

Efficiency of 1,4-dichlorobenzene degradation in water under photolysis, photocatalysis on TiO₂ and sonolysis

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Abstract

The rate of 1,4-dichlorobenzene (1,4-DCB) degradation and mineralization in the aqueous phase was investigated either under direct photolysis or photocatalysis in the presence of commercial or sol–gel synthesized TiO₂, or under sonolysis at 20 kHz with different power inputs. Two lamps, both emitting in the 340–400 nm wavelength range with different energy, were employed as irradiation sources. Photocatalysis ensured faster removal of 1,4-DCB with respect to sonolysis and direct photolysis. The highest degradation and mineralization rate was attained with the combined use of photocatalysis and sonolysis, i.e. under sonophotocatalytic conditions. The efficiency of the employed advanced oxidation techniques in 1,4-DCB degradation is discussed also in relation to their energy consumption, which might be decisive for their practical application. © 2007 Elsevier B.V. All rights reserved.

Keywords: Photolysis; Photocatalysis on TiO₂; Sonolysis; 1,4-Dichlorobenzene degradation; Energy consumption

1. Introduction

Chlorinated aromatic compounds form an important class of organic pollutants of industrial wastewater. Chlorobenzenes and other halo-aromatics, in fact, are widely employed as pesticides and raw materials for pesticide manufacture and have a variety of uses in chemical synthesis and other applications. Because of their acute toxicity, suspected endocrine, immuno- and neuro-toxicity [1] and bioaccumulation capability, they are of great health and environmental concern [2,3], for their potentiality to contaminate surface and groundwaters and also be the origin of marine pollution [3–5], though typically present at sub-ppm concentration. Most of them, in fact, are highly hydrophobic and possess very low vapor pressure and aqueous solubility.

Besides the traditional methods for the removal of chlorinated compounds from water, mainly based on their transfer from one phase to another and thus requiring additional processes to achieve the complete detoxification of the environment [6,7], the so called advanced oxidation processes (AOPs) [8] can be successfully employed to directly destroy such harmful species. AOPs consist of “clean” methods and reagents, e.g. ultraviolet

irradiation, ultrasound treatment, ozonation, hydrogen peroxide oxidation, which can efficiently be applied also in combination [9].

Aim of the present work is a comparison between the efficiency of different oxidation techniques, i.e. photolysis, photocatalysis on TiO₂ and sonolysis, employed under normal atmosphere in the absence of any oxidant chemical species, in the degradation and mineralization of 1,4-dichlorobenzene (1,4-DCB), chosen as a typical chlorinated pollutant of wastewaters and of contaminated areas. The photocatalytic degradation of such aromatic chlorinated compound has already been reported, e.g. in studies on the effects of TiO₂ surface modification [10–12] or, more recently, in investigations on the TiO₂ photocatalyst sensitivity to visible light [13]. Sonolytic investigations on this and other chlorinated aromatic substrates have also been carried out in recent years, usually employing high frequency ultrasound [14–16]. Following recent studies of our [17–21] and other research groups [22–26] on the combined use of sonolysis and photocatalysis in the degradation of various pollutants, possible synergistic effects at work in 1,4-DCB degradation under sonophotocatalytic conditions with low frequency ultrasound have been checked in the present work. Finally, the energy consumed under the different investigated operation conditions has been estimated. This aspect has received scarce attention so far, but could be decisive for large-scale applications. As our

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attention was mainly focused on the efficiency of the different techniques, on possible synergistic effects and on the energetic aspects of degradation processes, no detailed analysis of reaction intermediates and products has been made.

2. Experimental

2.1. Materials

1,4-Dichlorobenzene (1,4-DCB) was purchased from Aldrich (purity >99%). Degussa P25 titanium dioxide was generally employed as photocatalyst. Other TiO₂ samples, indicated as TiO₂-300, TiO₂-450 and TiO₂-600, were prepared by sol-gel synthesis starting from titanium isopropoxide, as already detailed [27], and calcined at different temperature (300, 450 and 600 °C, respectively). Their surface area was determined by BET analysis using a Coulter SA 3100 apparatus, via liquid nitrogen adsorption. Structural characterization was performed by X-ray diffraction using a Siemens D500 diffractometer with Cu K α radiation; the phase composition was determined from the intensities of the diffraction peaks at 25.3° (anatase), 27.5° (rutile) and 31° (brookite). Distilled water was used in the preparation of solutions and suspensions.

