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UNIVERSITÀ DEGLI STUDI DI TORINO

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Oxidative Degradation of Chlorophenol Derivatives promoted by Microwaves or Power Ultrasound: A Mechanism Investigation.

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ABSTRACT

Phenols are the most common pollutants in industrial wastewaters (particularly from oil refinery, resin manufacture and coal processing). In the last two decades it has become common knowledge that they can be effectively destroyed by non-conventional techniques such as power ultrasound (US) and microwave (MW) irradiation.

We studied the oxidative degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using advanced oxidation processes (AOPs), assisted either by US in aqueous solutions or by MW in the absence of solvents. The effect of US-frequency (20 and 300 kHz, respectively) was investigated and compared with those of conventional treatments. Detailed mechanisms of Fenton-type reactions under these conditions were suggested; products and intermediates were identified especially by GC-MS analyses. The results can also support the interpretation of previously published data and improve the understanding of the factors of direct degradation along different pathways.

We show that US and MW enhance the oxidative degradation of 2,4-D and that a considerable saving of oxidants and cutting down of reaction times is thereby achieved.

KEYWORDS

Oxidative Degradation; Fenton Reagent; Ultrasound; Microwaves; 2,4-Dichlorophenoxyacetic Acid.

INTRODUCTION

The presence in waste waters of phenols, persistent organic pollutants (POPs) deriving from chemical and petrochemical industries as well as the manufacture of paints, textiles and pesticides, is a serious environmental hazard.^[1] Chlorophenols in particular are highly toxic to aquatic life and may prove carcinogenic and mutagenic on humans; they are moreover extremely resistant to biological degradation by aerobic microorganisms. Conventional physical, chemical and biological treatments have been used to destroy phenolic compounds with poor to acceptable results. A more efficient degradation has been achieved by combining physico-chemical and biological treatments.^[2,3] In recent years advanced oxidation processes (AOPs) have emerged as powerful methods for converting organic pollutants, including phenols, to non-toxic degradation products.^[4,5] They are based on the reactivity in aqueous solution of free radicals, especially hydroxyl radicals, that rapidly, and usually non-selectively, attack most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom, resulting in a series of degradation/oxidation reactions; these ultimately lead to mineralization, i.e., complete conversion to CO₂, H₂O and inorganic ions.^[6] Transition metals (iron, copper), ozone or UV light can be employed to activate these reactions. As most advanced oxidation systems comprise more than one oxidant, the mechanisms of resulting transformations are quite complex. The Fenton (F) reaction is one of the most attractive AOPs because the reagent is easy to handle and environmentally benign.^[7] However, its application to the treatment of wastewaters is limited by its high running costs due to the large amounts of H₂O₂ required and the need to remove iron after the treatment.^[8]

During the oxidation of phenol with Fenton reagent numerous intermediate are generated through reaction mechanisms that are poorly understood. According to well-known fact,^[9] in the first stage of the oxidation sequence phenol is converted to aromatic compounds with two hydroxyl groups on the benzene ring (hydroquinone, resorcinol and catechol). Their oxidation in turn generates quinones; the next stage brings about a ring opening to form carboxylic acids with lower carbon numbers.

2,4-Dichlorophenoxyacetic acid (2,4-D) is a herbicide commonly used to control broadleaf weeds in cereal crops, sugarcane, turf and pastures. The fate in the environment of this chlorinated aromatic compound is of great interest because so much of it is used on farms and lawns, that it can

contaminate water supplies through runoff and in other ways. In water 2,4-D breaks down slowly, with a reported half-life ranging from 6 to 170 days, depending on environmental conditions.^[10] Although it is only mildly toxic (its oral LD₅₀ ranging from 370 to 666 mg/kg in small animals), it can be converted to highly toxic chloroorganic products.^[11] The United States Environmental Protection Agency (EPA) has classified 2,4-D as a suspected endocrine disruptor. Because in fresh water it can be mineralized by various microbiological processes only at concentrations not exceeding 10 ppb, alternative methods must be considered to eliminate it in groundwater. Many chemical and photochemical oxidation processes have been proposed to degrade it in aqueous solutions.^[12] Dichlorophenol (2,4-DCP), chlorohydroquinone and hydroquinone were detected as degradation intermediates. Several recent studies have used AOPs to break down 2,4-D to non-toxic substances and eventually mineralize it.^[13]

Although a large body of information concerning the rates of hydroxyl radical reactions with organic compounds has been collected,^[14,15] the reaction mechanisms are incompletely understood. In order to fully understand the degradation of environmentally dangerous compounds and to determine how damage is caused by them in organisms and can be prevented, the interactions of the hydroxyl radical with organic compounds must be elucidated in full detail.

In recent years, considerable interest has been focused on the application of ultrasound (US) to the cleanup of wastewaters containing hazardous chemicals.^[16-19] Aquasonolysis of pollutants is one of few physical treatments that in some cases can be scaled up for extensive employ.^[20,21] Acoustic cavitation provides a unique interaction of energy and matter resulting in high-energy chemical reactions. Water vapour and oxygen contained in the cavitation bubbles undergo thermal dissociation to yield hydrogen atoms and hydroxyl radicals as well as oxygen atoms and hydroperoxyl (HOO·) radicals.^[22] Organic solutes in the vicinity of collapsing bubbles or partitioned into the gas phase of the bubbles undergo thermal decomposition, and/or react with highly reactive radicals. The sonochemical degradation of phenol and substituted phenols has been extensively studied; ^[23-27] it is known that its products are short-chain organic acids, inorganic ions, CO, CO₂ and H₂O.^[28] In practice ultrasonic irradiation is not very effective unless it is combined with other methods such as AOPs, in particular the Fenton reaction.^[29,30]

During the last two decades the attention of chemists has also been attracted by microwaves (MW) irradiation, a source of molecular-level heating which promotes homogeneous and rapid thermal reactions.^[31] MW have been exploited to improve on several types of oxidation processes leading to environmental applications.^[32-35] Synergic effects of several MW-assisted AOPs were studied for the degradation of phenols.^[30,36,37] Sodium percarbonate (SPC) behaves as a dry carrier of H₂O₂ which is loosely bound in the solid and readily displaced by moisture when it disrupts the crystal

structure. Being inexpensive and non-toxic, it could be used in solvent-free POPs degradation under MW irradiation.^[33]

We report here on studies of the oxidative degradation of 2,4-D aiming to understand, on the basis of a pathway proposed in the literature,^[34-36] the mechanisms that are involved in its attack by hydroxyl radicals of in AOPs promoted by US (20 and 300 kHz) or MW. We studied the kinetics of sonochemical Fenton oxidation of 2,4-D in water and of its solvent-free degradation with SPC under MW irradiation. Reactions were monitored by GC-MS.

A better understanding of the factors that affect the reaction mechanism is required to assess the respective roles of US and MW.

