

Microwave Photochemistry and Photocatalysis. Part 1: Principles and Overview

Vladimír Církva* and Stanislav Relich

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

Abstract: The coupled activation of photochemical and photocatalytic reactions by using of two different types of radiation, microwave and UV/Vis, is covered by the new discipline called microwave photochemistry and photocatalysis. Such a connection might have a synergic effect on reaction efficiencies or, at least, enhance them by summing up the individual effects. The objective of this discipline 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 review article is focused on the general principles of microwave photochemistry and photocatalysis, i.e. generation of UV/Vis discharge in EDL (theory of the microwave discharges, construction of EDL, preparation of the thin titania films on EDL, spectral characteristics of EDL, and performance of EDL). Likewise, the various microwave photochemical and photocatalytic reactor types (batch with external or internal light source, flow-through with external light source, annular flow-through with internal EDL, and cylindrical flow-through surrounded with EDL) with different arrangement of the lamps are described. The concept of microwave photochemistry and photocatalysis as an important issue in synthetic chemistry and material science is presented in several tables.

Keywords: Batch and flow-through photoreactor, electrodeless discharge lamp, microwave, photocatalysis, photochemistry, thin titania films.

1. INTRODUCTION

Photochemistry is intrinsically an interdisciplinary field pertaining to all natural sciences and many technical disciplines [1]. Many synthetic chemists shy away from using key photochemical steps [2] that might substantially reduce the number of reaction steps required to synthesize a desired product. The great potential of synthesis lies in many cases when photochemistry achieves what ground-state chemistry cannot. However, the photoinduced reactions are only slowly accepted by the synthetic organic community (only about 1% of the procedures in *Organic Syntheses* and in *Organic Reactions* dealt with photochemistry) [3]. This effect results from two major problems: first, photochemistry is always linked to photophysical aspects of excited states, and second, photochemical processes require an appropriate expensive equipment.

In the meanwhile, the interdisciplinary chemical research became more and more essential. Therefore, a featured application of microwave (MW) energy on photochemical or photocatalytic reactions enables to solve the above mentioned problems. MW radiation is a non-classical energy source, with photoactivation, ultrasound, high pressure, mechanical activation, supercritical fluids, electrochemistry, or plasma discharge. MW activation increases the efficiency of many processes and can simultaneously reduce formation of the byproducts obtained from conventionally heated reactions. Since first reports of the use of MW heating to accelerate organic chemical transformations [4], numerous articles and books have been published on the subject of MW-assisted synthesis and related topics, *microwave chemistry*, has certainly become an important field of modern organic chemistry [5-9]. Chemical processes performed under the action of MW radiation are believed to be affected in part by superheating, hot-spot formation, and polarization [10]. The existence of a specific non-thermal MW effect has been a matter of controversy during the past years [5,11].

Coupled activation of photochemical and photocatalytic reactions by using two different types of radiation, MW and UV/Vis, is covered by the discipline called *Microwave Photochemistry* or *Microwave Photocatalysis*. 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 or photocatalytic change, and MW radiation subsequently affects the course of the subsequent reaction [12].

Microwave chemistry has been also utilized in combination with some other non-conventional activation processes. Such a connection might have a synergic effect on reaction efficiencies or, at least, enhance them by summing up the individual effects. Application of MW radiation to ultrasound (US)-assisted chemical processes has been recently described [13-14]. There have also been attempts to affect electrochemical [15], photochemical [16] and photocatalytic reactions [17].

An earlier comprehensive review on *Microwaves in Photochemistry* [12] was reported by Klán and Církva, and it covers the literature up to 2006 and gives a complete picture of current knowledge of microwave-assisted photochemistry and photocatalysis. This pioneer work provides the necessary theoretical background and some details about synthetic, analytical, environmental and technical applications. Církva and Žabová have published a review [18] that is limited to the thin titania films on the EDLs. It demonstrates outstanding improvement of degradative efficiency in *microwave photocatalysis*. Two other reviews [19,20] from Horikoshi deal with the application of EDLs on the advanced oxidation processes (AOPs) in the photocatalytic environmental remediation of actual pollutants (2,4-D herbicide, bisphenol-A, acetaldehyde, toluene, and dioxins).

This review article about *Microwave Photochemistry and Photocatalysis* is focused on principles and overview in theory of the microwave discharge in EDLs, their construction, spectral characteristics, preparation of titania-coated films, and their performance.

