

PHOTOCATALYTIC TREATMENT OF OLIVE MILLING WASTE WATER: OXIDATION OF PROTOCATECHUIC ACID

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ABSTRACT

The photocatalytic degradation of protocatechuic acid, a biorecalcitrant polyphenolic compound typically found in olive processing and wine distillery waste waters, has been investigated in aqueous heterogeneous solutions containing semiconductor powders (TiO₂, ZnO) as photocatalysts, both in the presence of artificial and natural illumination. The disappearance of the organic molecule follows, approximately a pseudo-first kinetic order according to the Langmuir-Hinshelwood model. Various commercial photocatalysts have been compared with respect to their overall efficiency as well as the production of CO₂. Among them, ZnO shows the highest photocatalytic activity. The effect of H₂O₂ on the reaction rate has been ascertained.

KEY WORDS: protocatechuic acid, TiO₂, ZnO, photocatalysis, photooxidation

INTRODUCTION

The elimination of toxic chemicals from waste water is presently of great concern, since their complete biodegradation is usually very slow and requires several days or weeks. These pollutants may originate from industrial applications or from household and personal care areas. The search of effective means of removing these compounds is of interest to regulating authorities worldwide.

Recently, it has been demonstrated that semiconducting materials mediating photocatalytic oxidation of organic compounds can be an alternative to conventional methods for the removal of organic pollut-

ants in water and air (Ollis et al., 1991; Hoffmann et al., 1995; Peral et al., 1997). A variety of semiconductor powders (oxides, sulfides and others) acting as photocatalysts has already been used. Most attention was given to TiO₂ because of its high photocatalytic activity, its resistance to photocorrosion, its biological immunity and its low cost. The appropriate illumination of these particles produces excited-state high energetic electron and hole pairs (e⁻/h⁺), that can migrate to the particles surface. These pairs are able to initiate a wide range of chemical reactions that may lead to complete mineralization of the pollut-

ants. In addition the photocatalytic process is operated under mild conditions and as it can be powered by sunlight, has a reduced electric power requirements and operating costs (Gupta and Anderson, 1991; Goswami, 1995).

Olive oil is a typical Mediterranean product and its nutritional and economical importance is well known. The waste water from the olive oil milling (extraction) process (OMW) is highly pollutant due to the high organic carbon content, substantial portion of which is present as phenols, polyphenols, tannins, (Zouari and Ellouz, 1996). The pollution potential of OMW, expressed as Chemical Oxygen Demand (COD) concentration, varies from 100-250 kg m⁻³. OMW is a serious environmental problem, not only due to its high organic load and the presence of recalcitrant compounds with biostatic action, but also because it is produced in very high quantities during a short period of time.

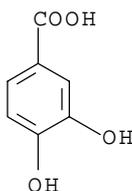
Several chemical and biological procedures are increasingly used in order to transform OMW into more biodegradable residues, some with success, but they are not widely implemented due to their high installation and operation costs (Borja et al., 1992; Matzavinos et al., 1996; Benitez et al., 1997).

In the present study, results are provided for the photocatalytic oxidation and mineralization of protocatechuic acid, which is abundantly present in the OMW, over TiO₂ and ZnO powders under various experimental conditions. Protocatechuic acid is a key polyphenolic pollutant and it belongs to a range of compounds together with gallic, gentistic, caffeic and p-coumaric acid, which are known to inhibit the biological treatment of wastewaters from agricultural origin.

In the recent literature some reports have dealt with the photodegradation of protocatechuic acid in the absence or presence of oxidants such as O₃ and H₂O₂ (Benitez et al. 1993; Benitez et al., 1996), but nothing, as far as we know, has been reported about its photocatalytic destruction.

EXPERIMENTAL

Protocatechuic acid (C₇H₆O₄, 3,4-dihydroxybenzoic acid) of purum quality was a Fluka product and was used as received. Its structure is presented beside:



TiO₂ P-25 from Degussa (anatase/rutile = 3.6/1, surface area 56 m² g⁻¹, non-porous) was used for all photocatalytic experiments, except otherwise mentioned in the text. TiO₂-A (pure anatase, 10 m² g⁻¹) and ZnO (10 m² g⁻¹) were obtained from Merck.

