

## The photo-fenton reaction and the TiO<sub>2</sub>/UV process for waste water treatment – novel developments

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### Abstract

Solar applications of photochemical waste water oxidation methods driven by UV and/or visible light, especially TiO<sub>2</sub>/UV and the Photo-Fenton reaction (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-VIS), have been investigated. Degradation results of 4-Chlorophenol and some other model compounds at laboratory scale are discussed. A photoreactor with immobilized TiO<sub>2</sub> has led to a higher quantum efficiency than the suspension treatment. Electron densities were calculated to predict the oxidizing properties of UV irradiated TiO<sub>2</sub>. Al doped TiO<sub>2</sub> powders showed better performance than undoped samples in laboratory scale degradation experiments. Experiments with different waste waters (e.g. landfill leachates, plastics industry, etc.) using the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-VIS system in a photoreactor prototype are reported. Solar treatment of a model waste water in a glass basin has been investigated. Furthermore, experiments performed at the Plataforma Solar de Almería (Spain) with different methods, reactor types and waste waters are compared. According to a comparison of costing the solar driven Fenton reaction is a cheap method for water treatment, also for highly contaminated effluents. ©1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Advanced oxidation process; Waste water treatment; Solar; Photo-Fenton; TiO<sub>2</sub>; Doping; LAPW calculations; Electron density; Nafion®; Immobilization

### 1. Introduction

The cube in Fig. 1 represents the whole amount of water existing on earth (the water of oceans, lakes, rivers, polar regions, glaciers, underground water, water of the biosphere and atmosphere). The small cube in the magnification represents the available drinking water [1]. This small cube of approximately 9000 km<sup>3</sup>

potential drinking water per year (20.8 km side length) clearly illustrates how a shortage of water can become a threat to mankind. Besides, the world suffers from growing health and hygienic problems. Eighty percent of diseases in developing countries are caused by a deficient water supply.

According to WHO estimations [2]

- 1.2 billion people (one quarter of the world's population) lack hygienic drinking water.
- 1.4 billion people are without satisfactorily hygienic waste water disposal.
- More than 80 countries (>40% of the world's population) suffer from water shortage.

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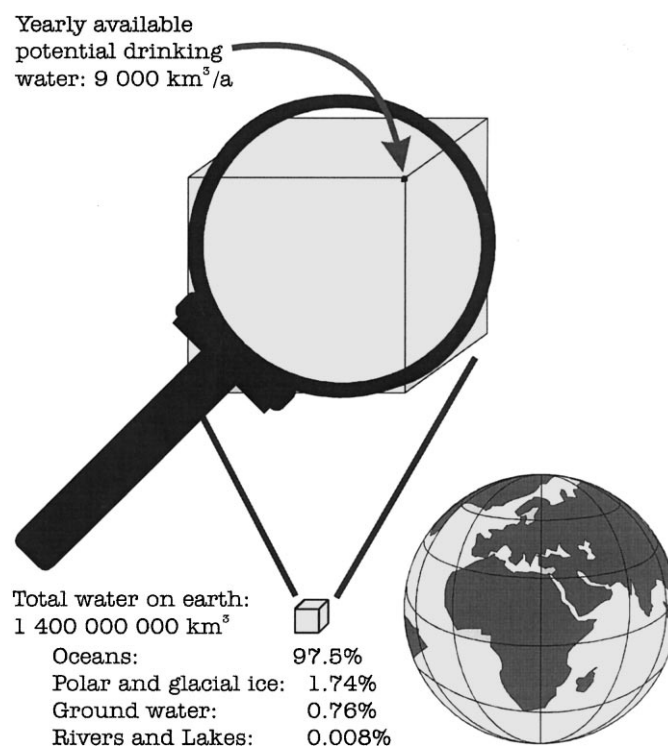


Fig. 1. Illustration of the world's water resources. The globe and the small cube are on the same scale. Data obtained from [1].

Two strategies of water treatment have to be forced to oppose these growing environmental problems: (a) chemical treatment of contaminated drinking-water, ground water and surface water; (b) chemical treatment of waste waters containing toxic or biologically non-degradable compounds.

For the last 25 years the research field of water purification has been extensively growing. Rigorous pollution control and legislation in many countries resulted in an intensive search for new and efficient water treatment technologies.

Advanced Oxidation Processes (AOPs) for the degradation of non-biodegradable organic contaminants in waste water are useful alternatives to established techniques like flocculation, precipitation, adsorption on granular activated carbon, air stripping or reverse osmosis [3]. Chemical treatment of waste water by AOPs can effect a complete mineralization of the pollutants to CO<sub>2</sub> and in case of halogenated compounds to halide ions. On the other hand, partial decomposition of non-biodegradable organic contaminants, like halogenated aromatics, by these AOPs is

straightforward, leading to biodegradable intermediates. Therefore combinations of an AOP as a preliminary treatment, followed by an inexpensive biological process, seem very promising from an economical viewpoint.

Although some authors [4] claim that there are other species involved, the active species responsible for destruction of contaminants in most cases seems to be the hydroxyl radical (OH•) with its very high oxidation potential. It 'burns' nearly all organic, but especially favors unsaturated compounds in aqueous solution.

This unstable and therefore very reactive radical can be generated by various techniques.

#### 1.1. OH• generation by direct photolysis of H<sub>2</sub>O<sub>2</sub>

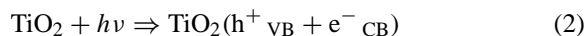


The quantum efficiency  $\Phi(\text{OH}^\bullet)$  for the direct photolysis of H<sub>2</sub>O<sub>2</sub> (1) is 0.98, but its absorption in the near UV-region is quite low [3]: the H<sub>2</sub>O<sub>2</sub>/UV photo-process needs low pressure mercury lamps

emitting short wave UV-radiation (254 nm), which is not available in the solar radiation. The high operating costs of the UV C lamps reduce the feasibility of application of this system on a large scale.

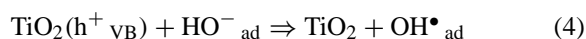
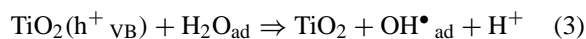
### 1.2. $\text{OH}^\bullet$ generation by excitation of $\text{TiO}_2$

The first step is a light induced ( $\lambda < 390 \text{ nm}$ ) generation of a hole ( $\text{h}^+$ )/electron ( $\text{e}^-$ ) pair (2).

