

# Microwave Photochemistry. Applications in Organic Synthesis

Vladimír Církva\* and Stanislav Relich

*Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojova 135, 16502 Prague 6, Czech Republic*

**Abstract:** This review article is the second of the comprehensive series on survey of the microwave photochemical and photocatalytic processes, and is focused specially on the microwave-assisted photochemical applications of the electrodeless discharge lamps (EDLs) in organic synthesis. The concept of microwave organic photochemistry is an important issue in synthetic chemistry and material science, and is presented in several schemes. Likewise, the various microwave photochemical reactor types (batch with external or internal light source, flow-through with external light source, annular flow-through with internal EDL, cylindrical flow-through surrounded with EDL, and mixed flow-through with internal EDL) with different arrangement of the lamps are described.

**Keywords:** Microwave, photochemistry, batch and flow-through photoreactor, electrodeless discharge lamp.

## 1. INTRODUCTION

The first review on *Microwaves in Photochemistry* [1] was reported by Klán and Církva, and it covered the literature up to 2006 and gave a complete picture of current knowledge of microwave (MW)-assisted photochemistry and photocatalysis. This pioneer work provided the necessary theoretical background and some details about synthetic, analytical, environmental and technical applications. Církva and Žabová have published the reviews [2,3] that were limited to the thin titania films on the electrodeless discharge lamps (EDLs) in *Microwave Photocatalysis*. Two other reviews [4,5] from Horikoshi deal with the application of EDLs on the advanced oxidation processes (AOPs) in the MW photocatalytic environmental remediation of actual pollutants (2,4-D herbicide, bisphenol-A, acetaldehyde, toluene, and dioxins).

In Part 1 of our comprehensive review the general principles and overview of microwave photochemistry and photocatalysis have been described [6]. This first article was focused on generation of UV/Vis discharge in the EDLs, i.e. theory of the MW discharges, construction of EDL, preparation of the thin titania films on EDL, spectral characteristics of EDL, and performance of EDL.

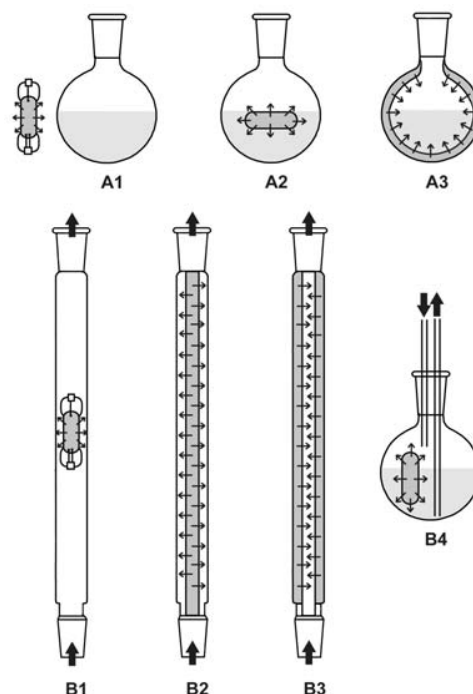
This sequel of review article about microwave photochemistry is focused on applications of a new method with EDLs in organic synthesis. The novel MW photochemical reactors with different arrangement of the lamps in the batch and the flow-through experimental set-up, and the presented photochemical reactions in several schemes are described in detailed.

## 2. MICROWAVE PHOTOCHEMISTRY

Coupled activation of photochemical reactions by using of two different types of radiation, MW and UV/Vis, is covered by the discipline called *Microwave Photochemistry*. The energy of MW radiation ( $E = 0.98 \text{ J mol}^{-1}$  at  $\nu = 2.45 \text{ GHz}$ ) is considerably lower than that of UV/Vis radiation ( $E = 600\text{--}170 \text{ kJ mol}^{-1}$  at  $\lambda = 200\text{--}700 \text{ nm}$ ), thus insufficient to disrupt the bonds of common organic molecules. We therefore assume that, essentially, UV/Vis is responsible for a photochemical change, and MW radiation subsequently affects the course of the subsequent reaction [1].

The photoreactor used for the MW-assisted experiments is an essential tool for experimental work. Such equipment enables simultaneous irradiation of compounds with both MW and UV/Vis radiation. Over the past decade, considerable experiences [7,8] have been obtained concerning the construction of the MW photochemical reactors [1]. The various lamp configurations in these types of the MW photoreactors are shown in Fig. (1), where the different arrangements of the lamp (external vs. internal UV/Vis source) and

their location in MW field (outside vs. inside) are plotted. As a result the batch and flow-through modes of seven fundamental types of MW photoreactors **A1-A3** and **B1-B4** were detached.



**Fig. (1).** Cross-sectional view of various microwave photoreactor types with different arrangement of the lamps: (A1) batch with external UV/Vis source (classical lamp); (A2) batch with internal EDL; (A3) batch with EDL inside of double wall; (B1) flow-through with internal UV/Vis source (classical lamp); (B2) annular flow-through with internal EDL; (B3) cylindrical flow-through surrounded with EDL; (B4) mixed flow-through with internal EDL.

The simplest types of MW photoreactors are a batch flask (Fig. 1, **A1**) or flow-through tube (**B1**) in MW field, which are irradiated by a light beam from an external UV/Vis source (classical lamp or EDL). This type of equipment makes possible to study effect of microwave radiation on the course of photoreaction. However, for practical reasons, the batch photoreactors (**A2**, **A3**) with EDL inside of MW oven has been widely applied.

The flow-through reactor types can be subdivided into an annular photoreactor (Fig. 1, **B2**) with EDL centered parallel to the axis of the reactor vessel; into a cylindrical photoreactor (**B3**) with a coaxial radiation field that is generated by surrounded EDL; and into a mixed flow-through photoreactor (**B4**) with an internal EDL inside of the circulating reaction solution. The many microwave photoreactor used in lab units are based on these designs.

\*Address correspondence to this author at the Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojova 135, 16502 Prague 6, Czech Republic; Tel: +420 220 390 343; Fax: +420 220 920 661; E-mail: cirkva@icpf.cas.cz

## 2.1. Microwave Photochemistry in Batch Reactors

Microwave photochemistry in batch reactor has been investigated over the past decade and can be implemented if external or internal lamps (classical UV lamp vs. EDL) are used. Combination of given variables may lead to the following three types of techniques for batch set-up in a MW field:

- external classical UV lamp (Fig. 1, A1)
- internal EDL (Fig. 1, A2)
- internal EDL inside of double wall (Fig. 1, A3)

### 2.1.1. Batch Photoreactors with External Classical UV Lamp (Type A1)

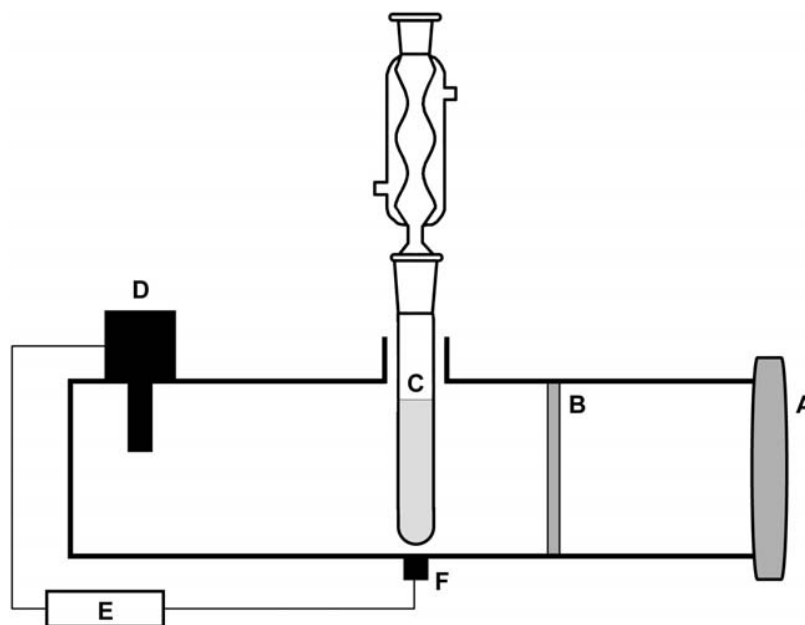
Chemat *et al.* [9] have developed an original MW/UV combined reactor (Fig. 2) based on a commercially available monomode MW reactor (Synthewave 402, Prolabo, France) and an external UV/Vis source (250 W medium-pressure Hg lamp).

The thermal rearrangement (Baker-Venkataraman) [10, 11] of 2-acetylphenyl benzoate in the presence of aluminum pillared bentonite gave 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione

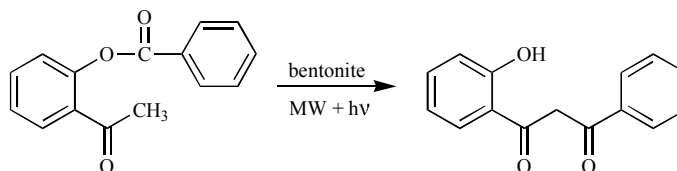
(Scheme 1) in methanol at atmospheric pressure. This reaction is sensitive to UV/Vis irradiation and thermal treatment [12]. Comparative studies were performed for three different conditions: under UV, MW, and simultaneous MW + UV radiation. In all cases, the temperature was kept at 80 °C and the significant activation effect for MW + UV system has been observed. However, the rearrangement was not studied in further detail.

Klán *et al.* [13] investigated the Norrish type II photoreaction of *p*-substituted alkyl aryl ketones (valerophenone, *p*-methylvalerophenone) on alumina or silica gel surfaces by use both monomode MW reactor (Synthewave 402, Prolabo, France) and an external UV/Vis source (200 W high-pressure Hg lamp) (Fig. 2).

