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A mild photochemical approach to the degradation of phenols from olive oil mill wastewater

Flavio Cermola [a], Marina DellaGreca [a], M. Rosaria Iesce [a,*], Stefania Montella [a], Antonino Pollio [b], Fabio Temussi [a]

[a] *Dipartimento di Chimica Organica e Biochimica, Università degli Studi di Napoli Federico II, Complesso Universitario Monte Sant'Angelo, via Cinthia, I-80126 Napoli, Italy*

[b] *Dipartimento di Biologia Vegetale, Universitàdegli Studi di Napoli Federico II, via Foria, 223 I-80139 Napoli, Italy*

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Abstract

Photooxidation of cathecol (**1**) is carried out in aqueous solution at $\lambda > 300$ nm using different sensitizers: rose bengal (RB), 9,10-dicyanoanthracene (DCA), 2,4,6-triphenylpyrylium tetrafluoroborate (Pyryl). The highest degradation is observed in the UV/RB-sensitized reaction (66% after 15 h of irradiation), mineralization and formation of dimers are the final events. This procedure has been extended to tyrosol (**2**), caffeic acid (**3**), vanillic acid (**4**), 4-hydroxycinnamic acid (**5**) and 4-hydroxybenzoic acid (**6**) as well as to a mixture of all phenols. A reduced toxicity of the UV/RB-irradiated solutions of cathecol and tyrosol towards alga *Ankistrodesmus braunii* is also verified.

Keywords: Cathecol; Tyrosol; Phenolic acids; Sensitized photooxidation; Rose bengal; *Ankistrodesmus braunii*

1. Introduction

Wastewaters from olive oil mills (OMW) have significant polluting properties, especially due to the high concentration of aromatic compounds (i.e. phenols and polyphenols) which are toxic (Hamdi, 1992; DellaGreca et al., 2001) and may inhibit biological treatment (Borja et al., 1997).

The disposal of 30 millions m^3 of OMW every year is a major environmental problem in the Mediterranean countries also because a large volume of this effluent is produced in a short period in wintertime. In European and North African countries OMW are usually released in the soil, and to reduce OMW pollution in soil within the limits required by law, different waste treatments have been devised: biological, chemical, physical, physico-chemical. To date none of these approaches appears as a universal solution so that great efforts of the scientific community are devoted to search effective processes for destroying or reducing these refractory contaminants. In the last decade due to the increasing interest on photochemical approaches for wastewater treatment (Legrini et al., 1993), great attention has been paid to the photodegradation of phenolic compounds, particularly of cinnamic and/or benzoic acids chosen as representative compounds. Photocatalytic oxidation has been used for the degradation of protocatheuic acid in aqueous heterogeneous solutions containing semiconductor powders (TiO_2, ZnO) as photocatalysts (Poulios et al., 1999). It was observed that ZnO is more efficient as a photocatalyst, both in respect of degradation as well as mineralization. Besides, the protocatheuic acid after the treatment is converted into biodegradable compounds. The utilization of systems based on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, (advanced oxidation processes—AOPs) is also a relevant topic. So, it has been recently

* Corresponding author. Tel.: +39-0816-74334; fax: +39-0816-74393.

E-mail address: iesce@unina.it (M.R. Iesce).

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described the kinetics of the oxidation of *p*-hydroxybenzoic acid in aqueous solutions by UV/H_2O_2 (Beltran-Heredia et al., 2001). Although a nearly complete degradation is reached, the main inconvenience of this application is related to the difficulty to control the H_2O_2 concentration. More promising appears the use of a 2,4,6-triphenylpyrylium salt as photosensitizer and sunlight as experimented by Miranda et al. (2000, 2001a,b) who obtained 20–40% of photodegradation of benzoic acid derivatives after 6 h of solar exposure and better results with pyrylium-containing silica gel (Miranda et al., 2002). Dye-sensitized photooxygenations have been examined for phenol derivatives (Matsuura et al., 1972a,b; Saito et al., 1972) or tyrosol (Breton et al., 1987) using methanol as solvent and rose bengal as sensitizer. Here, we report an investigation on the sensitized photooxidation, in aqueous solution, of cathecol (**1**) and other phenols **2**–**6** (Fig. 1). These compounds constitute the principal low-molecular-weight phenolic components from olive oil mill wastewaters and they have been re-examined in a recent study on the toxicity of OMW phenols (DellaGreca et al., 2001). Cathecol was the most abundant compound in the mixture and it also resulted the most toxic on the green alga *Ankistrodesmus braunii* (DellaGreca et al., 2001). This alga represents one of the assay organisms recommended for the standard algal assay procedure developed for aquatic systems (Pipe and Shubert, 1984). We therefore irradiated cathecol in water at $\lambda > 300$ nm under different conditions, hence the UV/rose bengal-sensitized photooxidation, which appeared to generate the most effective degradation, was extended to the other phenols.

