2 at \$1/kg, and sodium persulphate at \$2.3/kg. Other consumable costs are FeCl_3 at \$200/tonne, methylene blue at \$18/kg and CaO at \$140/tonne.

3.2 Results

Blanco and Malato² have published a cost analysis comparing CPC or parabolic trough solar concentrators with UV lamps for a TiO_2 -catalyzed water detox process with a mixed sodium persulphate-oxygen oxidizer. Their conclusions were that the CPC gave the lowest costs of the three alternatives, and was preferred to the parabolic trough because it delivered both direct and diffused sunlight.

Using the same general approach as Blanco and Malato, we assume \$300/m² cost for CPC collectors and balance of plant (i.e. primarily the cost the photons), 2200 kWhr per year global irradiation (includes 3.67% UV energy), and 15% per year capital and operating costs (without chemicals). These are now applied to 3 alternative photocatalysts in table 1.

The energy efficiency (defined as solar energy used/energy into photo-reactor) of the TiO_2 catalyst was determined by experiment². The energy efficiency of 10% for the $\text{FeCl}_3/\text{H}_2\text{O}_2$ system was based on oxidation of Orange II and *p*-coumaric acid at the Federal Institute of Technology (Lausanne)³ and the oxidation of phenol at the Weizmann Institute, Israel. When compared to the broad data base on compounds amenable to photo-oxidation with TiO_2 , the data base for FeCl_3 is limited and relatively unexplored.

Table 1. Cost of solar detox of water

Photocatalyst-oxidant	Assumed energy efficiency ⁴ %	Throughput m ³ water/m ² yr	Cost (\$/m ³)		
			Photons	Chemicals	Total
$\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8-\text{O}_2^{1,2}$	1.3	20	2.30	3.90	6.20
$\text{FeCl}_3/\text{H}_2\text{O}_2^3$	10	150	0.30	0.73	1.03
Methylene blue/ O_2^3	1	667	0.07	0.04	0.11

Notes: 1. Based on reduction of 100 ppm in total organic carbon.

2. Based on experimental data of Blanco and Malato².

3. Based on the degradation of 100 ppm of a contaminant of MV = 200.

4. Energy efficiency defined as solar energy used/energy into photoreactor.

The organic-dye photosensitizers have little potential for mineralizing organic constituents. However, they do offer possibilities for degradation of some toxic compounds and good prospects for disinfection. Where they are effective, even low energy efficiencies can provide low treatment costs, as indicated in table 1.

The costs of solar detox should ideally be considered as only part of the cost of an integrated water treatment system that may include biological treatment, filtration or other unit operations. Since biological treatment of aqueous wastes is generally cheaper than photochemistry, efforts should be made to integrate the two technologies to give optimal results.

4. Experimental approach

4.1 Solar tests

Three types of tests were set up,

- Solar furnace tests with flow at solar fluxes of 700–8000 kW/m² and exposure times of a fraction of a second.
- Tests at the solar tower where static samples are exposed to 10–200 kW/m² for periods from 5 seconds up to several minutes.
- Tests in ordinary sunlight.

The solar furnace (figure 1) is the principal test site. The furnace consists of a flat heliostat (100.m²) with two-axis tracking of the sun, mounted outdoors, that reflect to a spherical mirror which is made of 600-curved mirror facets located in a building. This 2-stage optical system produces a solar image approximately 5 cm in diameter in the focal plane. The range of solar flux is achieved by opening the door of the building,