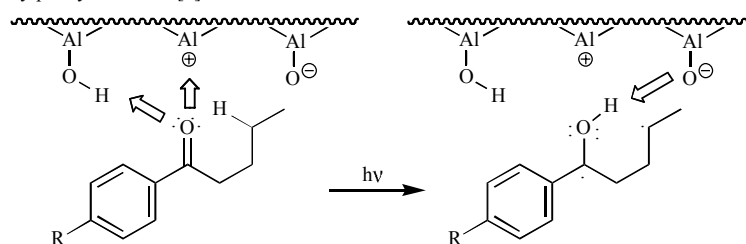
The reaction was studied in terms of the quantum efficiency and the photoproduct distribution as well as the influence of the reaction temperature. A model in which the short-lived biradical intermediate interacts with the surface, in addition to a polar effect on the excited triplet of ketone, has been proposed (Scheme 2). Both acidic and basic sites are present on the amphoteric alumina surface; while the acidic OH groups coordinate to the carbonyl oxygen, the basic groups (AlO<sup>-</sup>) are involved in hydrogen bonding with



**Fig. (2).** Reactor for microwave photochemical experiments based on the Synthewave (Prolabo): (A) external UV/Vis lamp; (B) window of vision; (C) reaction mixture; (D) magnetron; (E) regulation; (F) IR sensor. Adapted from ref. [9].



**Scheme 1.** Rearrangement of 2-acetylphenyl benzoate [9].

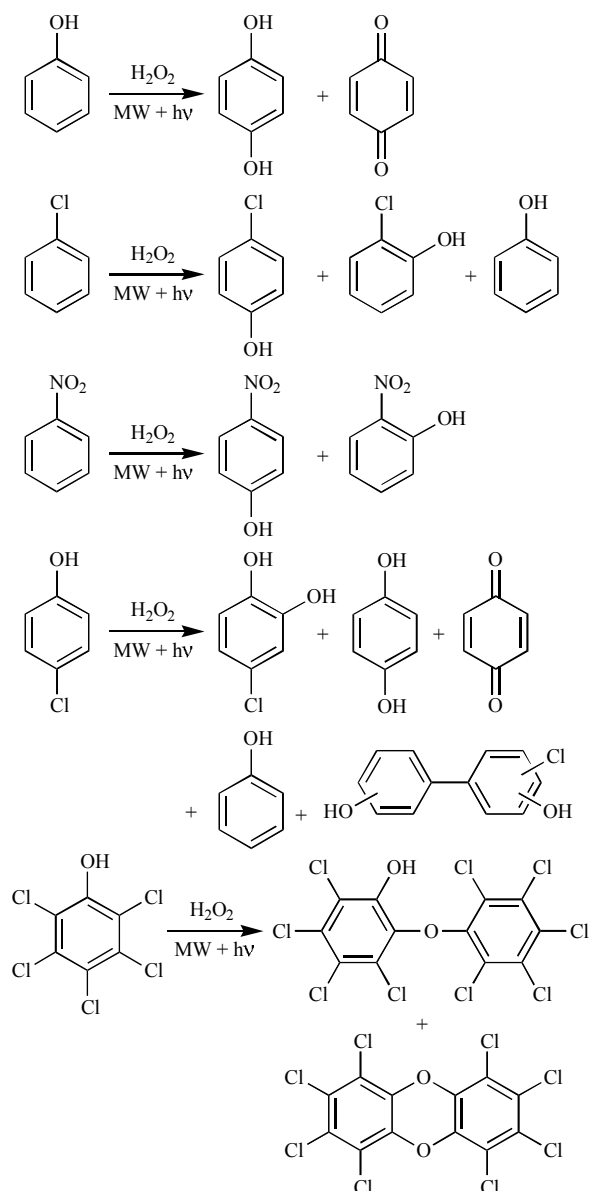


**Scheme 2.** Norrish type II photoreaction of valerophenones on alumina [13].

the OH group of the biradical intermediate. The change in the regioselectivity of the reaction as a result of MW heating was explained in terms of the weakening of such interactions with increasing temperature. The advantage of using the MW radiation for alumina photochemistry is especially in simplicity of both the experiment arrangement and the reaction temperature control.

Klán and Vavřík [14] studied degradation dynamics of five model aromatic compounds (phenol, chlorobenzene, nitrobenzene, 4-chlorophenol, and pentachlorophenol) in aqueous solutions by non-catalytic UV, MW, and combined MW/UV remediation techniques in the presence of  $H_2O_2$ , where the MW field has been used solely as a simple heating method. The combined MW/UV reactor consisted of a MW cavity (modified MW oven, Fig. 4), which had a quartz window for an external UV irradiation (400 W high-pressure Hg lamp) with  $\lambda = 254$  nm.

The degradation dynamics has been monitored to estimate the rate of disappearance of the starting material (relative initial pseudo first-order rate constants,  $k_{rel}$ ) and, in addition, the major photoproducts were identified (Scheme 3). The combined degradation effect



Scheme 3. Main degradation products from MW/UV/ $H_2O_2$  technique [14].

of UV and MW radiation was always larger than the sum of isolated effects. It was concluded that this overall efficiency increase is essentially based on a thermal enhancement of subsequent oxidation reactions of the primary photoreaction intermediates. Optimizations revealed that the simultaneous effect was particularly significant for samples containing low concentration of  $H_2O_2$ , although a large excess of  $H_2O_2$  was essential for complete destruction in most experiments. The results from this work showed that simultaneous MW/UV/ $H_2O_2$  remediation technique offer an attractive alternative to conventional oxidation or photocatalytic degradation methods for environmental remediation of polluted wastewaters. The absence of heterogeneous catalyst is in no doubt an important advantage of this technique.

### 2.1.2. Batch Photoreactors with Internal EDL (Type A2)

Den Besten and Tracy [15] reported on the especially useful and the convenient apparatus with EDL (Fig. 3) for small-scale laboratory photolysis of organic compounds in the solution or for irradiation of gases. In this arrangement the EDL was placed in a reaction solution and was operated by means of an external MW field from radio- or MW-frequency transmitter. The quantum output of the lamp was controlled by changing the output of the transmitter or by using a dilute ionic solution circulating through the cooling jacket. Placing EDL in the solution was quite advantageous, because the full quantum output was used.

Cirkva and Hájek [16] reported the UV or MW/UV initiated radical addition of THF to perfluorohexylethene (Scheme 4). Reactions were carried out under combined MW/UV radiation using a new simple photochemical reactor with quartz Hg-EDL developed for organic synthetic reactions.

In a typical design (Fig. 4), two holes were drilled into the walls of a domestic MW oven, one for a condenser tube in the oven top and second in the side for a fiber optic spectral probe. Part of the oven bottom was replaced with an aluminum plate to enable mag-

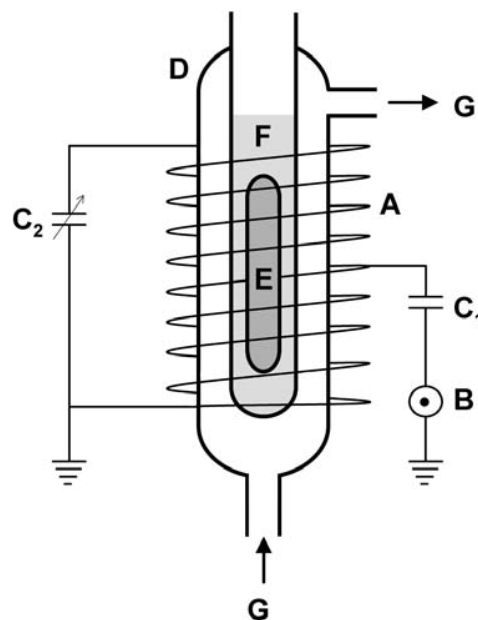
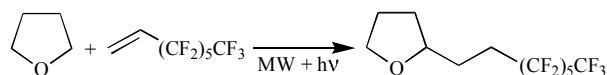
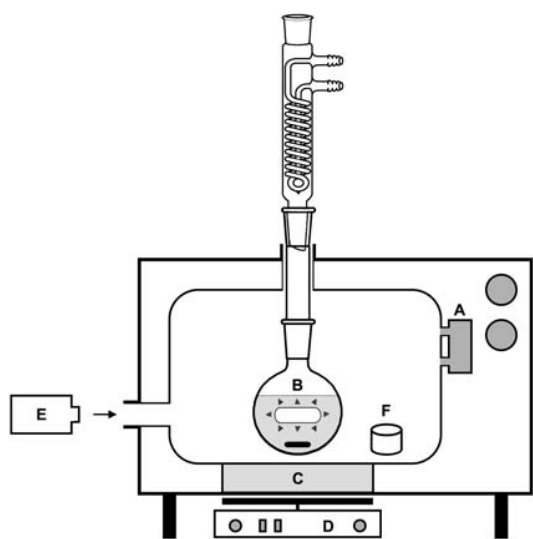


Fig. 3). Apparatus with EDL for UV/Vis irradiation: (A) antenna; (B) transmitter; (C) capacitors; (D) jacketed flask; (E) EDL; (F) reaction mixture; (G) circulating coolant. Adapted from ref. [15].



Scheme 4. Radical addition of THF initiated by MW/UV radiation [16].



**Fig. (4).** MW batch photochemical reactor: (A) reaction mixture with EDL and a magnetic stir bar; (B) Dimroth condenser; (C) aluminum plate; (D) magnetic stirrer; (E) fiber optic spectral probe; (F) dummy load inside the oven cavity [16].

netic stirring. The certain amount of a MW-absorbing solid material (dummy load: basic  $\text{Al}_2\text{O}_3$ , molecular sieve, etc.) was inserted when a small quantity of a non- or poorly absorbing sample was used. The material removed excess MW power and prevented the magnetron from being destroyed by overheating.

In the photochemical reaction, perfluorohexylethene was excited by UV light to a diradical-like triplet state that is able to abstract hydrogen atom from THF to generate the radicals starting a propagation cycle by addition to perfluorohexylethene, and giving the adduct-radical which is transformed to the final product. The comparative experiments with conventional mercury lamps (125 W and 400 W medium-pressure Hg lamp) showed the higher efficiency of EDLs providing high yield of final product in shorter reaction time under reflux of THF.