*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

Table 1. Research Groups Concerning with the Microwave-Assisted Photochemistry and Photocatalysis

Head Name, E-Mail Address	Country, Town	Institute	Area ^a
Christofi, Nick n.christofi@napier.ac.uk	Scotland, UK, Edinburgh	School of Life Sciences, Napier University	EDLs
Čírkva, Vladimír cirkva@icpf.cas.cz	Czech Republic, Prague	Institute of Chemical Process Fundamentals, Academy of Sciences	EDLs, MWP, MWPC
Dong, Wen-Bo wbdong@fudan.edu.cn	China, Shanghai	Institute of Environmental Science, Fudan University	EDLs, photolysis
Ferrari, Carlo; Longo, Iginio ferrari@icpf.cnr.it; longo@icpf.cnr.it	Italy, Pisa	Institute for Chemical and Physical Processes, National Research Council	MWP
Horikoshi, Satoshi horikosi@rs.noda.tus.ac.jp	Japan, Noda	Research Institute for Science and Technology, Tokyo University of Science	MWPC
Jou, C.-J. G. george@ccms.nkfust.edu.tw	Taiwan, China, Kaohsiung	Dept of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology	MWPC
Klán, Petr klan@sci.muni.cz	Czech Republic, Brno	Department of Organic Chemistry, Faculty of Science, Masaryk University	MWP
Leadbeater, Nicholas E. nicholas.leadbeater@unconn.edu	USA, CT, Storrs	Department of Chemistry, University of Connecticut	MWP
Leveque, Jean-Marc Jean-Marc.Leveque@univ-savoie.fr	France, Le Bourget du Lac	Laboratoire de Chimie Moléculaire et Environnement, University of Savoie	US MWP
Lu, Xiaohua lxh@hust-esri.com	China, Wuhan	Environmental Science Research, Huazhong University of Science and Technology	MWP, MWPC
Matusiewicz, Henryk Henryk.Matusiewicz@put.poznan.pl	Poland, Poznań	Department of Analytical Chemistry, Politechnika Poznańska	MWPC
Meyer, Andreas ame@umex.de	Germany, Dresden	UMEX GmbH	EDLs, MWP
Qu, Jiuhui; Zhang, Xiwang jhqu@rcees.ac.cn; xiwangzhang@126.com	China, Beijing	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	MWP, MWPC
Skudra, Atis; Revalde, Gita askudra@latnet.lv; gitar@latnet.lv	Latvia, Riga	Institute of Atomic Physics and Spectroscopy, University of Latvia	EDLs
Sun, Darren D.; Zhang, Xiwang ddsun@ntu.edu.sg; xwzhang@ntu.edu.sg	Singapore, Singapore	School of Civil and Environmental Engineering, Nanyang Technological University	MWPC
Yang, Shao-Gui; Sun, Cheng qhjh@nju.edu.cn; envidean@nju.edu.cn	China, Nanjing	School of the Environment, Nanjing University	MWP, MWPC
Wang, Peng pwang73@vip.sina.com	China, Harbin	School of Municipal and Environmental Engineering, Harbin Institute of Technology	MWPC
Zeng, Qing-Fu qfzeng@wuse.edu.cn	China, Wuhan	Engineering Research Center, Wuhan University of Science and Engineering	MWPC

^a see Abbreviations

Novel microwave photochemical and photocatalytic reactors with different arrangement of the lamps in the batch and the flow-through experimental set-up will be described. The presented photochemical and photocatalytic reactions are indexed into several tables, and their detailed description will be the subject of an upcoming review article.

2. MICROWAVE PHOTOCHEMISTRY AND PHOTOCATALYSIS IN THE WORLD

Microwave photochemistry and photocatalysis is a new and young scientific interdisciplinary branch. The investigation in this field includes the knowledge of microwave chemistry, photochemistry and photocatalysis, which are intensified by informations from plasma chemistry, electrotechnics and material sciences. This scien-

tific branch is now dynamically developing and the number of publications is exponentially increasing (2 papers in 1998, 6 papers in 2003, and 12 papers in 2008).

The research groups in the world concerning with microwave-assisted photochemistry and photocatalysis are mentioned in Table 1. Investigations are carried out mainly in Europe (Czech Republic, France, Germany, Italy, Latvia, Poland, UK) and Asia (China, Japan, Singapore); only one place is from North America (USA).

3. GENERATION OF UV/VIS DISCHARGE IN EDLS

The objective of MW-assisted photochemistry and photocatalysis 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 MW field [12].

The EDL [21] consists of a glass envelope tube filled with an inert gas and an excitable substance and it is sealed under a lower pressure. MW field can trigger gas discharge causing the emission of UV/Vis radiation. This phenomenon has been studied for many years and was well understood in the 1960s [22]. The term “electrodeless” means that the lamps lack the electrodes within the envelope and as such the EDLs may be at large shaped depending on application. The history of the scientific development and practical application of high-frequency EDLs as optical spectral source goes back to the 1930s [23]. Jackson [24] began to use the radiation of a discharge to study the hyperfine structure of the cesium, indium and rubidium lines. A similar design of the spectral source was used by William F. Meggers [25] to excite the spectra of various elements, i.e. the mercury isotope ^{198}Hg for a precise standard of length for use in spectroscopy and metrology.