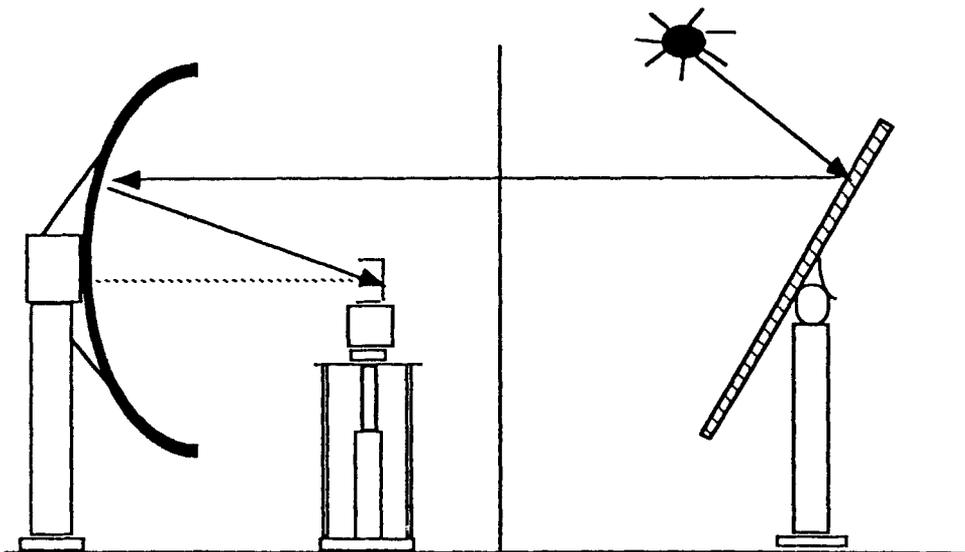


Figure 1. Schematic view of the solar furnace.

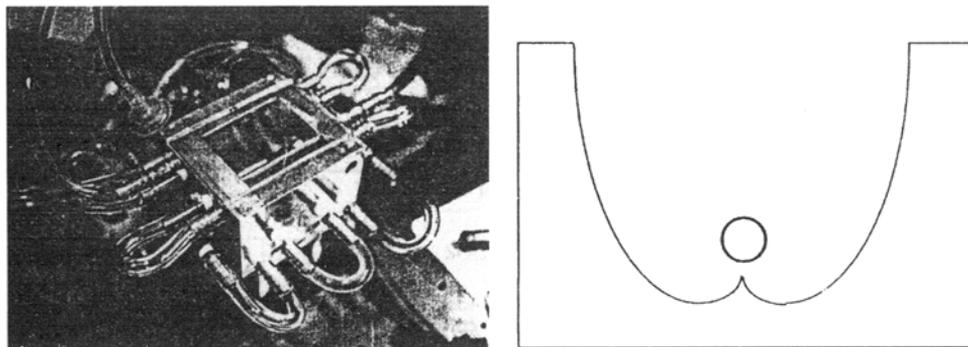


Figure 2. Photograph of the test reactor and side view of the quartz reactor tube mounted at the focus of the 2-dimensional CPC.

acting as a shutter. The receiver consists of a quartz tube 1 cm OD (0.8 cm ID), 7 cm long positioned at the focus of the furnace backed up by a 2-dimensional CPC (figure 2). The CPC is water-cooled. The solution to be tested was mixed in a large glass bottle serving as a reservoir. About 5 to 9 litres of solution were used in an experiment. Oxygen from a cylinder was bubbled through the water to saturate the solution. A pump circulated up to 3 litres of the solution per minute through the receiver, after which the water was discarded (once-through) or was recirculated to the reservoir. The pump and tubing were of teflon to minimize absorption of organics. The sample point was after the receiver. The solar beam insolation was recorded as was the temperature rise across the reservoir.

4.2 Chemical analysis

The objectives of the chemical analysis were:

- to determine the reduction in concentration of the target chemicals as the result of solar exposure, and
- to get information on the reaction products.

Most of the chemical analysis was conducted with a Cary 118 spectrophotometer. This was supplemented by HPLC to look for reaction products. HPLC is carried out using a Perkin–Elmer LC Model 250, with ISS-200 Autosampler, Photodiode Array Detector Model 235 C and 1020 LC Plus Controller and Software. GCMS analysis or total organic carbon analysis were used in some cases.

5. Results

5.1 Pesticides

A number of pesticides have been tested with organic dye and FeCl_3 photocatalysts. All of the pesticides could be degraded with $\text{FeCl}_3\text{-H}_2\text{O}_2$, but only some with methylene blue (table 2).

It was thought that it might be possible to enhance the catalysis of FeOH^{++} by complexing it with an organic dye that extended the spectral range of absorption.

Table 2. Summary of insecticide behaviour in sunlight. Methylene blue vs ferric chloride catalyst

Compound	Oxygen Methylene blue Alkaline pH	H ₂ O ₂ Ferric chloride pH 3 to 4
Bromacil C ₉ H ₁₃ O ₂ N ₂ Br	Rapidly degraded	Readily degraded
EPTC C ₉ H ₁₉ ONS	Degrades slowly	Rapidly degraded Degrades more slowly in sunlight with no catalyst
Tribufos C ₁₂ H ₂₇ OS ₃ P	No reaction	Rapidly degraded by H ₂ O ₂ dark. Degraded by FeCl ₃ + sun
Atrazine C ₈ H ₁₄ N ₅ Cl	No reaction	Readily degraded
Lindane C ₆ H ₆ Cl ₆	No reaction	Degraded

Experiments with FeCl₃, Orange[®] II (which complexes with Fe), oxygen and bromacil target gave results similar to solutions free of the dye. Some success was observed in oxidizing Atrazine with FeCl₃ and riboflavin catalysts, in the absence of hydrogen peroxide.