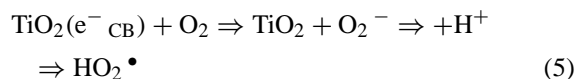


where  $\text{h}^+_{\text{VB}}$  is hole in the valence band,  $\text{e}^-_{\text{CB}}$  electron in the conduction band.

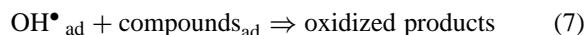
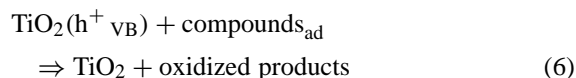
The oxidation of adsorbed water (3) or hydroxyl ions (4) by holes in the valence band at the excited surface produces the hydroxyl radicals.



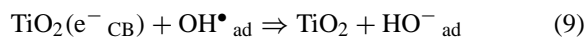
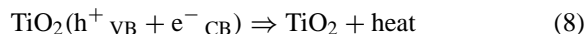
On the surface of the catalyst oxygen or other electron acceptors (e.g.  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_8$ ) are reduced (5).



Degradation of adsorbed compounds is possible either by direct oxidation on the catalytic surface (6) or by hydroxyl radicals (7).



Direct recombination of  $\text{h}^+/\text{e}^-$  pairs (8) and the reduction of adsorbed hydroxyl radicals by conduction-band electrons (9) are responsible for the low quantum efficiency of this method.



The system  $\text{TiO}_2/\text{UV}$  works with UV A light ( $\lambda < 390 \text{ nm}$ ), thus approximately 5% of the solar energy could be used for driving this process. However, three main problems have to be solved for its possible useful application:

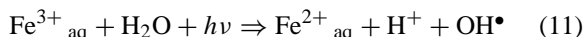
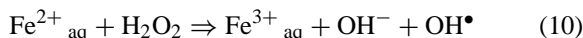
- Depth of penetration of excitation light into aqueous  $\text{TiO}_2$  suspensions has to be increased.
- Expensive separation procedures of  $\text{TiO}_2$  after the treatment have to be avoided.
- Increase of the low quantum efficiency of the decomposition process on the excited photocatalyst should be attained.

Immobilization of  $\text{TiO}_2$  on quartz glass fibers in a photoreactor helped to solve the first two problems [5]. The differences in the refractive indices of fused silica and the  $\text{TiO}_2$  coating cause excitation along the fibers. Photons not yet absorbed by one fiber can excite the coating of another fiber at the outer surface (Fig. 2). Therefore, optimal use is made of light as it illuminates the whole reactor (Fig. 3).

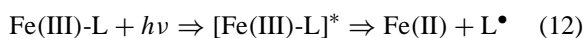
May be doping of  $\text{TiO}_2$  with different materials like Al, Nb, etc. to gain more holes at the surface of the excited photocatalyst could solve the third problem [6]. Before practical work electron densities of the excited surface of  $\text{TiO}_2$  have been calculated by a computer program (WIEN95) [7]. Trivalent ions are supposed to enhance the quantum efficiency by reducing the electron densities in the photonic excited state of  $\text{TiO}_2$  thus augmenting the hole densities.

### 1.3. $\text{OH}^\bullet$ generation by the Photo-Fenton reaction

This very complex photocatalytic reaction is among the most efficient methods to generate  $\text{OH}^\bullet$  radicals. Eqs. (10) and (11) describe the real reaction processes in a very simplified manner. Complexes and hydroxides of iron ions play an important role in these reaction cycles (possible ligands L are  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{HO}_2^-$ , carboxylates etc.).



Excited  $\text{Fe(III)}$  complexes undergo ligand-to-metal charge transfer (12). The broad absorption bands of these complexes are the reason why this reaction can be driven by visible light, too.



The superior efficiency of the Photo-Fenton reaction compared to  $\text{TiO}_2/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{UV}$  was clearly demonstrated in flask experiments for degradation of

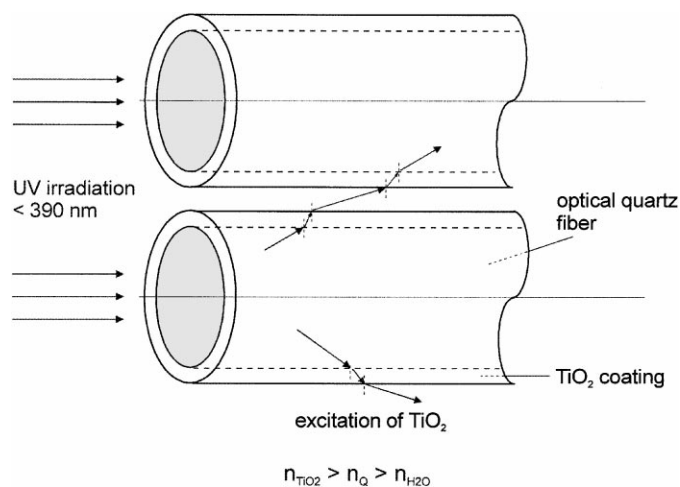


Fig. 2. Principle of the  $\text{TiO}_2$  coated fiber reactor: the refractive index of  $\text{TiO}_2$  is higher than the one of quartz, therefore light is refracted from quartz into the  $\text{TiO}_2$  layer.

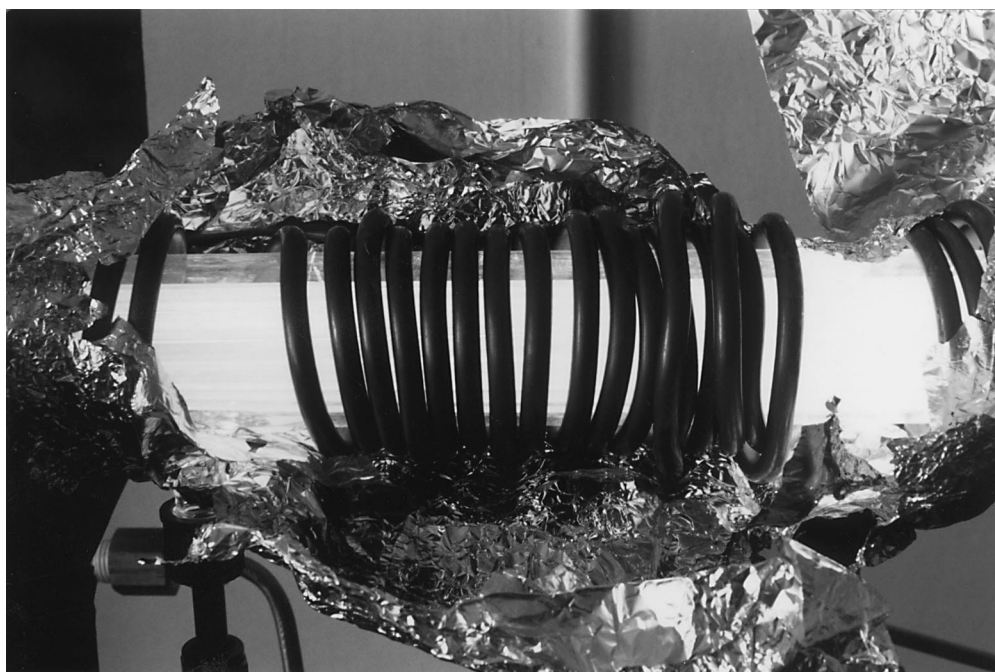


Fig. 3. A view of the  $\text{TiO}_2$  coated quartz fiber reactor with the fibers illuminated from the right hand side: light propagates into the whole reactor volume, in contrast to a suspension where light is completely absorbed within a short path.