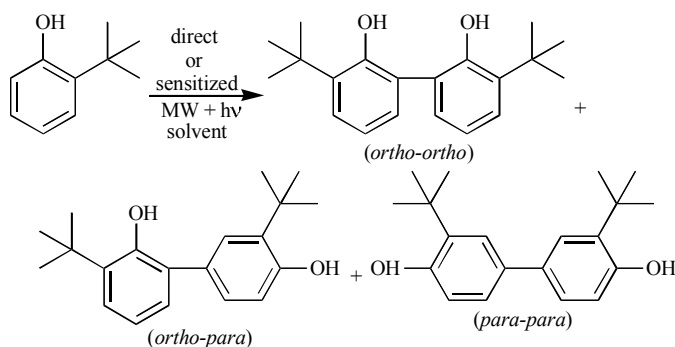
Čirkva *et al.* [17] have investigated an effect of UV and combined MW/UV irradiation on the transformation of 2-*tert*-butylphenol (2TBP) in the presence and the absence of sensitizers with different values of singlet and triplet energy, and in the presence of solvents with different polarity. Reactions were carried out under combined MW/UV irradiation for 2 h at the reflux temperature using a simple photochemical reactor (Fig. 4) with quartz Hg-EDL. No significant specific effects of the combined MW/UV radiation on the distribution of the photoproducts from 2TBP photolysis were observed.

The UV or combined MW/UV irradiation of the 2TBP gave three C-C dimers (Scheme 5): 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (*ortho-ortho*), 3,3'-di-*tert*-butylbiphenyl-2,4'-diol (*ortho-para*), and 3,3'-di-*tert*-butylbiphenyl-4,4'-diol (*para-para*). Their concentration ratios depended on the nature of the solvents and sensitizers used. In non-polar solvents (hexane, heptane, benzene, toluene), direct 2TBP irradiation led to the formation of two photoproducts where *ortho-para* was predominant over *ortho-ortho* dimer. However, irradiation in dipolar aprotic solvent 1,4-dioxane led only to *ortho-ortho* product, and in the case of acetonitrile only to *ortho-para* dimer. In polar solvents (acetic acid, water, methanol/water=1:1 v/v), it led to the formation of all three products.

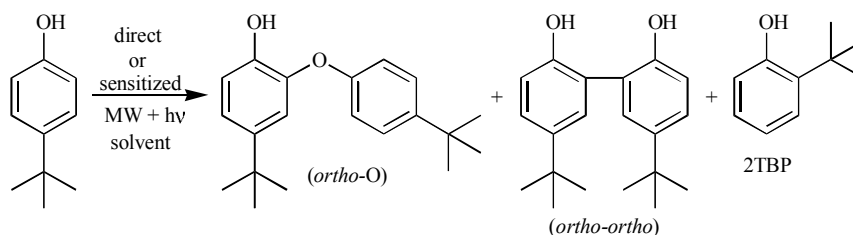
The sensitized 2TBP irradiation (acetophenone, benzophenone, naphthalene, acridine, and anthracene) in hexane gave also *ortho-ortho* and *ortho-para* dimers. The acridine-sensitized reaction in acetonitrile was found to give *ortho-para* and a greater amount of *para-para* dimers. Singlet-sensitized reaction (naphthalene, anthracene) in acetonitrile led to *ortho-para* dimer.

Čirkva *et al.* [18] have also investigated an effect of UV and combined MW/UV irradiation on the transformation of 4-*tert*-butylphenol (4TBP). Reactions were carried out under combined MW/UV irradiation for 2 h at the reflux temperature using a simple photochemical reactor (Fig. 4) with quartz Hg-EDL.

The UV or combined MW/UV irradiation of the 4TBP gave C-O and C-C photoproducts (Scheme 6): 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (*ortho-O*), 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (*ortho-ortho*), and 2TBP as an isomerization by-product. Their concentration ratios depended on the nature of solvents and sensitizers used. In non-polar solvents (hexane, heptane, toluene), direct



**Scheme 5.** Photoreaction products of 2-*tert*-butylphenol (2TBP) [17].



**Scheme 6.** Photoreaction products of 4-*tert*-butylphenol (4TBP) [18].

4TBP irradiation led to the formation of all photoproducts where *ortho-ortho* dimer was predominant over *ortho-O* ether. In acetonitrile *ortho-ortho* dimer was selectively formed under UV and MW/UV irradiation. In 1,4-dioxane and in methanol, no product formation was observed.

The sensitized 4TBP irradiation (acetophenone, benzophenone, naphthalene, and acetone) in acetone gave also all three photoproducts where *ortho-O* ether was predominant. In the presence of singlet sensitizer naphthalene, the reaction of 4TBP in hexane gave mainly *ortho-O* ether and 2TBP, whereas *ortho-ortho* dimer was not found. Triplet-sensitized reaction with acetophenone in hexane led selectively to *ortho-O* ether, while with benzophenone gave moreover 2TBP and its *ortho-ortho* and *ortho-para* dimers (Scheme 5). Again, no specific MW effect was observed.

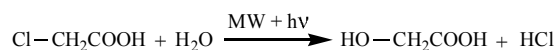
Cirkva and Relich [19] have studied photohydrolysis of aqueous mono-chloroacetic acid (MCAA) into hydroxyacetic acid and HCl (Scheme 7) as the model reaction to evaluate the low-pressure batch MW photoreactor (Fig. 5) equipped with quartz Hg-EDLs. Studies were carried out at relative high MCAA concentration (0.1 mol l<sup>-1</sup>), the desired temperature in the flow-through photoreactor was achieved by altering the total pressure of the system by pump, and the photoreaction course was monitored by the pH change in the solution.

This arrangement provided the unique possibility of studying photochemical reactions under extreme thermal conditions (determination of thermal dependence of photoreaction) with the technical difficulties occurring when the MW photochemical experiments are to be performed at temperature below the boiling point of the solvent.

The effects of operational parameters (reaction temperature, quantum yield) on the MCAA photohydrolysis were investigated. The MCAA conversion was optimized as a result of a trade-off between the thermal dependence of the photochemical quantum yield (which increases with increasing temperature) and the thermal dependence of the EDL light intensity of 254 nm line [20] (which increases with decreasing temperature).

Klán, Literák and Hájek [21] have studied the use of the Pyrex EDLs in a MW photoreactor as first consistent information about the technique, its scope and limitations. The application has been investigated in terms of (i) an operating MW power and temperature influence on the EDL, (ii) solvent polarity influence, (iii) EDL heating capabilities, and (iv) a dependence of the photoreaction efficiencies on the MW power output in various solvents (benzene, cyclohexane, acetonitrile, and ethanol).

It was found that the EDL produced enough heat to quickly warm up any liquid to boil even in case of 'transparent' liquids in the MW field. An efficiency of light-induced photofragmentation reaction of valerophenone (Norrish type II reaction, Scheme 8) was investigated as a function of the MW input power and solvent po-



Scheme 7. Photohydrolysis of mono-chloroacetic acid [19].

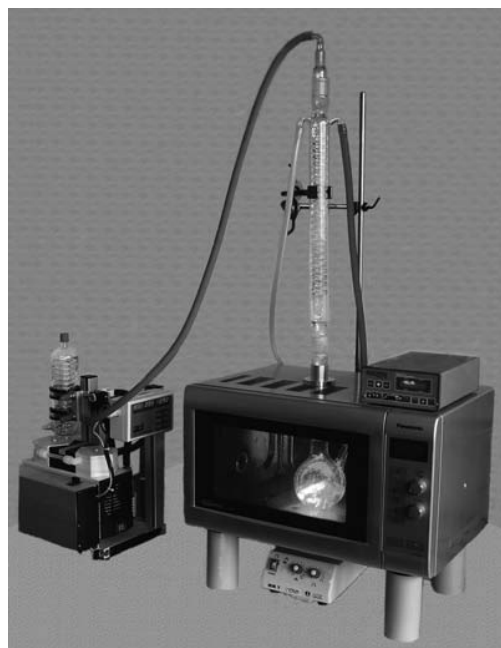
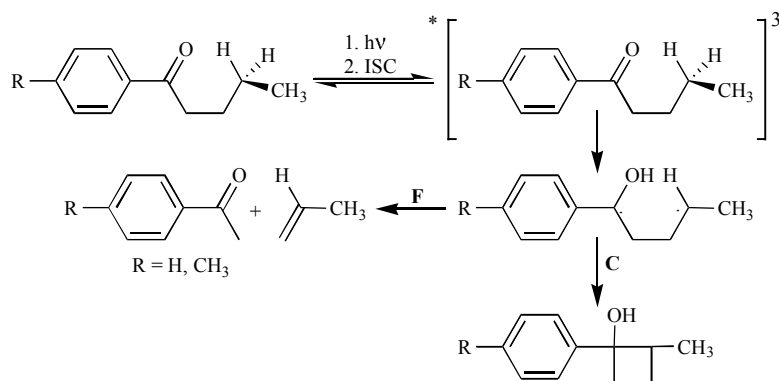


Fig. (5). Low-pressure batch microwave photoreactor [19].

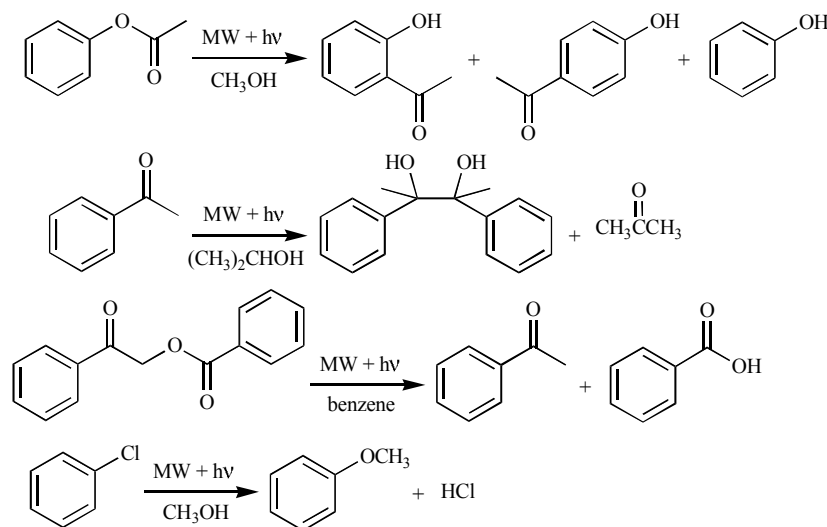
larity. It was found that conversions of acetophenone production showed almost linear dependence on the input MW power. Efficiencies in acetonitrile were higher than those obtained in benzene, only by a factor of 1.2, which was explained by lowering the EDL intensity, thanks to MW absorption by the solvent.

