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Interaction between *E. coli* inactivation and DBP-precursors — dihydroxybenzene isomers — in the photocatalytic process of drinking-water disinfection with TiO_2

Angela G. Rincón, Cesar Pulgarin*, Nevenka Adler, Paul Peringer

Institute of Environmental Engineering, Laboratory for Environmental Biotechnology, Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

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Abstract

The common drinking water disinfection procedures lead to the formation of disinfection by-products (DBPs), which come mainly from naturally occurring organic compounds disinfection by-products precursors (DBPPs). Solar disinfection by photocatalysis is a promising method, which could be applied to a drinking water treatment process in order to destroy a bacterial population and DBPPs as well.

The complete *E. coli* inactivation by light irradiation over TiO_2 suspension was reached in 20 min, while by light alone it was in 70 min. Illumination was produced by a Hanau Suntest lamp simulating natural radiation power of 80 mW cm^{-2}. The addition of DBPPs like $C_6H_4(OH)_2$: hydroquinone, resorcinol and catechol to bacterial suspension contained TiO_2, resulted in a decrease in sunlight germicidal activity. A correlation between photoreactivity of dihydroxybenzene isomers and photocatalytic bacterial disinfection was demonstrated. Experiments performed under dark conditions demonstrated either $C_6H_4(OH)_2$ or TiO_2 separately do not affect to a large extent the survival of *E. coli*, while mixing of both showed a bacterial deactivation between two- and one-order of magnitude in the presence of substances within 2 h. The order of decay in photodegradability was resorcinol > catechol > hydroquinone. The evolution of $C_6H_4(OH)_2$ degradation under light in the presence of both oxygen and H_2O_2 as electron acceptor was discussed.

Keywords: Water disinfection; Solar irradiation; TiO_2 photocatalysis; DBPs; Disinfection by-products precursors; Dihydroxybenzenes

1. Introduction

For drinking water at present, the control of microbiological risk is considered more important than the control of chemical risk. Unfortunately, drinking water disinfection procedures, commonly chlorination and ozonation, can lead to the formation of disinfection by-products (DBPs). The most important are the trihalomethanes (THMs), which are of interest due to their carcinogenic and mutagenic potential. THMs mainly derived from naturally occurring humic and fulvic acids and their derivative compounds, which combine with chlorine and bromine during the chlorination of drinking water. In order to minimize the risk to humans, conventional treatment modifications and other alternative methods of disinfection including the removal of DBPs have been proposed [1,2]. Much attention has been directed to the removal of humic substances in order to reduce the possibility for THMs formation [3]. Little has been studied concerning dihydroxybenzenes, e.g. resorcinol, hydroquinone and catechol which are disinfection by-products precursors (DBPPs). Standard water treatment techniques are often too expensive both in capital investment and operation, as well as maintenance for use in developing countries. In this respect, the use of solar energy as a primary alternative to chlorination could prove an economically viable technology in countries with a high degree of sunlight. Solar treatment could also be a good way to degrade organic precursors of DBPs making chlorinated drinking water harmless for human consumption.

Photocatalytic oxidation is a promising technology for the detoxification and disinfection of water and wastewater. When catalytic semi-conductor powders, such as titanium dioxide (TiO_2) are suspended in water and irradiated with near UV $\lambda < 385$ nm, $OH^\bullet$ free radicals are generated. The $OH^\bullet$ radical is highly toxic towards microorganisms and very reactive in the oxidation of organic substances like DBPPs. The photocatalytic degradation of various organic compounds by illuminated TiO_2 have been reported [4–8]. Photocatalytic inactivation of bacteria *E. coli*, *Bacillus pumilus* and spores of *Clostridium perfringens*, as well as virus Phage QB have been investigated [9–18]. In these

* Corresponding author. Tel.: +41-21-693-4720; fax: +41-21-693-4722.
E-mail address: cesar.pulgarin@epfl.ch (C. Pulgarin).

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photocatalytic disinfection studies, UV (250-400 nm) or sunlight-emitting lamps, were used as source of light.

The purpose of this paper is to investigate the photocatalytic bacterial inactivation with a solar-simulating lamp, as a source of light, in the presence of one group of DBPPs, such as dihydroxybenzene isomers $C_6H_4(OH)_2$: hydroquinone, catechol and resorcinol. These DBPPs are introduced into the environment through a variety of natural (degradation products of the humic acids) and industrial sources [19]. *E. coli* was selected as tested bacteria because of its common use as biological indicator of disinfection efficiency in water systems. In this paper, inactivation of *E. coli* suspension by sunlight in the presence of $C_6H_4(OH)_2$ solutions is studied with or without the addition of TiO_2. Particular emphasis is placed on the photoreactivity of dihydroxybenzene isomers in oxidative systems applied. The interaction between photocatalytic degradation of $C_6H_4(OH)_2$ present and the *E. coli* inactivation is studied.

1.1. Reaction mechanisms

The mechanisms for the primary events occurring at the surface of the catalyst have been described [20,21]. The irradiation of TiO_2 with photons of energy equal or greater than its band-gap (3.2 eV) resulted in the promotion of electrons from the valence band (VB) to the conduction band (CB) of the particle. The outcome of this process is a region of positive charge termed a hole (h^+) in the VB, and a free electron (e^-) in the CB (Eq. (1)):

$$TiO_2 + h\nu \rightarrow TiO_2 + e^-(CB) + h^+(VB) \quad (1)$$

At the TiO_2 particle surface, the holes react with surface hydroxyl groups (OH^-) and adsorbed H_2O, to form $OH^\bullet$ radicals (Eqs. (2) and (3)). Organic substances can be also adsorbed to the surface and directly oxidized (Eq. (4)):

$$OH^- + h^+ \rightarrow OH^\bullet \quad (2)$$

$$H_2O + h^+ \rightarrow OH^\bullet + H^+ \quad (3)$$

$$C_6H_4(OH)_2 + h^+ \rightarrow {}^\bullet C_6H_{4-}(OH)_2{}^{\bullet+} \quad (4)$$

In the absence of electron acceptors the electron–hole recombination is possible. The presence of oxygen prevents this recombination by trapping electrons through the formation of superoxide ions according to Eq. (5). The final product of the reduction may also be $OH^\bullet$ radical and the hydroperoxy radical $HO_2^\bullet$ (Eqs. (6) and (7)):