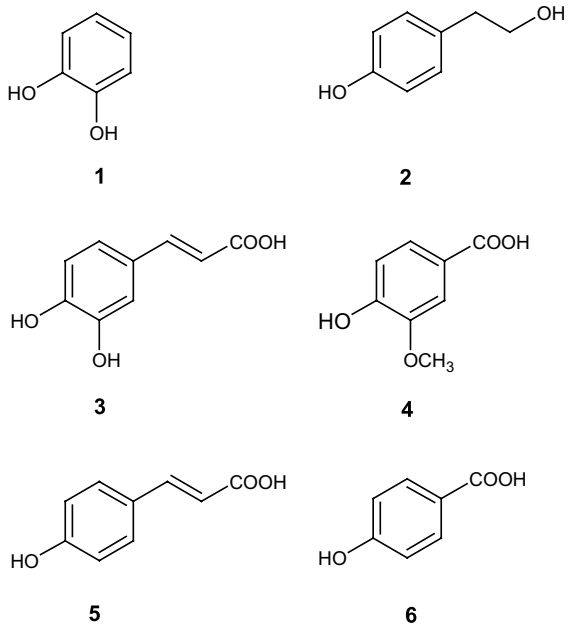


Fig. 1. Phenolic compounds from the low-molecular weight fraction of olive oil mill wastewaters.

2. Materials and methods

2.1. Chemicals

Analytical grade cathecol (**1**), tyrosol (**2**), caffeic acid (**3**), vanillic acid (**4**), 4-hydroxycinnamic acid (**5**) and 4-hydroxybenzoic acid (**6**) were obtained from Aldrich. These and all the other products were used without further treatment: rose bengal (RB, Aldrich), 9,10-dicyanoanthracene (DCA, Kodak), 2,4,6-triphenylpyrylium tetrafluoroborate (Pyryl, Avocado), 1,4-diazabicyclo [2.2.2] octane (DABCO, Merck), NaN_3 (Carlo Erba), oxalic acid (Aldrich).Phenol solutions were prepared using Milli-Q water. All other solvents were of HPLC grade.

2.2. Equipment and methods

HPLC experiments were carried out on a Agilent 1100 HPLC system equipped with a UV detector.

Nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz for [^{1}H] and 125 MHz for [^{13}C] on a Fourier Transform NMR Varian 500 Unity Inova spectrometer. The carbons multiplicity was evidenced by DEPT experiments. The proton couplings were evidenced by ^{1}H–^{1}H COSY experiments. The heteronuclear chemical shift correlations were determined by HMQC and HMBC pulse sequences. ^{1}H–^{1}H proximities through space within a molecule were determined by NOESY.

Mass spectra were carried out on a GCMS-QP5050A (Shimadzu) equipped with a 70 eV EI detector. The column used was Zebron ZB-5 30 m× 0.25 mm with a film thickness of 0.25 μm. The temperature of the injector as well as that of the detector was 230 °C and the acquisition mode was full scan. The following oven temperature was used; start temperature 60 °C followed by an increase to 160 °C at a rate of 20 °C/min where it was held for 8 min. Hence, temperature was increased to 280 °C at a rate of 20 °C/min an it was held for 8 min.

Irradiations were performed using a photoreactor (Helios Italquartz) equipped with a 500 W high-pressure mercury lamp (through a Pyrex filter) or a 650 W halogen lamp (General Electric).

2.3. Irradiation of cathecol and other phenols

In a typical procedure a solution of the phenol compound (10 mg, 100 ml of water) and the sensitizer (molar ratio phenol:sens = 10:1 or as otherwise indicated) in an open Pyrex tube was irradiated at room temperature at a distance of 15 cm from the lamp. When

exposed to the halogen lamp the reactor was kept at the desired temperature (20 °C) by immersion into a thermostated bath. In the experiment carried out under argon atmosphere the solution was saturated with the gas for 15 min before irradiation and then kept closed.