Klán and Literák [22] have investigated five different common photoreactions (Scheme 8 and 9) (Norrish type II reaction of valerophenone and its *p*-methyl derivative in cyclohexane, photo-Fries rearrangement of phenyl acetate in methanol, photoreduction of acetophenone by 2-propanol in cyclohexane, photolysis of a phenacyl benzoate in benzene, and photosubstitution of chlorobenzene in methanol).

The reaction conversions, product distributions, and the relative photochemical efficiencies have been studied in terms of the Hg-EDL quality (quartz vs. Pyrex), size, quantity, and the scale of the MW/UV experiment. In addition, MW experiments were compared to those using a conventional medium-pressure mercury UV lamp.



Scheme 8. Norrish type II reaction (F) and Yang cyclization (C) of valerophenones [21-23, 25].



Scheme 9. Photoreactions in MW field [22, 23].

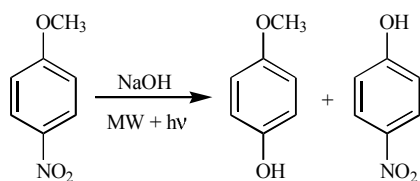
Klán, Literák and Relich [23] have reported the first study of temperature dependent solvent effects in the Norrish type II reaction (Scheme 8) and the photo-Fries reaction (Scheme 9) in the MW field using the quartz and Pyrex Hg-EDL (Fig. 4).

The former process exhibited a linear and reliable temperature dependence which served for the estimation of the microwave superheating effects in four different solvents (ethanol, *t*-butanol, acetonitrile, and methanol) under atmospheric pressure. Their magnitudes were in a perfect agreement with the measured temperature enhancements. Thus, this photochemical system has been proposed as a reliable molecular photochemical thermometer.

Klán *et al.* [24] have studied temperature-sensitive photochemical nucleophilic aromatic substitution ( $S_NAr$ ) of 4-nitroanisole by the sodium hydroxide (Scheme 10) in homogeneous solutions by use of MW heating and EDL (Fig. 4). Photoreaction provides two principal products: 4-methoxy-phenol and 4-nitrophenol. It was found that reaction regioselectivity dramatically changes with temperature in the region of -20 to 196 °C. The quantum yield of the 4-methoxyphenol formation was found to be temperature independent, in contrast to that of the 4-nitrophenol formation, suggesting that there is a temperature dependent process occurring after the partitioning between replacement of the nitro group and the methoxy group. A technique for microwave-assisted photochemical synthesis has been proposed as an efficient and practical tool for organic synthesis.

Klán, Müller and Loupy [25] have reported two temperature-sensitive photoreactions (Norrish type II of valerophenone,  $S_NAr$  of 4-nitroanisole) carried out in high-temperature water (100-200 °C) in a pressurized vessel under MW heating (MicroSYNTH Labstation, Milestone) with quartz Hg-EDL.

The excited valerophenone (Scheme 8) reacted according to the Norrish type II reaction (F) *via* the triplet state to produce triplet 1,4-biradical that can fragment (to acetophenone) (F), cyclize (2-methyl-1-phenyl-cyclobutan-1-ol) (C, Yang cyclization), or dispro-

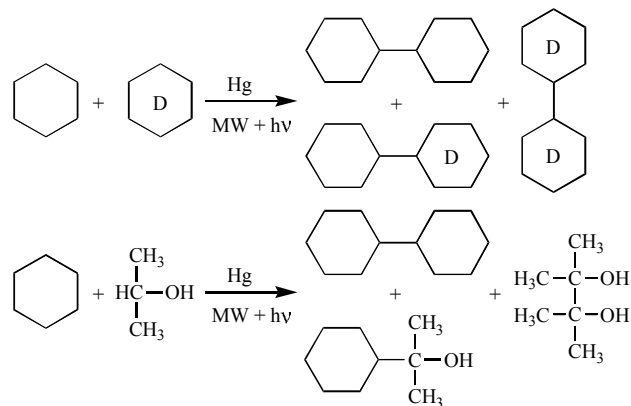
Scheme 10. Photochemical  $S_NAr$  of 4-nitroanisole [24, 25].

portionate back to the starting ketone. The temperature-dependent F/C ratios (i.e. reaction chemoselectivity) in water were increased (from 4.5 to 6.8) with raising temperature. The fact that high temperatures enhanced the fragmentation (F) at the expense of cyclization (C) has been presumably caused by lowering the energy barrier hindering the cleavage of  $C_{\alpha}$ - $C_{\beta}$  bond in the biradical, but above all, due to the favored formation of thermodynamically more stable product (acetophenone).

The second photoreaction studied,  $S_NAr$  on 4-nitroanisole in aqueous NaOH (Scheme 10), proceeded primarily by a thermal pathway. While the irradiation of 4-nitroanisole in basified solutions of aliphatic alcohols resulted in a formation of two photoproducts, only 4-nitrophenol was observed in water at temperatures ranging up to 170 °C.

Nüchter *et al.* [26] have demonstrated the productive power of the MW/UV method by the mercury-sensitized gas-phase dehydrodimerization of cyclohexane and perdeuterocyclohexane (Scheme 11) by use of quartz Hg-EDLs. The simple and multi-step recombination and disproportionation radical mechanisms have been discussed (formation of cyclohexenes and cyclohexylcyclohexenes). This MW/UV laboratory system was suitable for organic synthesis and for the degradation of water contaminants.

Lu *et al.* [27] have studied the synergistic effects of several microwave assisted advanced oxidation processes (MW/AOPs) for the degradation of 4-chlorophenol (4-CP) to hydroquinone and benzo-



Scheme 11. Dehydrodimerization of cyclohexane and perdeuterocyclohexane [26].

quinone (Scheme 3). The photoreactions were performed in a modified MW oven (Fig. 4) with the quartz Hg-EDL.

The efficiencies of the degradation of 4-CP in dilute aqueous solution for a variety of AOPs with or without MW irradiation were compared. The results showed that the synergistic effects between MW/UV and MW/UV/H<sub>2</sub>O<sub>2</sub> resulted in a high degradation efficiency for 4-CP. The degradation rates with MW irradiation were nearly double of those without MW. It seems likely that the role of microwaves in the integrated UV and H<sub>2</sub>O<sub>2</sub> process was to produce more HO• radicals (induced by the localized superheating of MW irradiation) and electronically excited states of 4-CP.

Lu *et al.* [28] have described the degradation of various chlorophenols by the MW-assisted UV photolysis (MW/UV) method in a modified MW oven (Fig. 4) with the quartz Hg-EDL.

The degradation sequences were obtained as 2-chlorophenol > 4-chloro-3-methylphenol > 4-chlorophenol > 2,4-dichlorophenol > 2,4,6-trichlorophenol > pentachlorophenol. The sequence suggests that the increase of chlorine atoms decreases the susceptibility of the aromatic ring to be attacked by the photons generated by the UV radiation.

Sun *et al.* [29] have investigated the photodegradation of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) in aqueous solution using the Pyrex Hg-EDLs. The main degradation product was 2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine (Scheme 12) according to dechlorination-hydroxylation mechanism. In addition, some other minor degradation products were formed, i.e. 2-chloro-4,6-diamino-1,3,5-triazine (dealkylation process) and N-(4-chloro-6-isopropylamino-1,3,5-triazin-2-yl)acetamide (alkylic-oxidation process).

An experimental design was conducted to assess the influence of various parameters: pH value, initial concentration, amount of EDL, initial solution volume, and coexisted solvent (acetone, methanol). Atrazine was degraded completely in a relatively short time.

Hong *et al.* [30] have studied the MW-assisted direct photolysis of bromophenol blue (BPB) in aqueous solutions using the Pyrex Hg-EDLs (Fig. 4). BPB was efficiently photodegraded (Scheme 13) into 2-hydroxybenzoic acid and 3,5-dibromo-4-hydroxybenzoic acid which were further mineralized. The influence of fac-

tors as MW output power, light intensity, and initial concentration of BPB on photodegradation was investigated.

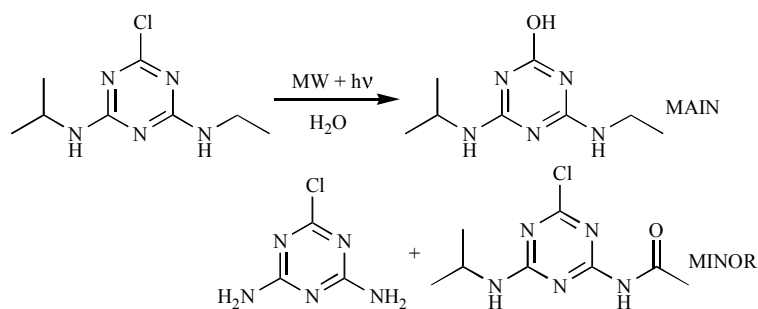
Horikoshi *et al.* [31] have developed a novel MW EDLs for wastewater treatment with Advanced Oxidation Processes (AOPs) using environment risk-free gases (*e.g.*, xenon, nitrogen, helium, oxygen, hydrogen, and argon alone or a mixture thereof). The EDLs were optimized through an examination of the light intensity of the emitted radiation in the UV/Vis spectral region at controlled pressures and gas-mixture ratios and to test whether the gases self-ignite on irradiation with microwaves.