However, such light sources have not been widely used because of technical difficulties connected with the creation of the high-frequency field (i.e. MW), the lack of pure noble gases and metals. The EDL is usually characterized by a higher emission intensity than that of hollow cathode lamps, lower contamination, because of the absence of the electrodes, and a longer lifetime [26]. The lamps were used in various applications as light sources as well as in atomic spectrometers.

3.1. Theory of the Plasma-Chemical Microwave Discharges

Plasma is an ionized gas, a distinct fourth state of matter. “Ionized” means that at least one electron is not bound to an atom, converting the atoms into positively charged ions, which make plasma electrically conductive, internally interactive, and strongly responsive to MW field [27].

The theory of Hg-EDL operation is shown in Fig. (1). Free electrons in the fill (i.e. electrons that have become separated from the environment because of the ambient energy) accelerate as a result of the MW field energy [12]. They collide with the argon atoms and ionize them to release more electrons. The repetitive effect causes the number of electrons to increase significantly over a short period of time, an effect known as an “avalanche”. The energetic electrons collide with the heavy-atom particles (argon or mercury) present in the plasma, exciting them from a ground state to higher energy levels. The excitation energy is then released as UV/Vis radiation with spectral characteristics which depend on the composition of the envelope. The excited molecular or atomic spe-

cies in the plasma can emit photons over very broad portion of the electromagnetic spectrum, ranging from x-rays to the IR [28].

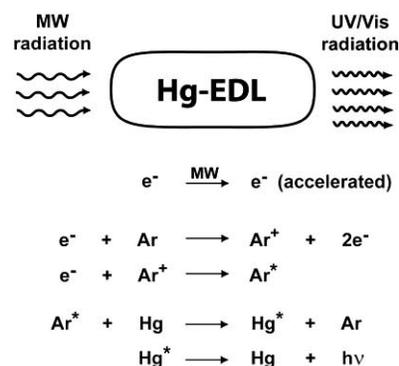


Fig. (1). Principle of Hg-EDL operation and the release of UV/Vis radiation [12].

3.2. Construction of the MW-powered EDLs

The EDL system is modular and consists of two basic parts, a gas filled bulb and a MW power supply with magnetron. A typical EDL is made of a quartz or Pyrex tube envelope, which contains a noble gas and an excitable substance. The envelope material must be impermeable to gases, an electrical insulator, and chemically resistant to the filling compounds at the temperature of operation.

The construction of microwave-excited EDLs is relatively straightforward but there are a number of operating parameters in their preparation which have to be considered in order to produce an intense light source. The desired characteristics and requirements for EDL are high intensity, great stability, long lifetime, and to a lesser extent, low cost and high versatility. In practice, it is very difficult to simultaneously meet all these desired characteristics.

General procedures of EDL construction are available in the literature [29-31]. However, many minor details which are critical for the lamp proper function are often omitted. The investigator who wants to make an EDL is thus faced with a very large amount of information dispersed in the literature, and finds that it is very difficult to reproduce these procedures to develop EDLs having desired properties. An experimental vacuum system for EDL (Hg, HgI_2 , Cd, I_2 , KI, P, Se, and S) construction has been recently designed by Církva *et al.* (Fig. 2) [32]. The Pyrex EDL blank was cleaned in a

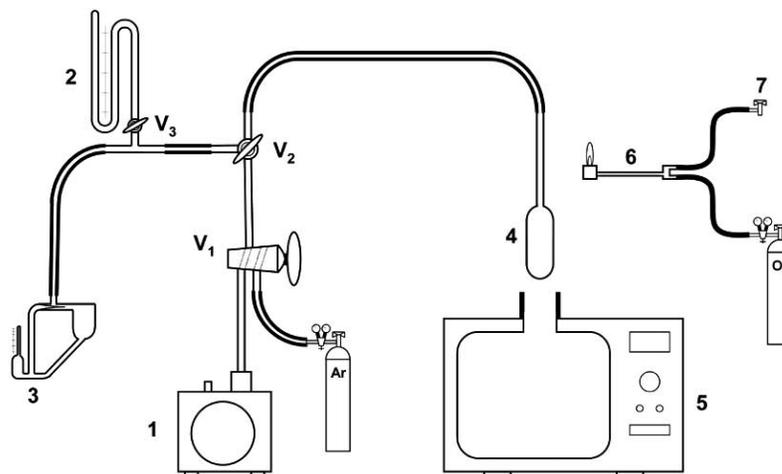


Fig. (2). Vacuum system for the EDLs construction: (1) rotary vacuum pump; (2) mercury manometer; (3) tilting-type McLeod pressure gauge; (4) EDL blank; (5) modified microwave oven; (6) glass-working burner; (7) natural gas; V_1 - V_3 are stopcocks [32].