The phenol concentration in samples withdrawn from the reactor at regular reaction times was determined by HPLC, equipped with a UV detector, using a RP-18 column (Phenomenex HYDRO RP-18, 4 μm, 250×4.5 mm). Detection was at 260 nm at a flow rate of 0.7 ml/min. The column was equilibrated with a mixture of A (H_2O containing 1% of acetic acid)/B (methanol containing 1% of acetic acid), 9:1 (v/v) and using the following program: isocratic run for 25 min, followed by an increase of B up to 60% in 30 min and a decrease down to 10% in 5 min.

To verify the presence of short chain fatty acids an aliquot (50 μl) was taken up and injected directly in the HPLC-UV system few minutes after irradiation (5 min, 15 min, 30 min, 45 min) setting the UV detector at 220 nm wavelength.

1,4-Diazabicyclo[2.2.2]octane (DABCO) and NaN_3 were used in a 1:3 molar ratio with the selected phenol.

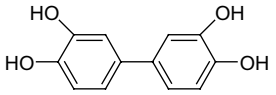
2.4. Photoproduct isolation and characterization

For quantitative scope and to fully characterize the photoproducts, samples of 100 mg were used. After 5 h of irradiation the solution was dried under vacuum and then chromatographed by flash chromatography, eluting with $CHCl_3$/MeOH, 9/1 v/v. All photoproducts were identified by means of their physical features. Details of the HPLC, MS and NMR analysis are given in Table 1.

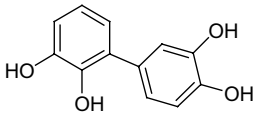
2.5. Phytotoxicity tests

The algal growth experiments were carried out on *A. braunii* cultures as previously described (DellaGreca et al., 2001). Inocula from axenic cultures of *A. braunii* in mid exponential phase were grown in test tubes containing solutions of the phenolic compound irradiated at 0, 5, 10 and 15 h, diluted with Bold Basal Medium (BBM). The concentration of phenols was 10^{-3} M and the final concentration of algae in the test tubes corresponded to 1×10^5 cells/ml. Controls containing either untreated cathecol or tyrosol at the above indicated

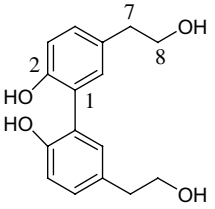
Table 1
Analytical and spectral data of isolated photoproducts



3,3′,4,4′-tetrahydroxybiphenyl (**1a**): (11%), t_R (42 min), MS: m/z 218 $[M]^+$. ^{1}H-NMR: $\delta(CD_3OD)$ 6.95 (1H, d, $J = 2.5$ Hz, H-2), 6.84 (1H, dd, $J = 8.0$ and 2.5 Hz, H-6), 6.76 (1H, d, $J = 8.0$ Hz, H-5). ^{13}C-NMR: $\delta(CD_3OD)$ 134.8 (C-1), 114.8 (C-2), 146.4 (C-3), 145.3 (C-4), 116.6 (C-5), 118.5 (C-6)



3,4,2′,3′-tetrahydroxybiphenyl (**1b**): (3%), t_R (46 min), MS: m/z 218 $[M]^+$. ^{1}H-NMR: $\delta(CD_3OD)$ 7.04 (1H, d, $J = 2.2$ Hz, H-2), 6.88 (1H, dd, $J = 8.0$ and 2.2 Hz, H-6), 6.78 (1H, d, $J = 8.0$ Hz, H-5), 6.64–6.76 (3H, overlapped signals H-4′, H-5′, H-6′). ^{13}C-NMR: $\delta(CD_3OD)$ 137.1 (C-1), 125.0 (C-1′), 114.8 (C-2), 143.9 (C-2′), 145.8 (C-3 and C-3′), 147.7 (C-4), 116.4 (C-4′), 118.1 (C-5), 122.6 (C-5′), 120.9 (C-6), 122.3 (C-6′)



2,2′-dihydroxy-5,5′-(2-hydroxyethyl)biphenyl (**2a**): (2%), t_R (48 min), MS: m/z 274 $[M]^+$. ^{1}H-NMR: $\delta(CD_3OD)$ 7.11 (2H, d, $J = 2.5$ Hz, H-6 and H-6′), 7.08 (2H, dd, $J = 8.5$ and 2.5 Hz, H-4 and H-4′), 6.85 (2H, d, $J = 8.5$ Hz, H-3 and H-3′), 3.74 (4H, t, $J = 7.0$ Hz, 2H-8 and 2H-8′), 2.78 (4H, t, $J = 7.0$ Hz, 2H-7 e 2H-7′). ^{13}C-NMR: $\delta(CD_3OD)$ 128.2 (C-1 and C-1′), 130.6 (C-6 and C-6′), 132.3 (C-5 and C-5′), 133.5 (C-4 and C-4′), 118.0 (C-3 and C-3′), 154.3 (C-2 and C-2′), 65.0 (C-8 and C-8′), 38.8 (C-7 and C-7′). Elemental analysis, found: C, 69.03; H 6.44. $C_{16}H_{18}O_4$ requires: C, 70.07; H 6.57%