The usefulness of the EDLs was assessed by examining the degradation of aqueous 2,4-dichlorophenoxyacetic acid (2,4-D) irradiated simultaneously by both MW and UV radiation. The decomposition efficiencies for the disposal of the 2,4-D herbicide were compared with the EDL in close contact (inside) and with the EDL located outside the reactor. Degradation of 2,4-D with the EDL was monitored spectroscopically and by the loss of total organic carbon (TOC).

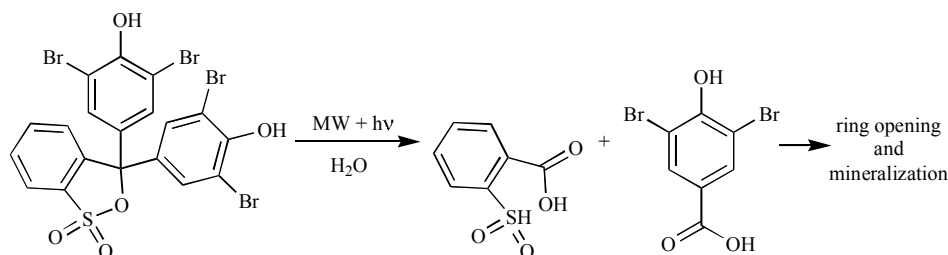
Knapp and Florian [32] have developed a novel, MW-assisted, high-temperature UV digestion procedure for the accelerated decomposition of interfering dissolved organic carbon (DOC) prior to trace element analysis of liquid samples such as industrial/municipal wastewater, body fluids, infusions, beverages, and sewage. The technique has been based on the closed multiwave MW digestion device (Fig. 6) equipped with a quartz pressure reaction vessel containing the quartz Hg-, Cd-, and Zn-EDLs (254, 228, and 213 nm). To enhance excitation efficiency (solution is shielding for the MW) an appropriate metal antenna (W wire and Mo foil in length 3 cm) was fixed on top of the EDL to focus the MW field.

The performance of each EDL prototype was evaluated by MW/UV oxidation of the tested solution (potassium hydrogen phthalate C<sub>8</sub>H<sub>5</sub>KO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, and HNO<sub>3</sub>) following the given digestion procedure and subsequent determination of the mineralization efficiency by the remaining DOC.

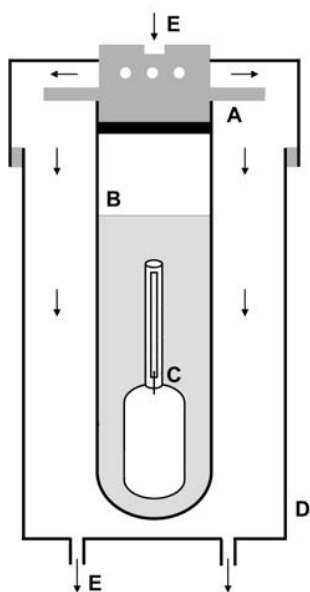
Limbeck [33] has developed a procedure for the selective determination of Pd in environmental aquatic solutions using a MW-assisted UV-digestion using the quartz Cd-EDL (228 and 326 nm). The method was applied to quantify the water-soluble fraction of Pd in urban road dust.



Scheme 12. Photodegradation of atrazine [29].



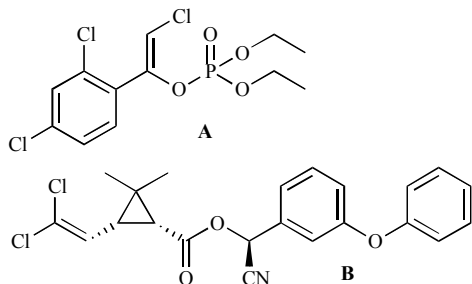
Scheme 13. Photodegradation of bromophenol blue (BPB) [30].



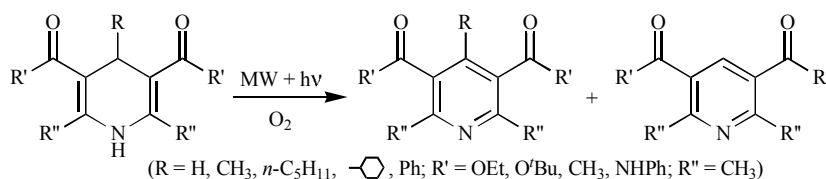
**Fig. (6).** Simplified schematic of a high-pressure digestion vessel with the quartz EDL: (A) plug and seal; (B) quartz pressure reaction vessel with a sample solution; (C) EDL with an antenna; (D) PEEK vessel jacket with a screw cap; (E) air flow. Adapted from ref. [32].

Matusiewicz and Stanisz [34] have developed a novel, MW-assisted, high-temperature/high-pressure UV-TiO<sub>2</sub> digestion procedure for the accelerated decomposition of four certified reference material (serum, urine, milk, arsenobetaine solution) using the quartz Cd-EDLs (228 nm).

Nogueira *et al.* [35] have evaluated the coupling of MW radiation with photo-Fenton reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + h\nu$ ) for the insecticide residues decomposition using the quartz Cd-EDLs (228 nm) [32]. This strategy was performed in a focused MW digestion oven with open quartz vessel (Fig. 6). The results were based on residual carbon content. The operational conditions were established considering the extent of decomposition (>98%) for a commercial insecticide concentrate: Chlorfenvinphos (2-chloro-1-(2,4-dichlorophenyl)vinyl diethyl phosphate) and Cypermethrin (cyano(3-phenoxyphenyl)methyl) 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (Scheme 14) used for the bovine ticks (*Boophilus microplus*) control.



**Scheme 14.** Chlorfenvinphos (A) and Cypermethrin (B) [35].

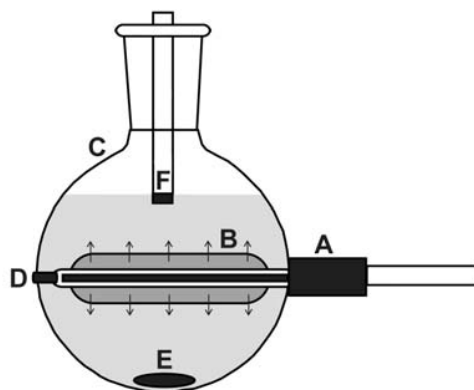


**Scheme 15.** Photooxidation of 1,4-dihydropyridines to pyridines [36].

Leadbeater *et al.* [36] have used the conjunction MW/UV radiation for the efficient oxidation of the 1,4-dihydropyridines to the corresponding pyridines (Scheme 15). The reactions were performed in sealed vessel in acetonitrile using molecular oxygen (1000 kPa) as the oxidant and quartz Hg-EDL as the irradiation source (150 °C, 30 min, 100% conversion). In an open vessel reactor at reflux and simply bubbling oxygen through the solution, the reaction gave only an 11% yield at 12% conversion. It has been shown that both oxygen and UV irradiation are keys to the success of the reaction.

The outcome of the oxidation depended on the 1,4-dihydropyridine substrate used. When the substituent at the 4-position was an aromatic ring, the only substituted pyridine was found. However, when an alkyl group was in 4-position, the formation of the corresponding de-alkylated pyridine product was also observed.

Ferrari *et al.* [37] have presented the characteristic features of a novel MW/UV photoreactor with the coaxial quartz Hg-EDL (Fig. 7) using an immersed MW source as the coaxial MW antenna connected with flexible coaxial cable without the need of a MW oven.

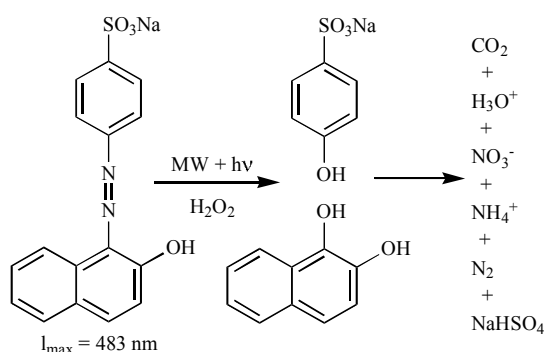


**Fig. (7).** Immersed microwave photoreactor with the coaxial dipole antenna: (A) MW antenna with coaxial cable; (B) coaxial quartz EDL; (C) quartz flask with reaction mixture; (D) clamping post; (E) magnetic stir bar; (F) spectral probe. Adapted from ref. [37].

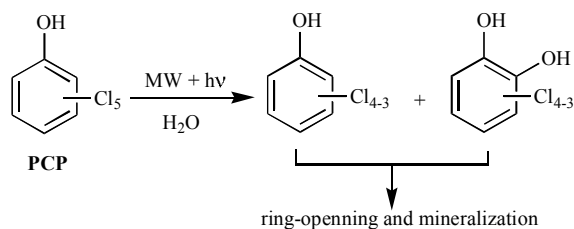
The new equipment was tested in MW/UV/H<sub>2</sub>O<sub>2</sub> process on the photo-decoloration of Acid Orange 7 azo dye (AO7; sodium 4-[(2-hydroxynaphthalen-1-yl)diazenyl]benzenesulfonate). The oxidative degradation of AO7 (Scheme 16) occurs in three stages and starts with the breaking of the azo bond to form sodium 4-hydroxybenzenesulfonate and naphthalene-1,2-diol. The second stage includes the hydroxylation to polyhydroxylated derivatives, which are oxidized in their turn to quinoid structures, they then lead to the formation of short-chain carboxylic acids. The third stage involves the oxidation to CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and NaHSO<sub>4</sub>.

Yang and Sun [38] have tested the MW-assisted direct photolysis (MADP) of aqueous solution of pentachlorophenol (PCP) using the quartz Hg-EDLs. The PCP was after excitation effectively decomposed by reductive dechlorination and the major intermediates were tetrachlorophenols, trichlorophenols, and chlorocatechols (Scheme 17), and finally the ring-opening and the complete mineralization have been observed.





Scheme 16. Photo-decoloration of Acid Orange 7 with  $\text{H}_2\text{O}_2$  [37].