4-Chlorophenol (4-CP) as a model waste water contaminant. The excellent results of the flask experiments encouraged us to construct a Photo-Fenton laboratory reactor for up to 15 l of waste water (Fig. 4). Measurements with this reactor exceeded the satisfactory re-

sults of the laboratory scale experiments, due to more efficient utilization of light energy [8].

Experiments in a glass basin covered by a window pane have been performed in Vienna to show the feasibility of solar waste water treatment even under

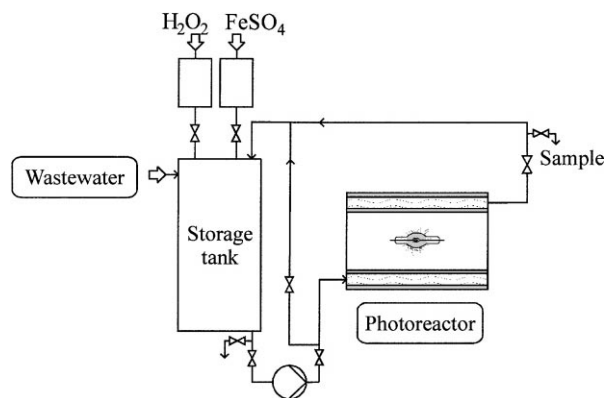


Fig. 4. Flow chart of the 151 Photo-Fenton laboratory reactor.

unfavorable light conditions. At the Plataforma Solar de Almería solar detoxification of pesticide containing waste water has been investigated as an example for the applicability of this solar driven process.

Currently efforts are made to immobilize Fe ions onto Nafion<sup>®</sup> membranes to avoid the need for iron separation from the waste stream after treatment, see also [9]. The need for acidification of a waste water stream is one of the major obstacles towards an industrial application of the Photo-Fenton reaction. Thus a possible extension of the useful pH range towards more neutral solutions would be of utmost interest.

## 2. Experimental

### 2.1. Analytical methods

Total organic carbon (TOC) was monitored with a TOC-Analyzer 5000 (Shimadzu) equipped with an auto sampler (ASI 5000). The determination of iron was performed with the spectrometric method using 1,10-phenanthroline with a Shimadzu UV-160A spectral photometer. The pH was measured by means of a WTW pH-Meter 537 equipped with a pH combination electrode E56. Chemical oxygen demand (COD) was determined by cuvette tests (Merck Spectroquant).

Amines and  $\text{NH}_4^+$  were determined by use of a Lichrosil<sup>®</sup> IC-CA (Merck) cationic column,  $5 \times 10^{-3}$  mol/l tartaric acid and  $10^{-3}$  mol/l pyridine-2,6-di-carboxylic acid as eluent. All eluents were made up with water from a Millipore ZFMQ 23004 System.

### 2.2. $\text{TiO}_2$ and Photo-Fenton 2 l flask experiments

$\text{TiO}_2$  suspensions (2 g/l Degussa P 25), Photo-Fenton ( $10^{-2}$  mol/l  $\text{H}_2\text{O}_2$  and  $2.5 \times 10^{-4}$  mol/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and  $\text{H}_2\text{O}_2/\text{UV}$  ( $10^{-2}$  mol/l  $\text{H}_2\text{O}_2$ ) experiments were performed in a stirred 2 l flask (borosilicate glass window, aperture 6 cm), thermostated at 25°C and under air bubbling. The solutions were irradiated with a 400 W medium pressure mercury lamp (Osram Ultramed). Initial concentration of 4-Chlorophenol (4-CP) was  $10^{-3}$  mol/l.

### 2.3. $\text{TiO}_2/\text{UV}$

#### 2.3.1. $\text{TiO}_2$ coated quartz fiber reactor

$\text{TiO}_2$  was immobilized on quartz glass fibers by a dip-coating procedure [5]. One hundred forty coated fibers with 2 mm diameter and 480 mm length were packed in a photocatalytic flow reactor with storage bulb and thermostat. A schematic draw of the principle and a picture of this reactor in operation can be seen in Figs. 2 and 3.

Model waste water containing 4-CP ( $10^{-3}$  mol/l) was degraded using a 400 W Hg medium pressure lamp (Osram Ultratech).

#### 2.3.2. LAPW calculations for predicting proper $\text{TiO}_2$ dopants

In order to predict suitable dopants, calculations of the electron densities of doped  $\text{TiO}_2$  were performed by use of the Linear Augmented Plane Wave (LAPW) computer program called WIEN95 [7], based on the Density Functional Theory (DFT). The electron density of the excited state was simulated by running a self consistent cycle (energy convergence down to  $10^{-4}$  Ry). Based on these results the electron densities with two additional electrons above the Fermi level were plotted.

#### 2.3.3. Flask experiments with Al doped $\text{TiO}_2$

Degradation experiments with diethylamine ( $5 \times 10^{-4}$  mol/l) over Al doped  $\text{TiO}_2$  (0.5 g/l) were performed in a 250 ml flask, thermostated at 20°C,  $\text{O}_2$  bubbling at 35 l/h, with a fused silica window. Irradiation source was a 150 W Xe short arc lamp, IR (10 cm water) filter, aperture 33 mm.

The doped TiO<sub>2</sub> powders were prepared by the coprecipitation method: Titanium(IV) isopropoxide (14.2 g), diethanolamine (5.3 g), aluminum trichloride and 0.9 ml water (Ti:H<sub>2</sub>O=1:1 M ratio) were dissolved in 100 ml ethanol. The solution was evaporated to obtain a slightly yellowish precipitate which was tempered in air for 15 h at 500°C.

