

Photochemical and photocatalytic degradation of *trans*-resveratrol†‡

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Photochemical and photocatalytic degradation of the emerging pollutant *trans*-resveratrol has been studied under different irradiation wavelengths and using different TiO₂ catalysts. *trans*-Resveratrol was more easily degraded when irradiated using the whole spectral range (UV-Vis) rather than with UV and near-UV to visible irradiation. The main intermediate of *trans*-resveratrol phototransformation was identified as its isomer *cis*-resveratrol. Different TiO₂ catalysts were used to carry out the photocatalytic degradation of *trans*-resveratrol. Catalysts properties such as crystallite dimensions, surface area and presence of hydroxy surface groups are shown to be crucial to the photocatalytic efficiency of the materials tested. From the point of view of *trans*-resveratrol abatement, the photocatalytic process was more efficient than the pure photochemical one resulting in higher degradation rates and higher organic content removal. Six photoproducts of *trans*-resveratrol phototransformation were identified mainly resulting from the attack of the hydroxyl radical to the organic molecule.

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1. Introduction

Worldwide concerns on water pollution have resulted in increasingly intensive research activity on new treatment technologies over the last few decades. On the other hand, contemporary social habits have led to the occurrence of new types of pollutants in natural watercourses. Biological treatments are not always sufficient to treat well waters polluted with many recalcitrant or persistent compounds.

Pharmaceuticals and personal care products (PPCPs) are a class of water contaminants that have emerged in the last few decades due to their massive use for personal health or cosmetic reasons.^{1,2} PPCPs comprise a diverse collection of chemical substances, including drugs, fragrances, lotions, and cosmetics. The introduction of these compounds in the environment includes human activity (e.g., household and hygienic uses, swimming), veterinary drug use, especially

antibiotics and steroids, residues from pharmaceutical manufacturing and also from hospitals.^{3,4} The concentration of PPCPs can be particularly high in pharmaceutical industry effluents, reaching several hundreds of mg L⁻¹.⁵

Heterogeneous photocatalysis has gained relevance among the existing advanced oxidation processes (AOPs) as a low-cost competitive process, mainly because it can be operated at ambient temperature and pressure.^{6,7}

In particular, titanium dioxide (TiO₂) has been widely used as a photocatalytic material for solving environmental problems, especially for removing chemical pollutants from wastewater.^{8,9} The widespread use of TiO₂ in photocatalytic applications is due to its strong oxidizing power, high chemical stability and relative inexpensiveness.⁸

In this work we have studied the photochemical and photocatalytic degradation of *trans*-resveratrol (3,4',5-trihydroxy-*trans*-stilbene), an antioxidant stilbenoid compound used in medical applications for lowering the risk of coronary heart disease, bearing also important anticarcinogenic properties.^{10–12} *trans*-Resveratrol can be found in grape skin, peanuts, soy, tea and other plants.¹³ It is introduced in the human diet mainly through the ingestion of wine in which both *trans*- and *cis*-isomers are found.¹⁴ *trans*-Resveratrol has emerged as a pollutant in wastewater since it has been synthesized in large scale to be included in the formulation of several personal care products with anti-aging effects.^{15,16}

To the best of our knowledge this is the first study dedicated to the photocatalytic degradation of *trans*-resveratrol.

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There are only a few references in the literature reporting the interaction of light (mostly in the UV range) with the *trans*-resveratrol molecule.^{17,18}

In this paper we have studied the photodegradation of *trans*-resveratrol under different irradiation wavelengths and irradiation intensities. The photocatalytic degradation of *trans*-resveratrol using TiO₂ as a photocatalyst is also described using different types of TiO₂ and different irradiation wavelength ranges.

2. Experimental

2.1 Reagents and materials

Titanium(IV) oxide powder anatase 99.8% metal basis (TiO₂-SA) and *trans*-resveratrol (≥99%) were purchased from Sigma-Aldrich. TiO₂ AEROXIDE® P25 (TiO₂-EP) was supplied by Degussa AG, now Evonik. TiO₂-SG was prepared by using a sol-gel procedure as described elsewhere.¹⁹