concentration or algae in BBM without phenols were also tested. The test tubes were incubated on a shaking apparatus illuminated by daylight fluorescent lamps (Philips TLD 30 w/55), with a total irradiance of 80 $\mu E\,s^{-1}\,m^{-1}$. The growth of the cultures was daily followed by counting the cell number with a Burker blood-counting chamber. Each bioassay was carried out in triplicate and was repeated three times. The inhibition of growth was measured as number of cells respect to control after 4 days. To test the statistical significance of the results, one-way ANOVA was performed at $\alpha = 0.05$. For each solution tested a comparison among means was performed using the Student–Newman–Keuel test (SNK) at $P = 0.05$. The SPSS statistical package (SPSS Inc. for Windows) was used.

3. Results and discussion

3.1. Irradiation of cathecol under different conditions

In the first stage we examined the photochemical behaviour of cathecol under different oxygenation conditions using the properly sensitizer. Rose bengal (RB) which absorbs in a wide region from far UV to visible wavelength acts predominantly via energy transfer to oxygen and it is one of the most efficient singlet oxygen sensitizers (quantum yield of singlet oxygen formation 0.76 in MeOH from Lamberts et al., 1984). 9,10-Dicyanoanthracene (DCA), an electron transfer sensitizer, absorbs in the UV region and can generate superoxide anion (Kavarnos and Turro, 1986), while 2,4,6-triphenylpyrylium tetrafluoroborate (Pyryl) works as an oxidation-reduction catalyst in an electron transfer mechanism which produces neither singlet oxygen nor superoxide and has an absorption band in the visible (Miranda and Garcìa, 1994). Photodegradation was monitored injecting directly an aliquot of the irradiated sample in the HPLC system after 5, 10 and 15 h. For longer times of irradiation we did not observe any significative variation.

As shown in Fig. 2, photodegradation occurs at higher extent using UV/RB conditions (66% of conversion) than using UV/DCA (10–15%), VIS/Pyryl (30%) or VIS/RB (20%). The difference in the rate removal using the same sensitizer (rose bengal) and the two different light sources can be due to different routes depending on the radiation used, as previously observed in the rose bengal-sensitized photooxygenation of resorcinol derivatives by Saito et al. (1972).

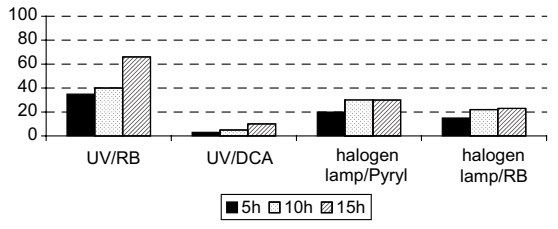


Fig. 2. Cathecol photodegradation (%) by different sensitizers.

Comparison of the results evidences that combination of UV radiation and rose bengal plays a determinant role in the cathecol photodegradation process. We then decided to investigate on the UV/RB irradiation also in order to gain information on the involved mechanism.

The UV/RB-sensitized irradiation led to a significant low mass balance while no substantial amounts of any intermediate were accumulated and concentrations suffered very few changes while reaction was occurring. This can be also due to the slow rate of reaction of cathecol; intermediates were formed very slowly and as they were formed they reacted, keeping a low constant concentration. Treatment of the mixture time by time with the KI reagent coloured the pale rose solution violet evidencing the involvement of peroxidic or hydroperoxidic intermediates (Pasto and Johnson, 1969). Oxalic acid was the only species detected few minutes after irradiation and was identified by comparison with an authentic sample. Small amounts of dimers **1a** and **1b** were also evidenced, and they were isolated with the yields of 11% and 3%, respectively, after 5 h of irradiation. Their structures were assigned on the basis of spectral data reported in Table 1 and by comparison with literature data (Forsyth and Quesnel, 1957; Mehta et al., 2001).