water-soap mixture, and then washed with distilled water, aqueous 10% hydrofluoric acid, and ethanol. 2.5 μl Hg and a stainless steel thin wire (3 cm) were placed to the EDL blank. The system was flushed with argon and sealed under 20 Torr vacuum. This technique is very simple and enables to prepare EDL in a common chemical laboratory.

The EDL length was 50 mm (diameter 20 mm) and the pictures of Hg-EDL and S-EDL are shown in Fig. (3). Testing the EDL performance was carried out in order to prepare the lamps for spectral measurements [32]. A typical experimental system for such a testing consisted of a round-bottom flask containing *n*-heptane, equipped with a fiber-optic temperature and spectral probe, a Dimroth condenser, and placed to a MW oven (Fig. 4).

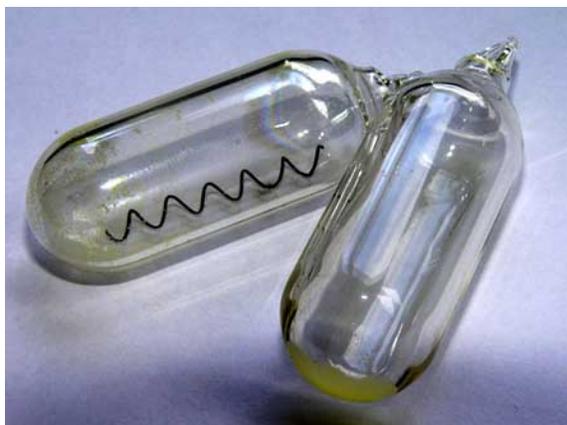


Fig. (3). Hg-EDL and S-EDL for photochemical applications.



Fig. (4). Testing the EDL performance in a Milestone's MicroSYNTH Lab-station [32].

Another novel environmental risk-free (Hg-free) EDLs were constructed by Horikoshi *et al.* [33] using the device illustrated in Fig. (5). A quartz ampoule (Ichikawa Pressure Industrial Ltd.) was connected to vacuum and was then arranged in the MW waveguide. The EDL length was 145 mm (diameter 18 mm), the initial internal pressure was set at 10^{-3} Torr (0.133 Pa), and the target gas (He, Ar, Xe, H_2 , N_2 , O_2 , or a binary gas mixture thereof) has been used. These EDLs were examined (at the optimized conditions) for using in AOPs (photo-assisted or photocatalyzed degradations).

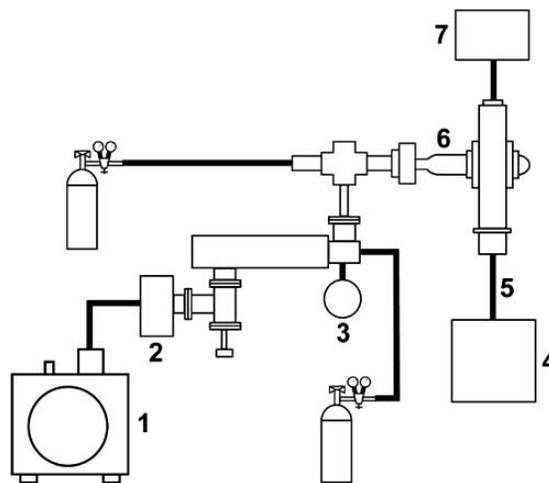


Fig. (5). Experimental setup for the examination of optimized conditions in the EDL system: (1) rotary vacuum pump; (2) turbo-molecular pump; (3) capacitance manometer; (4) MW generator; (5) MW coaxial cable; (6) EDL blank; (7) UV/Vis spectrometer [33].

