

Degradation of aqueous solutions of camphor by heterogeneous photocatalysis

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Abstract

In this study the photocatalytic degradation of aqueous solutions of camphor was investigated by using TiO_2 and ZnO photocatalysts. In the presence of artificial UV-light the highly photosensitive camphor was almost totally degraded after reaction times of 60 min. However, under these conditions the mineralization degree was lower than 25%. In the presence of semiconductors the degradation was complete after a treatment time of about 30 min. Moreover, the mineralization was considerably greater, mainly with the use of TiO_2 (>80% at reaction time of 60 min). Heterogeneous photocatalytic processes applied in the presence of solar radiation show a promising degradation capability. TiO_2 -based processes afforded mineralization degrees of about 90% after a reaction time of 120 min, when the system was assisted by aeration.

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1. Introduction

The occurrence of undesirable tastes and odors in drinking water and aquaculture supplies is a common problem in several regions of the world [1–4]. The perception by consumers of off-flavors compounds, even in very low concentration (ng L^{-1}), is an important issue for water suppliers and a major cause of consumer complaints [5]. Geosmin (1) and 2-methylisoborneol (MIB) (2) (Fig. 1) are the two compounds most frequently associated to musty/earthy odor and taste in drinking water. They are bicyclic tertiary alcohols produced by microorganisms, such as actinomycetes and cyanobacteria. In many studies, camphor was the precursor molecule in the MIB synthesis and one of biodegradation products of MIB by *Enterobacter* sp. [6] and *Pseudomonas putida* [7].

Even when a number of water treatment technologies have been successfully used to remove off-flavors compounds from water, including the use of granular activated carbon (GAC) [3], powdered activated carbon (PAC) [8], alum coagulation/sand

filtration [9] and ozonation [10], the evaluation of advanced oxidation technologies appears as a relevant task [11], mainly due to its customary high degradation efficiency toward recalcitrant substrates.

The efficiency of photocatalysis in the degradation of recalcitrant chemical compounds in water has been extensively documented [12–15]. However, as far as we know, only one study reported the destruction of 2-methylisoborneol and geosmin using titanium dioxide photocatalysis [11].

When TiO_2 or ZnO particles are illuminated with near UV radiation ($\lambda < 400 \text{ nm}$), electron–hole pairs are generated within the metal oxide semiconductor. The valence band hole has an intensive reduction potential and it leads to the generation of $\bullet\text{OH}$ radicals that are known to be powerful and non-selective oxidizing agents [16].

In this study, camphor, a more accessible compound, was used as a model substrate to investigate the potential of heterogeneous photocatalysis toward the degradation of 2-methylisoborneol, using TiO_2 and several irradiation systems. As some works have been related a high photochemical activity of the ZnO/UV system [17,18] the efficiency of this photocatalyst was also investigated. To optimize some relevant experimental conditions (pH and mass of photocatalyst) a factorial design system was used.

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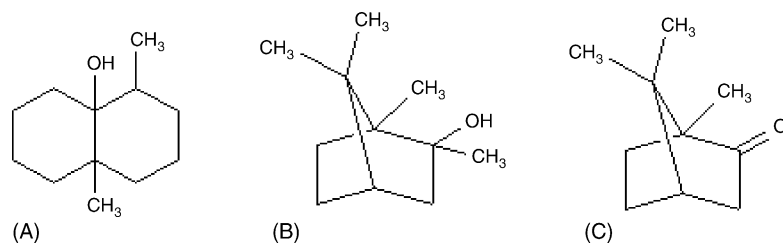


Fig. 1. Structures of (A) geosmin, (B) 2-MIB and (C) camphor.

2. Experimental

2.1. Chemicals

Camphor of pharmaceutical grade (98%) was prepared with deionized water at concentration of 50 mg L^{-1} . Titanium dioxide (Degussa® P-25, particle size: 30 nm, specific surface area: $55 \text{ m}^2 \text{ g}^{-1}$) and analytical grade ZnO (Merck®, particle size: 0.1–4 μm , specific surface area: $10 \text{ m}^2 \text{ g}^{-1}$) were used in suspension. Other reagents were of analytical grade.