RESULTS AND DISCUSSION
















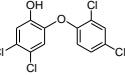
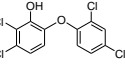
We had recently demonstrated the synergic effect of simultaneous^[37] and sequential^[38] US/MW irradiation on the oxidative degradation of POPs. Here we aimed to shed light on reaction mechanisms that are involved when AOPs are promoted by either energy source or conventional heating. All reactions were monitored by sequential sampling (after 15, 30, 60 and 120 min); samples were analyzed by GC-MS in order to detect all the intermediates generated during the process.

2,4-D was subjected to oxidation either with Fenton reagent under 300 kHz US in water (US/F) or in the absence of solvent with sodium percarbonate under MW (MW/SPC). In either case just a small excess of reagent was used, in fact much less than the amounts usually employed in these oxidative degradations.^[3,19,29,37,38] Results were compared with those obtained without irradiation under plain magnetic stirring or under US irradiation in the absence of oxidants; these control treatments were prolonged up to 4 hours, as shown in Tab. 1.

On the basis of analytical data obtained by GC-MS (Tab. 1) and those already published we could draw Scheme 1, in which the radical mechanisms involved in the degradation of 2,4-D are collected.

Table 1 Intermediates detected during the degradation of 2,4-D, amounts given as percentages of the initial charge (50 mg). Times of sampling are appended under each heading.

Intermediate	S/F ^a	S/F ^a	S/F ^a	US/F ^b	US/F ^b	US/F ^b	US ^c
	30'	60'	120'	30'	60'	120'	4h

	0.0	0.1	0.4	0.0	0.1	0.2	0.0
	0.0	0.1	0.0	0.1	0.0	0.0	0.0
	9.8	12.4	71.1	13.0	29.0	48.9	8.3
	0.9	2.6	17.0	0.9	1.2	1.7	0.9
	0.0	0.3	0.0	0.2	0.2	0.3	0.2
	0.0	0.3	0.7	0.2	0.2	0.5	0.6
	2.1	0.9	0.8	1.9	2.3	2.1	0.2
	0.2	0.9	0.5	0.1	0.5	0.9	1.1
	0.1	0.6	0.6	0.1	0.8	1.3	1.0
	0.3	1.0	1.3	0.1	0.5	1.2	0.9
	0.0	0.1	0.0	0.0	0.0	0.0	0.5
	2.3	0.7	0.8	1.5	2.4	2.8	0.4
	4.4	1.3	1.3	3.8	9.7	9.2	1.4
	78.2	78.3	5.3	76.3	51.3	27.9	83.4
	1.8	0.6	0.3	1.3	1.1	1.2	0.5
	0.0	0.0	0.0	0.4	0.5	1.5	0.5
	0.0	0.0	0.0	0.1	0.2	0.5	0.2

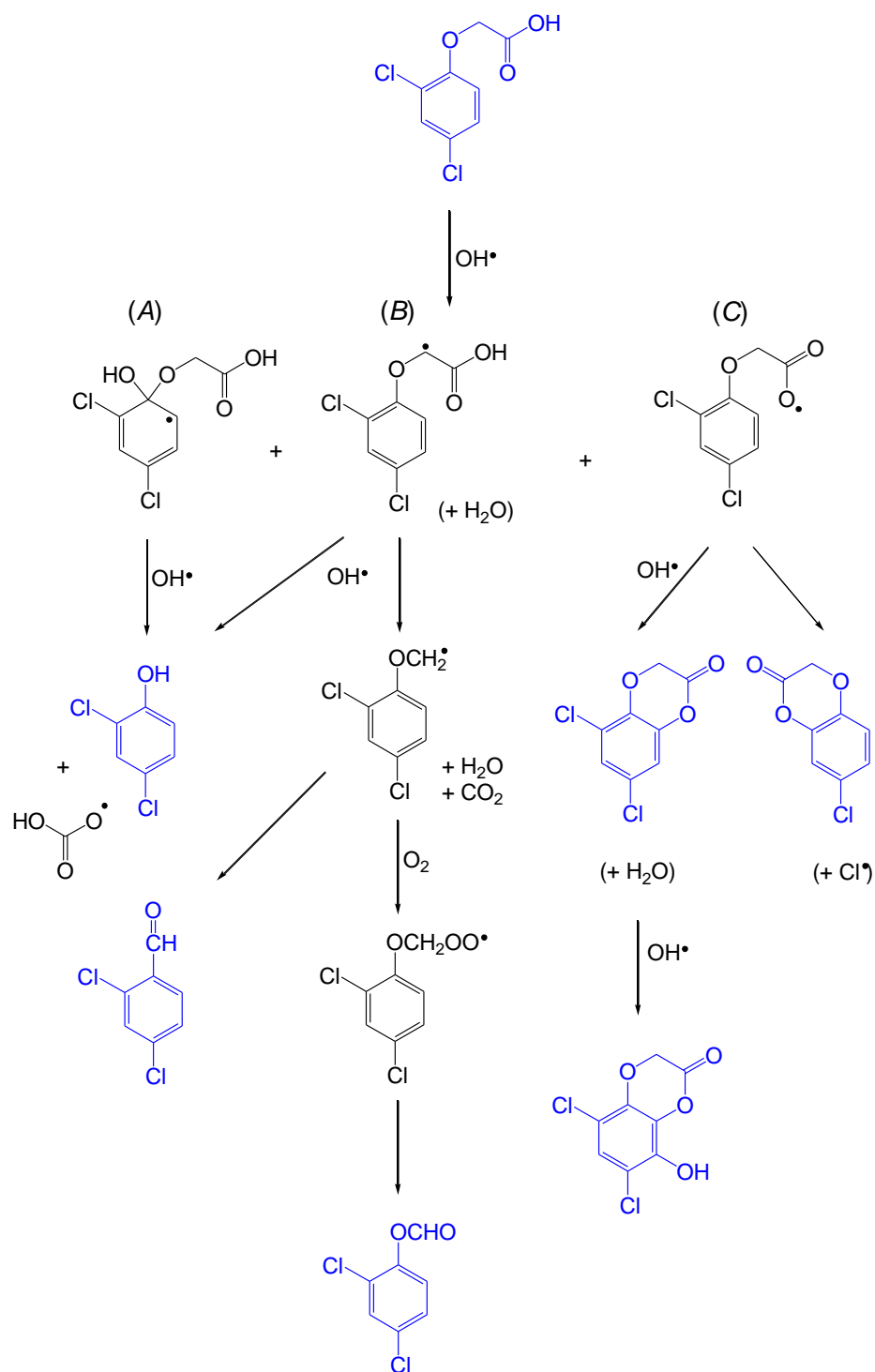
* Data for MW/SPC (SPC 7.5eq, MW 300W) are not reported because this treatment achieved complete mineralization in 15 min.

^a Magnetic stirring at room temp. in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (10.7eq).

^b US-300 kHz (120 W, 25°C) in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (10.7eq)

^c US-300 kHz (120 W, 25°C) in plain water (50 ml).