5.2 Destruction of bromacil with methylene blue photosensitizer and oxygen

The results of extensive testing of bromacil have been reported ⁴. To summarize,

- favoured by increasing pH in range 7–10
- kinetics more than proportional to the sunlight concentration (see figure 3).
- first-order kinetics relative to bromacil concentration
- favoured by increasing MB and O₂ concentration
- low degree of mineralization
- MB is also degraded
- Ca compounds had unexpected effects on kinetics, either positive or negative
- energy efficiencies up to 11.4% observed.

5.3 Phenol destruction with the Fenton reaction

Extensive tests were made using phenol as a model compound, with the following results:

- Effect of pH. Total organic carbon (TOC) reduction was favoured at pH of 3 to TOC vs exposure time. Linear destruction of TOC with time was observed at phenol concentrations above 100 ppm, after a fast initial dark reaction when phenol is mixed with FeCl₃-H₂O₂ (figure 4, table 3). First-order reaction kinetics (constant half-life of TOC) was generally observed at TOC between 10 and 50 ppm (table 3). At TOC

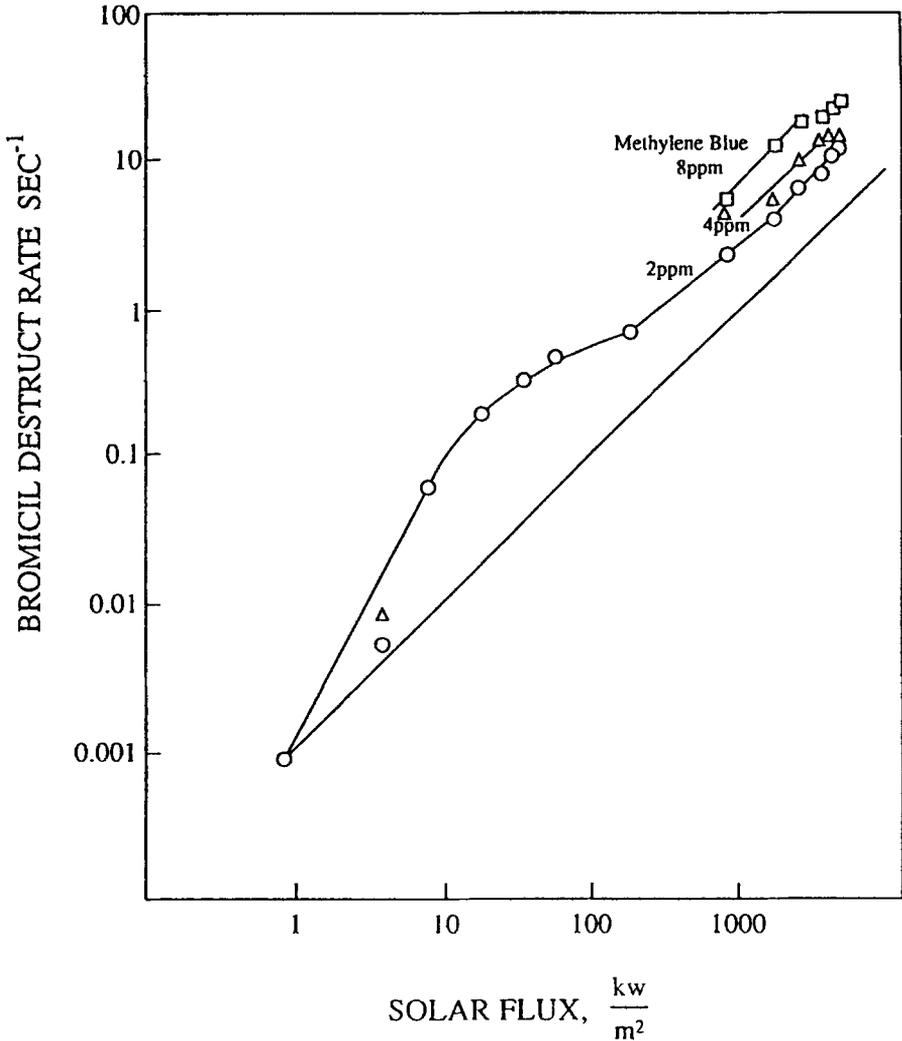


Figure 3. Bromacil destruction rate vs solar flux in the presence of methylene blue and NaHCO_3 .

below 10 ppm, the reaction is faster than first order provided the pH is optimal, the solution is clear and H_2O_2 is still in excess.