2.2. Apparatus

All degradation runs were carried out employing the experimental setup similar to that already described [20,28], which allows the use of different advanced oxidation techniques, either separately or simultaneously, without any modification in the geometry of the system. It consisted of a cylindrical, tightly closed Pyrex vessel (500 mL), which was irradiated by external lamps and/or subjected to ultrasound irradiation through an immersed horn. At the beginning of the runs the reactor was always almost completely filled up with the aqueous solution or suspension containing 1,4-DCB, in order to minimize the headspace of the reactor and thus any loss of the volatile substrate. All runs were carried out at (30 ± 1) °C under continuous or intermittent stirring at ca. 220 rpm.

Two external iron halogenide lamps (Jelosil, models HG 200 or HG 500), both emitting in the 340–400 nm wavelength range, were employed as irradiation sources. They will be indicated as lamp I and lamp II; their effective power consumption, measured amperometrically, were 550 and 640 W, respectively. Two ultrasound generators, both emitting at 20 kHz, were employed in sonolytic degradation runs. The first one was a W-385 Heat System-Ultrasonics apparatus, with a maximum emission power of 20 W and a tip diameter of 12 mm. Alternatively, the ultrasound source was an Omron H5CN system, produced by Stimin, Italy, with a tip diameter of 13 mm. Its emission power could be regulated through a potentiometer and was fixed at 40 W. The power effectively absorbed by the two ultrasound sources was 169 and 185 W, respectively (amperometric determination). During the runs, the emitting horns, immersed in the aqueous solution or suspension, were cooled through forced air circulation. Intermittent stirring (i.e. 15 min stirring followed by 15 min without stirring) was applied during the sonolytic

and sonophotocatalytic degradation runs. The Velp Scientifica magnetic stirrer consumed 46 W.

2.3. Procedure

Both lamps and ultrasound sources were always switched on at least 15 min before starting the runs. Aqueous solutions or suspensions initially contained a fixed 1,4-DCB concentration of 2.7×10^{-4} M. In photocatalytic runs, 0.1 g L⁻¹ of titanium dioxide was added to the solutions directly in the reactor. Samples (3 mL) were withdrawn from the reactor at different reaction times during the runs, through a rubber septum on the reactor cover, and analyzed spectrophotometrically in a Perkin-Elmer Lambda 16 apparatus. Prior to analysis, TiO₂ was separated from the suspensions by centrifugation at 4800 rpm for 10 min. According to a preliminary calibration up to a 1,4-DCB concentration of 3×10^{-4} M, the molar extinction coefficient of 1,4-DCB at $\lambda_{\max} = 223.2$ nm was taken as $(9.0 \pm 0.2) \times 10^3$ M⁻¹ cm⁻¹. The extent of mineralization was determined through total organic carbon (TOC) analysis using a Shimadzu TOC-5000A analyzer. The maximum duration of the runs was 6 h.

3. Results and discussion

3.1. Direct photolysis and photocatalysis in the presence of TiO₂

Two irradiation sources, both emitting in the low wavelength range of the solar spectrum (340–400 nm), though with different energy, were employed in the present study. As 1,4-dichlorobenzene (1,4-DCB) is able to absorb part of the emitted light, its direct photolytic degradation in the absence of any photocatalyst was first investigated kinetically, to be compared with that of its photocatalytic degradation in the presence of both commercial and home-synthesized TiO₂ samples. As shown in Fig. 1, direct photolysis employing the more powerful lamp II produced quite fast 1,4-DCB degradation, leading to a more than 70% decrease of absorbance at 223.2 nm after 6 h-long irradiation. The lower intensity irradiation originated by lamp I led to slower photolysis, as expected, the absorbance decrease being only around 25% after 6 h. Thus, 1,4-DCB electronic excita-

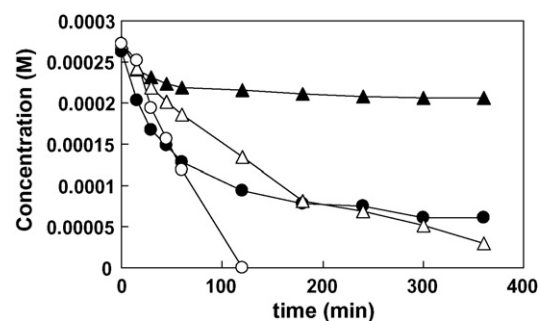


Fig. 1. 1,4-DCB degradation under photolysis (full symbols) and photocatalysis in the presence of 0.1 g L⁻¹ of TiO₂ P25 (open symbols) employing lamp I (triangles) or lamp II (circles).

tion subsequent to direct absorption of light leads to photolysis, whose first step is expected to be the C–Cl bond homolytic cleavage with formation of chloride anions, followed by the slower oxidation of the aromatic ring.