Scheme 1 Proposed mechanism for the oxidative degradation of 2,4-D (only the compounds drawn in blue were actually detected)



The hydroxyl radical generated by the Fenton reaction may determine:

(A) An *ipso* attack at position 1 of the aromatic ring resulting in the homolytic cleavage of the side chain;

(B) A radical attack in alpha position to the carboxyl group, resulting in the formation of a O-Neophyl-type radical and in the last instance the product 2,4-dichlorobenzaldehyde, cf. [39]









(C) The formation of a carboxylic radical, followed by lactonization and closure of a second ring. Two product structures support this pathway; the monochloro derivative was further hydroxylated on the aromatic ring. We had no evidence of the direct formation of the Cl-radical.








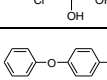
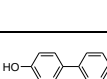
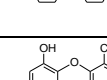
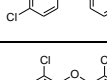
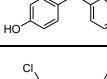
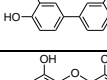
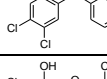
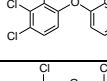
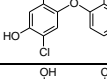
In pathway B the 2,4-dichloroanisole radical (D) can be generated by 1,3-H-shift to (C) and by following C-C-cleavage. While a solvent-free oxidation with SPC under MW caused complete mineralization within 15 minutes, the Fenton reaction under US strongly promoted the formation of radicals as depicted in pathways B and C. However, quantitative data reported in Table 4 show that the effect of US irradiation (300 kHz) was largest during the first 30 minutes.

Under conventional conditions (Fenton under magnetic stirring, “S/F”) at room temperature the Fenton reaction was much slower as the formation of 2,4-DCP.

In order to shed more light on radical pathways in the degradation of 2,4-D, we applied the same set of treatments to 2,4-DCP and phenol, the first two products that occur a step down in the degradation sequence. On the basis of results reported in Tab. 2 and data available in the literature, we drew Scheme 2 for the oxidative degradation of 2,4-DCP.

Table 2 Intermediates detected during the degradation of 2,4-DCP, amounts given as percentages of the initial charge (50 mg)

Intermediate	S/F ^a			US/F ^b			US ^c	MW/SPC ^d	
	15'	30'	60'	15'	30'	60'	4 h	15'	30'
	1.2	1.6	1.3	0.2	2.1	1.1	0.0	0.0	0.0
	0.6	1.2	0.7	0.0	0.0	0.9	0.0	0.0	0.0
	7.4	10.7	8.1	0.7	6.8	4.4	0.0	0.0	0.0
	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1.0	1.0	0.6	0.2	0.0	0.4	0.5	0.0	0.0
	0.7	1.5	1.1	0.0	0.0	0.4	0.0	0.0	0.0
	9.1	4.7	4.7	22.0	12.0	31.4	88.5	98.5	11.1
	28.0	34.2	33.9	12.0	43.4	39.0	1.1	0.0	0.0

	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.2	0.0
	2.5	1.7	1.7	11.6	3.4	4.3	2.0	0.0	0.0
	10.9	5.4	5.8	33.3	12.8	9.3	0.6	0.0	0.0
	17.1	15.5	12.6	14.4	14.5	6.3	3.4	0.0	0.0
	3.3	2.6	5.3	1.0	0.0	0.6	1.3	0.0	0.0
	0.3	0.4	0.5	0.2	0.0	0.4	0.0	0.0	0.0
	5.4	4.2	5.7	0.7	2.4	0.3	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.4
	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	2.6
	0.0	0.0	0.3	0.1	0.0	0.0	0.1	0.2	6.8
	0.0	0.2	0.6	0.2	0.0	0.0	0.1	0.2	4.6
	0.0	0.0	0.6	0.2	0.0	0.0	0.1	0.0	0.0
	4.5	5.5	5.5	0.4	0.0	0.6	0.5	0.8	31.6
	2.0	2.6	3.5	0.2	0.0	0.4	0.3	0.2	6.9
	0.9	0.8	1.1	0.0	2.6	0.0	0.1	0.0	24.1
	5.0	5.9	6.5	2.2	0.0	0.3	0.0	0.0	0.0

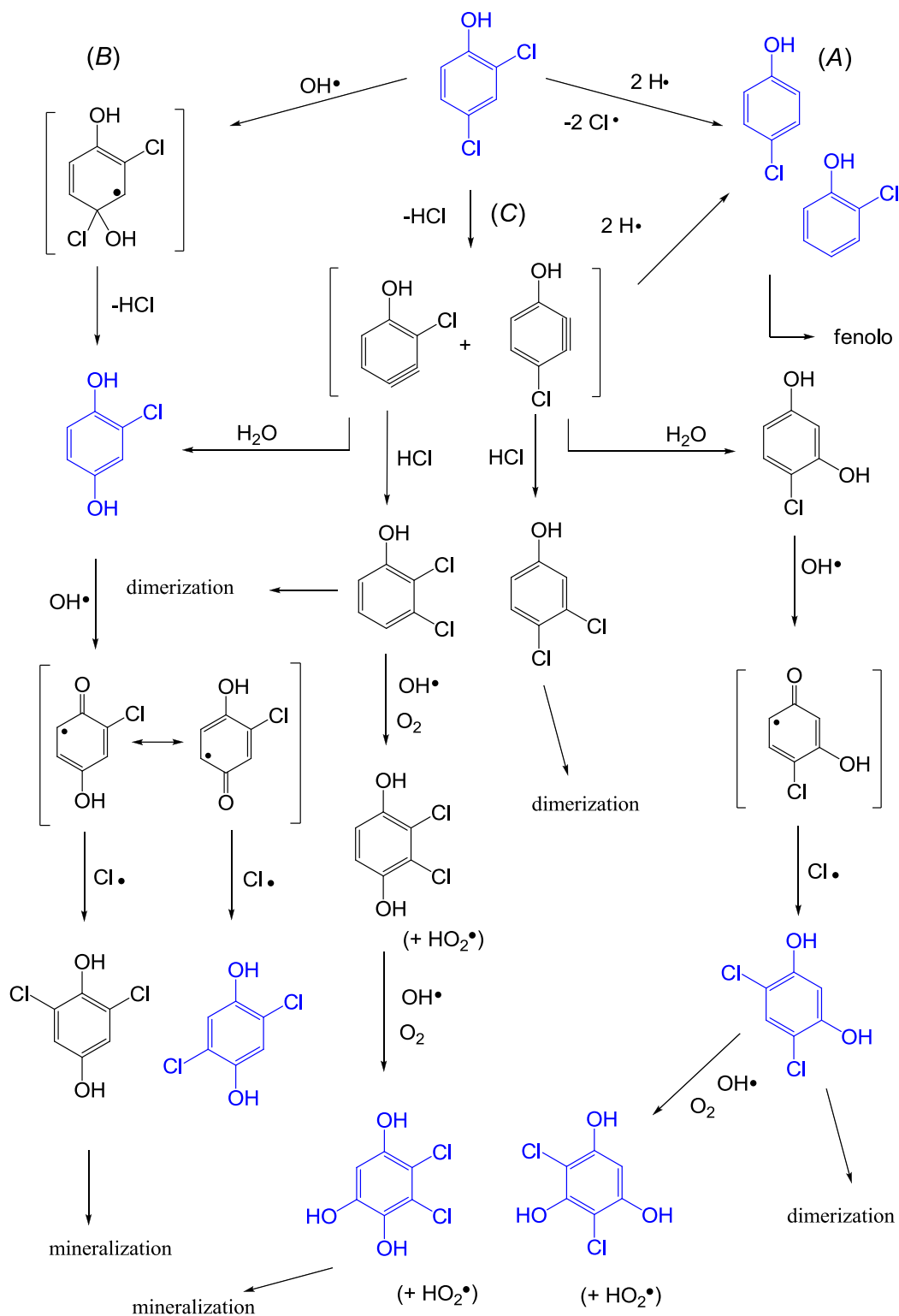
^a Magnetic stirring at room temp. in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (10.7eq),