2.2 Photodegradation experiments

The photodegradation of *trans*-resveratrol was carried out in a 300 mL glass immersion reactor with a gas inlet, a gas outlet and a sampling port. The photoreactor was equipped with distinct types of light sources located axially and held in a quartz immersion tube: a UV Heraeus TNN 15/32 low pressure mercury vapour lamp ($\lambda_{\text{exc}} = 254$ nm) and a UV-Vis Heraeus TQ 150 medium pressure mercury vapour lamp ($\lambda_{\text{exc}} = 254, 313, 365, 405, 436, 546$ and 578 nm). The light intensity of both lamps was approximately 50 mW cm^{-2} , as determined by using a UV-Vis spectroradiometer (USB2000+, OceanOptics, USA). A quartz jacket with water recirculation was employed to cool the irradiation source and cancel the infrared radiation, thus preventing any heating of the solution/suspension. In order to cut-off the UV-B and UV-C emission lines, a DURAN 50® glass cooling jacket was placed around the UV-Vis lamp (main resulting emission lines at $\lambda_{\text{exc}} = 365, 405, 436, 546$ and 578 nm, see ESI, Fig. SI1†). The different irradiation wavelength ranges were designated as UV (TNN 15/32 lamp), UV-Vis (TQ 150 lamp) and Vis (TQ 150 lamp with DURAN 50® cut-off filter). In a typical reaction, the reactor was charged with 250 mL of a 20 mg L^{-1} *trans*-resveratrol solution. A 20% vol. oxygen stream was continuously bubbled through the reaction system. Reactions were performed under natural pH conditions (pH = 5.6). In the case of photocatalytic reactions, TiO₂ was used as a catalyst with a load of 1 g L^{-1} . Before turning the light on, the suspensions were magnetically stirred for 15 min, to establish the adsorption-desorption equilibrium. The first sample was taken out at the end of the dark adsorption period, just before the light was turned on, in order to set the initial *trans*-resveratrol concentration in solution (C_0).

2.3 Analytical techniques

Diffuse reflection infrared Fourier transformed (DRIFT) spectroscopic analysis of TiO₂ samples was performed on a Nicolet 510P FTIR Spectrometer. The interferograms were converted

by the instrument software (OMINC) to equivalent absorption units in the Kubelka-Munk scale. The specific surface area (S_{BET}) of TiO₂ materials was determined by multipoint analysis of N₂ adsorption isotherms at 77 K using the BET method, with a Quantachrome NOVA 4200e multi-station apparatus.

During the photodegradation experiments, samples were regularly withdrawn from the reactor and centrifuged prior to analysis for separation of any suspended solid. The solutions were then analyzed by HPLC using a Hitachi Elite LaChrom liquid chromatograph equipped with an L-2450 diode array detector (DAD). The stationary phase consisted of a Purospher Star RP-18 endcapped column (250 mm × 4.6 mm, 5 μm particles) working at room temperature. The mobile phase was a mixture of water (A) and methanol with a gradient concentration at a flow rate of 1 mL min^{-1} . The gradient was as follows: 0 min, 70% A; 22 min, 37% A; 27 min, 37% A; 30 min, 70% A; 36 min, 70% A.

Selected samples were analyzed using a Thermo Accela HPLC equipped with a PDA detector, coupled to a Thermo LTQ Orbitrap Discovery mass spectrometer using ESI[−] ionization, operating in full-scan mode ($R > 30\,000$), between 50 and 400 uma . Separation was carried out using a Phenomenex Luna C18 column (150 mm × 4.6 mm, 5 μm particles) at a flow rate of 0.5 mL min^{-1} . The mobile phase gradient was similar to that used for HPLC-DAD analysis.

Total organic carbon (TOC) measurements were performed in a Shimadzu TOC-5000 analyzer.

3. Results and discussion

3.1 Photochemical degradation of *trans*-resveratrol under different irradiation wavelengths

Photochemical degradation of *trans*-resveratrol was carried out under different irradiation conditions: (i) monochromatic ultraviolet light with an emission line at 254 nm (UV); (ii) polychromatic light in the range 200–600 nm (UV-Vis); (iii) polychromatic light at $\lambda \geq 365$ nm (mostly visible light irradiation, Vis).

The UV-Vis spectrum of *trans*-resveratrol shows a maximum at 310 nm with a molar absorption coefficient at this wavelength of $26\,669 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. 1a). HPLC analysis of the samples taken during photochemical experiments revealed that the main intermediate of *trans*-resveratrol photochemical degradation is its geometrical isomer *cis*-resveratrol, identified by its UV-Vis absorption spectra, with a maximum at 286 nm (Fig. 1a).