No reaction was observed irradiating by UV/RB under argon atmosphere or by UV/oxygen without sensitizer, showing that both oxygen and rose bengal are needed to photodegrade cathecol. The involvement of singlet oxygen was confirmed by irradiating in the presence of NaN_3 or DABCO, two quenchers of this reactive species (Foote and Clennan, 1995). Indeed, in the presence of DABCO the reaction proceeds very slowly, and after 15 h only 5% degradation was observed, while it was completely inhibited when NaN_3 was added to the cathecol solution.

No appreciable variation was found with or without stirring, although the availability of air is not the same. Evidently, the rate of decomposition of cathecol is so slow that the air diffusing into the solution is enough to supply the oxygen consumed in the reaction. Two percent of sensitizer appears optimal while lower as well as higher amount produces a lesser extent of degradation (from 58% to 45% going from 0.5% to 5% of sensitizer). By changing pH from alkaline to acid a slight increasing of degradation was observed under alkaline conditions (70% at pH 13 vs. 55% at pH 3) as found with other phenols (Gerdes et al., 1997).

According to the mechanisms proposed by Matsuura and Saito who have extensively studied the dye-sensi-

tized photooxygenation of phenol derivatives (see for example, Matsuura et al., 1972a,b; Saito et al., 1972) the results can be easily explained through hydrogen abstraction by the primary formation of a phenoxy radical which may be produced either by the triplet excited sensitizer (via a) and/or by singlet oxygen (via b). In this case the latter should be predominant due to the inhibition of the reaction by NaN_3 or DABCO.

$$^1\text{sens} + h\nu \rightarrow {}^1\text{sens}^*$$

$$^1\text{sens}^* \rightarrow {}^3\text{sens}^*$$

via (a) $^3\text{sens}^* + \text{ArOH} \rightarrow \text{sensH}^{\cdot} + \text{ArO}^{\cdot}$

via (b) $^3\text{sens}^* + {}^3\text{O}_2 \rightarrow {}^1\text{sens} + {}^1\text{O}_2$

$$\text{ArOH} + {}^1\text{O}_2 \rightarrow [\text{ArOH}\text{- - -}\text{O}_2] \rightarrow \text{O}_2^{\cdot-} + [\text{ArOH}]^{\cdot+} \rightarrow \text{ArO}^{\cdot} + \text{H}^+$$

The fate of the phenoxy radical is to undergo dimerization or oxidative fragmentation (Matsuura et al., 1972a,b; Gerdes et al., 1997) to open-chain acids, e.g. oxalic acid, which mineralize to CO_2 and H_2O (Fig. 3). As evidenced by the positive test with KI, peroxidic or hydroperoxidic species should be involved and UV radiation might be a role in accelerating their further degradation (Foote and Clennan, 1995).

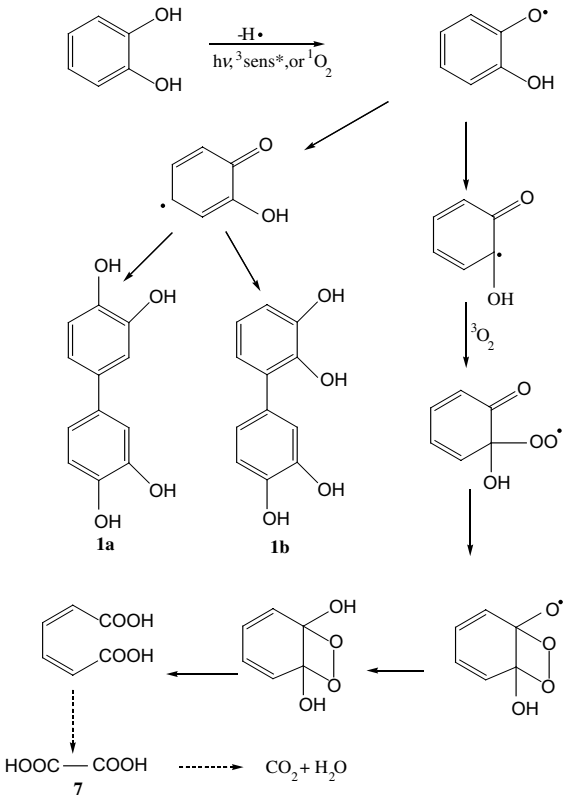


Fig. 3. Suggested mechanism of cathecol degradation by UV/RB-sensitized photooxygenation.

3.2. Photochemical treatment of tyrosol and other phenolic compounds

The higher efficiency of combination of UV radiation and rose bengal was also experimented in the degradation of tyrosol. Indeed, the conversion was of 45% after 15 h vs. 5–15% under the other three conditions (Fig. 4). As for cathecol, low mass balance was experimented and only a dimer was identified and isolated to which structure **2a** was assigned on the basis of analytical and spectral data (Table 1).