^b US-300 kHz (120 W, 25°C) in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (10.7eq),

^c US-300 kHz (120 W, 25°C) in plain water (50 ml),

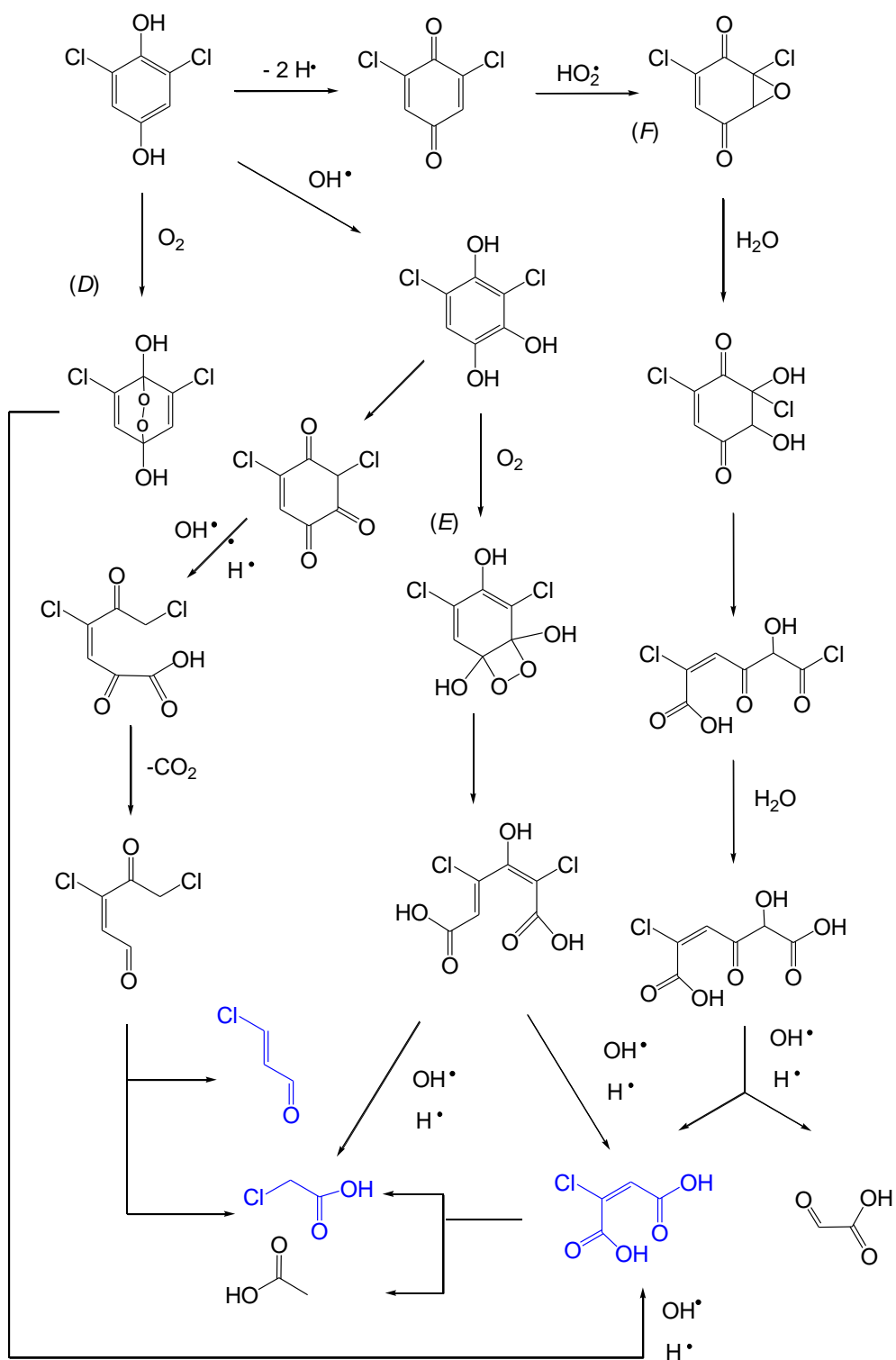
^d MW/SPC (SPC 15eq, MW 300 W).

Scheme 2 Proposed mechanism for the oxidative degradation of 2,4-DCP (only compounds drawn in blue were actually detected)



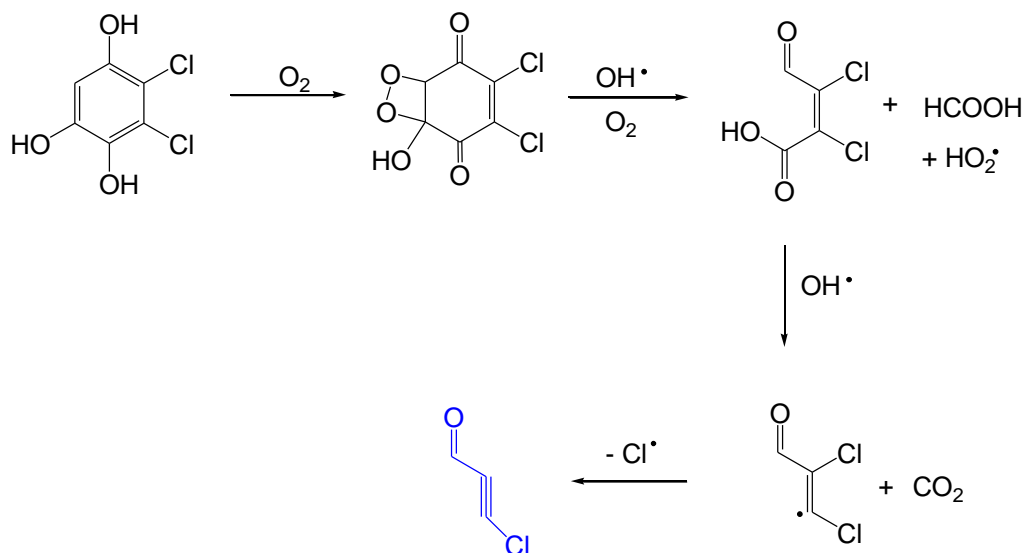
Besides dehalogenation to phenol by the action of hydrogen atom (*A*), we also suppose that an *ipso* attack by the hydroxyl radical on the aromatic ring occurs, resulting in an addition/elimination process (*B*).^[40] The hypothesis envisaging a benzyne intermediate ^[21] may explain the formation of 2,4-DCP isomers bearing the Cl atoms in 2,3 or 3,4 as well as that of polyhydroxy- and polychlorobenzenes (*C*). From these highly toxic derivatives, dimeric compounds can be generated as shown in Tab. 2. Considering the residual amounts of 2,4-DCP found at the end of treatments (Tab. 4) and the low residual amounts of any other intermediates, we may conclude that both S/F and US/F determine a marked mineralization (see Scheme 3). In all the above as well as in the following schemes only compounds drawn in blue were actually detected by GC/MS.