Photocatalytic degradation in the presence of 0.1 g L^{-1} of Degussa P25 TiO_2 proceeded at a considerably higher rate (Fig. 1), yielding the complete oxidative decomposition of the aromatic ring in less than 2 h, when lamp II was employed as irradiation source, and to ca. 90% absorbance decrease at 223.2 nm, under 6 h-long irradiation from lamp I. In the presence of TiO_2 particles, direct photolysis consequent to light absorption by 1,4-DCB is paralleled by a photocatalytic degradation path, originated by light absorption by the TiO_2 semiconductor, followed by the photoinduced promotion of electrons in the conduction band and the formation of holes in the valence band [29]. As a consequence of such photoinduced charge separation on the semiconductor surface, electron exchange reactions occur at the water-semiconductor interface. The superoxide radical anion $\bullet\text{O}_2^-$ is formed by interaction of photopromoted conduction band electrons with adsorbed dioxygen molecules, while the direct or $\bullet\text{OH}$ radical-mediated oxidation of adsorbed organic substrates simultaneously occurs, either via their direct interaction with valence band holes, or via valence band holes oxidation of adsorbed water or hydroxyl anions.

The photocatalytic degradation path, proceeding through the initial transformation of chlorobenzene compounds into chlorophenols, according to very recent results on chlorobenzene gas phase photocatalytic decomposition [30], is expected to be much more efficient than direct photolysis in ensuring the oxidative degradation of the benzene ring and the overall mineralization of aromatic compounds [31]. Chlorophenols, in fact, are known to undergo efficient degradation by means of different advanced oxidation processes [32]. It is worth noting, however, that with both lamps the initial degradation rate under photocatalytic conditions was slightly lower than under direct photolysis (Fig. 1), because of the simultaneous and competitive absorption of light by 1,4-DCB and by the TiO_2 photocatalyst particles, which are also able to scatter part of the light. However, the long-term better efficiency of photocatalysis with respect to photolysis in achieving the total removal of organics is out of discussion (Fig. 1).

The results of 1,4-DCB photocatalytic degradation in the presence of different TiO_2 samples prepared by the sol-gel method and subsequently calcined at different temperature are collected in Fig. 2. Though fairly active in 1,4-DCB degradation and all yielding much faster 1,4-DCB degradation with respect to direct photolysis, all such home-made TiO_2 photocatalysts showed less active than the notoriously well performing Degussa P25. The TiO_2 sample calcined at the lowest temperature, i.e. at 300°C , proved to be the best photocatalyst in this series, most probably as a consequence of both its higher surface area and high content of anatase phase (Table 1). Anatase, in fact, is widely recognized to be more photoefficient as catalyst than both rutile and brookite [29]. Moreover, the TiO_2 sample calcined at 300°C is expected to have a higher amount of surface hydroxyl groups: this guarantees a good hydrophilicity of the well dispersed photocatalyst particles in the irradiated suspen-

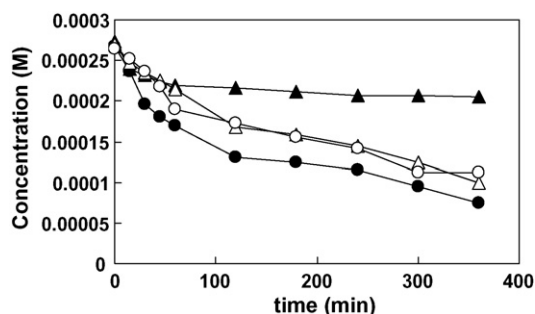


Fig. 2. 1,4-DCB degradation under photolysis (▲) and under photocatalysis in the presence of 0.1 g L^{-1} of TiO_2 -300 (●), TiO_2 -450 (△) and TiO_2 -600 (○). Irradiation source I.