Experiments were performed in an open thermostated Pyrex cell of 250 ml capacity (9 cm diameter, 3.5 cm height). The reaction mixture in the cell was maintained in suspension by magnetic stirring. The irradiation was carried out using four parallel 15 W blacklight blue fluorescent tubes mounted in standard 15W fluorescent tube holders (Philips TLD 15W/08, 45 cm length, 2.6 cm diameter). According to the producer, each tube has a total radiative output of 2.2 W, between 340-400 nm with maximum emission at 370 nm.

In all cases, during the experiments, 200 ml of the protocatechuic acid solution containing the appropriate quantity of the semiconductor powder were magnetically stirred before and during the illumination. At specific time intervals, samples of 5 ml were withdrawn. To remove the TiO₂ particles, the solution was filtered through a 0.45 μm filter (Schleicher and Schuell). Changes in the concentration of protocatechuic acid were observed from its characteristic absorption at 290 nm, using a UV-visible spectrophotometer (Shimadzu UV-160 A) or a high performance liquid chromatography system (Shimadzu LC 7A).

Experiments in the presence of sunlight were performed in July 1997, under the same conditions as those in the presence of artificial light, from 12 to 4 p.m. so that the irradiation was as intense as possible. Two series of experiments were carried out; one under abundant sunlight and the other under a cloudy sky.

In order to determine the CO₂ release, a second apparatus was used. It consisted of a borosilicate glass vessel of 6 cm diameter and 13.5 cm height hermetically sealed with a silicone rubber. The reaction vessel was fitted with a central 11 W lamp (Osram Dulux S 11W/78) and had inlet and outlet ports for bubbling the selected gas, for each reaction. Formation of CO₂ during the photooxidation in the reaction vessel, was followed by measurements of the conductivity increase of an ultra pure water, with the aid of a conductivity meter (Matthews et al. 1990). The pH value of the solutions was monitored by a Metrohm pH-meter and the reaction temperature was kept constant at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

Photodegradation experiments

It is well established that by the irradiation of an aqueous TiO₂ suspension with light energy greater than the band gap energy of the semiconductor ($h\nu > E_g = 3.2 \text{ eV}$), conduction band electrons (e^-) and valence band holes (h^+) are generated. After this primary event, part of the photogenerated carriers recombine in the bulk of the semiconductor with heat emission, while the rest reach the surface where the holes as well as the electrons act as powerful oxidants and reductants respectively. The photogenerated electrons react with the adsorbed molecular O₂ on the Ti(III)-sites reducing it to superoxide radical anion O₂^{•-}, while the photogenerated holes can oxidize either the organic molecules directly or the OH⁻ ions and the H₂O molecules adsorbed at the TiO₂ surface to OH[•] radicals (Fig. 1a). These together with other highly oxidant species (peroxide radicals) are responsible for the primary oxidizing step in photocatalysis, as reported by Pelizzetti and Minero, (1993). According to this, the relevant steps of the photodegradation process at the semiconductor surface can be summarized by the reactions in Fig. 1b.

The OH[•] radicals formed on the illuminated semiconductor surface are very strong oxidizing agents with an oxidation potential of 2.8 V. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus finally

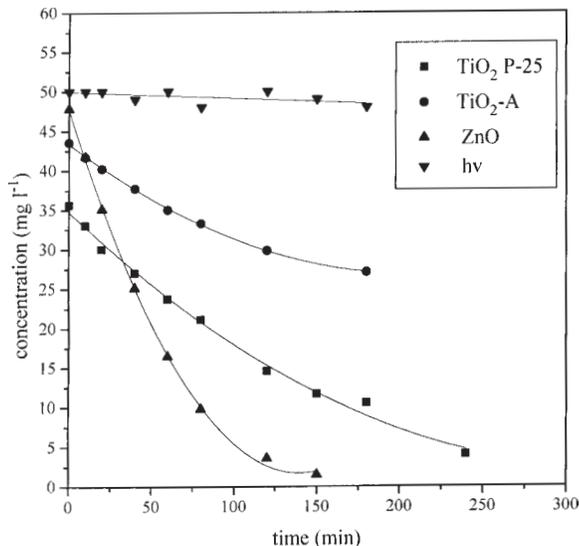


Figure 2. Photodegradation of 50 mg l⁻¹ protocatechuic acid as a function of irradiation time in the presence of (■) 1 g l⁻¹ TiO₂ P-25, (▽) 1 g l⁻¹ ZnO, (●) 1 g l⁻¹ TiO₂ -A and (□) without catalyst.

leading to their complete mineralization.