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \quad (5)$$

$$2O_2^{\bullet-} + 2H^+ \rightarrow 2OH^\bullet + O_2 \quad (6)$$

$$2O_2{}^{-\bullet} + H^+ \rightarrow HO_2^\bullet \quad (7)$$

The presence of other more powerful electron acceptors than O_2, for example the hydrogen peroxide, increases the efficiency of the oxidative reaction (Eq. (8)):

$$H_2O_2 + e_{cb}{}^\bullet \rightarrow OH^\bullet + OH^- \quad (8)$$

Hydroxyl radicals can oxidize the organic compounds adsorbed onto the semiconductor surface and inactivate microorganisms (Eqs. (9) and (10)).

$$C_6H_4(OH)_2 + OH^\bullet \rightarrow C_6H_3(OH)_3 + H^+ \quad (9)$$

$$\text{bacteria} + OH^\bullet \rightarrow \text{bacterial inactivation} \quad (10)$$

The photocatalytic process is accompanied by the release of protons (Eqs. (3) and (9)).

2. Experimental details

2.1. Materials

Hydrogen peroxide (H_2O_2) and the compounds studied (catechol, resorcinol, hydroquinone) were supplied by Fluka, puriss. The photocatalyst was TiO_2 Degusa P-25 (mainly anatase, surface area $50\,m^2\,g^{-1}$).

2.2. Photochemical experiments

Solution concentration of 1.0×10^{-2}, 4.2×10^{-3} and 2.0×10^{-3} M and the catalyst concentration of $1\,g\,l^{-1}$ were used. TiO_2 was separated by centrifugation and filtration before analysis. For experiments in the presence of H_2O_2 the concentration was 4×10^{-2} M. Illumination was produced by a Hanau Suntest (AM1) lamp with $80\,mW\,cm^{-2}$ radiating power. The lamp had a λ distribution with about 0.5% of emitted photons at wavelengths shorter than 300 nm (UV-C range) and about 7% between 300 and 400 nm (UV-B, A range). The profile of the photons emitted between 400 and 800 nm followed the solar spectrum.

2.3. Instrumental analysis

High performance liquid chromatography (HPLC) was carried out in a chromatograph Varian 9065 Unit, having a diode array (Varian, Switzerland). A spheriosorb silica column (ODS-2) with acetic acid (10% (v/v)) acetonitrile gradient evolution was used. Dissolved organic carbon (DOC) measurements were performed using a TOC analyser model 5050A (Shimadzu, Japan) with a solution of potassium phthalate as the calibration standard.

2.4. Disinfection experiments

TiO_2 concentration was $1\,g\,l^{-1}$. The bacteria used in inactivation studies was *E. coli* K12. Bacteria were grown in rich medium (PCA, Merck, Germany) prior to the experimental stage. Mili-Q water and solutions of dihydroxybenzene isomers were spiked with *E. coli* to yield starting concentrations of 10^7 colony forming units, CFU ml^{-1}. The solutions were irradiated for 2 h, at the ambient temperature up to 32°C. The samples were taken at the same intervals of time (each

5 min at the beginning and each 10 min after 40 min). Serial dilutions were performed if necessary in trypthone water, samples were spotted onto chromagar *E. coli* (ECC) plates and spread using standard techniques. Plates were incubated at 37°C for 24 h prior to enumeration. All experiments were carried out three times, the pH of the initial solutions being 6. De-ionized water was used to prepare the solutions.

3. Results and discussion

3.1. Bacterial inactivation by sunlight

The bacterial inactivation by sunlight occurs with or without TiO_2 addition. However, direct germicidal action of sunlight with the addition of TiO_2 presented in Fig. 1 (trace ∗) is better than the action of sunlight alone (trace +).

The total time of bacterial abatement is shorter in the presence of TiO_2 than without it. This is in accordance with previous findings [13]. Kinetics of bacterial disinfection has been expressed by Chick and Watson in 1908 [22]. Based on the Chick law the graph of $\ln(N/N_0)$ versus time should give a straight line, where N represents the number of microorganisms at time t, N_0 the initial number of microorganisms and t the contact time [23]. In Fig. 1 it can be seen that the curves of solar inactivation of *E. coli*, are in accordance with the Chick law. However, the sunlight affects bacteria but not immediately in both cases. The curve has a shoulder, which correspond to the initial period of latency, after that the inactivation rate increases considerably. In the dark, during 120 min of the stirring, up to 32°C with or without TiO_2 addition, all bacteria survive, the disinfection does not occur (Fig. 1). These results are consistent with the previous experiments reported in the literature showing that TiO_2 itself does not act as a germicide in the dark [10].

Solar disinfection with TiO_2 is a consequence of both direct action of the light on the microorganisms and the photocatalytic action of the excited TiO_2 particles. The ultraviolet part of the sunlight (3%) is directly responsible for a part of the bacterial inactivation. The inactivation of bacteria by UV irradiation results primarily from the absorption by DNA of the microorganisms resulting in dimerization of thymine bases in DNA. These thymine dimers obstruct the conformation of the double helix and interfere with normal DNA replication [24]. On the other hand, photocatalytic inactivation has been explained by the attack of radicals photogenerated at the surface of the catalyst like $O_2^{\bullet -}$, $HO_2^{\bullet}$ and $OH^{\bullet}$ (Eqs. (2), (3), (5) and (7)). All three species have bactericidal characteristics, but the hydroxyl radical is the most potent. The mechanism of cell death has been not elucidated. In 1988 Matsunaga et al. [25] suggested that the hole in the VB received an electron from coenzyme A (CoA) as the donor forming dimeric CoA. Dimerization of CoA inhibits respiration and causes death of the cells. More recently, in 1999 Maness et al. [26] reported that in the presence of TiO_2 the lipid peroxidation reaction takes place and that as a result, the normal functions associated with an intact membrane, such as respiratory activity, are lost. The same authors investigated the mechanisms of cell death with a focus on the features of cell wall and cytoplasmic membrane damages caused by TiO_2 photocatalytic reactions [27].