- Effect of the concentration of light. The half-life of TOC observed at the furnace was 2400 times faster than that observed under one sun. It should be noted that the ultraviolet portion of the solar spectrum is not properly concentrated in the furnace, especially the diffuse component. The ultraviolet photons are most effective for this process, although FeOH^{++} absorbs well into the visible spectrum. The ultraviolet beam radiation could be concentrated with aluminium reflectors instead of the back-surface silvered glass used.
- Effect of the concentration of FeCl_3 . It appears that the reaction rates are approximately proportional to FeCl_3 concentration in the range 40 to 100 ppm.

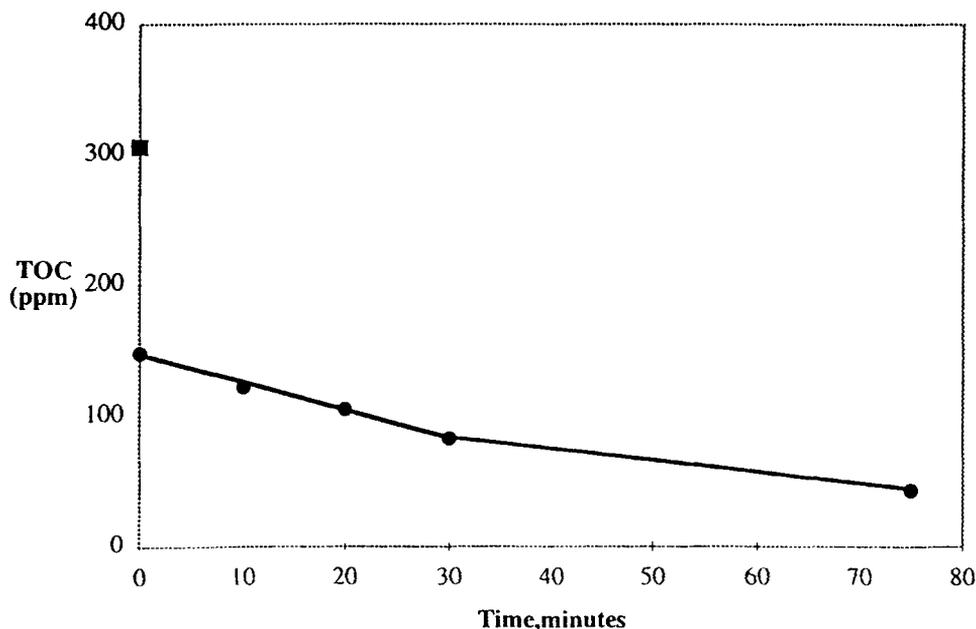


Figure 4. One-sun mineralization of phenol.
100 ppm Ferric chloride, hydrogen peroxide, 690 W per sq. metre

Table 3. Mineralization of phenol with Fenton reaction (100 ppm FeCl_3)

Time Min.	Condition	Phenol 450 ppm TOC(ppm)	pH	Phenol 300 ppm TOC(ppm)	pH	Phenol 150 ppm TOC(ppm)	pH
0	initial/dark	306	3.12	187		109.2	3.12
00	add H_2O_2	148	3.5	86.5	3.31	51.5	3.21
10	1 sun	122	3.7	71.7	3.54	41	3.24
20	1 sun	105	3.93	56.3	4.18	28	3.82
30	1 sun	83	4.2	46.2	5.14	17.3	4.1
75	1 sun	43	5.9				
	Solar Beam kW/m^2	690		660		610	
	Energy efficiency 00 to 30	29%		22%		20%	

- O_2 vs H_2O_2 . Much faster reaction occurs with H_2O_2 oxidizer.
- Energy efficiency up to 29% observed (table 3).

5.4 Microbiology

Both FeCl_3 and methylene blue are effective catalysts for the photo-destruction of *E. Coli* with sunlight. Figure 5 shows a factor of 10^6 reduction in concentration after a 10 min exposure with MB. Figure 6 shows 10^6 reduction in 45 min with Fe^{+++} concentration of 1.7 ppm, O_2 oxidizer.