At first, experiments concerning the photocatalytic decomposition of 50 mg l⁻¹ protocatechuic acid were performed, in the presence of semiconductor catalysts such as TiO₂ P-25, ZnO and TiO₂ -A. Among these, ZnO and TiO₂ P-25 produced the best results.

Results of the photolysis of a 50mg l⁻¹ protocatechuic acid solution containing 1 g l⁻¹ TiO₂ P-25, 1 g l⁻¹

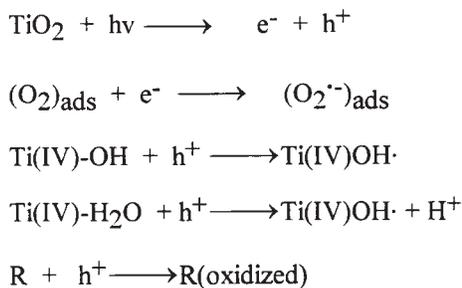
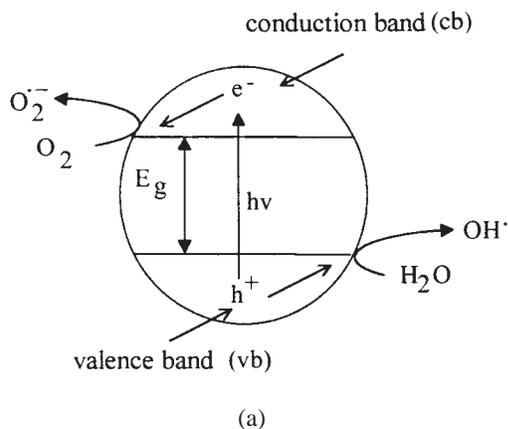


Figure 1. (a) The TiO₂/solution interface under UV- illumination (b) Reactions on the TiO₂ surface under UV-illumination.

ZnO or 1 g l⁻¹ TiO₂-A are shown in Fig. 2. The amount of the organic molecule present in the supernatant is plotted as a function of irradiation time. From Fig. 2, it is clear that the photolysis of an air equilibrated protocatechuic acid solution in the presence of the semiconducting catalysts could lead to the disappearance of the compound. Under these experimental conditions, in the presence of TiO₂ P-25, around 80% of the initial concentration of the acid was removed after 3 h of light exposure, while for the same time interval and in the presence of ZnO the degradation was almost completed. Due to the photocorrosion presented by ZnO, especially in low pH values and due to photostability and constant crystalline composition of anatase-based TiO₂ P-25 powders on the other hand, this catalyst was used throughout the whole work. The decomposition of protocatechuic acid in the presence of TiO₂-A, as can be seen in Fig. 2, is a slower process and after 3 h of illumination more than 50 % of the initial concentration remained in the solution. On the contrary, a very small decrease in the concentration of this compound was observed by illumination in the absence of any

Table 1. Initial reaction rates (r_0) from the photodecomposition of 50 mg.l⁻¹ protocatechuic acid under various experimental conditions.

Experimental Conditions	initial reaction rate (mg l ⁻¹ min ⁻¹)
TiO ₂ P-25 (1 g l ⁻¹)	0.324 ± 0.034
ZnO (1 g l ⁻¹)	0.540 ± 0.018
TiO ₂ Merck (1 g l ⁻¹)	0.196 ± 0.009
sunny day (9.5 mW cm ⁻²)*	0.637 ± 0.086
cloudy day (2.1 mW cm ⁻²)*	0.092 ± 0.014

*in the presence of 1 g l⁻¹ TiO₂ P-25

catalyst (Fig. 2). After 3 h of irradiation with UV light (hν > 340 nm), direct photolysis contributed less than 5 % to the degradation of protocatechuic acid.

The influence of the initial concentration of the solute on the photocatalytic degradation rate of most of the organic compounds is described by a pseudo-first kinetic order, which is rationalized in terms of the Langmuir-Hinselwood model, modified to accommodate reactions occurring at a solid-liquid in-

terface (Al-Ekabi and Serpone, 1988; Turchi and Ollis, 1990),

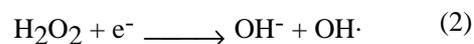
$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \quad (1)$$

where r is the rate of disappearance of the organic substrate and C is its concentration. K represents the equilibrium constant for adsorption of the organic substrate onto TiO₂ and k_r reflects the limiting rate of reaction at maximum coverage for the experimental conditions.