## 2.4. Photo-Fenton

### 2.4.1. Photo-Fenton laboratory reactor

These experiments were conducted in a prototype reactor depicted in Fig. 4. The photochemical reactor consisted of two coaxial hollow glass cylinders. A more sophisticated version of the photoreactor is equipped with an inner cylinder made of fused silica to utilize the higher energetic emissions of the UV lamps [8]. The experiments with 4-CP were carried out at room temperature in unbuffered aqueous solutions ( $V=10\text{ l}$ ,  $\text{pH}_0=2$ ) in which ferrous sulfate ( $2 \times 10^{-3}\text{ mol/l}$ ) and 4-CP ( $10^{-2}\text{ mol/l}$ ) were dissolved. The beginning of the experiment corresponded to the addition of hydrogen peroxide ( $1.4 \times 10^{-1}\text{ mol/l}$ ) and simultaneous start of irradiation (400 W Osram Ultramed Hg medium pressure). At defined intervals samples were taken and the following parameters were measured: TOC, pH, temperature, H<sub>2</sub>O<sub>2</sub>, iron content and COD. In most experiments hydrogen peroxide was added in several portions. TOC analyses were conducted immediately after sampling, for COD analyses residual peroxide was destroyed with MnO<sub>2</sub> at pH=11. The real waste water was acidified with sulfuric acid, then ferrous sulfate was added. The addition of the first portion of hydrogen peroxide and simultaneous start of irradiation again marked the starting time of the experiment.

### 2.4.2. Solar Photo-Fenton treatment in a glass basin

Twenty liter of a  $10^{-3}\text{ mol/l}$  4-CP in a 70 cm × 70 cm glass basin covered by a window pane were degraded using  $2 \times 10^{-4}\text{ mol/l}$  ferrous sulfate,  $1.4 \times 10^{-2}\text{ mol/l}$  hydrogen peroxide. The cover should prevent evaporation losses, but it did also cut off the UV edge of the solar irradiation.

### 2.4.3. Solar detoxification of pesticide waste waters at the Plataforma Solar de Almería

The effluents of a pesticide bottle recycling plant [10,11] were treated by various methods in solar driven reactors at the Plataforma Solar de Almería, southern Spain. Low concentrating solar collectors (CPC, compound parabolic collector) were used throughout these experiments. The collectors consist of three static modules mounted south orientated with a tilt angle similar to the latitude of the site (37°) to obtain the maximum yearly efficiency. Each module disposes of 3 m<sup>2</sup> aperture area with  $2 \times 60^\circ$  semi-aperture angle, concentration is ca. 1 sun, illuminated volume is 36 l per module. The absorber tubes (ID 48 mm) are made of a fluoropolymer, the reflectors are of polished aluminum. The efficiency of the collector was 0.72 [12]. Waste water was recirculated from a storage tank through the collectors by a centrifugal pump. Total volume was 250 l. UV irradiation (300–400 nm) was recorded by a Kipp and Zonen CUV3 detector, inclined 37° like the CPC modules.

The degradation experiments used a model mixture of 10 commercial pesticides [11] which are presented in Table 1. These compounds were selected in order to cover a wide range of organic substance classes. The model waste water was produced by adding equal TOC quantities of each pesticide (10 ppm) to distilled water. For Photo-Fenton  $10^{-3}\text{ mol/l}$  FeSO<sub>4</sub>·7H<sub>2</sub>O and the stoichiometrical amount of H<sub>2</sub>O<sub>2</sub> (33 wt.%) were added (H<sub>2</sub>O<sub>2</sub> in five portions). For the TiO<sub>2</sub> experiments 0.2 g/l Degussa P25 was used and the sodium persulfate concentration was maintained at a constant level of  $10^{-2}\text{ mol/l}$ .

### 2.4.4. Fe ion immobilization on Nafion<sup>®</sup> membranes

The Nafion<sup>®</sup> membrane was purchased from Sigma-Aldrich in the acid form with an equivalent weight of 1100. The thickness of 0.43 mm is due to a Teflon<sup>®</sup> grid which is used as reinforcing support. This reinforcement causes a continuous absorption background of about 0.2 in the range of 200–800 nm in all cases (dry, soaked and loaded membrane). Before application it was soaked in distilled water and then loaded with iron using an ion exchange method. On this purpose, the membrane was left for 24 h at room temperature in a solution containing  $10^{-2}\text{ mol/l}$  ferrous sulfate. The loading with ferrous

Table 1  
Model pesticides used for the study

Commercial name	Producer	Active ingredient	Formula
Rufast	Rhône-Poulenc	Acrinatrín	C <sub>26</sub> H <sub>21</sub> F <sub>6</sub> NO <sub>5</sub>
Vertimec	Merck	Abamectín	C <sub>48</sub> H <sub>72</sub> O <sub>14</sub>
Thiodan	AgrEvo	Endosulfan $\alpha$ - $\beta$	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S
Dicorzol	AgrEvo	Formetanate	C <sub>11</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>2</sub>
Confidor	Bayer	Imidacloprid	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>
Match	Ciba-Geigy	Lufenuron	C <sub>17</sub> H <sub>8</sub> Cl <sub>2</sub> F <sub>8</sub> N <sub>2</sub> O <sub>3</sub>
Tamaron 50	Bayer	Methamidofos	C <sub>2</sub> H <sub>8</sub> NO <sub>2</sub> PS
Vydate	DuPont	Oxamyl	C <sub>7</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> S
Scala	AgrEvo	Pyrimethanil	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub>
Previcur	AgrEvo	Propamocarb	C <sub>9</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>

sulfate caused a significant increase of the absorption at wavelengths lower than 300 nm.

For the photodegradation experiments over Nafion<sup>®</sup> membranes 1 l of an aqueous solution (pH = 7.5) containing  $1.4 \times 10^{-3}$  mol/l 4-CP, ferrous ion loaded Nafion<sup>®</sup> membrane and  $2.3 \times 10^{-2}$  mol/l hydrogen peroxide were irradiated (Osram, 400 W Hg lamp) under continuous stirring. Experiments were carried out over an irradiation time of 300 min and without temperature compensation, temperature increased from about 20°C to approximately 30°C. The lamp housing (Polytec GmbH, LH-151/3, including a condensing system LHC-151/3) was equipped with a 90° light tube (LHA-154/3).