2.2. Degradation procedures

Photocatalytical experiments were carried out in a jacketed borosilicon-glass vessel (250 mL), equipped with magnetic stirrer, water refrigeration (operating temperature: $25 \pm 2^\circ\text{C}$) and oxygenation system (oxygen flow: 45 mL min^{-1}). The UV radiation was provided by a medium-pressure mercury vapor lamp (125 W, maximal emission wavelength centered at 254 nm), without the original glass-bulb, immersed in the samples by means of a quartz jacket (Fig. 2). Under these conditions, the measured UV photon flux was $9.7 \times 10^{-5} \text{ Einstein s}^{-1}$ (uranyl-oxalate actinometry).

Experiments involving solar radiation were carried out in Curitiba city (latitude $25^\circ 25' \text{N}$ and longitude $49^\circ 16' \text{E}$), in sunny days of the spring. The reactor was located at the center of a parabolic collector covered with aluminum foil. Under these conditions, the measured UV photon flux was $1.0 \times 10^{-5} \text{ Einstein s}^{-1}$.

The intensity of the artificial and solar light were measured with a cosmoLUX®-UVATEST 3000 radiometer.

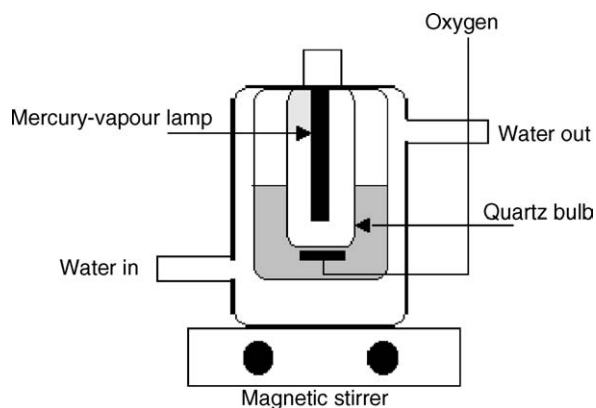


Fig. 2. Schematic representation of the photochemical reactor.

Samples of 250 mL were placed in the reactor and irradiated for different times, using a photocatalyst mass and a working pH previously optimized by factorial design. The pH of the samples was adjusted with aqueous solutions of HNO_3 and NaOH . Samples were collected at intervals of 5 min and submitted to analytical control.

2.3. Analytical control

The camphor degradation was monitored by GC-FID analysis after extraction in methylene chloride. The chromatographic analysis was carried out in a Shimadzu 14B gas chromatographer, equipped with flame ionization detection (FID) and a Shimadzu C-RGA area integrator. A $30 \text{ m} \times 0.25 \text{ mm i.d.}$, $0.25 \mu\text{m}$ film thickness DB-Wax (J & W Scientific) capillary column was used. Peak-area ratios between camphor and the internal standard (*n*-octanol) were used to construct a calibration curve over the range of $5\text{--}50 \mu\text{g mL}^{-1}$. The typical variance coefficient of the determination was 2.5%.

The total organic carbon (TOC) content was determined in a Shimadzu VCPH TOC analyzer. The calibration curve was made from a standard aqueous solution of potassium hydrogen phthalate over the range $0\text{--}500 \text{ mg L}^{-1}$. The typical variance coefficient of the determination was 2.0%.

3. Results and discussion

3.1. Heterogeneous photocatalysis with artificial radiation

Initially, the influence of relevant operational variables (pH and mass of semiconductor) in the efficiency of the photocatalytic degradation of camphor was evaluated by the factorial designs shown in Table 1. This kind of procedure have been extensively used in our works, mainly due to the low number of experiments involved in the optimization of controlling parameters. In general, only two levels are selected for each variable (*n*), which permit that 2^n experiments have necessities to explore all possible combinations. Usually, an additional central point is assayed in triplicate to facilitate the study of tendencies and to calculate the typical deviation of the involved analytical determination. Variables and levels are carefully chosen, mainly taking into account the previous knowledge about the studied system. In this case, other experimental parameters such as O_2 flow and stirring speed were fixed considering previous results [19].