In Table 1 the initial reaction rate (r_0) values from the photodecomposition of the above compound under various experimental conditions are presented. The r_0 values were independently obtained by polynomial fitting of the concentration data (with respect to time) for the first 40 minutes of the reaction, Figs. 2 and 5. Due to the fact that protocatechuic acid is adsorbed particularly strongly on the TiO₂ surface, the equilibrium concentration instead of the initial one has been used in the kinetic study (Cunningham et al., 1994). It must be pointed out that the comparison of the r_0 -values of the three oxides, under the given experimental conditions, is of a more or less qualitative character. Their different physicochemical characteristics (BET, extend of adsorption, etc.) do not allow absolute conclusions as regards the comparison of their photocatalytic activities.

Effect of oxidants

The addition of other powerful oxidizing species such as H₂O₂ or K₂S₂O₈ to TiO₂ suspensions is a well known procedure and in many cases leads to an increase of the rate of photooxidation (Graetzel et al., 1990; Pelizzetti et al., 1991). H₂O₂ is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (eq. 2). It also forms OH· radicals according to eq. 3.



In our case the photocatalytic degradation of 50 mg l⁻¹ protocatechuic acid has been studied at different H₂O₂ concentrations. The effect of the amount of H₂O₂ on the initial reaction rate is shown in Fig. 3. The photocatalytic efficiency increases when the

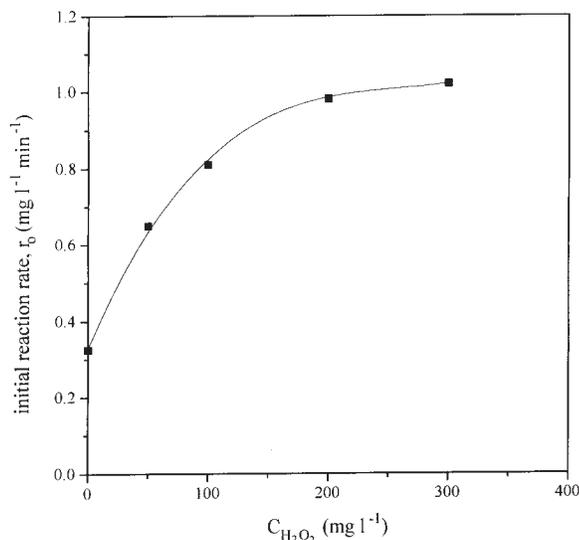


Figure 3. Effect of the H_2O_2 concentration on the photodegradation of 50 mg l^{-1} protocatechuic acid in the presence of 1 g l^{-1} TiO_2 P-25.

concentration of H_2O_2 increases and reaches a maximum in the region of $200\text{--}300 \text{ mg l}^{-1}$. Beyond this maximum, the photocatalytic efficiency starts decreasing. It is well known that H_2O_2 may act as a hole or $OH\cdot$ scavenger or react with TiO_2 and form peroxy compounds, which are detrimental to the photocatalytic action. This explains the need for an optimal concentration of H_2O_2 for the maximum effect. Under these conditions, the addition of 200 mg l^{-1} H_2O_2 accelerates the degradation by a factor of 4.3. This positive effect is comparable to the one observed during photooxidation in other cases (Wolfrum and Ollis, 1994).

Photomineralization experiments

As mentioned above, the complete decomposition of organic compounds to CO_2 via photocatalytic reactions is of great significance in water treatment, because it is the unequivocal evidence for their total destruction of organic compounds in water. For this reason, the conversion of protocatechuic acid to CO_2 was studied in a separate apparatus described in the experimental section.