### 3. Results and discussion

#### 3.1. TiO<sub>2</sub> and Photo-Fenton 2 l flask experiments

The experiments (Fig. 5) showed that 2 l of a  $10^{-3}$  mol/l 4-CP solution were completely mineralized after 30 min by the homogeneous Photo-Fenton reaction, while the heterogeneous TiO<sub>2</sub>/UV process (slurry) needed 24 h to eliminate only 40% of the pollutant. An explanation for this difference is recombination of the photogenerated charge carriers (h<sup>+</sup>/e<sup>-</sup> pairs). Under these conditions H<sub>2</sub>O<sub>2</sub>/UV (studied only for the sake of comparison) was not very efficient either. Absorbance of H<sub>2</sub>O<sub>2</sub> in the used wavelength range is very weak and the amount of generated OH• radicals is very small. TOC reduction after 24 h was only 51%.

#### 3.2. TiO<sub>2</sub>/UV

##### 3.2.1. TiO<sub>2</sub> coated quartz fiber reactor

By this reactor design [5], degradation was substantially enhanced compared to TiO<sub>2</sub> slurries. As shown in Fig. 6, TOC degradation of a 4-CP solution by this reactor was clearly more efficient than by the conventional TiO<sub>2</sub> slurry treatment using the same light flux. Excitation light permeates the total volume of the photoreactor (see Fig. 3), in contrast to the suspension treatment. Other attempts to immobilize TiO<sub>2</sub> on different supports like plates, coils, tubes, glass beads, or membranes always had caused a decrease in the overall process efficiency, whereas here an increase in the quantum efficiency could be achieved. Stability of the coated fibers was remarkable, no measurable loss in activity was detected after more than 600 h of degradation on the same catalytic surface. This reactor with the same coated fibers — which have been in use for waste water treatment — is currently successfully used for photo-detoxification of waste air streams [13].

##### 3.2.2. Electron densities of doped TiO<sub>2</sub>

In Fig. 7 the influence of the dopant (Al) on the electron density — inversely proportional to the hole density — is depicted. We can see a 3-D view of part of a (010) plane containing the atoms we are interested in. X- and y-axis are position coordinates, and the z-axis represents the electron density [e<sup>-</sup>/Å]. The higher peaks are the titanium atoms, the lower ones are oxygens, dopants are located in the center of this plot. The 'inverted' electron density is due to this type of representation — the electron density of the excited state, however at a much lower level (see the abso-

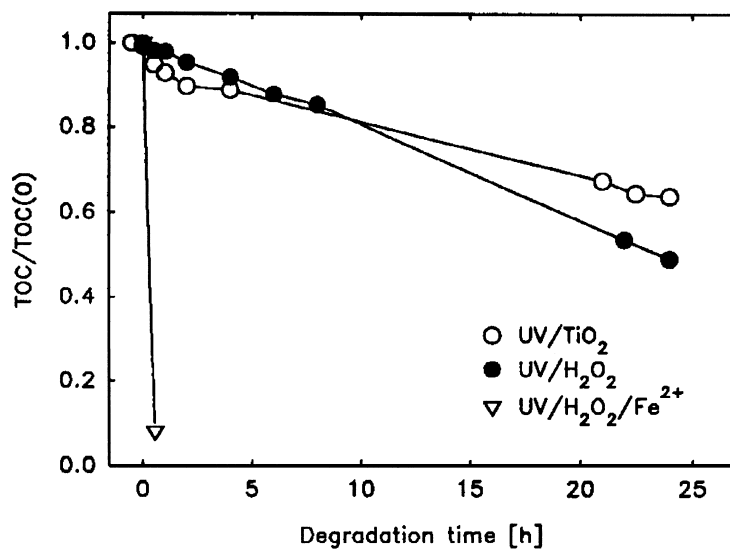


Fig. 5. The superior performance of the Photo-Fenton process ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-VIS}$ ) vs.  $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{TiO}_2/\text{UV}$  is obvious from this chart. Initial 4-CP concentration was  $10^{-3}$  mol/l throughout these experiments, 400 W Hg medium pressure lamp (Osram Ultramed).  $\text{TiO}_2$  suspensions: 2 g/l Degussa P 25; Photo-Fenton  $c_0$ :  $10^{-2}$  mol/l  $\text{H}_2\text{O}_2$ ,  $2.5 \cdot 10^{-4}$  mol/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{H}_2\text{O}_2/\text{UV}$   $c_0$ :  $10^{-2}$  mol/l  $\text{H}_2\text{O}_2$ .

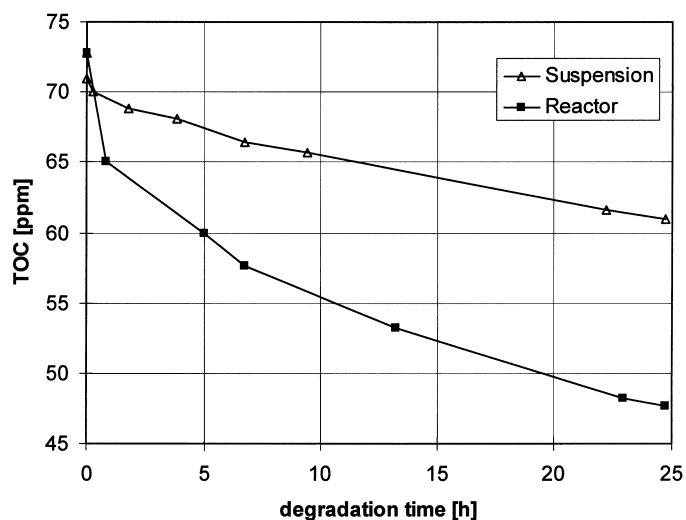


Fig. 6. Comparison of the  $\text{TiO}_2$  coated fiber reactor's efficiency to an aqueous slurry of  $\text{TiO}_2$  (2 g/l Degussa P25) in the degradation of 21 4-CP solution.  $c_0$ :  $10^{-3}$  mol/l 4-CP, 400 W Hg medium pressure lamp (Osram Ultramed).

lute values of the electron densities), seems to be inverted compared to the ground state (with higher electron density at oxygens). Al significantly decreases electron density of the excited state in this plane and therefore should be a suitable dopant, enhancing hole densities.