Scheme 3 Proposed mechanism pathways for oxidative opening of the aromatic ring (only compounds drawn in blue were actually detected)



It is known that the opening of the aromatic ring proceeds via formation of peroxydic groups ^[41,42] and the epoxydation of one double bond to yield a quinone intermediate, followed by ring opening. The formation of chloromaleic and chloroacetic acids then follows. Presumably 3-chloropropynal derives from the opening of 5,6-dichloro-1,2,4-benzenetriol followed by decarboxylation (see Scheme 4).
















Scheme 4 Proposed mechanism pathways for the formation of 3-chloropropenal (only compound drawn in blue was actually detected)



Dimerization is disfavoured by US/F, as the amounts of dimeric structures progressively decreased during sonication through either polymerization or radical disruption. 4-Chlorophenol was detected in experiments with US and in traces under MW irradiation. This means that US can dechlorinate selectively position 2. Trials with MW/SPC confirmed a rapid pyrolytic mechanism, as neither linear products nor products deriving from direct attack by hydroxyl radicals were found. Under such conditions, the extent of dimerization is very modest.

Table 3 reports data on the degradation of phenol. MW/SPC was the most efficient method, leading to rapid mineralization besides some dimerization. During oxidation in water a peculiar role of hydroxyl radicals emerged, with attacks in ortho/para of the aromatic ring.

Table 3 Intermediates detected during the degradation of phenol, amounts given as percentages of the initial charge (50 mg).

Intermediate	S/F ^a 15'	S/F ^a 1 h	US/F ^b 15'	US/F ^b 1 h	US ^c 1 h	US ^c 7 h	MW/SPC ^d 15'
	0.0	0.1	0.0	0.0	0.0	0.0	0.0
	0.2	0.0	0.0	0.0	0.0	0.0	0.0
	94.2	3.3	32.7	7.1	96.5	84.3	25.0
	0.0	0.0	0.1	0.0	0.0	0.0	0.0
	0.1	56.6	44.2	52.8	2.1	10.1	0.0
	0.0	14.9	17.1	20.7	1.0	3.7	0.0
	0.0	4.9	0.0	5.5	0.3	1.1	0.0
	0.0	0.1	0.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.3	0.1	0.4	0.0	0.0	0.0	0.0
	1.1	0.6	0.1	0.3	0.0	0.16	7.3
unknown	0.00	0.10	0.00	0.10	0.00	0.00	0.00
	0.55	0.04	0.03	0.10	0.00	0.00	0.00
	0.00	0.12	0.06	0.11	0.00	0.00	0.00
	3.2	1.0	0.3	0.8	0.1	0.3	30.9
unknown	0.0	17.4	5.1	11.6	0.0	0.0	0.0
unknown	0.0	0.3	0.0	0.2	0.0	0.0	4.2
unknown	0.0	0.2	0.0	0.1	0.0	0.0	10.6
unknown	0.0	0.1	0.0	0.0	0.0	0.0	3.8
	0.1	0.0	0.5	0.2	0.0	0.3	0.3

^a Magnetic stirring at room temp. in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (5 eq),

^b US-300 kHz (120 W, 25°C) in water (50 ml) with FeSO₄ (15 mg) and 30% H₂O₂ (5 eq),

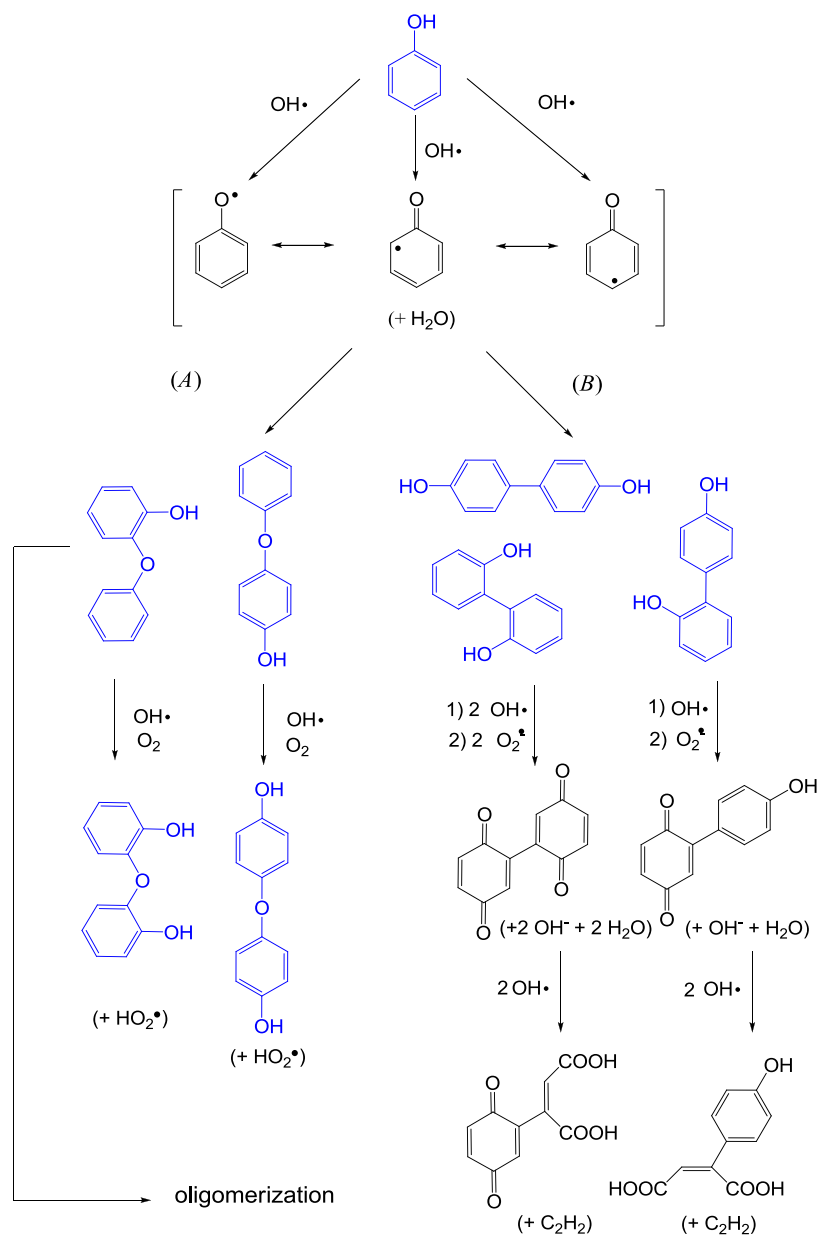
^c US-300 kHz (120 W, 25°C) in plain water (50 ml),

^d MW/SPC (SPC 7.5 eq, MW 300 W).