The processed response corresponds to the degradation of camphor (%) at a reaction time of 15 min. When the effects,

Table 1
Factorial design (2^2) for optimization of the UV/TiO₂ and UV/ZnO processes

Variables	Levels		
	–	0	+
pH	4	6	8
Photocatalyst mass (mg)	25	50	75

Experiment	pH	Mass	Camphor degradation (%)	
			TiO ₂	ZnO
1	–	–	78	87
2	+	–	73	90
3	–	+	81	89
4	+	+	71	94
5	0	0	81 ± 2.5	72 ± 2.5

Camphor, 250 mL; 50 mg L⁻¹; O₂, 45 mL min⁻¹; reaction time, 15 min.
TiO₂/effects: pH, -7.5 ± 2.5 ; mass, 0.5 ± 2.5 ; pH × mass, -2.5 ± 2.5 .
ZnO/effects: pH, 4.0 ± 2.5 ; mass, 3.0 ± 2.5 ; pH × mass, 1.0 ± 2.5 .

calculated according to procedures described by Box et al. [20] are compared with the deviation observed in the triplicate analysis of the central point (2.5%) it is possible to deduce that, at the selected levels, the effect of the mass is irrelevant for both photocatalysts.

On the other hand, the effect of pH shows a differentiated significance for both semiconductors. That is, for TiO₂ the degradation efficiency is favored at low pH conditions (pH 4), while for ZnO significant enhancement of the degradation efficiency can be observed under alkaline conditions (pH 8). Normally, the different behavior of each semiconductor in relation to pH can be explained by unlike modifications of the surface properties [21], mainly related to the isoelectrical point (pH 6.0 for TiO₂ and 9.0 for ZnO). According to Zhao et al. [22] and Finklea [23], positive charges on the TiO₂ surface at pH lower than 6 favor the migration of photo-produced electrons and suppress electron–hole recombination, a fact that enhance the efficiency of the photochemical process.

In contrast, the lack of photocatalytic activity of ZnO at low pH values can originate from either acidic/photochemical corrosion of the catalyst (Eqs. (1) and (2)), as appointed by Comparelli et al. [24]. In our experimental conditions, low dissolution of ZnO was observed in acidic media.



Taking into account the preliminary results the conditions of the central point (pH 5 and semiconductor mass of 50 mg) were selected for further experiments. Even when the degradation efficiency is slightly sacrificed at these conditions, some practical advantages justify the choice (example the natural pH of camphor aqueous solutions is 5.2).

As the photocatalytic process can involve four individual processes that can contribute to the elimination of the substrates, that is: adsorption on the photocatalyst surface, degradation by photolysis, oxygen-assisted volatilization and heterogeneous

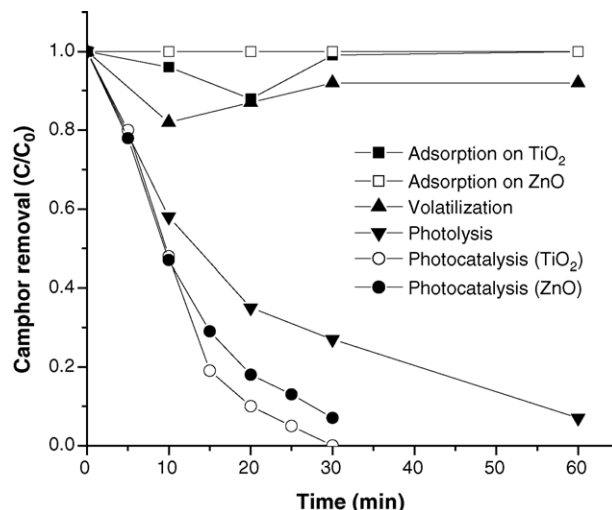


Fig. 3. Contribution of the isolated processes to the camphor removal (C/C_0). Camphor: 250 mL, 50 mg L⁻¹; pH: 5.2; TiO₂ or ZnO: 50 mg; O₂: 45 mL min⁻¹.

photocatalysis, their effect in the removal of camphor was evaluated in a preliminary manner.

The results (Fig. 3) demonstrated that the losses of camphor by adsorption and volatilization are not very significant, contributing with elimination lower than 20% at reaction times of 60 min. In contrast, nearly 90% of the camphor content can be removed by photolysis, a fact that demonstrates the photosensitivity of the substrate. Under conditions of heterogeneous photocatalysis, the removal of camphor shows a more favorable profile, with almost total elimination at reaction times of 30 min.