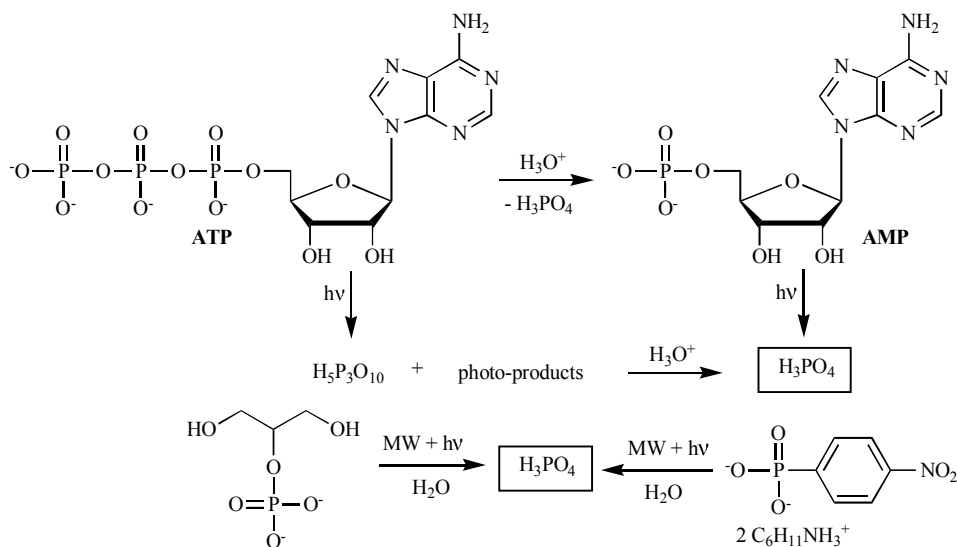


Scheme 17. Photolysis of pentachlorophenol (PCP) [38].

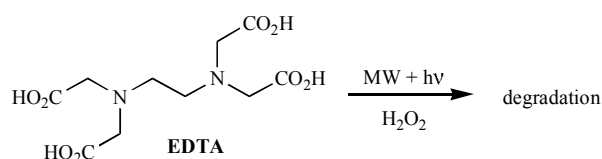
### 2.1.3. Batch Photoreactors with EDL Inside of Double Wall (Type A3)

Howard *et al.* [39] have employed the novel beaker shaped quartz Hg-EDL in the breakdown of organophosphates (ATP, 2-glycerophosphate, and 4-nitrophenylphosphate) into  $\text{H}_3\text{PO}_4$  (Scheme 18) in preparation for colorimetric phosphate determination.

Peralta-Zamora *et al.* [40] have reported the hydrogen peroxide-assisted photodegradation of ethylenediaminetetraacetic acid (EDTA) using the MW-activated quartz Hg-EDL photoreactor (Umex, Germany). The effect of pH and  $\text{H}_2\text{O}_2$ /EDTA molar ratio on the efficiency of the EDTA degradation (Scheme 19) has been evaluated. The optimized experimental conditions (pH of 2 and  $\text{H}_2\text{O}_2$ /EDTA molar ratio of 10) and monitoring the EDTA degradation by TOC analysis have led to the mineralization ratios higher than 90% at reaction times of 6 min.



Scheme 18. Decomposition of organophosphates to  $\text{H}_3\text{PO}_4$  [39].



Scheme 19. Photodegradation of EDTA [40].

Grassi *et al.* [41] have evaluated the efficiency of a new procedure for the digestion of natural waters, based on a MW-activated quartz Hg-EDL photochemical reactor (Umex, Germany). Fluorescence spectra showed a 100% reduction in the emission of humic acid solution in the presence of  $\text{H}_2\text{O}_2$  and in the concentration of dissolved organic carbon (DOC).

Bergmann *et al.* [42] have developed the MW photoreactors (Umex, Germany) equipped with quartz Hg-EDL for the disinfecting drinking, waste and feed waters with microorganism suspension (*Bacillus subtilis*, *Saccharomyces cerevisiae*, and *Escherichia coli*). The experiments have been performed both in a batch and a flow-through mode.

## 2.2. Microwave Photochemistry in Flow-through Reactors

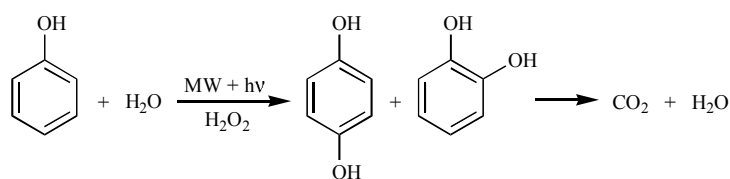
Microwave photochemistry in a flow-through reactor has been investigated over the past decade and can be implemented if classical UV lamp vs. EDL has been used. The combination of given variables may lead to the following four types of techniques for flow-through set-up in a MW field:

- internal classical UV lamp (Fig. 1, B1)
- annular reactor with internal EDL (Fig. 1, B2)
- cylindrical reactor surrounded with EDL (Fig. 1, B3)
- mixed reactor with internal EDL (Fig. 1, B4)

### 2.2.1. Flow-through Photoreactors with Internal Classical UV Lamp (Type B1)

Han *et al.* [43] have investigated the oxidative decomposition of aqueous phenol (Scheme 20) into hydroquinone, catechol, and consequently to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in MW/UV/ $\text{H}_2\text{O}_2$  system equipped with one low-pressure Hg lamp located at the center of the reactor. The removal photoefficiency was determined by TOC measuring.

It was claimed that MW radiation could considerably enhance the phenol degradation even under a suppression of thermal effect. The kinetic analysis showed that an indirect reaction of phenol with



**Scheme 20.** Oxidative photodecomposition of phenol [43].

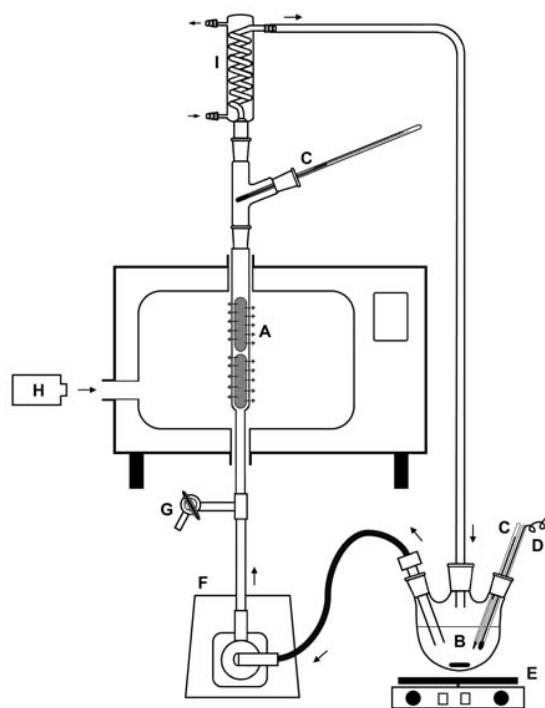
OH<sup>•</sup> radical might be dominant in the absence of MW radiation, meanwhile a direct reaction of phenol with H<sub>2</sub>O<sub>2</sub> might be dominant in the presence of MW radiation except for low concentrations of H<sub>2</sub>O<sub>2</sub>.

### 2.2.2. Annular flow-through Photoreactors with Internal EDL (Type B2)

Cirkva and Relich [19] have studied photohydrolysis of aqueous mono-chloroacetic acid (MCAA) into hydroxyacetic acid and HCl (Scheme 7) as the model reaction to evaluate the flow-through MW photoreactor (Fig. 8, 9) equipped with quartz Hg-EDLs. Studies were carried out at relative high MCAA concentration (0.1 mol l<sup>-1</sup>), the desired temperature in the flow-through photoreactor was achieved by adjustment of the pump flow speed, and the photoreaction course was monitored by the pH change in the solution.

The effects of operational parameters (reaction temperature, quantum yield) on the MCAA photohydrolysis were investigated. The MCAA conversion was optimized as a result of a trade-off between the thermal dependence of the photochemical quantum yield (which increases with increasing temperature) and the thermal dependence of the EDL light intensity of 254 nm line [20] (which increases with decreasing temperature).

Ferrari *et al.* [37] have also presented the characteristic features of a novel flow-through MW/UV photoreactor with the coaxial quartz Hg-EDL (analogy to Fig. 7, Chap. 2.1.2.) using an immersed MW source as the coaxial MW antenna connected with flexible



**Fig. (8).** MW flow-through photochemical reactor: (A) reaction tube with EDLs; (B) glass reservoir with magnetic stir bar; (C) thermometer; (D) pH electrode; (E) magnetic stirrer; (F) PTFE diaphragm pump; (G) outlet; (H) spectrometer with a fiber-optic probe; (I) cooling condenser [19].

coaxial cable without the need of a MW oven. The new equipment was tested in MW/UV/H<sub>2</sub>O<sub>2</sub> process on the photo-decoloration of Acid Orange 7 azo dye (Scheme 16).

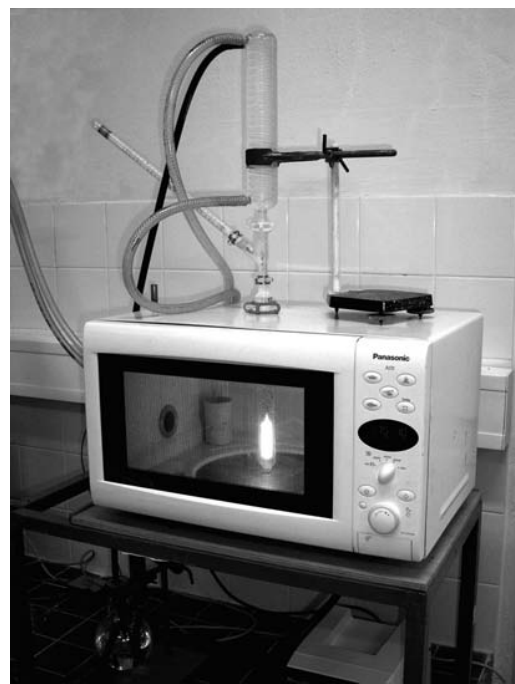
Dong, Hou *et al.* [44] have studied the photolysis of simulating low concentration (25 mg m<sup>-3</sup>) of hydrogen sulfide malodorous gas under UV irradiation emitted by the self-made quartz EDLs (Hg: 185.0 and 253.7 nm; I<sub>2</sub>: 178.3, 180.1, 183.0, 184.4, 187.6, 206.2, and 342 nm) in the flow-through gas MW/UV process.