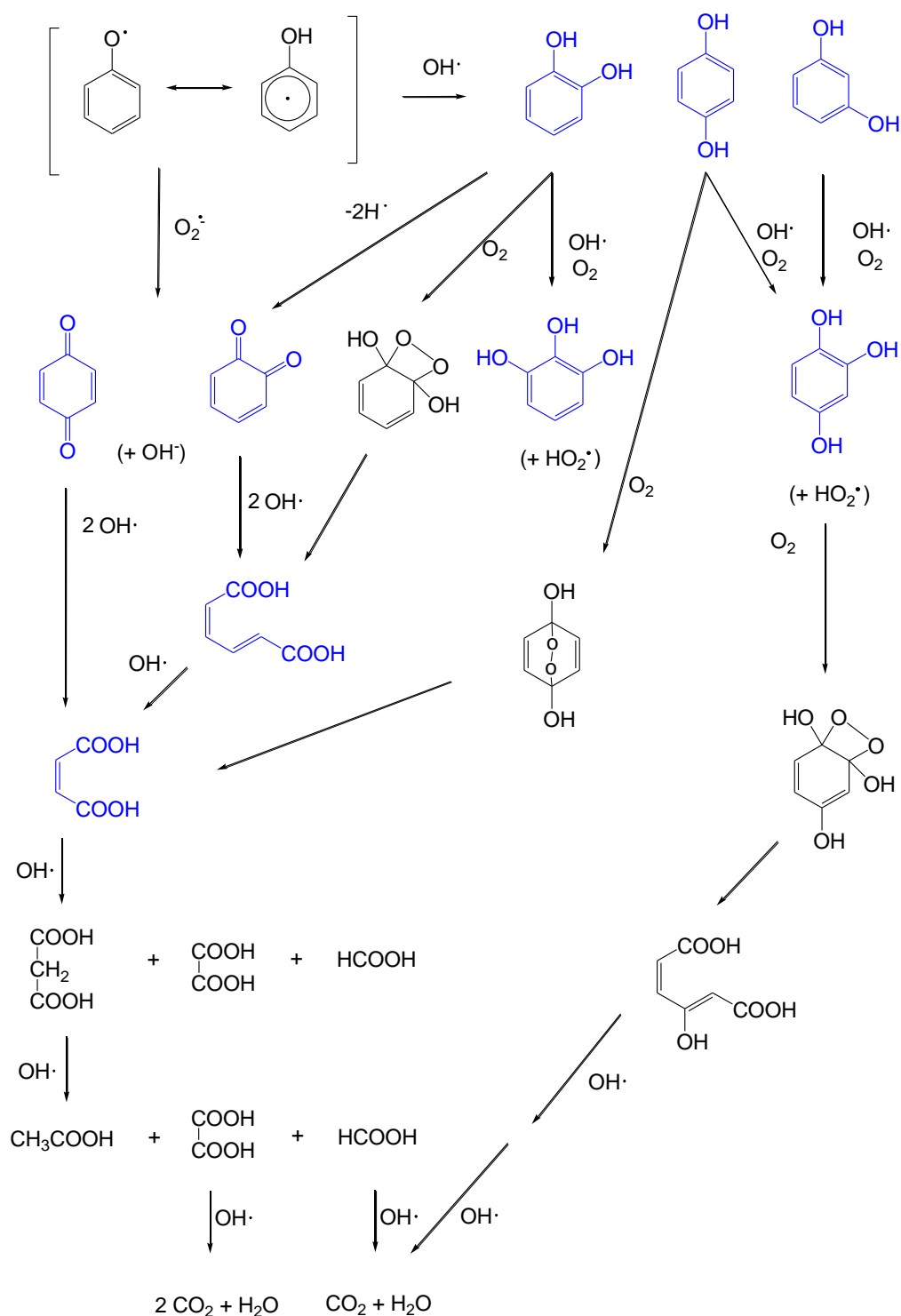
Under 15 minutes stirring C-C- or C-O-bridged dimers were favoured, a trend that was not seen under US.

As depicted in Scheme 5, hydroxyl attack may yield phenoxy radical ^[43-45] that can generate dimers or oligomers, mainly C-O bridged (A). C-C Dimers undergo the insertion of peroxidic bridges ^[41] before ring opening.

Scheme 5 Proposed mechanism pathways for phenol dimerization (only compounds drawn in blue were actually detected).



Scheme 6 Proposed mechanism for radical attack and ring opening (only compounds drawn in blue were actually detected)



By further hydroxyl attack phenoxyl radicals (Scheme 6) may undergo oxidation to catechol, hydroquinone and, in lesser amounts, to resorcinol. 1,2,3- and 1,2,4-benzenetriol can be generated by reaction with other hydroxyl radicals; further oxidation will open the aromatic ring and yield bicarboxylic acids such as muconic and maleic acid. Other oxidation products are the malonic, oxalic, acetic and formic acids, on the way down to complete mineralization to water and carbon

dioxide.^[46,47] The same products can also derive from the opening of *p*- and *o*-quinones, intermediates from hydroquinone and catechol. The two latter compounds can also dimerize.

Table 4 shows residual starting materials after treatments of 50 mg 2,4-D, 2,4-DCP, and phenol. Probably the low concentration of Fenton reagent and the several radical reactions, including dimerization, can explain the unexpected higher residual amount of 2,4-D.

Table 4. Amounts (mg) of residual starting material after treatments on 50 mg 2,4-D, 2,4-DCP, and phenol. Values determined by GC-MS (for experimental conditions see Tables 1, 2 and 3).

starting material	S/F	S/F	S/F	US/F	US/F	US/F	US	MW/SPC	MW/SPC
	30'	1 h	2 h	30'	1 h	2h	4h	15'	30'
2,4-D	32.3	8.0	0.1	23.6	5.3	1.2	6.0	0.0	0.0
2,4-DCP	4.0	1.1	0.0	0.4	0.2	0.1	20.0	8.8	0.0
phenol	42.0	0.2	0.0	5.6	0.8	0.0	49.1	3.6	0.0

In preliminary studies towards the optimization of the reagent/substrate ratio, the minimum amount of Fenton reagent for complete degradation of 2,4-D under US in about 30 min was determined to be 750 μ l 30% H₂O₂ and 40 mg FeSO₄ for 50 mg 2,4-D. These conditions achieved 85% degradation in 15 min (7.5 mg residual amount). With the aim to carefully monitor the degradation and detect all the intermediates during the treatment we reduced the Fenton concentration by about three-fold (30% H₂O₂ 250 μ l, FeSO₄ 15 mg).