3.3. Preparation of the Thin Titania Films on the EDLs

Photocatalysis is an efficient, attractive and clean technology for pollution abatement in water under mild conditions [34]. Titanium(IV) oxide, known as titania, is the archetypical photocatalytic material since it is endowed with an inherent photocatalytic activity. Moreover, it is inexpensive, very chemical and thermal stable, nontoxic and available in large amounts [35]. For better recovery and reuse, titania can be prepared in immobilized form as a thin film on glass substrate as a catalyst support. A major advantage here is that the reaction products and photocatalyst do not have to be separated unlike in the cases with powder or colloidal suspensions (slurry) of the photocatalyst [36]. However, the immobilized films produced by common sol-gel methods exhibit relatively low photocatalytic activity because of their low surface area and small film thickness. Also, TiO_2 is photoactive only under UV/Vis irradiation with an adsorption edge wavelength of typically less than 388 nm (i.e. 3.2 eV band gap). Likewise, the fast recombination rate (mean e^-/h^+ lifetime is about 30 ns) of photoinduced electron-hole pairs is leading to low photoactivity of titania. Doping TiO_2 with transition metal ions [37] has been frequently attempted not only to retard the fast charge pair recombination but also to enable visible light absorption by providing defect states in the band gap.

Sol-gel route is one of the most successful techniques for preparing nanosized metallic oxide materials with high photocatalytic activities. By tailoring the chemical structure of primary precursor and carefully controlling the processing variables, nanocrystalline products with very high level of chemical purity can be achieved [38]. In sol-gel processes, TiO_2 is usually prepared by the reactions: hydrolysis and polycondensation of titanium alkoxides, $\text{Ti}(\text{OR})_4$ ($\text{R} = i\text{-Pr}, n\text{-Bu}$), to form oxopolymers, which are then transformed

into an oxide network [39]. The overall reaction is usually written as follows: $\text{Ti}(\text{OR})_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{ROH}$.

The condensation is usually accomplished by gelization and calcination. The condensation pulls together the constitute particles of the gel into a compact mass, thus building up the metal oxide crystal. The calcination temperature is especially important for removing the organic molecules from the final products. The sol-gel derived precipitates are amorphous in nature, requiring further heat treatment at a high temperature to induce crystallization.

The sol-gel method within templates of surfactants assemblies organized as reverse micelles is effective strategy for generation of uniform metal oxide nanoparticles finalized as thin films [40]. In this process the alkoxide hydrolyses inside a reverse micelle with a limited amount of water. Then the polycondensation step could proceed simultaneously and is highly competitive. Compared to other methods the surfactant mediated sol-gel provides a good control of the hydrolysis rate [41].

The titania photocatalyst on Hg-EDLs can be prepared using a sol-gel method:

(a) from titanium(IV) isopropoxide, $\text{Ti}(i\text{-PrO})_4$ [42]: The titania sol was prepared by hydrolysis of $\text{Ti}(i\text{-PrO})_4$ according to the method described by Kluson *et al.* [43]. The hydrolysis was carried out in the reverse micelles of Triton X-100 in cyclohexane. The molar ratios of initial compounds were 1:1:1 (water/Triton X-100/ $\text{Ti}(i\text{-PrO})_4$) and volume ratio Triton X-100/cyclohexane was 0.45.

(b) from titanium(IV) butoxide, $\text{Ti}(n\text{-BuO})_4$ [44]: $\text{Ti}(n\text{-BuO})_4$ was dissolved in acetylacetone and ethyl alcohol in volume ratio 1:1:1. Then the water used for hydrolysis was added dropwise (molar ratio $\text{Ti}(n\text{-BuO})_4/\text{water}$ was 0.1) under mechanical stirring to form sol and gel.

As in the case of all surface-finishing techniques, it is also important to maintain a high level of surface cleanliness to ensure good adhesion between the substrate and the surface coating [42]. Prior to the film deposition, the support (EDL) was thoroughly cleaned in a water-soap mixture, rinsed with distilled water, soaked in a solution of HCl (1.0 mol l^{-1}), rinsed with water and ethanol, respectively. In this method the support is slowly dipped into and withdrawn from a tank containing the gel (by dip-coating machine), with a uniform velocity (6 cm min^{-1}), in order to obtain a uniform coating. The films were then dried at room temperature for one hour and finalized by thermal treatment at $500 \text{ }^\circ\text{C}$ for 2 h ($2 \text{ }^\circ\text{C/min}$) [42,44] to form the titania-coated Hg-EDLs (Fig. 6).



Fig. (6). Prepared titania-coated Hg-EDL.

Transition metals titania-doped (M/TiO_2) thin films have been also prepared [44] by sol-gel method using $\text{Ti}(n\text{-BuO})_4$ and transition metal acetylacetonate as precursors. For the preparation of M/TiO_2 sol, transition metal acetylacetonate (0.1-0.95 g) was dis-

solved in a 10 ml of acetylacetone. After that, $\text{Ti}(n\text{-BuO})_4$ was added followed by the addition of 0.1 ml of concentrated nitric acid and 10 ml of ethanol. Finally, 4 ml of water was added dropwise. In order to obtain a homogeneous mixture of M/TiO_2 , the solution was stirred vigorously for 2 h. Fig. (7) shows the flow chart for the preparation of transition metals titania-doped thin films. Typical sol was prepared for various transition metals ($\text{M} = \text{Zr, V, Cr, Mn, Fe, Co, Ni, and Ag}$) [44] and various wt.% of transition metal concentrations (1, 3, 5, and 9 wt.%).