Table 1

Surface area from BET analysis and phase composition from XRD analysis of the employed TiO_2 photocatalysts

Sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Percent phase composition		
		Anatase	Brookite	Rutile
Degussa P25	55	80		20
TiO_2 -300	151	60	40	
TiO_2 -450	131	65	35	
TiO_2 -600	11	20		80

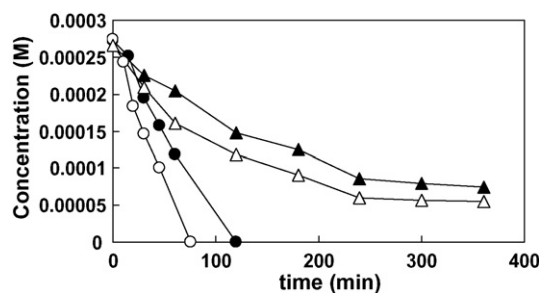


Fig. 3. 1,4-DCB degradation under sonolysis at 20 W (▲) and 40 W (△), under photocatalysis in the presence of 0.1 g L^{-1} of TiO_2 P25 (●), and under sono-photocatalysis with ultrasound at 40 W (○). Irradiation source II.

sion and the ready availability of OH groups, to be involved in interface electron transfer reactions.

3.2. Sonolytic and sonophotocatalytic degradation

1,4-DCB underwent degradation also under sonolysis at 20 kHz. As shown in Fig. 3, very similar degradation curves were obtained when employing the 20 or 40 W ultrasound source, with only a modest increase in degradation rate when the specific ultrasound power was doubled. The final percent decrease of absorbance were 72% and 79% with the 20 and 40 W ultrasound sources, respectively, corresponding to an overall percent mineralization of 65% and 71% after 6 h, as determined by TOC analysis. Intermittent stirring (15 min on, 15 min off) was adopted during the sonolytic degradation runs, because this was found to ensure higher degradation rates respect to continuous stirring in the case of the sonolytic degradation of volatile organic substrates [20], such as 1,4-DCB.

Table 2

Percent 1,4-DCB degradation attained after 6 h, time and energy required for attaining 60% 1,4-DCB degradation under photolysis (UV), photocatalysis (UV + TiO₂), sonolysis (US) or sonolysis + photocatalysis (sonophotocatalysis, US + UV + TiO₂)

System	Light source	Photo-catalyst	US power (W)	%Degradation ^a	Time ^b (min)	Energy ^c (kWh)
UV	I	–	–	25	>360	
UV	II	–	–	77	95	1.01
UV + TiO ₂	I	P25	–	90	150	1.49
UV + TiO ₂	I	TiO ₂ -300	–	72	263	2.61
UV + TiO ₂	I	TiO ₂ -450	–	63	340	3.38
UV + TiO ₂	I	TiO ₂ -600	–	58	>360	
UV + TiO ₂	II	P25	–	100	64	0.73
US	–	–	20	72	206	0.66
US	–	–	40	79	142	0.49
US + UV + TiO ₂	II	P25	40	100	41	0.58

Initial 1,4-DCB concentration: 2.7×10^{-4} M.

^a Percent 1,4-DCB degradation after 6 h.

^b Treatment time necessary to attain 60% degradation, evaluated from 1,4-DCB degradation curves (Figs. 1–3).

^c Energy consumed to attain 60% degradation, calculated on the basis of the effective power consumption of the light and/or ultrasound sources, and of the magnetic stirrer (see Section 2).

Sonolysis of aqueous solutions is known to produce •OH radicals and other radical species through water scission under the extreme temperature and pressure conditions created by the implosion of cavitation bubbles [33]. •OH radicals may rapidly initiate the degradation of 1,4-DCB through the direct attack on the aromatic ring, the rate constant of the •OH radical reaction with chlorobenzene in water solution being $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [34]. Under ultrasound, however, volatile and rather hydrophobic organic compounds, such as 1,4-DCB, may undergo degradation also through a completely different path, i.e. through their direct pyrolysis in the vapor phase of pulsating or collapsing cavitation bubbles, within the hot interfacial region between the vapor and the surrounding liquid phases [35]. Indeed, the ultrasound-induced degradation rate constants of a series of volatile organic compounds appear to be clearly related to their Henry's law constants [36]. Stirring may perturb cavitation [33], and this explains the above-mentioned beneficial effect of intermittent stirring with respect to continuous stirring.