The overall equation, valid after long irradiation time in the presence of excess oxygen, which describes the photocatalytic mineralization of protocatechuic acid is presented below:

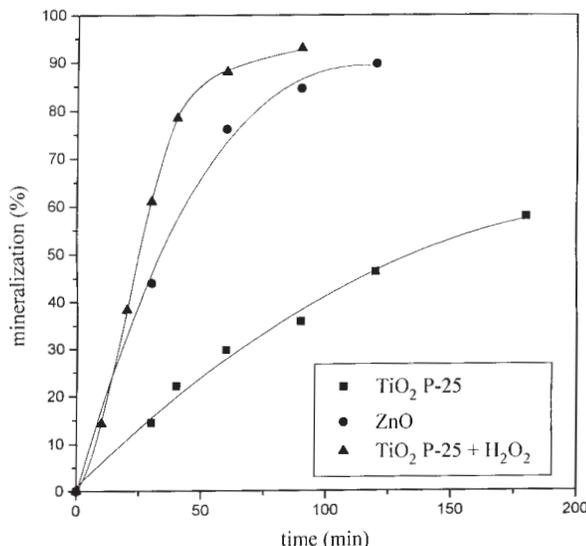


Figure 4. CO_2 formation as a function of irradiation time during the photocatalytic degradation of 50 mg l^{-1} protocatechuic acid in the presence of 1 g l^{-1} TiO_2 -P25 (■), 1 g l^{-1} TiO_2 P-25 + 200 mg l^{-1} H_2O_2 (p), 1 g l^{-1} ZnO (●),

Fig. 4 shows the formation of CO_2 vs. illumination time of a solution containing 50 mg l^{-1} protocatechuic acid in the presence of TiO_2 P-25, ZnO or TiO_2 P-25 + 200 mg l^{-1} H_2O_2 . The concentration of 200 mg l^{-1} H_2O_2 , according to Fig. 3, is the one with the greater influence on the acceleration of the photodegradation of protocatechuic acid.

In the presence of TiO_2 P-25, only 58% of protocatechuic acid was converted to CO_2 in the first 3 h of illumination, while 80% (Fig. 2) was decomposed in the same time showing the presence of intermediates. Full oxidation requires longer irradiation time. The addition of 200 mg l^{-1} H_2O_2 in a suspension of TiO_2 P-25/protocatechuic acid, as shown in Fig. 4, alters significantly the photomineralization process and in the first one and half hour, 90% of the parent compound was converted to CO_2 . This is also in agreement with the results depicted in Fig. 3, where the degradation rates in the presence of various concentrations of H_2O_2 are shown.

As can also be seen in Fig. 4, in the presence of ZnO, the mineralization process under the given experimental conditions is faster compared to that in the presence of TiO_2 P-25. From Figs. 2 and 4, it is clear that in the case of ZnO, the reaction rate of the degradation, as well as the mineralization, is higher than the corresponding of TiO_2 . This fact could be

explained as a result of the generation of H_2O_2 on the ZnO surface, due to the reaction of the photogenerated electrons in conduction band with the adsorbed O_2 molecules, leading thus to an increase of the initial rate of mineralization. According to Kormann et al. (1988), the quantum yield of H_2O_2 production in illuminated aqueous suspensions of ZnO was found to be one order of magnitude higher than the corresponding value for TiO_2 (Kormann et al., 1988; Hoffman et al., 1994).

In the case of TiO_2 -A the photomineralization proceeds with lower efficiency compared to the one when TiO_2 P-25 or ZnO has been used and after 3 h of illumination only 44 % of the initial carbon content has been converted to CO_2 .

The better performance of TiO_2 P-25 may be attributed to the morphology of crystallites, which was proposed to be one of the most critical properties for the photocatalytic efficiency of P-25, among various grades of TiO_2 . Crystallographic study shows that it consists of multiphases of amorphous, anatase and rutile forms. The close proximity of these phases and in some cases the overlapping of forms has been cited to be the reason for long lasting excitation of electrons from the valence to the conductive bands, allowing for efficient and effective degradation of organic compounds (Nargiello et al., 1993).

The photocatalytic degradation of protocatechuic acid is a complicated process with a mechanism involving several chemical and photocatalytic stages and a great number of intermediates. The details of the mechanism are not yet entirely clear. On the basis of our preliminary experimental results and some pertinent suggestions of other researchers concerning the photodecomposition of various carboxylic acids (Trillas et al. 1993; Tunesi and Anderson 1991; Sun and Pignatello 1995), the dual hole-radical mechanism may be proposed for the protocatechuic acid photooxidation, in which direct h^+ oxidation of the carboxylic group takes place under CO_2 liberation, in competition with the $OH\cdot$ attack of the aromatic ring. In the latter case, the resulting OH adduct is finally decomposed and, as a result of the ring opening, the formation of carbonyl compounds and carboxylic acids takes place. Irradiation of the suspension for longer time leads, according to eq. (4), to complete conversion of the parent compound, as well as of the intermediate products to CO_2 (Pelizzetti et al., 1993).