3.2. Effect of DBPPs on sunlight E. coli inactivation

3.2.1. Effect of $C_6H_4(OH)_2$ on bacterial suspension with and without TiO_2 in dark conditions

The addition of one dihydroxybenzene isomers $C_6H_4(OH)_2$ to bacterial suspension caused the inactivation of bacteria in the dark (Fig. 2) to a different extent for each isomer (between 0.5- and 1.5-orders of magnitude). This is probably due to specific inhibitor (toxic) effect of each substance on *E. coli* at the relatively high concentration of $C_6H_4(OH)_2$ used in this work. The effect on cell inactivation decreased in order: hydroquinone, catechol and resorcinol. The initial

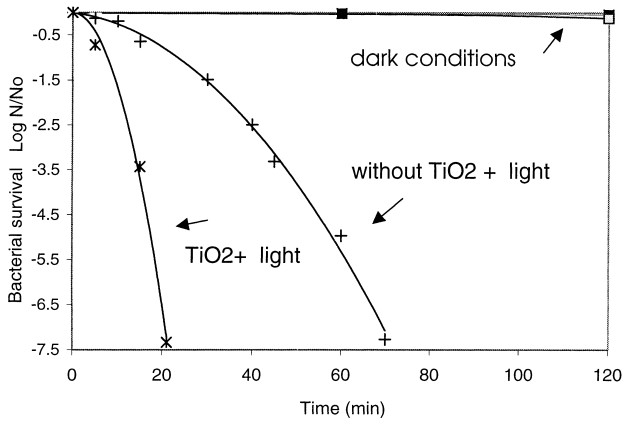

Fig. 1. Effect of TiO_2 (1 g l^{-1}) on *E. coli* survival in the dark as a function of time. Initial concentration 10^7 cell ml^{-1} with (■) and without (□) TiO_2 addition. Inactivation of *E. coli* by sunlight with (×) and without TiO_2 (+) addition as a function of time. TiO_2 (1 g l^{-1}).

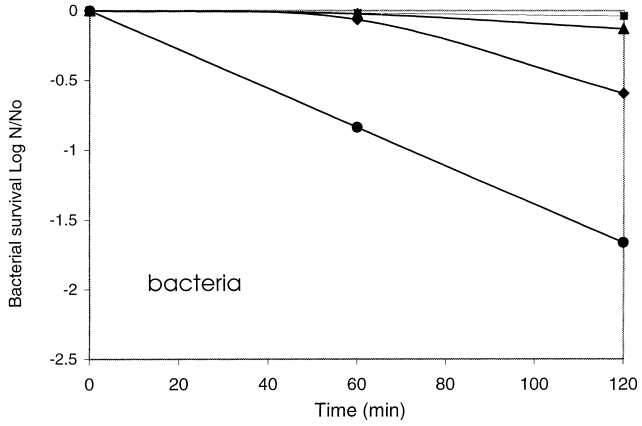

Fig. 2. Effect of dihydroxybenzene isomers (2.0×10^{-3} M) on *E. coli* survival in the dark as a function of time for an initial concentration of 10^7 cell ml^{-1}. Catechol (◆); hydroquinone (●); resorcinol (▲); not DBPPs (■).

bacterial concentration of 10^7 cell per milliliter decreased to about 10^5 in 2 h in the presence of hydroquinone. Resorcinol has a longest latency time which induces higher bacterial resistance.

When TiO_2 is added to the bacterial suspension containing $C_6H_4(OH)_2$ in the dark (Fig. 3), the bactericidal effect is better than without TiO_2 addition, in spite of adsorption of $C_6H_4(OH)_2$ on the surface of catalyser. Bacterial inactivation between 2.5- and 1-order of magnitude for hydroquinone, resorcinol and catechol was reached within 2 h. The addition of $C_6H_4(OH)_2$, influences the bacterial inactivation according to the following sequence: hydroquinone > resorcinol > catechol. We explain this order by the degree of adsorption of different dihydroxybenzene isomers on the catalyst. Since the chemical adsorption increases from hydroquinone to catechol, free surface available for bacterial adsorption is decreased and, consequently, the bactericidal effect of these dihydroxybenzene decreased (Fig. 3). The $C_6H_4(OH)_2$ that is more adsorbed on TiO_2 surface (catechol), protects the bacteria from adsorption to TiO_2 the most and in the same time limits its own bactericidal action which is blocked by adsorption on TiO_2. By comparing Figs. 2 and 3, we conclude that addition of TiO_2 to solutions containing $C_6H_4(OH)_2$ increases the deactivation rate of bacteria by a probable substance–TiO_2 synergistic effect.

3.2.2. Evolution of $C_6H_4(OH)_2$ with TiO_2 addition in dark conditions

The evolution of dihydroxybenzene concentrations measured by HPLC in dark conditions (Fig. 3, insert) is directly related to the extent of the adsorption of the compound on TiO_2. For 4 h $C_6H_4(OH)_2$ concentrations are slightly decreased due to adsorption on the TiO_2 surface. Catechol concentration decreased about 3%, and there is no significant difference between resorcinol and hydroquinone (about 1%).

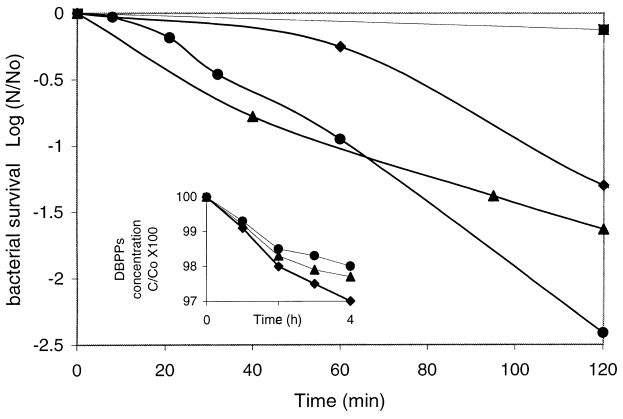

Fig. 3. Effect of dihydroxybenzene isomers (2.0×10^{-3} M) on *E. coli* survival in TiO_2 ($1\,g\,l^{-1}$) suspension under dark conditions vs. time for an initial concentration of 10^7 cell ml^{-1}. The insert contains evolution of compound (1.0×10^{-2} M) concentration measured by HPLC, containing $1\,g\,l^{-1}$ TiO_2 as a function of time under dark conditions. Catechol (◆); hydroquinone (●); resorcinol (▲); not DBPPs added (■).