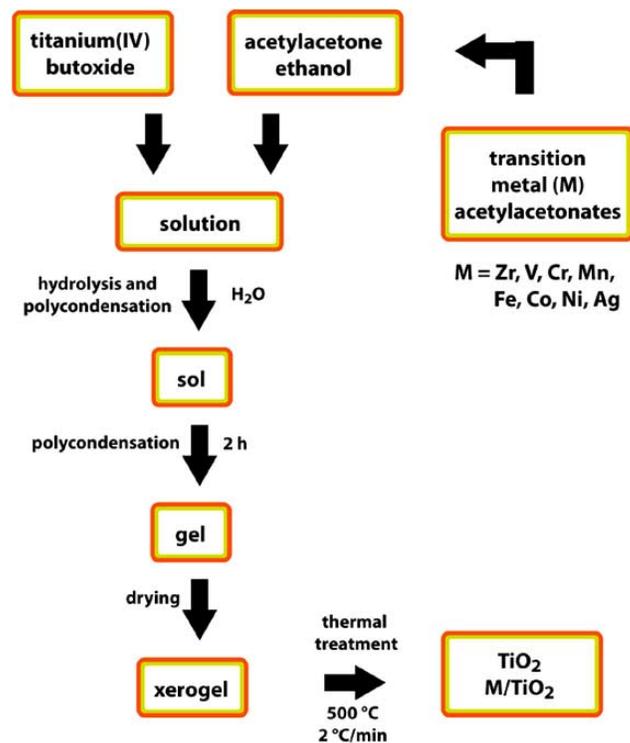


Fig. (7). Flow chart for the sol-gel processing of titania-doped thin films [18,44].

The prepared titania and titania-doped (M/TiO_2) thin films were characterized [18,44] by several techniques: X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV/Vis absorption spectroscopy. Also, the photocatalytic activity of titania films was examined by the decomposition test of Rhodamine B (RhB) [18,44].

3.4. Spectral Characteristics of the EDLs

The knowledges of spectral characteristics of EDL [45,46] are clearly essential for planning the microwave-assisted photochemical and photocatalytic experiments. The suitable choice of EDL envelope and fill material can be very useful in planning an efficient course of the photochemical or photocatalytic process without necessity of filtering off the undesirable part of the UV/Vis radiation by other tools, such as glass, solution filters or monochromators.

The total emission output of Hg-EDL in the region of 200-700 nm is approximately the same as that of the electrode lamp with the same power input [47]. The distribution of radiation is, however, markedly different, as a result of a much higher Hg pressure and the greater number of atoms that are present in the plasma. EDL emits