Fig. 1b shows the decay of *trans*-resveratrol concentration following UV, Vis and UV-Vis irradiation. *trans*-Resveratrol is more easily converted when irradiated over the whole spectral range (UV-Vis), which is attributed to better overlap of the excitation light with its absorption spectrum.

In opposition, the slowest reaction rate was observed when UV light ($\lambda_{\text{exc}} = 254$ nm) was used. At this wavelength *trans*-resveratrol shows a minimum of absorbance, which accounts for the lower photodegradation efficiency observed. As shown

in Fig. SI1,† the cut-off filter transmission uptake is at *ca.* 350 nm. *trans*-Resveratrol shows residual absorption at $\lambda \geq 350$ nm, which can explain the slow rate observed for the photochemical degradation reaction when radiation in the Vis range is used.

Independently of the irradiation wavelength used, the kinetics of the photodegradation reactions followed a first order rate law. Kinetic rate constants of the photochemical

degradation process (*k*), determined by non-linear curve fitting to the experimental data, are shown in Table 1, as well as the percentage of *trans*-resveratrol conversion and TOC removal after, respectively, 5 min ($X_{5 \text{ min}}$) and 3 h of irradiation ($X_{\text{TOC}, 3 \text{ h}}$).

As shown in Table 1, *k* increases with the irradiation wavelength following the order UV < Vis < UV-Vis. The same tendency was observed for *trans*-resveratrol conversion at 5 min of the reaction, with almost complete elimination when irradiating in the whole UV-Vis spectrum. Nevertheless, although total conversion of both *trans*- and *cis*-resveratrol was achieved at the end of the reactions using both UV and Vis irradiation, no TOC removal was observed, which indicates that both isomers are converted into other organic by-products but not mineralized to CO₂ and H₂O. On the other hand, UV-Vis irradiation leads to 87% TOC removal, indicating that both *trans*-resveratrol and organic intermediates are almost completely mineralized.

In order to study the influence of different light intensities in the photodegradation of *trans*-resveratrol under UV-Vis irradiation, a dye (C.I. Direct Green 26) solution was circulated through the quartz jacket placed around the irradiation source, acting as a light filter. This dye shows absorption in the range 200–750 nm (Fig. SI2,†), with maxima at 254, 382 and 610 nm and molar absorption coefficients at these wavelengths of 32 346, 28 931 and 25 745 M^{−1} cm^{−1}, respectively. Solutions of the dye with different concentrations were used to filter different light fractions. Radiation intensities were determined by ferrioxalate actinometry²⁰ and treated as fractions of the initial flow (ϕ/ϕ_0), *i.e.*, the photonic flow obtained when water is passing through the quartz jacket. Results show that the rate of transformation of *trans*-resveratrol increases with UV-Vis light intensity (Fig. 2a). It was also found that at an early stage of the reaction (5 min), *trans*-resveratrol conversion is linearly proportional to light intensity (Fig. 2a inset), which indicates that the number of photons absorbed by the system is proportional to the number of *trans*-resveratrol molecules being transformed. Fig. 2b shows the time evolution of the area of the HPLC peak corresponding to *cis*-resveratrol. Kinetics of formation and disappearance of *cis*-resveratrol are also light intensity dependent. For high intensities the low amounts of *cis*-resveratrol formed are rapidly degraded under those