Even inducing significant modifications in the chemical structure of the substrates, the photolysis commonly shows a low mineralization capacity. For instance, working at high camphor concentrations (1000 mg L⁻¹) the formation of a white solid was observed in photolytic experiments, probably related to polymeric forms of camphor [25].

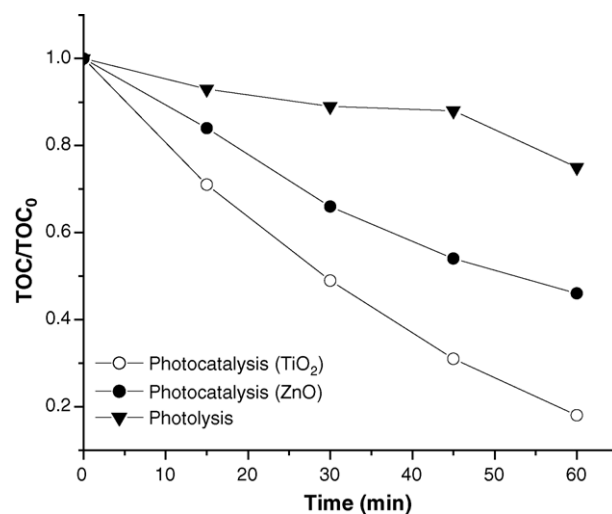


Fig. 4. TOC evolution (TOC/TOC_0) during the photochemical treatment of camphor with artificial radiation. Camphor: 250 mL, 50 mg L⁻¹; pH: 5.2; TiO₂ or ZnO: 50 mg; O₂: 45 mL min⁻¹.

As confirmed by the evolution of the TOC content (Fig. 4) the photolytic process leads to low mineralization ratios (<25%), even for long reaction times (60 min). Some byproducts of the photolytic degradation process were identified by GC-MS, as illustrated in Fig. 5.

The mineralization efficiency of both catalyzed systems was clearly better, mainly for the UV/TiO₂ system that allows mineralization ratios higher than 80%. Probably, the better efficiency of TiO₂-mediated processes should be connected with the high adsorption capacity shown by the photocatalyst for these experimental conditions (Fig. 3), primary condition for heterogeneous photocatalytical degradation processes.

Muruganandham and Swaminathan [26] have been studied the effect of various photocatalysts, such as TiO₂-P25 and ZnO, on the decolourisation and degradation of a reactive azo dye. The results have been demonstrated that the TiO₂ is more active than ZnO, due to slow recombination of electron-hole pair and large surface area. Additionally, ZnO has the disadvantage of undergoing photocorrosion under illumination.

3.2. Heterogeneous photocatalysis with solar radiation

Aiming at the simplification of the photocatalytic system, degradation procedures assisted by solar radiation were carried out, using homemade parabolic collectors constructed in aluminium-covered plastic material (diameter: 20 cm). The photochemical reactor was located at the center of the collector, applying the photochemical processes at the previously optimized experimental conditions (pH ≈ 5.2; semiconductor mass: 50 mg). In this case, oxygen was not bubbling through the suspension. The treatment time was extended up to 240 min, in view of the significant differences between the

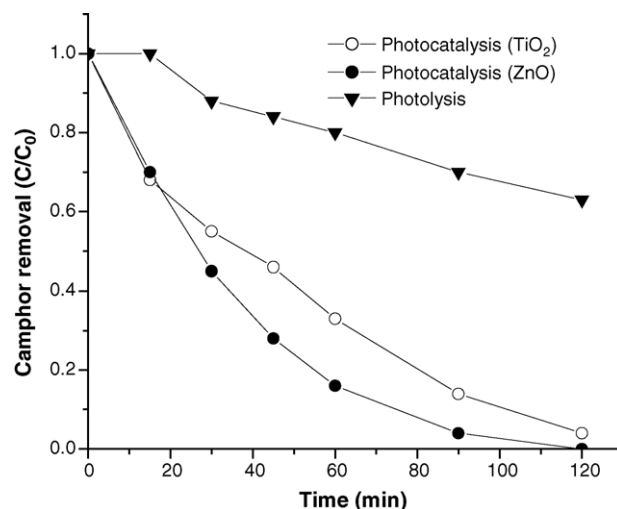


Fig. 6. Removal of camphor (C/C_0) by photochemical treatment with solar radiation. Camphor: 250 mL, 50 mg L⁻¹; pH: 5.2; TiO₂ or ZnO: 50 mg; O₂: without.