Solar and biodegradability experiments

For the solar exposure experiments the same open Pyrex cell, as for the previous measurements under artificial light, is adapted. The photodegradation of protocatechuic acid under solar illumination on a sunny day (9.5 mW cm^{-2}) and on a cloudy day (2.1 mW cm^{-2}) is shown in Fig. 5. In the same figure the photodegradation under artificial irradiation is also presented. The time required for a 50% degradation of 50 mg l^{-1} protocatechuic acid, under the given experimental conditions, was 26 min in the case of the sunny day, approximately 2 times faster than with the blacklight fluorescent tubes and more than 2.5 times slower in the case of the cloudy day. Consequently, protocatechuic acid can be effectively degraded in a TiO_2 suspension under solar exposure.

Finally, some preliminary experiments concerning the biodegradability of this compound were carried out. The Biochemical Oxygen Demand in 5 days (BOD_5) of a 50 mg l^{-1} protocatechuic acid solution was measured before and after the photocatalytic oxidation. From the results in Table 2 it is clear that after the photocatalytic pretreatment protocatechuic acid, a non biodegradable compound, is converted into intermediates and/or end products, which can be more readily attacked by the microorganisms. The aromatic ring cleavage and the appearance of the aliphatic products, which are more biodegradable, is responsible for this behaviour.

CONCLUSIONS

This study presents results of the photocatalytic oxidative degradation of protocatechuic acid, a biorecalcitrant polyphenolic compound typically found in olive processing and wine distillery waste waters. It was observed that, ZnO is more efficient as a photocatalyst, both in respect of degradation as well as mineralization. Due to the photocorrosion presented by ZnO, especially in low pH on the one, and due to photostability and constant crystalline composition of anatase-based TiO_2 P-25 powders on the other hand, this catalyst was used throughout the work. The combination of the catalysts with H_2O_2 leads to an increase of the photooxidation rates, due to the higher concentration of the hydroxyl radicals generated from the synergetic effect of the semiconductor with the hydrogen peroxide.

The results from the biodegradability experi-

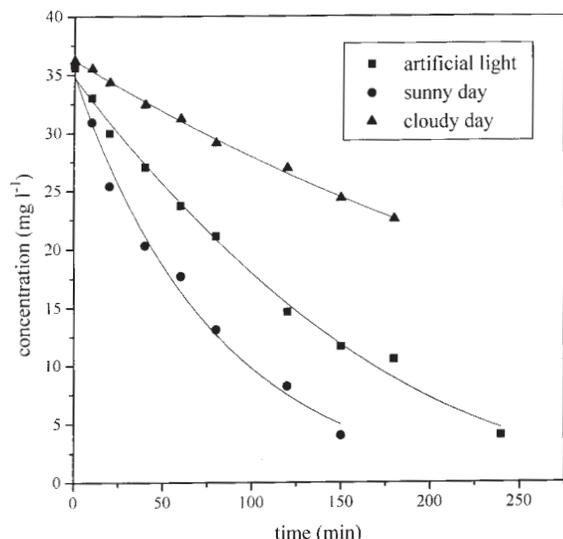


Figure 5. Photocatalytic degradation of 50 mg l⁻¹ protocatechuic acid under artificial and natural illumination in the presence of 1 g l⁻¹ TiO₂ P-25.

Table 2. BOD₅ of 50 ppm protocatechuic acid before and after photocatalytic treatment*

Photocatalytic pre-treatment (h)	BOD ₅ (mg l ⁻¹)
0	0
1	4.5 ± 0.37
3	10.3 ± 0.85

*in the presence of 1 g l⁻¹ TiO₂ P-25

ments had shown, that protocatechuic acid after the photocatalytic treatment is converted into compounds, which can be more readily attacked by the microorganisms. An integrated photocatalytic-biological system, under solar exposure, for the destruction of biorecalcitrant polyphenolic compounds, seems a logical choice for the treatment of waste waters such as from the olive milling process.

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