The UV/RB procedure was then extended to the other phenolic compounds **3**–**6** and the results summarized in Fig. 5 indicate a less effective degradation as expected considering the well-known electrophilicity of singlet oxygen (Foote and Clennan, 1995) and the reduced electron-donor nature of the acids with respect to cathecol or tyrosol.

A synthetic mixture of all phenolic compounds **1**–**6** was also photoxidated. Comparison of Figs. 5 and 6 indicates that for each compound only a slight decrease of degradation was observed in mixture if compared with the irradiation of the single component. Significantly, trace amounts of dimers **1a** and **2a** were found

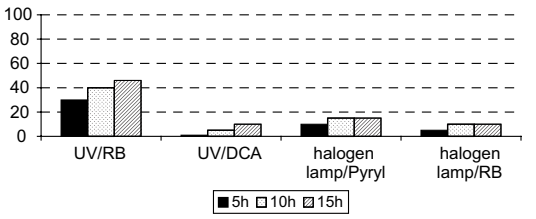


Fig. 4. Tyrosol photodegradation (%) by different sensitizers.

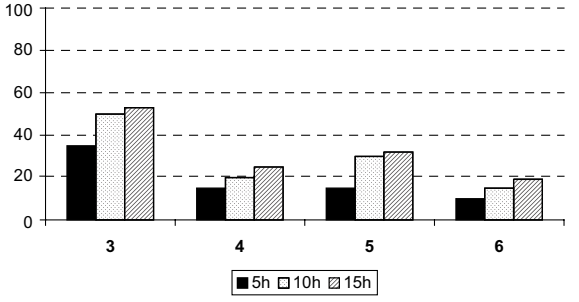


Fig. 5. UV/RB-sensitized photodegradation (%) of phenolic acids (**3**–**6**).

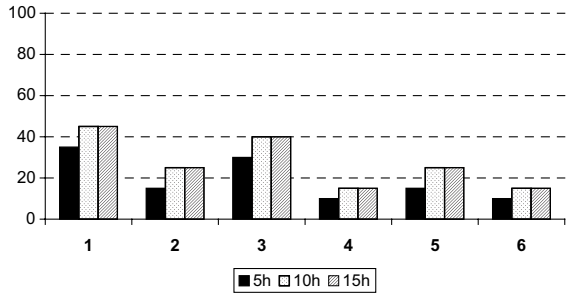


Fig. 6. UV/RB-sensitized photodegradation (%) of phenolic mixture (**1**–**6**).

Table 2
Inhibition of cathecol and tyrosol solutions, at increasing time of UV/RB-sensitized photooxidation, on *A. braunii* expressed as percent of inhibition with respect to the control

Irradiation time (h)	Inhibition by catechol solution (%)	Inhibition by tyrosol solution (%)
0	95a	82a
5	85b	76a
10	70c	62b
15	60d	54c

Values followed by different letters are statistically significant. Student–Newman–Keuls test, $P = 0.05$.

while no cross dimers between different phenols were detected.

4. Toxicity tests on the UV/RB irradiation solutions of cathecol and tyrosol

Each of the phototreated solutions of cathecol and tyrosol at 5, 10 and 15 h has been tested on *A. braunii* cultures by measuring the inhibition, respect to control, of the algal growth at increasing time of irradiation. As shown in Table 2, the toxicity of the solutions decreases with increasing irradiation times and it is reduced of ≈50% after 15 h of irradiation.

5. Conclusions

UV/Rose bengal-sensitized photooxygenation in water has been applied to cathecol and to other five low-molecular-weight phenolic compounds from olive oil mill wastewaters. Although this procedure leads to a partial degradation, some considerations make it attractive. The irradiation for each compound has been carried out at comparable concentration as they occur in OMW. Moreover there is no appreciable difference in the percentage of degradation for each component when irradiated singularly or in mixture. Significantly, toxicity tests carried out directly on the phototreated solutions of cathecol and tyrosol show a reduced toxicity, close to 50% for the highly noxious cathecol. So, the above mild photochemical approach appears promising to be coupled to other treatment, e.g. to biological treatment. The coupling of photoassisted and aerobic biological processes for the wastewater treatment is today receiving great attention (Sarria et al., 2002). The possibility of employing polymer-bound rose bengal (Schaap et al., 1975) represents a further attractive aspect due to the advantage of a reusable sensitizer in a heterogeneous process.

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