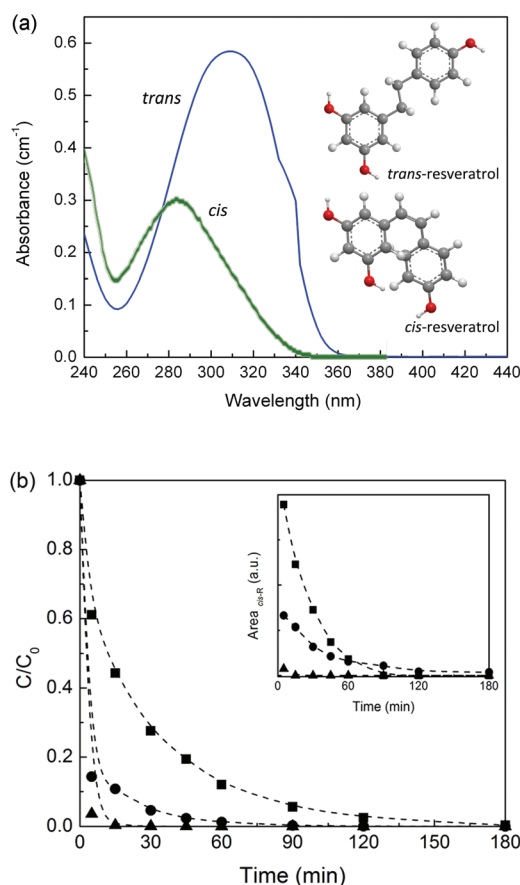


Fig. 1 UV-Vis spectra of *trans*- and *cis*-resveratrol and respective molecular structure (a). Evolution of the normalized concentration (C/C_0) of *trans*-resveratrol ($C_0 = 20 \text{ mg L}^{-1}$) during the photodegradation reactions under UV (■), Vis (●) and UV-Vis (▲) irradiation – inset: area of the HPLC peak corresponding to *cis*-resveratrol (b).

Table 1 Rate constants (k_{app} and k), *trans*-resveratrol conversion after 5 min of irradiation ($X_{5 \text{ min}}$) and TOC removal at 3 h of reaction ($X_{\text{TOC}, 3 \text{ h}}$), obtained for photocatalytic experiments using different reaction conditions

Reaction conditions	$k (\times 10^{-1} \text{ min}^{-1})$	$k_{\text{app}} (\times 10^{-1} \text{ min}^{-1})$	k_{app}/k	$X_{5 \text{ min}} (\%)$	$X_{\text{TOC}, 3 \text{ h}} (\%)$	Photo-products
UV	0.49 ± 0.06	—	—	39	0	2, 3, 5, 6
Vis	3.8 ± 0.6	—	—	86	0	1, 2, 3
UV-Vis	6.63 ± 0.07	—	—	96	87	1, 3, 4
Vis/TiO ₂ -SA	—	2.21 ± 0.03	0.58	66	74	n.a.
Vis/TiO ₂ -EP	—	3.0 ± 0.1	0.79	79	72	n.a.
Vis/TiO ₂ -SG	—	5.9 ± 0.2	1.55	94	75	1, 2, 3, 4
UV/TiO ₂ -SG	—	0.94 ± 0.07	1.92	44	65	1, 2, 3, 4
UV-Vis/TiO ₂ -SG	—	8.9 ± 0.3	1.34	98	90	n.d.

n.a.: not analyzed; n.d.: not detected.