The adsorption capacity on TiO_2 surface depends on the chemical nature of the substance and the functional groups and their positions on the aromatic ring. Thus, the results could be explained by the difference in the structure of the dihydroxy isomers. In 1992 Tunesi and Anderson [28] reported the results of the adsorption of different derivatives of benzoic acids on TiO_2 surface studied by diffuse reflectance spectroscopy DRIFT. They have argued that the adsorption of substituted benzoic acids at the surface of titanium dioxide (anatase), takes place upon substitution of water or hydroxide ligands and formation of inner-sphere complexes at the cation center. Hydroxyl groups also are capable of forming metal complexes [4,29]. The formation of these complexes is influenced by the steric properties. Therefore, in the case of catechol, the formation of the complex is most probably due to the more favorable positions of hydroxyl groups in *ortho* position thus have two sites of fixation to the catalyst, than in the case of the other two isomeric dihydroxybenzenes, resorcinol in *meta* and hydroquinone in *para* position. Furthermore, the quantity of phenate ions responsible for the adsorption on TiO_2 surface is higher at pH 6 than in more acidic conditions. This has a positive influence on the formation of complexes with TiO_2 due to adsorption. The adsorption experiments made in our laboratory demonstrated that the K_{ads} at pH 6 increases in the sequence hydroquinone > resorcinol > catechol, which is consistent with the decrease of concentration of compounds in the dark (see insert of Fig. 3).

The evolution of the dihydroxybenzene isomers in TiO_2 suspensions in dark conditions was not significantly modified by the presence of the bacteria *E. coli*. This indicates that during the experiments there are no detectable amounts of $C_6H_4(OH)_2$ metabolized or adsorbed by the microorganisms. Thus, in our experiments, the dihydroxybenzene isomers are not a source of carbon for the bacteria.

3.2.3. Effect of $C_6H_4(OH)_2$ on E. coli inactivation by sunlight

It has been reported that the presence of organic substances, mainly suspended material, and substances absorbing at 254 nm (emission height pression Hg UV lamp), can affect the efficiency of UV disinfection. According to our knowledge, the extent of this effect as well as for solar wavelength (<290 nm) has never been reported. It could be expected that intermediates formed from organic compounds under solar irradiation have a synergistic or antagonistic effect on disinfection depending on the chemical characteristic of the compounds.

If we compare the evolution of bacterial inactivation by sunlight only, trace (+) in Fig. 4 with the other curves, it is evident that the influence of the light on bacteria was more pronounced in the absence rather than in the presence of the $C_6H_4(OH)_2$. This means that the addition of these substances resulted in a decrease in UV germicidal activity. Dihydroxybenzene isomers initially protect the bacteria from the UV irradiation because they receive a part of the

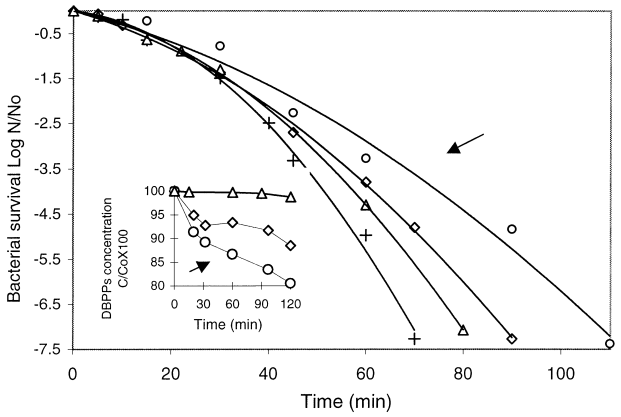

Fig. 4. Effect of DBPPs (2.0×10^{-3} M) on *E. coli* inactivation by solar light for an initial concentration of 10^7 cell ml^{-1}. Catechol (◇); hydroquinone (○); resorcinol (△); (+) not DBPPs. Insert contains a plot of the phenol evolution by HPLC in presence of bacteria under sunlight irradiation vs. time.

photon flux which otherwise would attack bacteria. This consequently, causes a negative effect on the disinfection.

Inverse order was observed for photoreactivity of $C_6H_4(OH)_2$ and bacterial inactivation. The order of dihydroxybenzene degradation, molar absorption, light coefficient and water solubility was the same: hydroquinone > catechol > resorcinol. Therefore, the $C_6H_4(OH)_2$ which absorbs the light less (resorcinol) is also the substance that less protects the bacteria, as shown in Fig. 4 and its insert. Consequently, the total time of bacterial abatement is shorter in the presence of resorcinol by comparing with other isomers. Furthermore, the bacterial inactivation sequence in presence of $C_6H_4(OH)_2$ is correlated with both the Ka values and the pH of the solutions after phototreatment: resorcinol > catechol > hydroquinone. The UV bacterial protection of dihydroxybenzene isomers is linked with chemical structure of the substances and therefore with their chemical properties like acidity, water solubility and molar extinction coefficient. In addition to these effects two more points should be considered: (i) in $C_6H_4(OH)_2$ solutions the bacteria are not living in an optimal nutrient media, which is a factor that contributes to "natural" bacterial inactivation, and (ii) the direct absorption of light by some of these compounds might result in their photochemical transformation, producing compounds which could be more toxic to bacteria than their precursors, thereby influencing the bacterial inactivation. However, this last phenomena does not seem to play a role in this case, since the more the $C_6H_4(OH)_2$ are degraded, the slower is the bacterial inactivation (Fig. 4 and insert).

In the period of time necessary to reach the total bacterial inactivation under sunlight illumination, we did not obtain either a complete elimination of the substances or a significant DOC decrease. These substances have two main UV absorption bands, 190 and 270–288 nm. In this range of wavelengths, solar light intensity is reduced considerably when it reaches the surface of the earth, where only 3% of the sunlight corresponds to UV radiation. In this case photolysis does not play a significant role in the degradation of $C_6H_4(OH)_2$. In the presence of hydroquinone *E. coli* required about 2 h for total inactivation, but only 17% of hydroquinone was eliminated during this period. Thus, direct photolysis of organic molecules present in water might also occur but its degradation is weak when compared with the bacterial inactivation (Fig. 4 and insert).

To find out the influence of some DBPPs presence on bactericidal activity during photocatalytic disinfection with TiO_2, the series of dihydroxybenzene photocatalytic degradation experiments without bacteria were performed.