Similar experiments were carried out for comparison at 300 kHz and 20 kHz, cf. Tab. 5 and 6, the reaction outcome being monitored each 15 minutes for one hour. Working at the higher frequency only traces of intermediates were detected (traces of 2,4-DCP, but no dimer at all); in spite of a little residual amount of starting material the mineralization of 2,4-D was almost complete within 45 min.

Table 5. Degradation of 2,4-D (50 mg dissolved in 50 ml of distilled water) under US (300 kHz, 120 W)/F (10.7 eq) at 25 °C at different irradiation times. Residual amounts of 2,4-D and amounts of 2,4-DCP produced are reported, as determined by GC-MS.

Time (min)	Residue (mg)	Residual 2,4-D (mg)	2,4-DCP found (mg)
15	35.8	32.1	5.6

30	31.7	23.6	6.1
45	27.2	14.5	6.3
60	21.9	5.3	7.4

Table 6. Degradation of 2,4-D (50 mg dissolved in 50 ml of distilled water) under US (20 kHz, 50W) /F(10.7 eq) at 25 °C at different irradiation times. Residual amounts of 2,4-D and amounts of 2,4-DCP produced are reported, as determined by GC.MS

Time (min)	Residue (mg)	Residual 2,4-D (mg)	2,4-DCP (mg)
15	27.8	22.0	1.2
30	25.6	18.5	2.7
45	8.2	1.6	1.5
60	4.1	0.1	1.2

CONCLUSION

The present study aimed to shed light on the effect and mechanism of US- and MW-promoted oxidative degradation of 2,4-D, with and without the addition of Fenton reagent. Oxidative pathways were proposed by a careful monitoring of the reactions and detection of intermediates by GC-MS. MW-promoted degradation under solvent-free conditions with solid Fenton-like reagents (*viz.* SPC) is extremely efficient and mainly follows pyrolytic pathways. Power US strongly accelerates the degradation of 2,4-D in water through a rapid generation of highly reactive radicals; it does not lead to the formation of more toxic dimers. Results obtained under non-conventional conditions were compared with those obtained under plain magnetic stirring at room temperature.

EXPERIMENTAL

GC-MS analyses were performed with an Agilent 6890 with a MS-Network 5973 detector equipped with a HP-5 MS: column: length 30 m, i.d. 0.25 mm, film thickness 0.25 μm . The identification of products was achieved by the NIST 05 library (National Institute of Standards and Technology) and by comparison with analytical standards when available.

MW oven: Milestone MicroSYNTH (Soriso, Italy).

The following US reactors have been developed in collaboration with Danacamerini (Torino, Italy):

- thermostatted 300-kHz reactor with a titanium cup-horn (max. volume 70 ml)
- 20 kHz probe with titanium immersion-horn.

2,4-D degradation

2,4-D (50 mg, 0.227 mmol) was dissolved in distilled water (50 ml); pH was adjusted to 3 with dilute H_2SO_4 . Then FeSO_4 (15 mg) and 30 % H_2O_2 (0.25 ml, 10.7 eq) were stirred in. This solution was treated in three different ways:

- magnetic stirring at room temperature (30, 60, 120 min).
- US-300 kHz (120 W; T: 25 °C; 15, 30, 45, 60, 120 min).
- US-20 kHz (50 W; T: 25 °C; 15, 30, 45, 60 min).

Another water solution of 2,4-D (50 mg in 50 ml) was sonicated at 300 kHz (1, 4, and 7 h) without Fenton reagent.

Work-up: Reaction mixtures were acidified to pH 2 with dilute H_2SO_4 and extracted with ether (20 ml x3). Organic phases were washed with brine, dried on anhydrous Na_2SO_4 and evaporated to dryness. Residues were dissolved in ether and analyzed by GC-MS: column HP 5-MS; split 1:20; injector temperature 250 °C; Helium as carrier gas at 1,2 ml/min; temperature program: firstly 40 °C (2 min), then a 5 °C/min increase up to 300 °C (held for 10 min).

2,4-DCP degradation

2,4-DCP (50 mg, 0.309 mmol) was dissolved in distilled water (50 ml); pH was adjusted to 3 with dilute H_2SO_4 . Then FeSO_4 (15 mg) and 30 % H_2O_2 (0.25 ml, 10.7 eq) were stirred in. This solution was treated in three different ways:

- magnetic stirring at room temperature.

- US-300 kHz (120W; T: 25 °C).
- US-300 kHz (120W; T: 25 °C) without Fenton reagent.

Aliquots were taken every 15 min for 1 h in the first two cases while in the latter after 1 and 4 h. Work-up and GC-MS analyses were carried out as detailed above.

Phenol degradation

Phenol (50 mg, 0.532 mmol) was dissolved in 50 ml distilled water; pH was adjusted to 3 with dilute H₂SO₄. Then FeSO₄ (15 mg) and 30 % H₂O₂ (0.25 ml, 4.9 eq) were stirred in. This solution was treated in three different ways as described for 2,4-DCP and products were analyzed by GC-MS.

Solvent-free degradation under MW

Compounds under study were finely dispersed in a mortar with SPC and distilled water (50 µl); the mixture was placed in pressure-resistant pyrex tubes (ACE Glass Inc.) and irradiated with MW (power: 300 W).

Work-up: Reaction mixtures were extracted with ether (20 ml×3) under US irradiation for 2 min in a common cleaning bath. Organic phases were washed with brine, dried on anhydrous Na₂SO₄ and evaporated to dryness. Residues were dissolved in ether and analyzed by GC-MS: column HP 5-MS; split 1:20; injector temperature 250 °C; Helium as carrier gas at 1,2 ml/min; temperature program: firstly 40 °C (2 min) then a 5 °C/min increase up to 300 °C (held for 10 min).

Acknowledgments

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REFERENCES

- [1] Australian Government, Department of the Environment, Water, Heritage and the Arts, The National Pollutant Inventory (NPI) 2008. Available at <http://www.npi.gov.au/database/substanceinfo/profiles/70.html> (checked at ...).