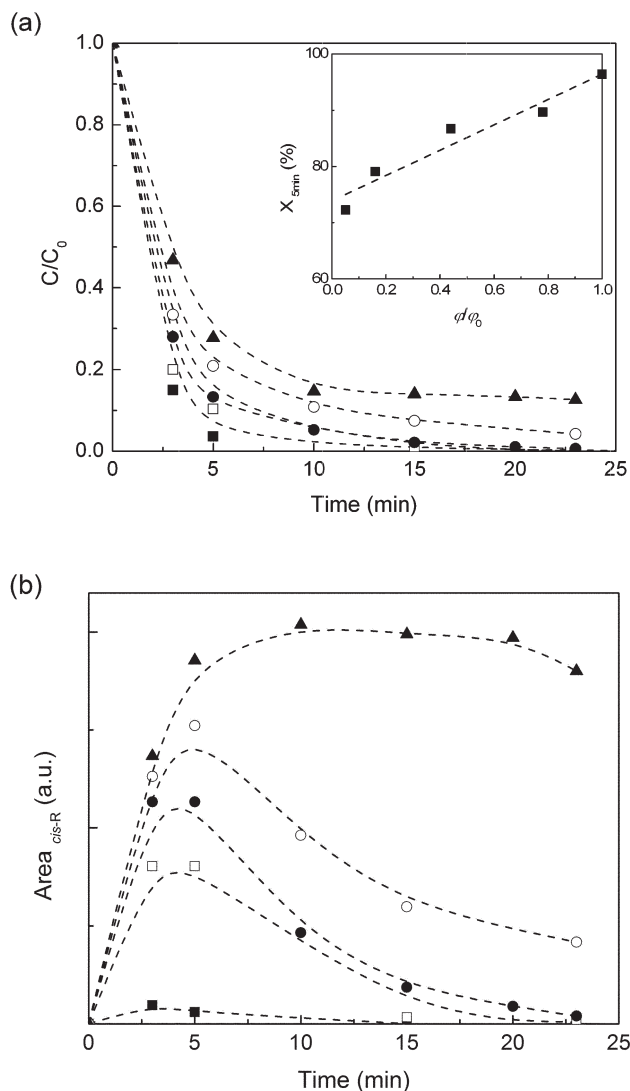


Fig. 2 Evolution of the normalized concentration (C/C_0) of *trans*-resveratrol (a) and area of the HPLC peak corresponding to *cis*-resveratrol (b) during photochemical degradation reactions under different UV-Vis irradiation intensities: $\phi/\phi_0 = 1$ (■); $\phi/\phi_0 = 0.78$ (□); $\phi/\phi_0 = 0.44$ (●); $\phi/\phi_0 = 0.16$ (○); $\phi/\phi_0 = 0.05$ (▲). Inset (a): correlation between light intensity and *trans*-resveratrol conversion after 5 min of irradiation ($X_{5\text{ min}}$).

conditions. As light intensity decreases, there is a progressive increase in the amount of *cis*-resveratrol being formed (and not being degraded) with a gradual decrease in its disappearance rate.

The slower rates observed for *trans*- and *cis*-resveratrol depletion when low intensities are used can be attributed to the lower ratio between the amount of photons available and the number of molecules in solution.

3.2 Photocatalytic degradation of *trans*-resveratrol

3.2.1 Effect of TiO_2 nature. Photocatalytic degradation of *trans*-resveratrol was performed under irradiation at $\lambda \geq 365$ nm using different TiO_2 catalysts. This wavelength interval was selected because no mineralization was observed in the

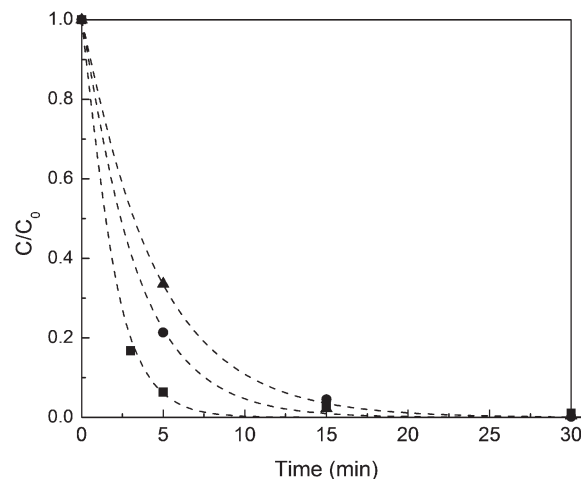


Fig. 3 Evolution of the normalized concentration (C/C_0) of *trans*-resveratrol during the photocatalytic experiments under Vis irradiation using TiO_2 -SG (■), TiO_2 -EP (●) and TiO_2 -SA (▲) catalysts.

absence of catalyst, and it may serve to simulate conditions of solar irradiation. TiO_2 P25 (EP) has been widely used in numerous photocatalytic studies being generally accepted as the benchmark catalyst for this type of reaction. It is constituted by 80% of anatase and 20% of rutile allotropes. Both TiO_2 -SA and TiO_2 -SG are constituted by pure anatase nanoparticles. Results show that for all cases total removal of *trans*-resveratrol was achieved after 30 min of irradiation (Fig. 3).

Kinetics of photocatalytic degradation of *trans*-resveratrol follow a pseudo-first order rate model (as predicted by the Langmuir-Hinshelwood model²¹), the corresponding apparent kinetic rate constants (k_{app}) being summarized in Table 1. TiO_2 -SG showed the best photocatalytic performance with the highest k_{app} , followed by TiO_2 -EP and TiO_2 -SA. Using this catalyst, a practically complete degradation was achieved after just 5 min of visible-light irradiation. The rate constants obtained for reactions using TiO_2 -EP and TiO_2 -SA were one half and one third lower than those obtained with TiO_2 -SG, respectively.