UV-A intensity of solar (40 W m⁻²) and artificial (180 W m⁻²) radiations.

Under these conditions, the better efficiency of the semiconductor-catalyzed photochemical processes becomes evident (Fig. 6), with almost total elimination at reaction times of 120 min. The evolution of the TOC content (Fig. 7) reveals a high mineralization capacity of the process mediated by titanium dioxide (mineralization higher than 80% for a reaction time of 180 min) and an obvious low efficiency of the ZnO-based process, even lower than those shown by the photolytic process. Probably, the high photoreactivity of TiO₂ is due to slow recombination of electron-hole pairs [26], a fact that becomes particularly important when the process

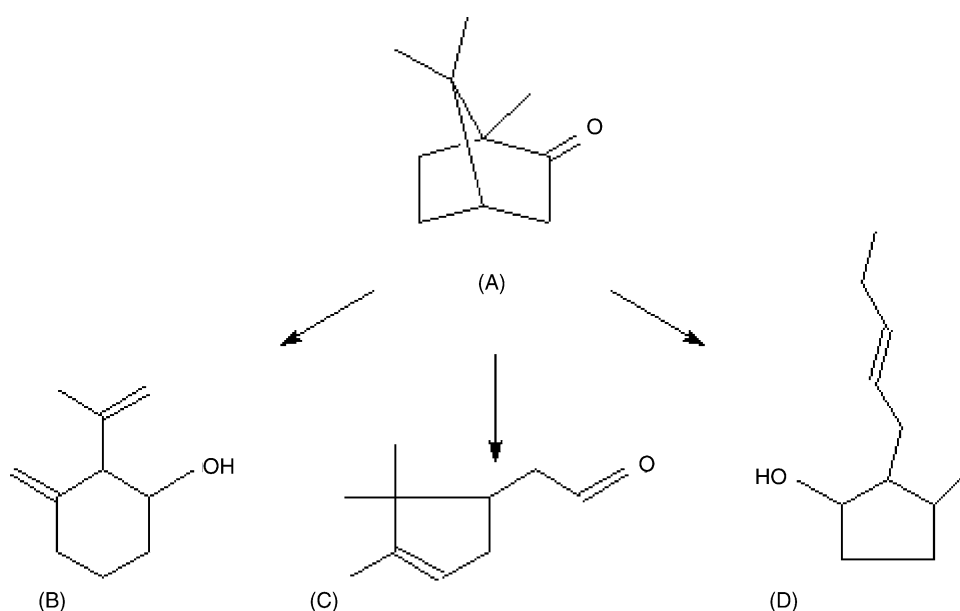


Fig. 5. Byproducts identified in the photolytic degradation of camphor: (A) camphor, (B) *ortho*-mentha-1(7)8-dien-3-ol, (C) 3-cyclopentene-1-acetaldehyde,2,2,3-trimethyl and (D) cyclopentanol,3-methyl-2-(2-pentenyl).

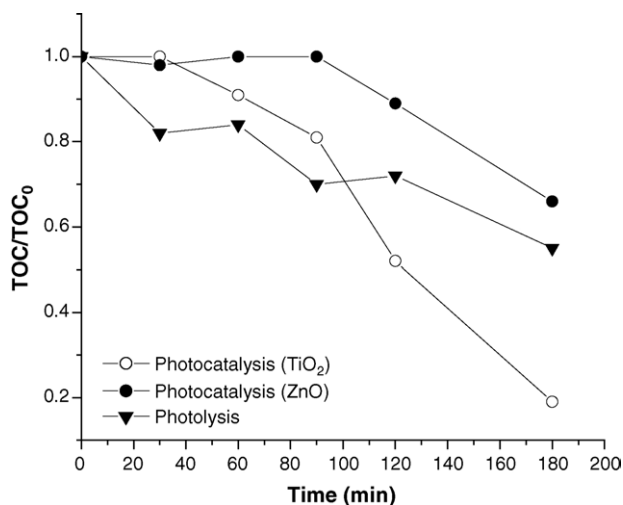


Fig. 7. TOC evolution (TOC/TOC₀) during the photochemical treatment of camphor with solar radiation. Camphor: 250 mL, 50 mg L⁻¹; pH: 5.2; TiO₂ or ZnO: 50 mg; O₂: without.

is applied in the absence of electron scavengers (molecular oxygen).