### 3.2.3. Al doped $\text{TiO}_2$ slurries

For the degradation of diethylamine, an optimum in Al content was found for 0.5–1 at.%, as shown in Fig. 8. This corresponds to results from Al doped  $\text{TiO}_2$  layers where an optimum Al content was found for 0.1–0.2 at.% [14]. Some of the properties of this doped



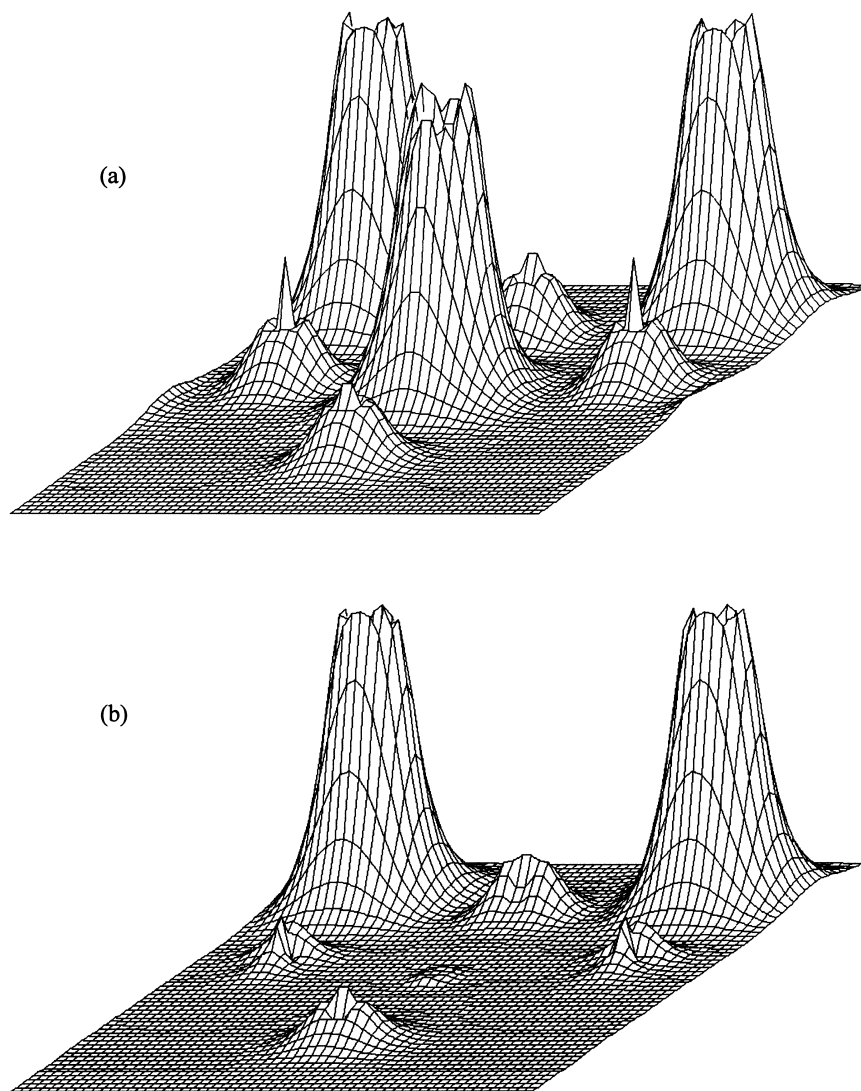


Fig. 7. Electron density of undoped (a) vs. doped (b)  $\text{TiO}_2$  (anatase) in the (010) plane, photonicallly excited  $e_g + t_{2g}$  states, as calculated by use of WIEN95 [7].

titania are summarized in Table 2. The color changed to slightly yellowish due to the doping and annealing processes, in spite of the fact of the increasing band gap at higher doping levels. This indicates the introduction of electronic states into the band gap. By the way, Al is insoluble in  $\text{TiO}_2$  [15], maybe due to the differences in ionic radii:  $\text{Ti}^{4+}$ : 61 pm,  $\text{Al}^{3+}$ : 54 pm (both for sixfold coordination, [16]). Note that [17] reported antagonistic effects of doping, however a lower

oxidation quantum efficiency for Al doped (0.5 at.%) than for undoped  $\text{TiO}_2$ .

### 3.3. Photo-Fenton

#### 3.3.1. Photo-Fenton laboratory reactor

These experiments resulted in nearly complete TOC removal of 10 l of  $10^{-2}$  mol/l 4-CP solution after 40 min by the homogeneous Photo-Fenton re-

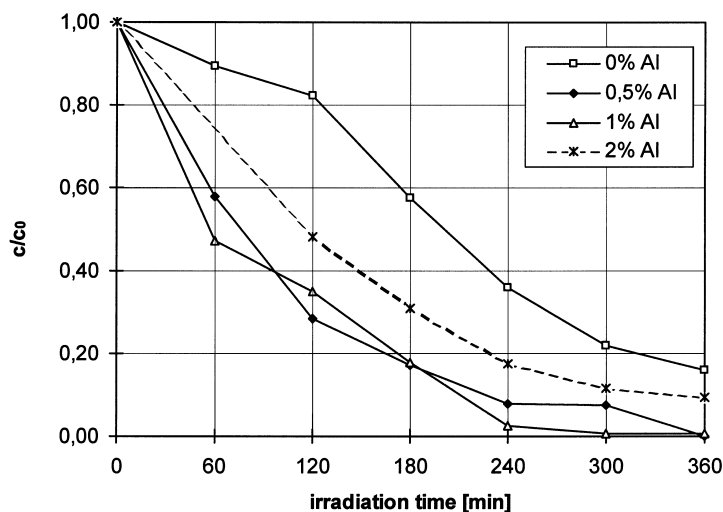


Fig. 8. Diethylamine ( $c_0 = 5 \times 10^{-4}$  mol/l) degradation over Al doped  $\text{TiO}_2$  powders (0.5 g/l);  $V = 250$  ml,  $20^\circ\text{C}$ ,  $\text{O}_2$  bubbling at 35 l/h. One hundred fifty watt Xe short arc lamp, IR water filter.

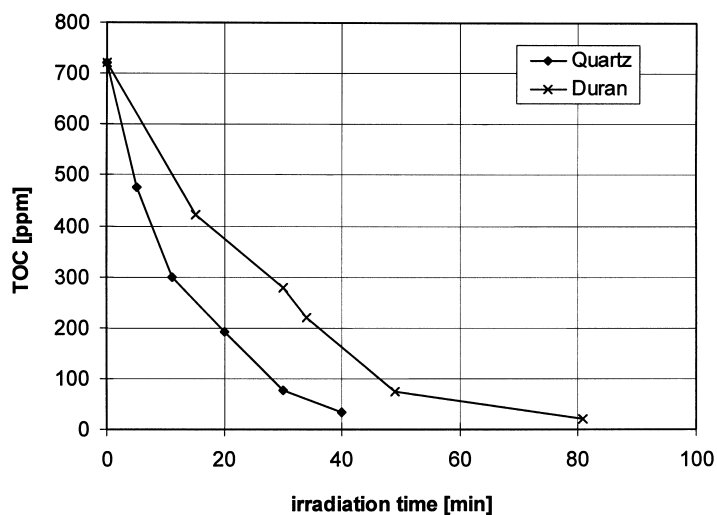


Fig. 9. Degradation of 4-CP in the Photo-Fenton prototype reactor with different glass sorts of the inner cylinder.  $C_0$ :  $10^{-2}$  mol/l 4-CP,  $1.4 \times 10^{-1}$  mol/l  $\text{H}_2\text{O}_2$ ,  $2 \times 10^{-3}$  mol/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{pH} = 2$ ;  $V = 10$  l; 400 W Hg medium pressure lamp (Osram Ultramed).