Noteworthy, regardless of the catalyst being used, high levels of TOC removal were attained at the end of 3 h of irradiation. However, k_{app} for the reactions using TiO_2 -EP and TiO_2 -SA at the studied conditions were lower than the rate constant (k) of the corresponding photochemical degradation reaction (Table 1). As shown before, in the pure photochemical regime using the same irradiation conditions, no TOC conversion was observed, which means that organic molecules are only being photo-transformed and not actually eliminated. In the case of the photocatalytic process, not only *trans*-resveratrol is being removed from the solution but also most of the intermediate compounds are being degraded up to complete mineralization.

The different results obtained with the various TiO_2 catalysts can be ascribed to the distinct physico-chemical characteristics of the materials. It has been recognized that TiO_2 photocatalytic efficiency is related to surface and structural properties of the semiconductor such as crystal structure,

surface area, particle size distribution, porosity, band gap and surface hydroxyl density.⁸ In this case, all TiO₂ samples are mainly constituted by anatase crystallites, but with different particle sizes. TEM images of the different TiO₂ materials (not shown) confirm the presence of anatase crystallites of sizes around 10 nm, 30 nm and 50 nm for TiO₂-SG, TiO₂-EP and TiO₂-SA, respectively. Particle size and, ultimately, crystallite dimensions play an important role in the photoactivity of a semiconductor catalyst, since the electron/hole recombination process has been shown to be particle size dependent.²² Generally it is assumed that the smaller the particle (in a nanometric range), the higher the efficiency of the photocatalytic process. Nevertheless, some studies revealed that the photocatalytic efficiency does not monotonically increase with decreasing particle size, and there exists an optimal particle size of about 10 nm for the pure nanocrystalline TiO₂ photocatalyst.^{22,23} Among the materials tested, TiO₂-SG is the one constituted by smaller crystal particles, which could be one of the reasons for the higher efficiency observed with this material.

Another important characteristic that contributes to the performance of TiO₂ photocatalysts is the presence of surface hydroxy groups. The presence of OH surface groups was confirmed by DRIFT analysis of the TiO₂ materials (Fig. SI3†). DRIFT spectra of the different materials show the presence of a weak band at around 1640 cm⁻¹ caused by the bending vibration of coordinated water as well as from Ti-OH groups.²⁴ The presence of a broad band located between 2600 and 3800 cm⁻¹ attributed to the stretching vibration of hydrogen-bonded surface water molecules and hydroxy groups can also be observed.^{19,25} This vibration is much more pronounced for TiO₂-SG, which suggests the existence of a higher availability of OH groups at the surface of this material. In photocatalytic reactions, the surface OH groups and adsorbed water react with photogenerated holes leading to the formation of hydroxyl radicals (HO·) with strong oxidation power that are able to degrade organic compounds until their mineralization.

The surface area of the photocatalysts is another aspect to be taken into account since it is directly related to the concentration of active sites for adsorption and reaction. In this case, the measured BET surface areas for the TiO₂ materials used were 99, 56 and 14 m² g⁻¹ for TiO₂-SG, TiO₂-EP and TiO₂-SA. After the dark adsorption period a decrease of 31% on the concentration of *trans*-resveratrol was observed when TiO₂-SG was used and of 22% and 23%, respectively, for the photocatalytic reactions using TiO₂-EP and TiO₂-SA. This indicates that adsorption of *trans*-resveratrol on the surface of the TiO₂-SG catalyst may play an important role in the efficiency of the photocatalytic degradation process. It is known that the adsorption process on the photocatalyst surface depends also on the electrical charge of both the organic substrate and the catalyst. Due to the amphoteric character of TiO₂, either a positive or negative charge can develop on its surface depending on the pH range. The point of zero charge of TiO₂, *i.e.*, the pH at which the surface charge is neutral, is around pH = 6.²⁶ Since reactions were performed at pH = 5.6, it is expected that the catalyst's surface may be slightly positively charged. On the

other hand, the pK_a values of *trans*-resveratrol corresponding to the mono-, di- and tri-protonation of the molecule are 9.3, 10.0 and 10.6, respectively.²⁷ At the working pH conditions *trans*-resveratrol is, therefore, in its non-ionized form. Thus, it is not expected that electronic interactions between the catalyst's surface and the organic molecule play a major role in the photocatalytic process.

Overall, the smaller crystallite size, the higher content on hydroxy surface groups and the higher surface area are believed to be the main features that make TiO₂-SG the most efficient catalyst for *trans*-resveratrol photodegradation.