Besides molecular oxygen, irreversible electron acceptors such as (NH₄)₂S₂O₈ can be used to enhance the degradation capacity of the photochemical systems [27]. Favorable effects have been observed mainly due to minimization of the electron-hole recombination process, by reaction of persulphate with the photogenerated electron (Eq. (3)), generation of strong oxidizing agents (example sulphate radical anion) and an increment in the hydroxyl radical concentration (Eq. (4)) [26]. However, no significant effects were observed in the mineralization of camphor (Fig. 8) for the experimental conditions adopted (S₂O₈²⁻: 1–3 g L⁻¹), probably on account of adsorption of sulphate anions on the semiconductor surface, with consequent reduction of its catalytic activity, or reaction of sulphate anions with hydroxyl radicals with formation of the

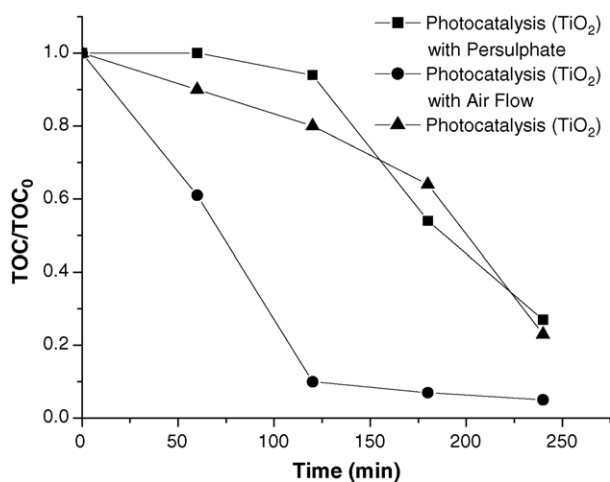
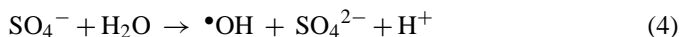
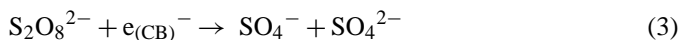


Fig. 8. TOC evolution (TOC/TOC₀) during the photochemical treatment of camphor with solar radiation in the presence of persulphate and air. Camphor: 250 mL, 50 mg L⁻¹; pH: 5.2; TiO₂: 50 mg; S₂O₈²⁻: 1.8 g L⁻¹; air: 140 mL min⁻¹.

less reactive sulphate radical anion (Eq. (5)).



On the other hand, the use of an air flow of about 850 mL min⁻¹, provided by a small aquarium pump, showed a very remarkable effect on the degradation process, inducing a mineralization higher than 90% at a reaction time of 120 min.

3.3. Kinetic study

Generally, the heterogeneous photocatalytic degradation process follows the kinetic expression of Langmuir–Hinshelwood [28], represented as:

$$r = \frac{kKC}{1 + KC}$$

where, C is the camphor concentration at time “ t ”, k a constant that includes various parameters, such as: mass of photocatalyzer and photon efficiency, among others and K is the adsorption constant. However, working at low initial camphor concentration (50 mg L⁻¹) the term KC in the denominator of the expression can be neglected and the reaction, apparently, obeys a first-order kinetic:

$$r = \frac{-dC}{dt} = kKC = k_a C$$

where, k_a is a pseudo first order constant

Later, the integration in the form of $C = f(t)$ leads to the relations:

$$-\ln \frac{C}{C_0} = k_a t$$

$$t_{1/2} = \ln \frac{2}{k_a}$$

where, $t_{1/2}$ expresses the time required for the concentration of the species under consideration, in this case the camphor, to diminish to half of its initial value.