3.3. Photocatalytic degradation of $C_6H_4(OH)_2$ without bacteria

3.3.1. Degradation of $C_6H_4(OH)_2$ with TiO_2 addition

The zero-order kinetics was found for the dihydroxybenzene isomers degradation rate in the illuminated TiO_2 suspensions. If initial concentration of $C_6H_4(OH)_2$ increases from 2×10^{-3} to 1×10^{-2} M photodegradation rate decreases. Degradation rates decreased from 20×10^{-5} to 7×10^{-5}, from 8×10^{-5} to 4×10^{-5} and from 5×10^{-5} to 3×10^{-5} mol h^{-1} l^{-1} for resorcinol, catechol, and hydroquinone, respectively. At high substrate concentrations the degradation rate is limited by the weak light penetration into the bulk of the solution making the photoactivity of the catalyst less effective. In dilute solutions the light penetrates more easily and arrive at the surface of the catalyst. In this case the reactivity of the compounds and not the penetration of light becomes determining factor. We must also note that the adsorption coefficient on the TiO_2 is not the same for all three molecules and consequently, their reactivity could not be affected to the same extent when their concentration is modified.

Fig. 5 shows hydroquinone and resorcinol concentration measured by HPLC and DOC during irradiation of solutions

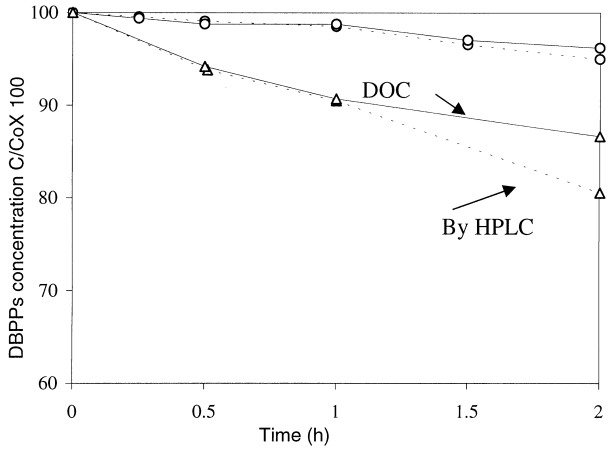

Fig. 5. Evolution of dissolved organic carbon (DOC) (—) and $C_6H_4(OH)_2$ concentration, measured by HPLC (- -) with TiO_2 (1 g l^{-1}) as a function of time of irradiation. Initial concentration of 2×10^{-3} M (144 mg C l^{-1}). Resorcinol (△); hydroquinone (○).

in absence of *E. coli* when the initial concentration for both substances was 2×10^{-3} M. DOC values indicate the degree of mineralization, and concentration by HPLC indicate the evolution of each compound during the treatment. Since in Fig. 5 both values (concentration determined by HPLC and by DOC) evolve together up to 1 h of treatment, we conclude that there is no meaningful accumulation of intermediates. The intermediates accumulate later on. The final pH of the irradiated solution decreased by about one or two pH units during treatment (up to 3.2), indicating that H^+ ions were formed by the process of degradation (Eqs. (3) and (9)). Further, we found a direct correlation between the photoreactivity of each $C_6H_4(OH)_2$ and their acidity, but the final pH of solutions treated after 2 h were in reverse order.

3.3.2. Degradation of dihydroxybenzenes in the presence of TiO_2 and H_2O_2

The $C_6H_4(OH)_2$ degradation without bacteria were carried out in the presence of H_2O_2 as electron acceptor, instead of oxygen of air applied in previous experiments. The evolution of $C_6H_4(OH)_2$ degradation adding TiO_2 and H_2O_2 in the dark (Fig. 6a) and exposed to sunlight (Fig. 6b) were studied. It was observed that there is a relevant decay of catechol even in the dark (Fig. 6a), but not that of hydroquinone and resorcinol. This phenomenon is due to the adsorption of compounds on TiO_2 surface, as shown in Fig. 3 (insert), and to the higher oxidability of catechol toward H_2O_2.

Under light, the addition of H_2O_2 (as electron acceptor) with TiO_2, increases the degradation rates by production of hydroxyl radicals (Eq. (8)). The $OH^\bullet$ radicals are also produced by photolysis of H_2O_2 (Eq. (11)):

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet, \qquad \lambda < 222\,\text{nm} \tag{11}$$

However, the molar absorption coefficient of H_2O_2 is high only for UV irradiation (222 nm). Consequently, the generation of $OH^\bullet$ involved in oxidation of $C_6H_4(OH)_2$ is not efficient at the lower wavelengths which is sunlight used here. The reaction rate constants were calculated in the photocatalytic process of $C_6H_4(OH)_2$ degradation with and without the H_2O_2 addition. The order of magnitude of k values with H_2O_2 addition is 10^3 times higher than without it (Table 1).

The effect of light on dihydroxybenzenes degradation rate is illustrated in Fig. 6b. By comparing Fig. 6a and b, the positive effect of light is evident. The order of degradation is not the same with and without illumination while it depends on the influence of different parameters on different

Table 1
Calculated degradation rates of dihydroxybenzene isomers in illuminated TiO_2 suspension with and without H_2O_2 addition[a]

Substance	With H_2O_2 k (h^{-1})	Without H_2O_2 k ($mol\,l^{-1}\,h^{-1}$)
Resorcinol	6.3×10^{-2}	7×10^{-5}
Catechol	3.8×10^{-2}	4×10^{-5}
Hydroquinone	3.1×10^{-2}	3×10^{-5}

[a] Initial concentrations are 1.0×10^{-2} M.