Experiments results showed that the removal H<sub>2</sub>S efficiency ( $\eta_{\text{H}_2\text{S}}$ ) was decreased with increasing initial H<sub>2</sub>S concentration and increased slightly with gas residence time. Also, effect of the radial UV radiation diffusion was observed on the H<sub>2</sub>S removal efficiency that it was decreased dramatically with enlarged pipe diameter. The primary photolysis of H<sub>2</sub>S produced HS + H both direct and indirect (O<sup>•</sup>, HO<sup>•</sup>) reaction. The main photoproduct was confirmed to be SO<sub>4</sub><sup>2-</sup> with ion chromatography.

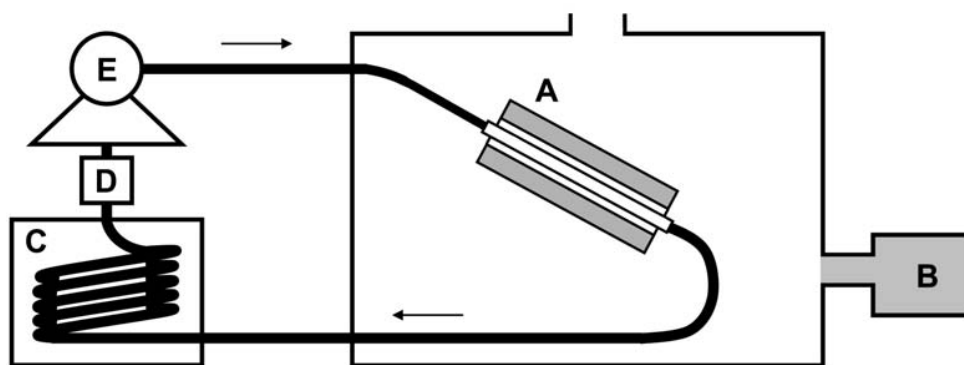
### 2.2.3. Cylindrical flow-through Photoreactors Surrounded with EDL (Type B3)

Horikoshi *et al.* [45] have proposed the novel double cylindrical photoreactor (Fig. 10) equipped with the quartz Hg/Ne-EDL for photosensitization of an aqueous rhodamine-B solution. The extent of photodegradation was monitored by UV/Vis spectroscopy and by decrease of TOC.

Bergmann *et al.* [42] have also developed the flow-through MW photoreactor (Umex, Germany) equipped with quartz Hg-EDL for the disinfecting drinking, waste and feed waters with microorganism suspension (*Bacillus subtilis*, *Saccharomyces cerevisiae*, and *Escherichia coli*).



**Fig. (9).** Flow-through microwave photochemical reactor [19].



**Fig. (10).** MW flow-through photochemical reactor: (A) cylindrical quartz Hg-EDL with sample solution; (B) magnetron; (C) cooling device; (D) thermometer; (E) peristaltic pump. Adapted from ref. [45].

#### 2.2.4. Mixed Flow-Through Photoreactors with Internal EDL (Type B4)

Lu *et al.* [46] have studied the degradation of aqueous 4-chlorophenol (4-CP) by direct photolysis in a MW-assisted EDL system (quartz Hg-EDL). The effect of operational parameters was assessed and the degradation was enhanced in alkaline solution by increasing the irradiation EDL intensity, purging with oxygen, and adding  $\text{H}_2\text{O}_2$  to the solution.

The 4-CP degradation methodology follows pseudo-first-order decay kinetic and a general reaction pathway for the degradation of 4-CP was proposed. The major intermediates (GC/MS analysis) were hydroquinone, benzoquinone, and 4-chlorocatechol (see Scheme 3). Key reactions involved in the photodegradation of 4-CP were: (a) hydroxylation of the aromatic ring, (b) substitution of chlorine by  $\text{OH}^\cdot$ , and (c) oxidation to major intermediates (*vide supra*).

Zhang *et al.* [47, 48] have studied the oxidative degradation of Acid Orange 7 azo dye (AO7; sodium 4-[(2-hydroxynaphthalen-1-yl)diazonyl]benzenesulfonate) (see Scheme 16) in the MW/UV/ $\text{H}_2\text{O}_2$  process using the quartz Hg-EDL. The removal photoefficiency (decolorization and mineralization) was determined by TOC measuring.

The simultaneous effect of both UV/Vis light and MW radiation was investigated: the EDL process was 32% more effective than process with traditional electrode lamp. Also, the effect of operation parameters (initial AO7 concentration,  $\text{H}_2\text{O}_2$  dosage, and pH) was studied. The kinetic model (pseudo-first order reaction) showed that not only the  $\text{OH}^\cdot$  radical oxidation but also the direct photolysis were considered.

Horikoshi *et al.* [49] have examined the photo-oxidative destruction of bisphenol A (BPA) and 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous media by the VUV-transparent quartz W-triggered Hg-EDL (185 and 254 nm) under MW irradiation in the flow-through process. The 185 nm radiation causes homolytic cleavage of the water molecule to produce  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  radicals and oxidize molecular oxygen to ozone and to singlet oxygen as the powerful oxidizing agents. This novel EDL provides an additional light source for AOPs without the need for a metal-oxide photocatalyst.

Horikoshi *et al.* [50] have developed a metallic condensing cone that concentrates MW radiation (equivalent to an optical lens) into the MW/UV photoreactor and used as part of a system to activate the quartz Hg-EDL (185 and 254 nm) in the oxidative treatment of wastewaters. This approach to self-ignition of an EDL immersed in solution led to considerable energy savings in such treatments.

System performance was examined for investigating the photolytic transformation (direct photolysis vs. oxidation by  $\text{OH}^\cdot$  radicals) of aqueous solutions of the three contaminants: 4-chlorophenol

(4-CP), 2,4-dichlorophenoxyacetic acid (2,4-D), and 4,4'-isopropylidenediphenol (bisphenol-A; BPA). The effect of operational parameters (MW power, immersion level, aeration) was also assessed.

### 3. CONCLUSION

In this review, we present a new method for carrying out photochemical reactions with high efficiency in the microwave field. The objective of microwave photochemistry is frequently, but not necessarily, connected to the electrodeless discharge lamp (EDL) as a novel light source which generates efficiently UV/Vis radiation when placed into a microwave field. This article is focused on applications of the EDLs in organic synthesis. Novel microwave photochemical reactors with different arrangement of the lamps both in a batch and a flow-through experimental set-up are described.

We have discussed how the concept of microwave photochemistry is already an important issue in synthetic chemistry and material science. Although still in the beginning, detailed analysis of past and present literature confirms explicitly the usefulness of this method of chemical activation. The application of EDL simplifies the technical procedure, especially in the field of organic photochemical synthesis, environmental chemistry, or analysis.

In the offing we are able to prepare the Part 3 of our comprehensive review about *Microwave photocatalysis*.

### ABBREVIATIONS

AOPs	=	Advanced oxidation processes
DOC	=	Dissolved organic carbon
EDLs	=	Electrodeless discharge lamps
MW	=	Microwave
MADP	=	MW-assisted direct photolysis
TOC	=	Total organic carbon
UV/Vis	=	Ultraviolet/visible

### ACKNOWLEDGMENT

Thanks are due to the Grant Agency of the Czech Republic (104/07/1212) for funding this research. We are also grateful to Milestone s.r.l. (Italy) for their technical support.

### REFERENCES

- [1] Klán, P.; Cirkva, V. *Microwaves in Photochemistry*; In: *Microwaves in Organic Synthesis*; Loupy, A., Ed.; Wiley-WCH: Weinheim, Germany, 2006; Vol. 2, pp. 860-897.
- [2] Cirkva, V.; Žabová, H. *Thin Nanoporous Titania Films on the Electrodeless Discharge Lamps For Photocatalysis*. In: *Handbook of Photocatalysts*:

- Preparation, Structure and Applications*; Castello, G.K., Ed.; Nova Science Publishers: New York, USA, 2010; Chap. 3.
- [3] Cirkva, V.; Žabová, H. *Photocatalysis on Titania-Coated Electrodeless Discharge Lamps*; Nova Science Publishers: New York, USA, 2010.
- [4] Horikoshi, S.; Abe, M.; Serpone, N. Novel design of microwave discharge electrodeless lamps (MDEL) in photochemical applications. Use in advanced oxidation processes. *Photochem. Photobiol. Sci.*, 2009, 8, 1087-1104.
- [5] Horikoshi, S.; Serpone, N. Photochemistry with microwaves. Catalysts and environmental applications. *J. Photochem. Photobiol. C*, 2009, 10, 96-110.
- [6] Cirkva, V.; Relich, S. Microwave photochemistry and photocatalysis. Part 1: Principles and overview. *Curr. Org. Chem.*, 2011, 15, 248-264.
- [7] Braun, A.M.; Maurette M.-T.; Oliveros, E. *Photochemical Technology*; Wiley & Sons: Chichester, UK, 1991.
- [8] Oppenländer, T. *Photochemical Purification of Water and Air*; Wiley-VCH: Weinheim, Germany, 2003.
- [9] Chemat, S.; Aouabed, A.; Bartels, P.V.; Esveld, D.C.; Chemat, F. An original microwave-ultra violet combined reactor suitable for organic synthesis and degradation. *J. Microw. Power Electromagnet. Energy*, 1999, 34, 55-60.
- [10] Baker, W. Molecular rearrangement of some o-acyloxyacetophenones and the mechanism of the production of 3-acylchromones. *J. Chem. Soc.*, 1933, 1381-1389.
- [11] Mahal, H.S.; Venkataraman, K. Synthetical experiments in the chromone group. XIV. Action of sodamide on 1-acyloxy-2-acetonaphthones. *J. Chem. Soc.*, 1934, 1767-1769.
- [12] Bansal, V.; Singh, P.K.; Khanna, R.N. New synthesis of 1,3-diarylpropane-1,3-diones. *Indian J. Chem.*, 1996, 35, 586-587.
- [13] Literák, J.; Klán, P.; Heger, D.; Loupy, A. Photochemistry of alkyl aryl ketones on alumina, silica-gel and water-ice surfaces. *J. Photochem. Photobiol. A*, 2003, 154, 155-159.
- [14] Klán, P.; Vavrik, M. Non-catalytic remediation of aqueous solutions by microwave-assisted photolysis in the presence of H<sub>2</sub>O<sub>2</sub>. *J. Photochem. Photobiol. A*, 2006, 177, 24-33.
- [15] Den Besten, I.E.; Tracy, J.W. Electrodelessly discharged photochemical lamps. *J. Chem. Educ.*, 1973, 50, 303.
- [16] Cirkva, V.; Hájek, M. Microwave photochemistry. Photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation. *J. Photochem. Photobiol. A*, 1999, 123, 21-23.
- [17] Cirkva, V.; Kurfürstová, J.; Karban, J.; Hájek, M. Microwave photochemistry II. Photochemistry of 4-tert-butylphenol. *J. Photochem. Photobiol. A*, 2004, 168, 197-204.
- [18] Cirkva, V.; Kurfürstová, J.; Karban, J.; Hájek, M. Microwave photochemistry III. Photochemistry of 4-tert-butylphenol. *J. Photochem. Photobiol. A*, 2005, 174, 38-44.
- [19] Cirkva, V.; Relich, S.; Hájek, M. Microwave photochemistry V: Low-pressure batch and continuous-flow microwave photoreactors with quartz mercury electrodeless discharge lamps. Photohydrolysis of mono-chloroacetic acid. *J. Chem. Technol. Biotechnol.*, 2010, 85, 185-191.
- [20] Müller, P.; Klán, P.; Cirkva, V. The electrodeless discharge lamp: a prospective tool for photochemistry. Part 4. Temperature- and envelope material-dependent emission characteristics. *J. Photochem. Photobiol. A*, 2003, 158, 1-5.
- [21] Klán, P.; Literák, J.; Hájek, M. The electrodeless discharge lamp: a prospective tool for photochemistry. *J. Photochem. Photobiol. A*, 1999, 128, 145-149.
- [22] Literák, J.; Klán, P. The electrodeless discharge lamp: a prospective tool for photochemistry. Part 2. Scope and limitation. *J. Photochem. Photobiol. A*, 2000, 137, 29-35.
- [23] Klán, P.; Literák, J.; Relich, S. Molecular photochemical thermometers: investigation of microwave superheating effects by temperature dependent photochemical processes. *J. Photochem. Photobiol. A*, 2001, 143, 49-57.
- [24] Klán, P.; Růžička, R.; Heger, D.; Literák, J.; Kullhánek, P.; Loupy, A. Temperature-sensitive photochemical aromatic substitution on 4-nitroanisole. *Photochem. Photobiol. Sci.*, 2002, 1, 1012-1016.
- [25] Müller, P.; Loupy, A.; Klán, P. The electrodeless discharge lamp: a prospective tool for photochemistry Part 6. Photochemistry of valerophenone and 4-nitroanisole in high-temperature water. *J. Photochem. Photobiol. A*, 2005, 172, 146-150.
- [26] Nüchter, M.; Ondruschka, B.; Jungnickel, A.; Müller, U. Organic processes initiated by non-classical energy sources. *J. Phys. Org. Chem.*, 2000, 13, 579-586.
- [27] Ai, Z.; Yang, P.; Lu, X. Degradation of 4-chlorophenol by microwave irradiation enhanced advanced oxidation processes. *Chemosphere*, 2005, 60, 824-827.
- [28] Wu, G.; Yuan, S.; Ai, Z.; Xie, Q.; Li, X.; Lu, X. Degradation of various chlorophenols by electrochemical, electro-Fenton, microwave assisted photolytic and microwave assisted photocatalytic methods. *Fresenius Environ. Bull.*, 2005, 14, 703-708.
- [29] Ta, N.; Hong, J.; Liu, T.; Sun, C. Degradation of atrazine by microwave-assisted electrodeless discharge mercury lamp in aqueous solution. *J. Hazard. Mater. B*, 2006, 138, 187-194.
- [30] Hong, J.; Ta, N.; Yang, S.-Q.; Liu, Y.-Z.; Sun, C. Microwave-assisted direct photolysis of bromophenol blue using electrodeless discharge lamps. *Desalination*, 2007, 214, 62-69.
- [31] Horikoshi, S.; Kajitani, M.; Sato, S.; Serpone, N. A novel environmental risk-free microwave discharge electrodeless lamp (MDEL) in advanced oxidation processes: Degradation of the 2,4-D herbicide. *J. Photochem. Photobiol. A*, 2007, 189, 355-363.
- [32] Florian, D.; Knapp, G. High-temperature, microwave-assisted UV digestion: A promising sample preparation technique for trace element analysis. *Anal. Chem.*, 2001, 73, 1515-1520.
- [33] Limbeck, A. Microwave-assisted UV-digestion procedure for the accurate determination of Pd in natural waters. *Anal. Chim. Acta*, 2006, 575, 114-119.
- [34] Matusiewicz, H.; Stanisz, E. Characteristics of a novel UV-TiO<sub>2</sub>-microwave integrated irradiation device in decomposition processes. *Microchem. J.*, 2007, 86, 9-16.
- [35] Gromboni, C.F.; Kamogawa, M.Y.; Ferreira, A.G.; Nóbrega, J.A.; Nogueira, A.R.A. Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water. *J. Photochem. Photobiol. A*, 2007, 185, 32-37.
- [36] Kormos, C.M.; Hull, R.M.; Leadbeater, N.E. Microwave heating in conjunction with UV irradiation: a tool for the oxidation of 1,4-dihydropyridines to pyridines. *Aust. J. Chem.*, 2009, 62, 51-57.
- [37] Ferrari, C.; Longo, I.; Tombari, E.; Bramanti, E. A novel microwave photochemical reactor for the oxidative decomposition of Acid Orange 7 azo dye by MW/UV/H<sub>2</sub>O<sub>2</sub> process. *J. Photochem. Photobiol. A*, 2009, 204, 115-121.
- [38] Yang, S.; Fu, H.; Sun, C.; Gao, Z. Rapid photocatalytic destruction of pentachlorophenol in F-Si-comodified TiO<sub>2</sub> suspensions under microwave irradiation. *J. Hazard. Mater.*, 2009, 161, 1281-1287.
- [39] Howard, A.G.; Labonne, L.; Rousay, E. Microwave driven ultraviolet photodecomposition of organophosphate species. *Analyst*, 2001, 126, 141-143.
- [40] Kunz, A.; Peralta-Zamora, P.; Durán, N. Hydrogen peroxide assisted photochemical degradation of ethylenediaminetetraacetic acid. *Adv. Environ. Res.*, 2002, 7, 197-202.
- [41] Sodr , F.F.; Peralta-Zamora, P.G.; Grassi, M.T. Microwave-assisted photochemical digestion of natural waters: application in partition and speciation studies of copper. *Quim. Nova*, 2004, 27, 695-700.
- [42] Bergmann, H.; Iourtchouk, T.; Sch ps, K.; Bouzek, K. New UV irradiation and direct electrolysis-promising methods for water disinfection. *Chem. Eng. J.*, 2002, 85, 111-117.
- [43] Han, D.-H.; Cha, S.-Y.; Yang, H.-Y. Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H<sub>2</sub>O<sub>2</sub> process and kinetic study. *Water Res.*, 2004, 38, 2782-2790.
- [44] Xia, L.-Y.; Gu, D.-H.; Tan, J.; Dong, W.-B.; Hou, H.-Q. Photolysis of low concentration H<sub>2</sub>S under UV/VUV irradiation emitted from microwave discharge electrodeless lamps. *Chemosphere*, 2008, 71, 1774-1780.
- [45] Horikoshi, S.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV-illumination method II. Characteristics of a novel UV-VIS-microwave integrated irradiation device in photodegradation processes. *J. Photochem. Photobiol. A*, 2002, 153, 185-189.
- [46] Ai, Z.; Yang, P.; Lu, X. Comparison of the direct photolysis and photocatalytic degradation of 4-chlorophenol in a microwave-assisted UV system. *Fresenius Environ. Bull.*, 2004, 13, 550-554.
- [47] Zhang, X.; Wang, Y.; Li, G.; Qu, J. Oxidative decomposition of azo dye C.I. Acid Orange 7 (AO7) under microwave electrodeless lamp irradiation in the presence of H<sub>2</sub>O<sub>2</sub>. *J. Hazard. Mater. B*, 2006, 134, 183-189.
- [48] Zhang, X.; Li, G.; Wang, Y.; Qu, J. Microwave electrodeless lamp photolytic degradation of acid orange 7. *J. Photochem. Photobiol. A*, 2006, 184, 26-33.
- [49] Horikoshi, S.; Miura, T.; Kajitani, M.; Serpone, N. Microwave discharge electrodeless lamps (MDEL). III. A novel tungsten-triggered MDEL device emitting VUV and UVC radiation for use in wastewater treatment. *Photochem. Photobiol. Sci.*, 2008, 7, 303-310.
- [50] Horikoshi, S.; Tsuchida, A.; Sakai, H.; Abe, M.; Sato, S.; Serpone, N. Microwave discharge electrodeless lamps (MDEL) Part IV. Novel self-ignition system incorporating metallic microwave condensing cones to activate MDELs in photochemical reactions. *Photochem. Photobiol. Sci.*, 2009, 8, 1618-1625.