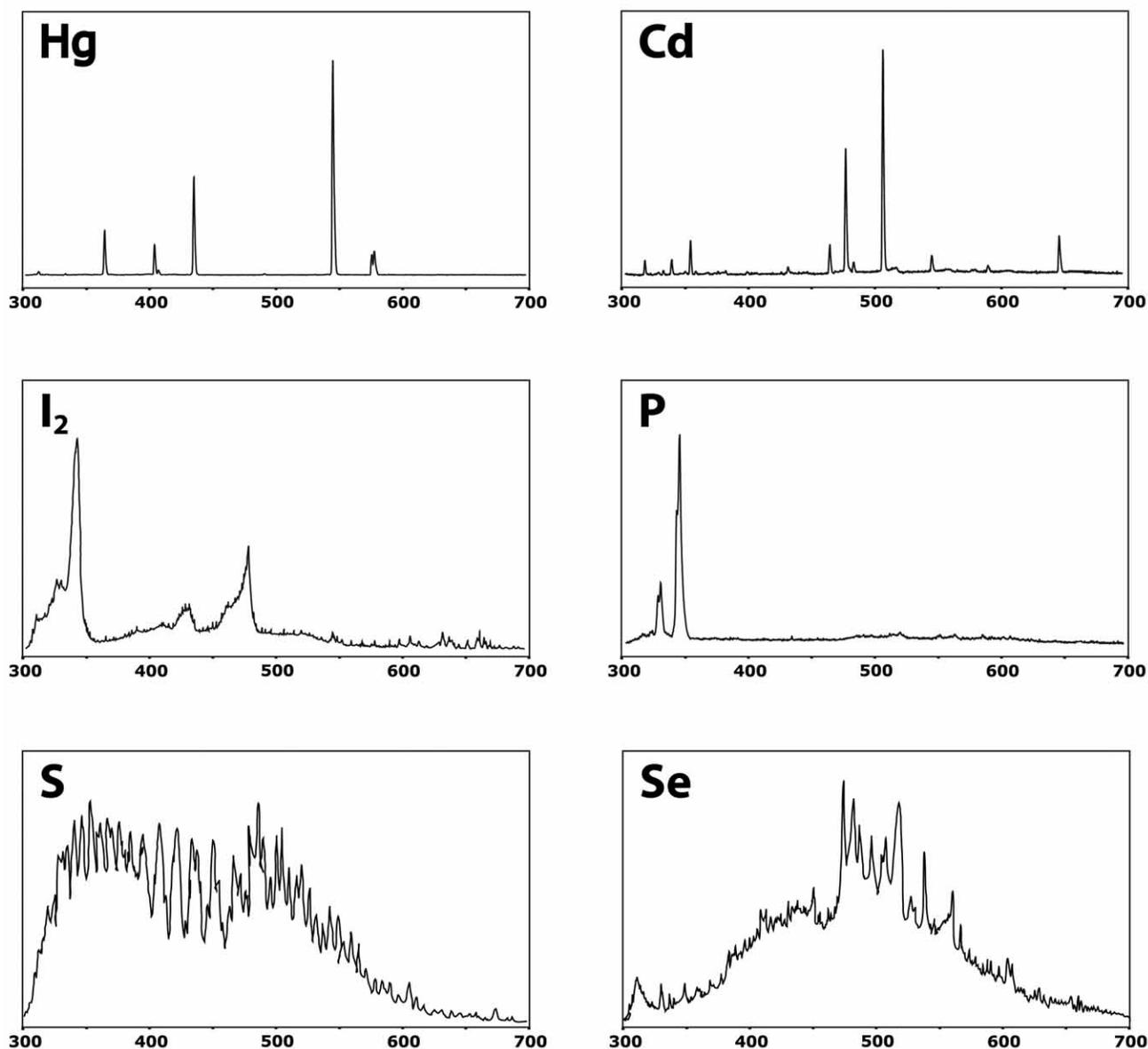


Fig. (8). Emission spectra of Hg-, Cd-, I-, P-, S-, and Se-EDL (Pyrex; 5 Torr of Ar) [32,46].

over three times as much UV and over a half as much IR as a conventional lamp.

The spectral measurements were accomplished in MW oven (such as in Fig. 4) described elsewhere [45], which had a window for UV/Vis radiation coming from EDL to a spectrometer. Its power was adjusted to the maximum in order to guarantee a continual MW irradiation. Every liquid is immediately boiling since EDL produces a considerable amount of infrared radiation. Spectral measurements of prepared EDLs (light intensity in $\mu\text{W}\cdot\text{cm}^{-2}$) were carried out on the spectrometer AVS-S2000 with AvaSoft software package and the spectrometer USB2000 with an optical fiber probe and operating software package OOIrrad-C (Ocean Optics) [32,45,46].

Müller, Klán, and Církva have reported [46] the emission characteristics of various EDL containing different fill material (such as, Hg, HgI_2 , Cd, I_2 , KI, P, Se, or S) in the region of 250–650 nm.

While distinct *line emission peaks* were found for the mercury, cadmium, and phosphorus fills (Fig. 8), the iodine-, selenium-, and sulfur-containing EDL (Fig. 8) emitted *continuous bands*. Sulfur-containing EDL has been proposed to assist phototransformations that are of environmental interest because the emission flux is comparable to solar terrestrial radiation.

Another novel Hg-free EDL has been developed by Horikoshi *et al.* [33] using only gases (He, Ar, Xe, H_2 , N_2 , O_2 , or a binary gas mixture thereof). This EDL was optimized through an examination of the light intensity at controlled pressures and gas-mixture ratios. The most suitable EDL with lines (296, 315, 336, 353, and 357 nm) concentrated in the 300–400 nm spectral range was obtained with a N_2/Ar ratio of 20/80 by volume at pressure around 5 Torr (700 Pa).

In addition, the EDL spectra could be easily modified by the choosing a suitable EDL envelope glass material, fill material, nature and pressure of the inert fill gas, temperature, MW output

power, and solvent polarity according to the needs of a photochemical or photocatalytic experiment [45] (see also chap. 3.5).