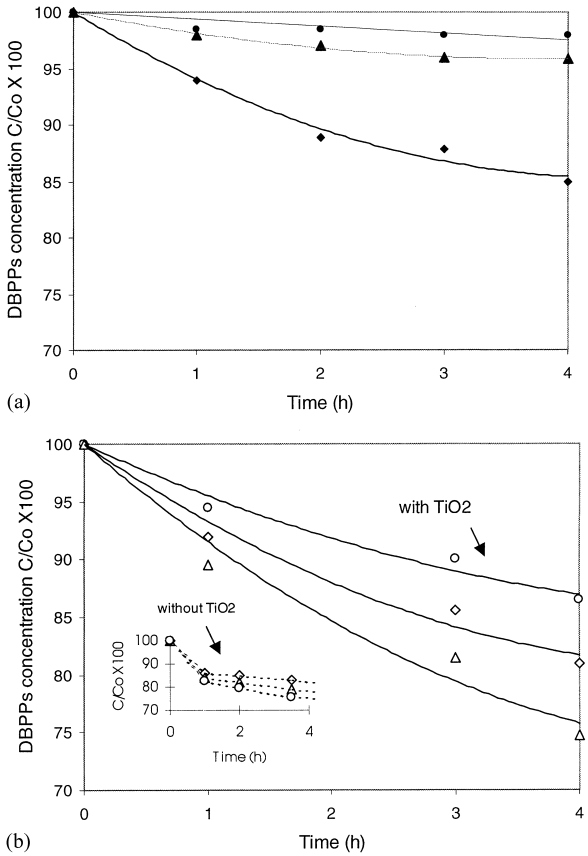

Fig. 6. Evolution of $C_6H_4(OH)_2$ (1.0×10^{-2} M) concentration by HPLC in the presence of TiO_2 ($1\,g\,l^{-1}$) suspension, H_2O_2 (4×10^{-2} M), as a function of time: (a) under dark conditions. Catechol (◆); hydroquinone (●); resorcinol (▲); (b) under sunlight irradiation. The insert contains a plot of the evolution of phenolic compounds by HPLC under sunlight irradiation in the presence of only H_2O_2 (4×10^{-2} M) vs. time. Resorcinol (△); catechol (◇); hydroquinone (○).

$C_6H_4(OH)_2$. Catechol has been more adsorbed than the other dihydroxybenzenes on TiO_2 surface either under light or in the dark. However, under light the OH attack is the most important factor influencing degradation. That is why resorcinol is the most degradated one under light and not catechol.

Comparison of the experiments with and without TiO_2 addition under irradiation showed that in the absence of TiO_2 (Fig. 6b insert) the dihydroxybenzenes degradation was lower, but not significantly, than with TiO_2. At this relatively high concentration of the substance (1.0×10^{-2} M) the TiO_2–H_2O_2 illuminated system described by Eqs. (1)–(9) was equally efficient as the system with only illuminated H_2O_2 represented by Eq. (11), where H_2O_2 is the sole source of $OH^\bullet$ radicals.

It was found out that the best system to degrade $C_6H_4(OH)_2$ is a combination of $h\nu$, TiO_2 and H_2O_2. It appears that the substance concentration play an important role in the extent of degradation of each of isomers. Fig. 7 shows the effect of photocatalytic reaction with the H_2O_2 addition at more than two times lower substance concentration than in the previous experiments, i.e. 4.2×10^{-3} M.

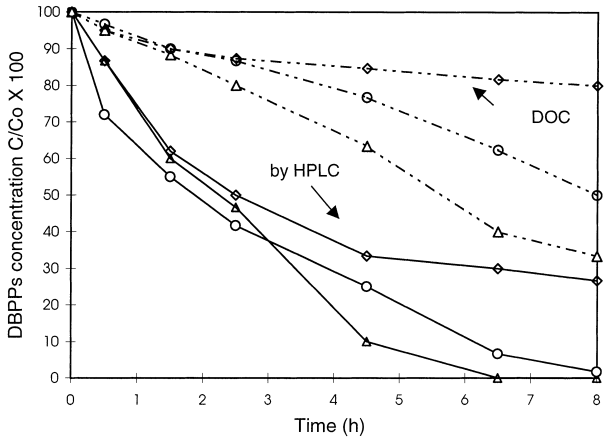

Fig. 7. Evolution of dissolved organic carbon (DOC) (full lines) and $C_6H_4(OH)_2$ concentration measured by HPLC (dashed lines), under irradiated TiO_2 ($1\,g\,l^{-1}$) suspension in the presence of H_2O_2 (4×10^{-2} M) vs. time. Initial concentration 4.2×10^{-3} M of catechol (◇); resorcinol (△); hydroquinone (○).

When H_2O_2 is added to illuminated TiO_2 suspensions a large quantity of $OH^\bullet$ is generated, the kinetics are much faster than in the experiments without H_2O_2 addition and reactivity of substance becomes more important. All isomers follow a pseudo-first-order degradation kinetic (full lines in Fig. 7).The decrease of initial substrate concentration has an effect on the kinetics of $C_6H_4(OH)_2$ photodegradation. The degradation rate constants obtained for 1.0×10^{-2} and 4.2×10^{-3} M increase of chemical rate from 6×10^{-2} to 50×10^{-2}, from 4×10^{-2} to 24×10^{-2}, and from 3×10^{-2} to $29 \times 10^{-2}\,h^{-1}$ for resorcinol, catechol and hydroquinone, respectively. Thus, in the case of H_2O_2 addition, the penetration of light into the bulk is a second factor with relation to the massive increase of $OH^\bullet$ generated from H_2O_2.

As shown clearly in Fig. 7, the observed differences between concentrations of dihydroxybenzenes, measured by HPLC (all lower) and DOC (all higher) suggests an accumulation of intermediates during the phototreatment. Therefore, the reactivity of the intermediates formed is lower than those of initial compounds, which are, thus, in competition with accumulated intermediates. This observation can be of great importance, because the formation and persistence of intermediates in the solution may have an influence on chemical properties of phototreated water and, consequently, on solar disinfection of drinking water with TiO_2. When intermediates are formed and accumulated they could affect the survival of bacteria in two opposite ways: (i) in an inhibitory sense if the products formed are more toxic than the initial compounds, (ii) if they are not toxic they could become a carbon source to bacteria having, in this case, a beneficial effect on bacterial reactivation and growth after phototreatment.

3.3.3. Relative photoreactivity of dihydroxybenzenes

For the three isomers under illumination in the presence of TiO_2 but in absence of H_2O_2, both HPLC and DOC concentration values indicated a similar order in their relative photoreactivity. Catechol seems to be the most reactive substance probably for the following two reasons. The first is related to its high adsorption on TiO_2, which favored a strong catalytic effect between TiO_2 and catechol. But, the main factor influencing photoreactivity seems to be the activation of the aromatic rings with respect to electrophilic substitution of $OH^\bullet$ radical. This generally corresponds to the first oxidation stage of aromatic substances. Chemical structure and, especially, the position of the electron donors hydroxyl groups on the benzene ring are important in these processes. The attack by the $OH^\bullet$ radicals is favorable in positions *ortho* and *para* related to an OH substituent on the benzene ring already present. For this reason, resorcinol which has three positions with double activation (Fig. 8) reacts much faster compared to catechol and hydroquinone which positions are the ones activated for electrophilic attack. In photochemical experiments without H_2O_2 addition, the photoreactivity of $C_6H_4(OH)_2$ does not follow the classic sequence of aromatic ring activation for electrophilic attack: resorcinol > hydroquinone > catechol. Catechol and hydroquinone change position in this series of experiments. This could be due to the keto–enolic tautomery of hydroquinone oxidoreductive effect illustrated in Fig. 9. Benzoquinone is one of the intermediate products of hydroquinone degradation, which can be reduced to hydroquinone by the electrons of the conduction band of the TiO_2 semiconductor. Simultaneously, hydroquinone can be oxidized to benzophenone by the holes in the VB. Thus, this effect diminishes the rate of the degradation of hydroquinone considerably.