3.2.2 Effect of irradiation wavelength. Similarly to the photochemical degradation study, the photocatalytic degradation of *trans*-resveratrol was performed using TiO₂-SG under different irradiation wavelengths: UV, Vis and UV-Vis (Fig. 4). As in the case of pure photochemical reactions, *trans*-resveratrol was more easily removed when UV-Vis light was used and the lower photocatalytic efficiency was obtained under UV irradiation.

Pseudo-first order apparent rate constants (k_{app}) for the photocatalytic reactions performed under different irradiation sources are listed in Table 1. The highest value of k_{app} was obtained for the UV-Vis system and the lowest for the reaction under UV light. Since *trans*-resveratrol absorbs at the different wavelength ranges of irradiation, one cannot exclude the contribution of direct photodegradation when studying the photocatalytic process. In order to quantify the effect of the photocatalytic contribution, we calculated the ratio between the kinetic rate constants obtained for photocatalytic (k_{app}) and photochemical (k) reactions. It was observed for all cases that the utilization of TiO₂-SG photocatalyst produced an increase in the kinetics of *trans*-resveratrol degradation. This enhancement of the kinetics of the process was more evident when UV irradiation was used, with an increase of almost 100% on the value for the kinetic rate constant. For Vis and UV-Vis photocatalytic systems the increase was 55% and 34%, respectively.

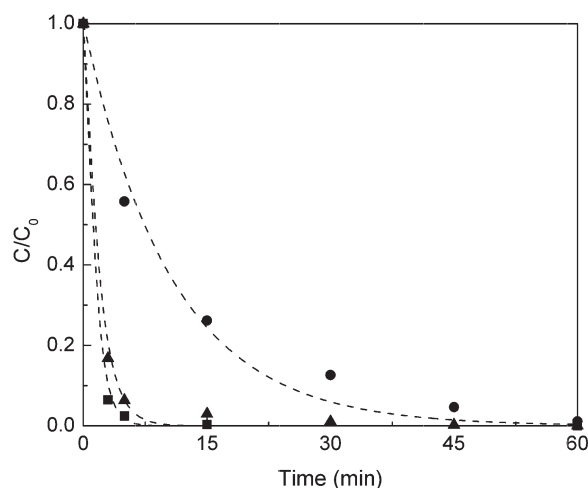


Fig. 4 Evolution of the normalized concentration (C/C_0) of *trans*-resveratrol during the photocatalytic experiments using TiO₂-SG and different irradiation wavelengths: UV-Vis (■), Vis (▲) and UV (●).

It is also relevant to notice that in the pure photochemical regime, when UV and Vis irradiation was used, no TOC removal was observed after 3 h of irradiation. In the case of the photocatalytic process, 65% and 75% of TOC reduction was achieved using UV and Vis irradiation, respectively. These results indicate that in the presence of a photocatalyst (TiO_2 -SG in this case), *trans*-resveratrol is not only more rapidly converted to its intermediates but there is also mineralization of other organic compounds present in the reaction media to CO_2 and H_2O .

3.3 Reaction mechanism

Samples taken at 15 min of irradiation were analyzed to determine the reaction photoproducts by high-resolution mass spectroscopy, as described above. The chromatograms showed a number of peaks, of which only the main ones were identified as a function of the working conditions (Table 1). Considering the observed photoproducts, we propose the mechanism described in Scheme 1 for both the direct and photocatalyzed degradation of *trans*-resveratrol ($t_R = 17.1$ min, $m/z = 227$ g mol $^{-1}$). *cis*-Resveratrol was also identified ($t_R = 20.7$ min) as an intermediate, probably generated following a photoisomerization.

Two different pathways are proposed: (i) a multi-step dehydration process to yield intermediate 1 ($t_R = 17.7$ min, 3,4',5-trihydroxydiphenylacetylene, $m/z = 225$ g mol $^{-1}$)¹⁸ which may derive from hydrogen abstraction from the double bond of *trans*-resveratrol ($t_R = 17.1$ min) by two hydroxyl radicals (HO^\cdot) with loss of two water molecules or from addition of two hydroxyl radicals to both of the carbon atoms of the double bond followed by subsequent dehydration of the so-formed diol; (ii) addition of HO^\cdot to the double bond followed by capture of a hydrogen (H^\cdot) to yield photoproduct 2 ($t_R = 8.4$ min, 5-(1-hydroxy-2-(4-hydroxyphenyl)ethyl)benzene-1,3-diol, $m/z = 245$ g mol $^{-1}$). Two different types of bond cleavage in 2 may lead to intermediates 3, 4 and 5. If the bond cleavage