The values of K and $t_{1/2}$ calculated for the different photochemical systems are summarized in Table 2. From these results, the following consideration can be made:

1. Camphor can be degraded to a great extent by artificial UV radiation. The degradation necessarily involves the generation of transient species, probably open-chain aldehydes [25], a fact that implies an unfavorable mineralization profile. By using semiconductor-assisted processes, the degradation and mineralization efficiency can be practically doubled.
2. Similar considerations can be made with respect to the use of solar-light. However, in this case the degradation capacity is considerably less, due to the low intensity of the solar radiation in the spectral region of the TiO₂-bandgap (387 nm). The degradation and mineralization efficiency of the process assisted by solar-light can be significantly enhanced by the

Table 2
Kinetics parameters for the photochemical degradation of camphor

Radiation	Photocatalyst	Condition	Camphor degradation	
			K (min ⁻¹)	$t_{1/2}$ (min)
Artificial UV	–	With O ₂	0.043	16.18
Artificial UV	ZnO	With O ₂	0.089	7.82
Artificial UV	TiO ₂	With O ₂	0.115	6.02
Solar (40 W m ²)	–	Without O ₂	0.016	43.56
Solar (40 W m ²)	ZnO	Without O ₂	0.036	19.36
Solar (40 W m ²)	TiO ₂	Without O ₂	0.027	25.86
Camphor mineralization				
Solar (40 W m ²)	–	Without O ₂	0.003	232.3
Solar (40 W m ²)	TiO ₂	Without O ₂	0.005	139.4
Solar (40 W m ²)	TiO ₂	With S ₂ O ₈ ²⁻	0.005	139.4
Solar (40 W m ²)	TiO ₂	With air	0.013	53.61

use of a high flow of air (140 mL min⁻¹), certainly by the positive effect of molecular oxygen on the hole–electron pair separation process.

4. Conclusions

Heterogeneous photocatalytic processes mediated by TiO₂ or ZnO can effectively degrade aqueous solutions of camphor. The degradation process is significantly enhanced by the use of artificial UV-light. However, the use of inexpensive solar radiation leads to results that entail an interesting potential. The close similarity between camphor and 2,4-methylisoborneol clearly suggests a promising potential of the photochemical process for the treatment of drinking water contaminated by odorous pollutants.