In contrast, in the presence of H_2O_2 this recombination mechanisms favored by adsorption of $C_6H_4(OH)_2$ on TiO_2 become "secondary" related to the massive attack of a high concentration of $OH^\bullet$ generated by H_2O_2 (Eqs. (8) and (11)). The photoreactivity of each dihydroxybenzenes is clearly differentiated and is related to the general rules of aromatic electrophilic substitution.

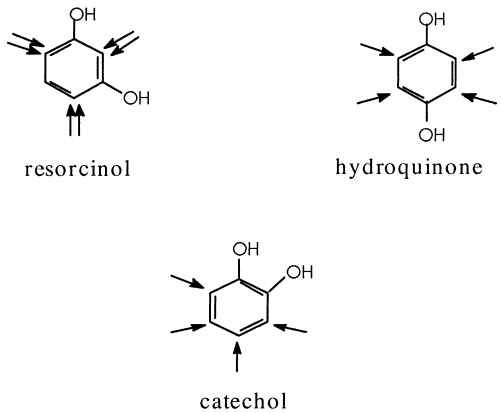

Fig. 8. Schematic representation from electrophilic attack of $OH^\bullet$ radical on dihydroxybenzene isomers $C_6H_4(OH)_2$ (↖).

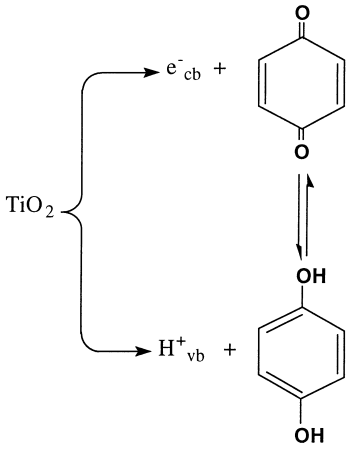

Fig. 9. Keto–enolic oxydoreductive effect of the hydroquinone.

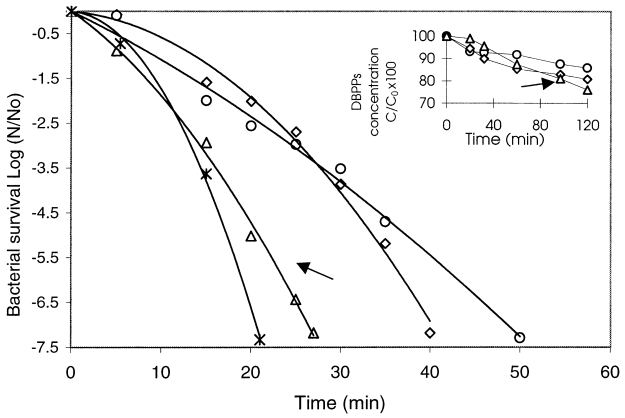

Fig. 10. Effect of DBPPs (2.0×10^{-3} M) on photocatalytic bacterial inactivation as a function of time. Catechol (◇); hydroquinone (○); resorcinol (△); without DBPPs (×); for an initial concentration of 10^7 cell ml^{-1}. The insert contains a plot of the simultaneous evolution of DBPPs concentration in a TiO_2–bacteria suspension vs. time.

3.4. Effect of DBPPs on bacterial inactivation by sunlight with TiO_2 addition

The results presented in Fig. 10 show that the time for complete bacterial photoinactivation with TiO_2 was longer when the dihydroxybenzenes are present, than without it.

This can be explained by a double competition, which induces a protective effect on bacteria. Firstly, dihydroxybenzenes competes with TiO_2 regarding light absorption (bacterial protection towards light). Secondly, $OH^\bullet$ formed on the TiO_2 surface has two potential targets: $C_6H_4(OH)_2$ that can be oxidized (bacterial protection towards $OH^\bullet$ radicals) and bacterial membranes, where $OH^\bullet$ attack of bacteria takes place. The photocatalytic process degrade $C_6H_4(OH)_2$ as well as inactivate bacteria. The determining factor of all these processes seems to be the photocatalytic formation of $OH^\bullet$. If we compare results shown in Figs. 4 and 10, it is evident that *E. coli* photocatalytic inactivation is higher when TiO_2 (generator of $OH^\bullet$) is added (Fig. 10) and its extent was directly proportional to the photochemical reactivity of the dihydroxybenzenes (consumers of $OH^\bullet$) present in solution. Both bacterial and chemical photoreactivity in the presence of TiO_2 were directly correlated with the pH of the solution after phototreatment and with the acidity ($K\alpha$). Photoreactivity of $C_6H_4(OH)_2$ with TiO_2 is similar in presence or absence of bacteria. The substance that is degraded much faster, resorcinol (Fig. 10, insert), does not induce the highest protective effect for bacteria against OH radicals. Therefore, in the presence of resorcinol the total time of bacterial inactivation is shorter in comparison with catechol and hydroquinone (Table 2).

The intermediates more or less reactive, which are formed during the degradation process of $C_6H_4(OH)_2$ generate the free radicals other than $OH^\bullet$, $HO_2^\bullet$ and $O_2^{-\bullet}$, commonly found in TiO_2 mediated systems. These supplementary radicals could be organic germicides and, therefore, accelerate the bacterial abatement. The intermediate compounds could be more toxic than the parent compounds. Consequently, the intermediates affect also the bacterial survival.

The study of bacterial inactivation and DBPPs degradation in different systems simultaneously showed that photocatalytic system with TiO_2 addition was the best process, regarding both purposes: to inactive bacteria and to degrade organic substance present, in our study with $C_6H_4(OH)_2$.

The bacterial inactivation and photocatalytic degradation of dihydroxybenzenes were in the same order, i.e. resorcinol > catechol > hydroquinone.

The experimental rate of photocatalytic *E. coli* inactivation can be expressed by first-order kinetics and were about 10^2 times higher than the photocatalytic degradation rates of the dihydroxyphenols. It was also demonstrated that the time of total bacterial inactivation without TiO_2 addition in the presence of $C_6H_4(OH)_2$was longer (Table 2).