Finally, the combined use of photocatalysis and sonolysis was also investigated. Intermittent stirring in this case was essential for maintaining the photocatalyst in the illuminated part of the suspension. As shown in Fig. 3, the highest 1,4-DCB degradation rate was attained under sonophotocatalytic conditions employing lamp II and the 40 W ultrasound source, leading to the complete decomposition of the aromatic moiety in less than 1 h and to almost complete mineralization in less than 6 h. 1,4-DCB concentration vs. time curves obtained under both photocatalysis and sonophotocatalysis conformed to a first order rate law, the calculated rate constants being $k_{\text{UV+TiO}_2} = (2.4 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ for photocatalysis and $k_{\text{US+UV+TiO}_2} = (3.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$ for sonophotocatalysis. Also 1,4-DCB concentration under sonolysis followed an exponential decay, with a final sort of plateau. The first order rate constant obtained for the concentration profile recorded when employing the 40 W ultrasound source is $k_{\text{US}} = (9.9 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$. Thus, being $(k_{\text{US}} + k_{\text{UV+TiO}_2}) \leq k_{\text{US+UV+TiO}_2}$, a small synergistic effect between sonolysis and photocatalysis can hardly be envisaged outside the limits of the experimental uncertainty. This points to

the conclusion that simultaneous sonolysis and photocatalysis exhibit an almost additive effect on 1,4-DCB degradation under the adopted experimental conditions, in line with the ultrasound-induced degradation of this volatile chlorinated substrate mainly occurring in the vapor phase of the cavitation bubbles and not in the bulk aqueous phase. Indeed, the synergistic effect between low frequency sonolysis (e.g. at 20 kHz) and photocatalysis, observed with less volatile substrates [17–21,23–26], has been attributed to the ultrasound-increased scission of the photocatalytically produced hydrogen peroxide [18], as well as to increased mass transfer. Both these effects would contribute to enhance the rate of substrate degradation only in the aqueous phase.

3.3. Efficiency comparison and energy consumption

The efficiency of the different degradation systems investigated in the present work can easily be compared in terms of the percent 1,4-DCB degradation values attained after 6 h, reported in Table 2. Photocatalysis and sonophotocatalysis under high intensity irradiation ensured total 1,4-DCB degradation in less than 6 h, while sonolysis at 20 kHz and photolysis under irradiation in the near UV showed less efficient.

The investigated degradation systems can be compared also in terms of time necessary to achieve a certain 1,4-DCB percent degradation and of the corresponding energy consumption required. Indeed, although energy consumption aspects should be obviously considered when dealing with the industrial scale application of water purification techniques, they usually do not receive adequate attention in the literature.

This calculation was limited to the energy required to reach 60% degradation of 1,4-DCB, as this percent degradation was attained within 6 h by most of the employed techniques. The energy consumption relative to the different experimental techniques could be easily calculated from the effective power consumption of the employed equipments (see Section 2) and the time needed to attain 60% degradation evaluated from the concentration vs. time curves reported in Figs. 1–3. The results

reported in Table 2 lead to the following energy consumption scale: US (40 W) < US + UV + TiO₂ < US (20 W) < UV + TiO₂ (lamp II) < UV (lamp II) < UV + TiO₂ (lamp I).

Thus, ultrasound treatment proved to be more convenient than photocatalysis and photolysis in the degradation of 1,4-DCB, though it requires longer treatment with respect to photocatalysis. It is worth underlining, however, that under simultaneous sonolysis and photocatalysis 1,4-DCB degradation proceeded at a more than three-times higher rate than under sole sonolysis (see also the rate constant values reported in Section 3.2), with only a 20% increase in energy consumption (Table 2).

4. Conclusions

The following conclusions may be drawn from the present kinetic and energy consumption analyses of 1,4-DCB degradation:

- Photocatalysis on TiO₂ particles leads to relatively fast 1,4-DCB degradation, though a relatively high amount of energy is consumed by the irradiation sources.
- Ultrasound, though inducing 1,4-DCB degradation at a lower rate, ensures parallel mineralization with lower energy consumption.
- The fastest degradation rate was attained under sonophotocatalytic conditions, with slightly higher energy consumption respect to sole photocatalysis.
- Synergy between sonolysis and photocatalysis could hardly be observed in the degradation of this volatile chlorinated aromatic substrate, most probably because the two techniques imply parallel mechanisms involving different phases.

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