- [2] Agarry S.E. ; Durojaiye A. O.; Solomon B.O. *Int. J. Env. Pollut.* **2008**, 32 , 12-28.; Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. *J. Hazard. Mater.* 2008, 160, 265-288
- [3] Cravotto, G.; Di Carlo, S.; Mantegna, S.; Binello, A.; Girlanda, M.; Lazzari, A. *Water Air Soil Pollut.* **2008**, 187, 353-359.
- [4] Gogate P.R.; Pandit. B. *Adv. Environ. Res.* **2004**, 8, 501-551.
- [5] Gimeno, O., Carbajo, M., Beltran, F.J., Rivas, F.J. *J. Hazard. Mater.* **2005**, 119, 99-108.
- [6] Bhargava, S.K.; Tardio, J.; Prasad, J.; Foger, K.; Akolekar, D.B.; Grocott, S.C. *Ind. Eng. Chem. Res.*, 45 (4) 1221-1258, 2006
- [7] Jones, C.W. *Applications of Hydrogen Peroxide and Derivatives* Royal Society of Chemistry: Cambridge, UK. **1999**, 264. DOI: 10.1021/op000003w.
- [8] J. Barrault, J.; Abdellaoui, M.; Bouchoule, C.; Majesté, A.; Tatiboüet, J.M.; Laulodi, A.; Papayannakos, N.; Gangas, N.H. *Appl. Catal. B. Environ.* **2000**, 27, 225-230.
- [9] Devlin, H.R.; Harris, I.J. *Ind. Eng. Chem. Fundam.* **1984**, 23, 387-392.
- [10] Aly, O.M.; Faust, S.D. *J. Agric. Food Chem.* **1964**, 12, 541-546.
- [11] Kaioumova, D.; Kaioumov, F.; Opelz, G.; Susal, C. *Chemosphere* **2001**, 43, 801-805.
- [12] Matos, J.; Laine, J.; Hermann, J.M. *J. Catal.* **2001**, 200, 10-20.
- [13] Yasman, Y.; Bulatov, V.; Gridin, V.; Agur, S.; Galil, N.; Armon, R.; Schechter, I. *Ultrasonic Sonochem.* **2004**, 11, 365-372.
- [14] Du, Y.; Zhou, M.; Lei, L. *Wat.Res.* **2007**, 41, 1121-1133.
- [15] Buxton, G.; Greenstock, C.; Helman, W.P.; Ross, A.B. *J. Phys. Chem. Ref. Data* **1988**, 17, 513-886.
- [16] Stavarache, C.; Yim, B.; Vinatoru, M.; Maeda, Y. *Ultrasonics Sonochem.* **2002**, 9, 291-296.
- [17] Petrier, C.; Y. Jiang, Y.; Lamy, M.F. *Environ. Sci. Technol.* **1998**, 32, 1316-1318.
- [18] Kidak, R.; Ince, N.H. *Ultrasonic Sonochem.* **2006**, 13, 195-199.
- [19] Bremner, D.; Di Carlo, S.; Chakinala, A. G.; Cravotto, G. *Ultrasonic. Sonochem.* **2008**, 15(4), 416-419.
- [20] Mason, T.J. *Ultrasonics* **1992**, 30, 192-196.
- [21] Goskonda, S.; Catallo, W.J.; Junk, T. *Waste Manag.* **2002**, 22, 351-356.
- [22] Riesz, P.; Kondo, T. *Free Radical Biol. Med.* **1992**, 13, 247-270.
- [23] Berlan, J.; Trabelsi, F.; Delmas, H.; Wilhelm, A.M.; Petrignan, J.F. *Ultrasonics Sonochem.* **1994**, 1, S97-S102.
- [24] Jiang, Y.; Waite, T.D. *Wat. Sci. Technol.* **2003**, 47, 85-92.

- [25] Papadaki, M.; Emery, R.J.; Abu-Hassan, M.A.; Díaz-Bustos, A.; Metcalfe, I.S.; Mantzavinos, D. *Sep. Purific. Technol.* **2004**, *34*, 35-42.
- [26] Hao, H.; Chen, Y.; Wu, M.; Wang, H.; Yin, Y.; Lü, Z. *Ultrasonics Sonochem.* **2004**, *11*, 43-46.
- [27] Tauber, A.; Schuchmann, H.P.; von Sonntag, C. *Ultrasonic Sonochem.* **2000**, *7*, 45-52.
- [28] Liang, J.; Komarov, S.; Hayashi, N.; Kasai, E. *Ultrasonics Sonochem.* **2007**, *12*, 201-207.
- [29] Cravotto, G.; Di Carlo, S.; Tumiatti, V.; Roggero, C.; Bremner, D. *Environ. Technol.* **2005**, *26*, 721-724.
- [30] Menéndez, J.A.; Inguanzo, M.; Pis, J.J. *Water Res.* **2002**, *36*, 3261-3264.
- [31] Ai, Z.H.; Yang, P.; Lu, X.H. *Chemosphere* **2005**, *60*, 824-827.
- [32] Cravotto, G.; Ondruschka, B.; Di Carlo, S.; Roggero, C.; Tumiatti V. *Chemosphere* **2007**, *69*, 1326-1329.
- [33] Abramovitch, R.A.; Michael, C. *Chemosphere* **2003**, *50*, 955-957.
- [34] Polaert, I.; Estel, L.; Ledoux, A. *Chem. Engin. Sci.* **2005**, *60*, 6354-6359.
- [35] Zhihui, A.; Peng, Y.; Xiaohua, L. *Chemosphere* **2005**, *60*, 824-827.
- [36] Yu, Ying-hui.; Ma, Jun; Yan-jun Hou *J. Environ. Sci. (Beijing)* **2006**, *18*, 1043-1049; Song, Qijun; Niu, Tao; Wang, Haijun *J. Mol. Struct. Theochem* **2008**, *861*, 27-32
- [37] Wu, Z.-L.; Ondruschka, B.; Cravotto, G. *Environ. Sci. Technol.* **2008**, *42*, 8083-8087.
- [38] Cravotto, G.; Di Carlo, S.; Curini, M.; Tumiatti, V.; Roggero, C. *J. Chem. Tech. Biotechnol.* **2007** *82*, 205-208.
- [39] Antunes, C.S.A.; Bietti, M.; Ercolani, G.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 3884-3891; Falvey, D.E.; Khambatta, B.S.; Schuster, G.B. *J. Phys. Chem.* **1990**, *94*, 1056-1059
- [40] Peller, J.; Wiest, O.; Kamat, P.V. *J. Phys. Chem. A* **2001**, *105*, 3176-3181.
- [41] Gopalan, S. ; Savage, P.E. : *J. Phys. Chem.* **1994**, *98*, 12646-12652.
- [42] X. Li, X.; Cubbage, J.W.; Jenks, W.S. *J. Org. Chem.* **1999**, *64*, 8525-8536.
- [43] Uyama, H.; Maruichi, N.; Tonami, H.; Kobayashi, S. *Biomacromol.* **2002**, *3*, 187-193.
- [44] Yu, J.; Taylor, K.E.; Zou, H.; Biswas, N.; Bewtra, J.K. *Environ. Sci. Technol.* **1994**, *28*, 2154-2160.
- [45] Higashimura, H.; Fujisawa, K.; Kubota, M.; Kobayashi, S. *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *43*, 1955-1962.
- [46] Zazo, J.A.; Casas, J.A.; Mohedano, A.F.; Gilarranz, M.A.; Rodríguez, J.J. *Environ. Sci. Technol.* **2005**, *39*, 9295-9302.
- [47] Lesko, T.; Colussi, A.J.; Hoffmann, M.R. *Environ. Sci. Technol.* **2006**, *40*, 6818-6823.