Table 2
Total *E. coli* inactivation and DBPPs degradation in irradiated experiments

DBPPs	Time of total bacterial inactivation (min)		Photoctalytic inactivation rate k	
	With TiO_2	Without TiO_2	Bacteria (min^{-1})	Substance ($mol\,l^{-1}\,h^{-1}$)
None	20	70	1.0417	–
Resorcinol	30	80	0.6078	20×10^{-5}
Catechol	70	100	0.3165	9×10^{-5}
Hydroquinone	110	120	0.2945	5×10^{-5}

4. Conclusions

The simultaneous elimination of bacteria and some DBPPs such as $C_6H_4(OH)_2$ by solar photocatalytic treatment as an interesting alternative process for water treatment has been elucidated. The chemical composition of water is an important factor that can influence the sensitivity of bacteria to solar light and the extent of the DBPPs photodegradation.

We have demonstrated that the presence of hydroquinone, catechol and resorcinol in water inhibit the bacterial growth in the dark, while under irradiation increase bacterial growth. The same effect was found by the addition of TiO_2.

These structural isomers of dihydroxybenzenes had negative influences on the *E. coli* inactivation by solar light with or without TiO_2 addition. The extent of bacterial inactivation and photodegradation of $C_6H_4(OH)_2$ were highly dependent on chemical structure of the substance, and, therefore, of chemical and physical properties as acidity, absorption coefficient and water solubility. The influence of the $C_6H_4(OH)_2$ on *E. coli* was to protect the bacteria from: (a) solar, (b) photocatalytic inactivation, and (c) adsorption on TiO_2. These three kind of protections are a consequence of: (a) the concurrent absorption of the light by the bacteria and the compounds, (b) photocatalytic degradation of the compounds, and (c) adsorption onto TiO_2 surface of DBPPs. Direct correlation between photocatalytic bacterial inactivation and photocatalytic degradation of DBPPs was observed.

Zero-order kinetic model describes the degradation of these compounds. Photochemical degradation was improved by addition of H_2O_2. It is possible that after photocatalytic treatment of water, the residual concentration of H_2O_2 (as a substitute for chlorine) could improve the inactivation of the microorganisms. This method could be a successful alternative to disinfection by chlorination.

Solar disinfection is an interesting alternative process for water treatment, due to two important reasons. The first reason is the rapid inactivation of microorganisms, the second is the reduction of DBPPs, which is interesting if a subsequent chlorination process is applied. Therefore, solar photocatalytic disinfection should be carefully examined in order to assess the application of the process to natural waters.

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References

[1] W.J. Cooper, E. Cadavid, M.G. Nickelsen, K.J. Lin, C.N. Kurucz, T.D. Waite, J. Am. Water Work Assn. 85 (1993) 106.
[2] S.D. Richardson, A.D. Thruston, T.W. Collette, K.S. Patterson, B.W. Lykins, J.C. Ireland, Environ. Sci. Technol. 30 (1996) 3327.
[3] M. Bekbolet, I. Balcioglu, Water Sci. Technol. 34 (1996) 73.
[4] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[5] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1523.
[6] D.W. Hand, D.L. Perram, J.C. Crittenden, J. Am. Water Work Assn. 87 (1995) 84.
[7] J. Kiwi, C. Pulgarin, P. Peringer, M. Gratzel, New J. Chem. 17 (1993) 487.
[8] L. Minsker, C. Pulgarin, P. Peringer, J. Kiwi, New J. Chem. 18 (1994) 793.
[9] T. Matsunaga, R. Tomoda, T. Nakajima, H. Wake, FEMS Microbiol. Lett. 29 (1985) 211.
[10] T. Matsunaga, M. Okochi, Environ. Sci. Technol. 29 (1995) 501.
[11] J.C. Ireland, P. Klostermann, E.W. Rice, R.M. Clark, Appl. Environ. Microbiol. 59 (1993) 1668.
[12] C. Wei, W.Y. Lin, Z. Zainal, N.E. Williams, K. Zhu, A.P. Kruzic, R.L. Smith, K. Rajeshwar, Environ. Sci. Technol. 28 (1994) 934.
[13] M. Bekbolet, Water Sci. Technol. 35 (1997) 95.
[14] S. Lee, K. Nishida, M. Otaki, S. Ohgaki, Water Sci. Technol. 35 (1997) 101.
[15] S. Lee, M. Nakamura, S. Ohgaki, J. Environ. Sci. Health A 33 (1998) 1643.
[16] I.M. Butterfield, P.A. Christensen, T.P. Curtis, J. Gunlazuardi, Water Res. 31 (1997) 675.
[17] H.N. Pham, T. McDowell, E. Wilkins, J. Environ. Sci. Health A Envirion. 30 (1995) 627.
[18] R. Armon, N. Laot, N. Narkis, I. Neeman, J. Adv. Oxid. Technol. 3 (1998) 145.
[19] P.W. Milligan, M.M. Haggblom, Environ. Toxicol. Chem. 17 (1998) 1456.
[20] D.F. Ollis, Environ. Sci. Technol. 19 (1985) 480.
[21] N. Serpone, Solar Energy Mater. Solar Cells 38 (1995) 369.
[22] H. Chick, J. Hyg. 8 (1908) 92.
[23] C. Haslay, H. Lecrec, Microbiologie des eaux d'alimentation, H.C.a. Lecrerc. (Ed.), Technique & documentation Lavoisier, 1973.
[24] G.D. Harris, V.A. Dean, L.S. Darwin, M.S. Curtis, Water Res. 21 (1987) 687.
[25] T. Matsunaga, T. Tomoda, T. Nakajima, N. Nakamura, T. Komine, Appl. Environ. Microbiol. 54 (1988) 1330.
[26] P.-C. Maness, S. Smolinski, D.M. Blake, Z.H.E.J. Wolfrum, W.A. Jacoby, Appl. Environ. Microbiol. 65 (1999) 4094.
[27] Z. Huang, P. Maness, D.M. Blake, E.J. Wolfrum, J. Photochem. Photobiol. A 130 (2000) 163.
[28] S. Tunesi, M.A. Anderson, Langmuir 8 (1992) 487.
[29] D. Robert, S. Parra, C. Pulgarin, A. Krzton, J.V. Weber, Appl. Surf. Sci. 167 (2000) 51.