action (Fig. 9). Several real waste waters have been treated with good results in this reactor e.g. 83% of TOC of a landfill leachate ( $\text{TOC}_0 = 558$  ppm;  $V = 8$  l;  $c_0 = 1.9 \times 10^{-1}$  mol/l  $\text{H}_2\text{O}_2$ ,  $1.51 \times 10^{-3}$  mol/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were degraded after 6 h, 73% of TOC of a waste water from plastics industry (containing styrene and latex,  $\text{TOC}_0 = 83$  ppm) were mineralized after 100 min of irradiation.

**3.3.1.1. Influence of lamp power in the Photo-Fenton reactor on degradation rate and costs** In a series of experiments the influence of the power of the irradiation source on the degradation rate was studied. For a detailed spectrum of the lamps used in this study see [8]. The degradation rate increased proportionally with the number of 150 W lamps used. The rate for one 400 W lamp fits in between the curves of two

Table 2  
Properties of the Al doped TiO<sub>2</sub> samples

Al (atomic%)	BET-surface (m <sup>2</sup> g <sup>-1</sup> )	Band gap (eV)
0	33.8	3.08
0.5	42.8	3.14
1	55.2	3.20
2	60.1	3.22
3	74.1	3.23

and three 150 W lamps according to prediction. The degradation curve for a 1000 W lamp was nearly identical to that of the 400 W lamp, in both experiments 90% of TOC were removed within the first hour. The 1000 W lamp could only be used with a cooling fan, while the 150 W lamps could only be used without. It should be taken into account in the judgment of the 1000 W's performance that the 400 W lamp yielded a much slower degradation rate when used with a fan. As expected, the highest costs are caused by the 1000 W lamp (33.4 Euro/kg TOC). The costing of the experiments with one, two and three 150 W lamps was rather similar (23.1–23.5 Euro/kg TOC). The costs of the 400 W experiment with fan (25.8 Euro/kg TOC) are 10% higher than the costs of the experiment without.

**3.3.1.2. Comparison of degradation rates of Photo-Fenton reactors with different glass sorts** A further focus of studies was the influence of the use of Duran or quartz glass [8]. The reactor used has the lamp fitted in the axis of two coaxial glass cylinders, the inner one was changed from Duran to quartz. In Fig. 9 the improvement of the inner quartz cylinder on the degradation rate is obvious. This behavior can be explained by an acceleration of the Photo-Fenton reaction by irradiation with shorter wavelengths [18].

### 3.3.2. Solar Photo-Fenton treatment in a glass basin

In bright sunshine the TOC of the 4-CP solution could be removed in 60 min, in diffuse daylight (cloudy weather) it took only 30 min longer. Papermill waste water could be degraded in 3 h. Bright sunlight as well as diffuse daylight could be efficiently used by this process. Judging these results, it should be noted that the glass cover of the basin also filters the useful UV part of solar irradiation.

### 3.3.3. Solar detoxification of pesticide waste waters

Irradiation times were calculated as  $t_R = (V_R/V_T) t_T$  where  $t_T$  is the total time elapsed,  $V_R$  the (illuminated) reactor volume and  $V_T$  the total volume. For comparison of experiments in different weather conditions, irradiation time was substituted by the total UV energy absorbed, calculated according to Eq. (13),

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_n \frac{A_{CPC}}{V_{TOT}}$$

$$\Delta t_n = t_n - t_{n-1} \quad (13)$$

where  $\overline{UV}_n$  is the average incident UV radiation (W/m<sup>2</sup>) on the collector surface within each  $\Delta t$  interval,  $t_n$  is the experimental time for each sample,  $A_{CPC}$  is the collector surface,  $V_{TOT}$  is the total plant volume and  $Q_{UV,n}$  is the accumulated energy per unit volume (kJ/l) incident on the reactor for each sample taken during the experiment.

Under average sunny conditions 10 kJ/l are collected in 1 h irradiation time, this corresponds to 2.3 h total time of the experiment.

Fig. 10 illustrates the higher efficiency of the Photo-Fenton process compared to the reactions catalyzed by TiO<sub>2</sub>. A cost estimation for all three processes has been performed [11], based on the assumption of 375 kg TOC to be treated every year. Costs for catalyst separation (microfiltration for TiO<sub>2</sub>, neutralization plus sedimentation for iron in the Photo-Fenton process) as well as a final granulated active carbon treatment are included. As shown in Fig. 11 and Table 3, the costs for Photo-Fenton are the lowest, which is due to two facts: as longer residence times are required for TiO<sub>2</sub>, the investment costs are higher because of larger collector area, especially when no persulfate is added. On the other hand, the chemicals consumed (mainly sodium persulfate) are also more expensive than for Photo-Fenton (hydrogen peroxide). Without persulfate, chemical costs are negligible, but the investment costs overcompensate this advantage. Besides, personnel costs are the same for all cases and therefore should be excluded from the comparison, even more favoring the Photo-Fenton option.

### 3.3.4. Fe ion immobilization on Nafion<sup>®</sup> membranes

The influence of the membrane area on the degree of degradation is depicted in Fig. 12. The loading of