takes place through "a)" (see Scheme 1), one of the fragments may undergo oxidation with HO^\cdot to photoproduct 3 ($t_R = 10.9$ min, 4-hydroxybenzaldehyde, $m/z = 121$ g mol $^{-1}$), while the other fragment may also add HO^\cdot to yield 4 ($t_R = 9.0$ min, 3,5-dihydroxybenzaldehyde, $m/z = 137$ g mol $^{-1}$). If, in turn, the bond cleavage takes place through "b)", addition of HO^\cdot leads, in various steps, to photoproduct 5 ($t_R = 7.6$ min, 2-(3,5-dihydroxyphenyl)-2-hydroxyacetic acid, $m/z = 183$ g mol $^{-1}$). Finally, intermediate 3 may undergo further oxidation by HO^\cdot addition to yield 6 ($t_R = 8.8$ min, 4-hydroxybenzoic acid, $m/z = 137$ g mol $^{-1}$).

From the results above it is clear that HO^\cdot is the main reactive species in the photodegradation of *trans*-resveratrol. Similar observations were reported by Bader *et al.*, who found also intermediates 3, 4 and 5 as products of γ -ray radiolysis of aerated *trans*-resveratrol solutions.²⁸

4. Conclusions

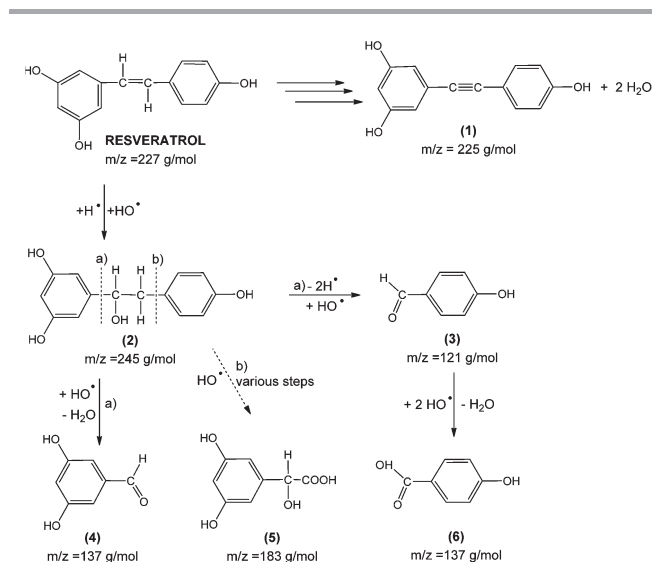
Photochemical and photocatalytic degradation of *trans*-resveratrol can be achieved under different irradiation wavelengths, ranging from the UV to the Visible. In both cases, the main degradation intermediate is its geometrical isomer, *cis*-resveratrol. In the absence of a catalyst, irradiation in the whole spectral range (UV-Vis) leads to *trans*-resveratrol conversion faster than when only UV or Vis light is used. The degree of *trans*-resveratrol conversion has been shown to be proportional to the UV-Vis irradiation intensity. Additionally, under UV-Vis irradiation a decrease in the organic content is observed, as a result of the partial mineralization of *trans*-resveratrol and of its photodegradation intermediates.

TiO_2 can be successfully used as a catalyst for the photocatalytic degradation of *trans*-resveratrol. The efficiency of this material depends on its intrinsic physical-chemical properties. Among the materials tested, the best performance was obtained for TiO_2 produced by a sol-gel method, which is constituted by anatase crystallites of very small dimensions and shows higher surface area and a higher amount of hydroxy surface groups. The photocatalytic process shows better efficiency for *trans*-resveratrol mineralization than the photochemical one. The best photocatalytic system is the one using TiO_2 -SG as a catalyst and UV-Vis irradiation, producing the fastest *trans*-resveratrol degradation and the highest organic content elimination.

The identification of six photoproducts allowed us to propose a reaction mechanism for *trans*-resveratrol photodegradation, mainly based on successive reactions with HO^\cdot leading to oxidation and fragmentation of the molecule.

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Scheme 1 Proposed mechanism for direct and photocatalyzed degradation of *trans*-resveratrol.

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