References

- [1] J. Ellis, W. Korth, Removal of geosmin and methylisoborneol from drinking water by adsorption on ultrastable zeolite-Y, *Water Res.* 27 (4) (1993) 535–539.
- [2] G. Izaguirre, W.D. Taylor, Geosmin and 2-methylisoborneol production in a major aqueduct system, *Water Sci. Technol.* 31 (11) (1995) 41–48.
- [3] P. Pendleton, S.H. Wong, R. Schumann, G. Levay, R. Denoyel, J. Rouquero, Properties of activated carbon controlling 2-methylisoborneol adsorption, *Carbon* 35 (8) (1997) 1141–1149.
- [4] I.M.K. Saadoun, K.K. Schrader, W.T. Blevins, Environmental and nutritional factors affecting geosmin synthesis by *Anabaena* sp., *Water Res.* 35 (5) (2001) 1209–1218.
- [5] W.F. Young, H. Horth, R. Crane, T. Ogden, M. Arnott, Taste and odour threshold concentrations of potential potable water contaminants, *Water Res.* 30 (2) (1996) 331–340.
- [6] A. Tanaka, T. Oritani, F. Uehara, A. Saito, H. Kishita, Y. Niizeki, H. Yokota, K. Fuchigami, Biodegradation of a musty odour component, 2-methylisoborneol, *Water Res.* 30 (3) (1996) 759–761.
- [7] E. Oikawa, A. Shimizu, Y. Ishibashi, 2-Methylisoborneol degradation by the cam operon from *Pseudomonas putida* PpG1, *Water Sci. Technol.* 31 (11) (1995) 79–86.
- [8] D. Cook, G. Newcombe, P. Sztajnbock, The application of powdered activated carbon for mib and geosmin removal: predicting pac doses in four raw waters, *Water Res.* 35 (5) (2001) 1325–1333.
- [9] R. Sävenhed, H. Borén, A. Grimvall, B.V. Lundgren, P. Balmér, T. Hedberg, Removal of individual off-flavour compounds in water during artificial groundwater recharge and during treatment by alum coagulation/sand filtration, *Water Res.* 21 (3) (1987) 277–283.
- [10] D.J. Smith, C.R. Moss, The Development Of Ozone For Potable Water-Treatment Within The United-Kingdom, *Ozone Sci. Eng.* 15 (6) (1993) 515–532.
- [11] L.A. Lawton, P.K.J. Robertson, R.F. Robertson, F.G. Bruce, The destruction of 2-methylisoborneol and geosmin using titanium dioxide photocatalysis, *Appl. Catal. B: Environ.* 44 (1) (2003) 9–13.
- [12] P. Peralta-Zamora, S.G. de Moraes, R. Pelegrini, M. Freire Jr., J. Reyes, H. Mansilla, N. Durán, Evaluation of ZnO, TiO₂ and supported ZnO on the photoassisted remediation of black liquor, cellulose and textile mill effluents, *Chemosphere* 36 (9) (1998) 2119–2133.
- [13] T.M. Wang, H.Y. Wang, P. Xu, X.C. Zhao, Y.L. Liu, S. Chao, The effect of properties of semiconductor oxide thin films on photocatalytic decomposition of dyeing waste water, *Thin Solid Films* 334 (1–2) (1998) 103–108.
- [14] R. Pelegrini, J. Reyes, N. Durán, P.P. Zamora, A.R. de, Andrade, Photoelectrochemical degradation of lignin, *J. Appl. Electrochem.* 30 (2000) 953–958.
- [15] I. Arslan-Alaton, H. Selcuk, A. Erdem-Senatarlar, Screening of polyoxometalates, semiconductor metal oxides and zeolites for photocatalytic activity and selectivity, *Fresenius Environ. Bull.* 13 (11b) (2004) 1248–1252.
- [16] A. Mills, S. LeHunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol.* 108 (1) (1997) 1–35.
- [17] A. Akyol, H.C. Yatmaz, M. Bayramoglu, Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions, *Appl. Catal. B: Environ.* 54 (2004) 19–24.
- [18] V. Kandavelu, H. Kastien, K.R. Thampi, Photocatalytic degradation of isothiazolin-3-ones in water and emulsion paints containing nanocrystalline TiO₂ and ZnO catalysts, *Appl. Catal. B: Environ.* 48 (2004) 101–111.
- [19] C.A.K. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, N. Nagata, P. Peralta-Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, *Chemosphere* 40 (2000) 433–440.
- [20] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters*, John Wiley & Sons, 1978, pp. 50–57.
- [21] R.J. Candal, S.A. Bilmes, M.A. Blesa, Eliminación de Contaminantes por Fotocatálisis Heterogénea, Chapter 4 Semiconductores con Actividad Fotocatalítica, *Gráfica 12 y 50, La Plata* (2001), 79–95.
- [22] S. Zhao, J. Xu, X.B. Zhong, Kinetic study on the photo-catalytic degradation of pyridine in TiO₂ suspension systems, *Catal. Today* 93–95 (2004) 857–861.
- [23] H.O. Finklea, *Semiconductor Electrodes*, Elsevier, 1988, pp. 10–11, Chapter 1.
- [24] R. Comparelli, E. Fanizza, M.L. Curri, P.D. Cozzoli, G. Mascolo, A. Agostiano, UV-induced photocatalytic degradation of azo dyes by organic-capped ZnO nanocrystals immobilized onto substrates, *Appl. Catal.* 60 (1–2) (2005) 1–11.
- [25] P.G. Gassman, *Chemistry of the Monoterpenes—An Encyclopedic Handbook, Part B*, Marcel Dekker Inc., New York, 1985.
- [26] M. Muruganandham, M. Swaminathan, Solar photocatalytic degradation of a reactive azo dye in TiO₂-suspension, *Solar Energy Mater. Solar Cells* 81 (4) (2004) 439–457.
- [27] S.M. Rodríguez, C. Richter, J.B. Gálvez, M. Vincent, Photocatalytic degradation of industrial residual waters, *Solar Energy* 56 (5) (1996) 401–410.
- [28] A. Fernández, G. Lassaletta, V.M. Jiménez, A. Justo, A.R. González-Elipse, J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, Preparation and characterization of TiO₂ photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification, *Appl. Catal. B: Environ.* 7 (1–2) (1995) 49–63.