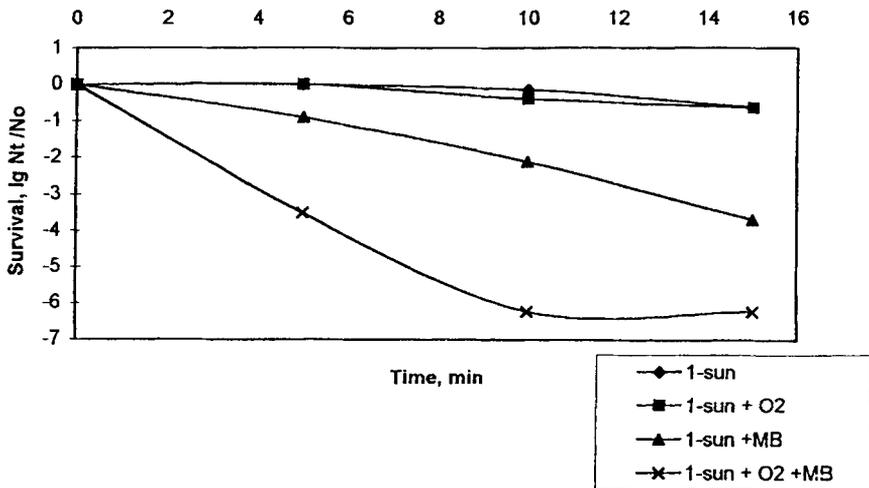


Figure 5. Influence of O₂, MB and combination of O₂ and MB on *E. coli* CECT 473 reduction.

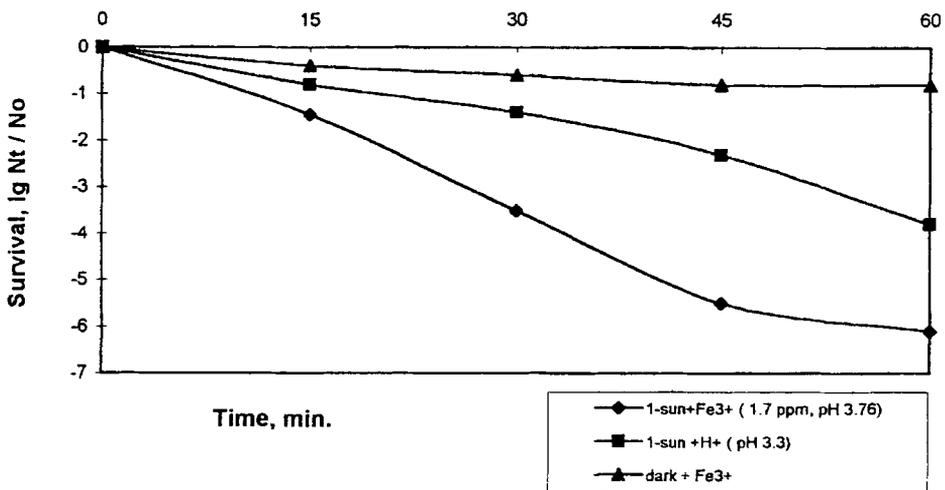


Figure 6. Influence of Fe³⁺ on *E. coli* CECT 473 reduction.

6. Conclusions and recommendations

- Organic dye photosensitizers are effective for disinfection and for oxidizing some organic compounds with sunlight.
- The ferric - hydrogen peroxide system in sunlight provides more powerful oxidation than the organic dye photosensitizers.
- These systems, in combination with other water treatment unit operations, appear to offer possibilities for low-cost improvement of water quality. For example, pH must be adjusted after treatment and photosensitizers filtered out.

Therefore, additional research and development are needed to optimize their use in specific applications.

The systems are effective over the range of sunlight intensity investigated (1–8000 suns). However, lacking a strong incentive for higher concentrations, the most cost-effective concentrator might be a compound parabolic collector (CPC) in cylindrical geometry oriented at the latitude angle with the ground, and controlled to rotate at fixed speed to follow the sun.

References

1. Turnheim R-Ashkenazi 1993 *Use of concentrated sunlight for photochemical inactivation of organic pollutants in water* MS thesis, Weizmann Institute of Science, Israel
2. Blanco Galvez J and Malato Rodriguez S 1996 In *Tecnologia de Fotocatalisis Solar* Instituto de Estudios Almerienses de la Diputacion de Almeria, Spain chap. 8
3. Kiwi J 1996 (personal communication)
4. Spiewak I, Yogev A, Benmair R, Ronen D, Turnheim R-Ashkenazi, Messalem R, Mizerikhin E 1996 *8th Intl. Symp. Solar Thermal Concentration Technologies* (Heidelberg: C F Müller Verlag) pp. 1509–1519