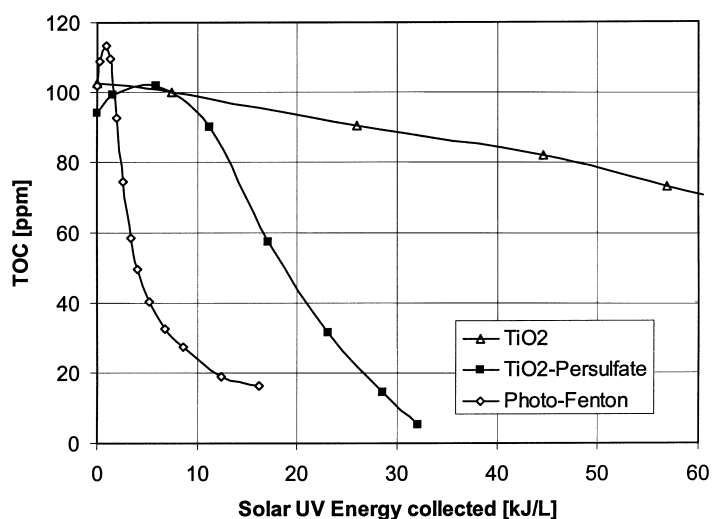


Fig. 10. Comparison of solar pesticide degradation in the CPC collectors. A mixture of 10 commercial pesticides was treated ( $V=2501$ ). Under average sunny conditions  $10 \text{ kJ/l}$  are collected in 1 h irradiation time, this corresponds to 2.3 h total time of the experiment. Photo-Fenton  $c_0$ :  $10^{-3} \text{ mol/l}$   $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  (33 wt.%) stoichiometrical amount (added in five portions).  $\text{TiO}_2$ :  $0.2 \text{ g/l}$  Degussa P25, sodium persulfate maintained at a constant level of  $10^{-2} \text{ mol/l}$ .

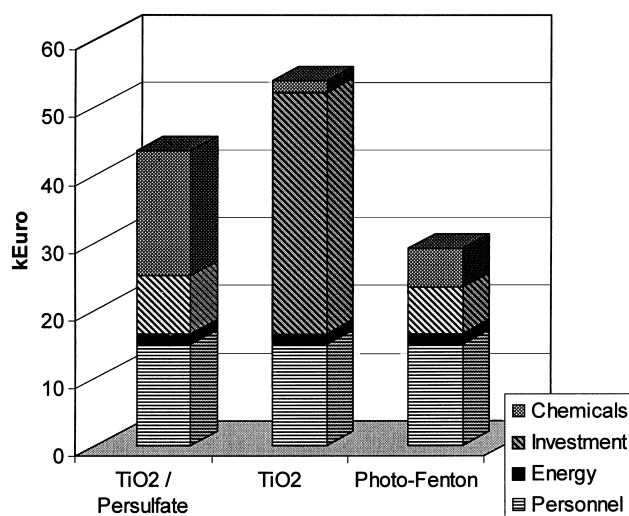


Fig. 11. Estimation of yearly operation costs for various pilot plants applying one of the sunlight driven AOPs considered in the 'El Ejido' study [11] for degradation of the pesticide containing waste water.

the membrane was approximately  $0.01 \text{ g Fe/g}$  membrane [19]. The increase of area in case of the one layer system ( $70 \text{ cm}^2$  versus  $100 \text{ cm}^2$ ) was 43% and in case of the two layer system ( $100 \text{ cm}^2$  versus  $2 \times 100 \text{ cm}^2$ ) 100%. TOC removal after 300 min of irradiation increased by 11 and 61%, respectively.

## 4. Conclusions

### 4.1. $\text{TiO}_2/\text{UV}$

Currently  $\text{TiO}_2/\text{UV}$  does not seem to be suitable for large scale waste water purification until the third

Table 3  
Estimation of yearly costs for a water treatment plant [10,11]

	TiO <sub>2</sub>	TiO <sub>2</sub> /persulfate	Photo-Fenton
Reactor area required (m <sup>2</sup> )	1446	280	168
Yearly costs (Euro)			
Investment (10 years)	35581	8530	6848
Chemicals	1710	18444	5816
Energy	1500	1500	1500
Personnel	15000	15000	15000
Total	53791	43474	29164

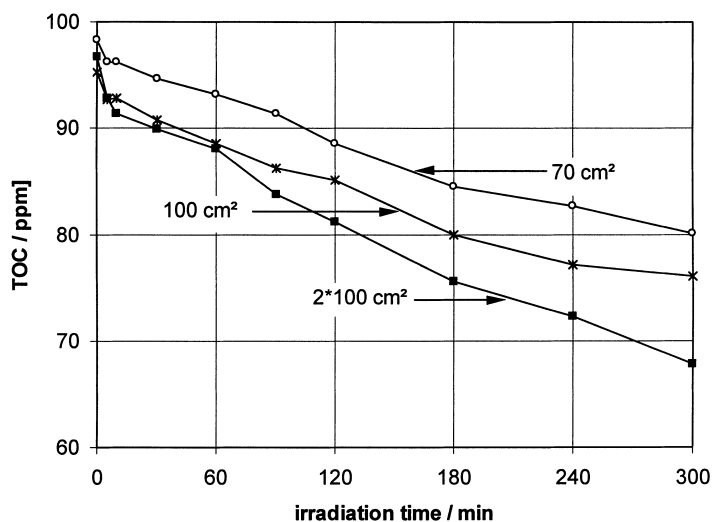


Fig. 12. Fe ion immobilization on Nafion<sup>®</sup> membranes: comparison of different membrane areas with respect to TOC reduction of 4-CP performed with a 0.43 mm thick Nafion<sup>®</sup> membrane.  $c_0$ :  $1.4 \times 10^{-3}$  mol/l 4-CP,  $2.3 \times 10^{-2}$  mol/l H<sub>2</sub>O<sub>2</sub>, pH=7.5,  $V=11$ , 400 W Hg medium pressure lamp (Osram Ultramed).

problem, which is caused by the fast recombination of photogenerated hole/electron pairs has been solved. This could be done by doping the TiO<sub>2</sub> coating. Experiments with TiO<sub>2</sub> coatings on conductive glass seem very promising: this way TiO<sub>2</sub> can be biased by a positive potential to dispose of more holes (oxidation centers) at the catalytic surface while the electrons are attracted by the positive potential.

More fundamental research in the field of TiO<sub>2</sub> doping is necessary. The advantages of this semiconductor (e.g. low cost, stability, no need for additives, possibility of decontamination of acidic as well as alkaline waste water, etc.) should encourage deployment of more resources for further development in this field.

#### 4.2. Photo-Fenton

It is evident that the Photo-Fenton process under solar irradiation is a very efficient and inexpensive waste water treatment process. It has potential for treating highly contaminated water. However, the disadvantage of the Photo-Fenton reaction is its sensitivity to pH. Before use on large scale the need for acidification of the waste water (at pH > 4 ferric hydroxide starts to precipitate) and the separation of iron after treatment have to be considered. Current research aims at extending the applicability of the Photo-Fenton reaction towards neutral and alkaline solutions. These interesting efforts have yielded first promising results. Immo-

bilization of Fe ions on Nafion<sup>®</sup> membranes has been accomplished and it is now possible to carry out the Photo-Fenton reaction in a wider pH range without additional separation of iron after the treatment process.

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