3.5. Performance of the EDLs

The performance of EDLs depends strongly on many preparation and operating parameters:

a) Envelope Material of the EDL

High quality quartz is the most widely used lamp envelope material but early EDL manufacturing used glass, Vycor, or Pyrex [29]. In addition, the envelope glass material is filtering off the part of the UV/Vis radiation from EDL. Fig. (9) shows a comparison of the emission spectra of quartz and as Pyrex Hg-EDLs [45,48]. The Pyrex glass completely removed the 254 and 297 nm bands, however, the intensity of the remaining bands was the same.

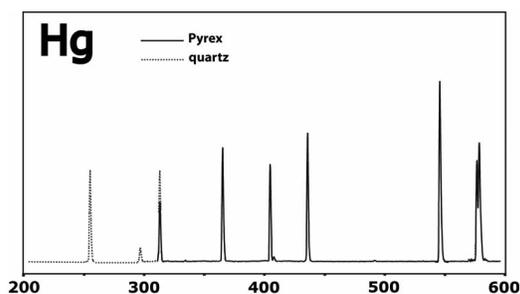


Fig. (9). Emission spectra of quartz and Pyrex Hg-EDLs in hexane [45].

b) Fill Material

The choice of the fill material initiating the discharge is very important. Together with a standard mercury fill it is often desirable to incorporate an additive in the fill material that has a low ionization potential and a sufficient vapor pressure (Cd, S, Se, Zn) [50,51]. One category of low-ionization-potential materials is the group of alkali metals or their halides (LiI, NaI) but some other elements, such as Al, Ga, In, Tl [52,53], Be, Mg, Ca, Sr, La, Pr, or Nd [54-56], can be used. Other metal-containing compounds have been utilized to prepare EDL, including amalgams of Cd, Cu, Ag, and Zn. Multi-element EDL have been prepared using combinations of elements (e.g., Li-Na-K, As-Sb, Co-Ni, Cr-Mn, Bi-Hg-Se-Te, Cd-Zn, Ga-In, Se-Te) [57]. The spectral output from each individual element is very sensitive to temperature [58]. It has been found that no inter-element interferences occur in the lamp.

The EDLs filled with a variety of compounds and the corresponding EDL emission wavelengths reported in the literature are summarized in Table 2.

c) Nature and Pressure of Inert Fill Gas:

The arc chamber contains a buffer noble gas (usually Kr, Xe, or Ar) which is inert to the extent that it does not adversely affect the lamp operation. Helium has a higher thermal conductivity than other noble gases and, therefore, higher thermal conduction loss is observed [83]. The inert gas easily ionizes at low pressure but its transition to the thermal arc is slower and the lamp requires a longer

Table 2. Fill Material and Emission Wavelength of EDLs

Fill Material (inert gas)	Excited Species	Emission Wavelength, λ [nm]	Refs
AlBr ₃ (Ne)	AlBr [*]	278	[59]
AlCl ₃ (Ne)	AlCl [*] , Al	261, 308, 394, 396	[60,61]
Ar (Ar)	Ar ₂	126, 107-165, 812	[28,62]
Br ₂ (Xe)	XeBr [*]	282	[82]
Cd (Ar)	Cd	229, 327, 347, 361, 468, 480, 509, 644	[46,63-65, 106-108]
Cl ₂ (Ar)	ArCl [*]	175	[28,62]
Cl ₂ (Xe)	XeCl [*]	308	[28,62]
CuCl (Ar)	Cu	325, 327	[63]
FeCl ₂ (Ar)	Fe	248, 272, 358, 372-376	[63]
GaI ₃ (Ar)	Ga	403, 417, 380-450	[66,67]
Hg (Ar)	Hg	185, 254, 297, 313, 365, 405, 436, 546, 577, 579	[46,49,63,64, 66,68-70]
HgI ₂ (Ar)	Hg, HgI ⁺	Hg lines + 440	[46]
I ₂ (Ar)	I ₂ [*]	342	[46]
I ₂ (Kr)	I + I ₂ [*]	178, 180, 183, 184, 188, 206, 342	[81,118]
InI ₃ (Ar)	In	410, 451	[67]
Mg, H ₂ (Ar)	MgH [*]	518, 521, 480-560	[71]
N ₂ (Ar)	N ₂	296, 315, 336, 353, 357	[33]
NaI (Xe, Kr)	Na	589	[72,73]
P (Ar)	P	325, 327, 343	[46]
S (Ar)	S	320-850, 525	[46,52,74-76]
Se (Ar, Xe)	Se	370-850, 545	[46,75-78]
SnI ₂ (Ar)	Sn	400-850, 610	[79,80]
Te (Ar)	Te	390-850, 565	[75,76,78]
TlI (Ar)	Tl	277, 352, 378, 535	[63,67]
Zn (Ar)	Zn	214, 330, 468	[63,64,67]

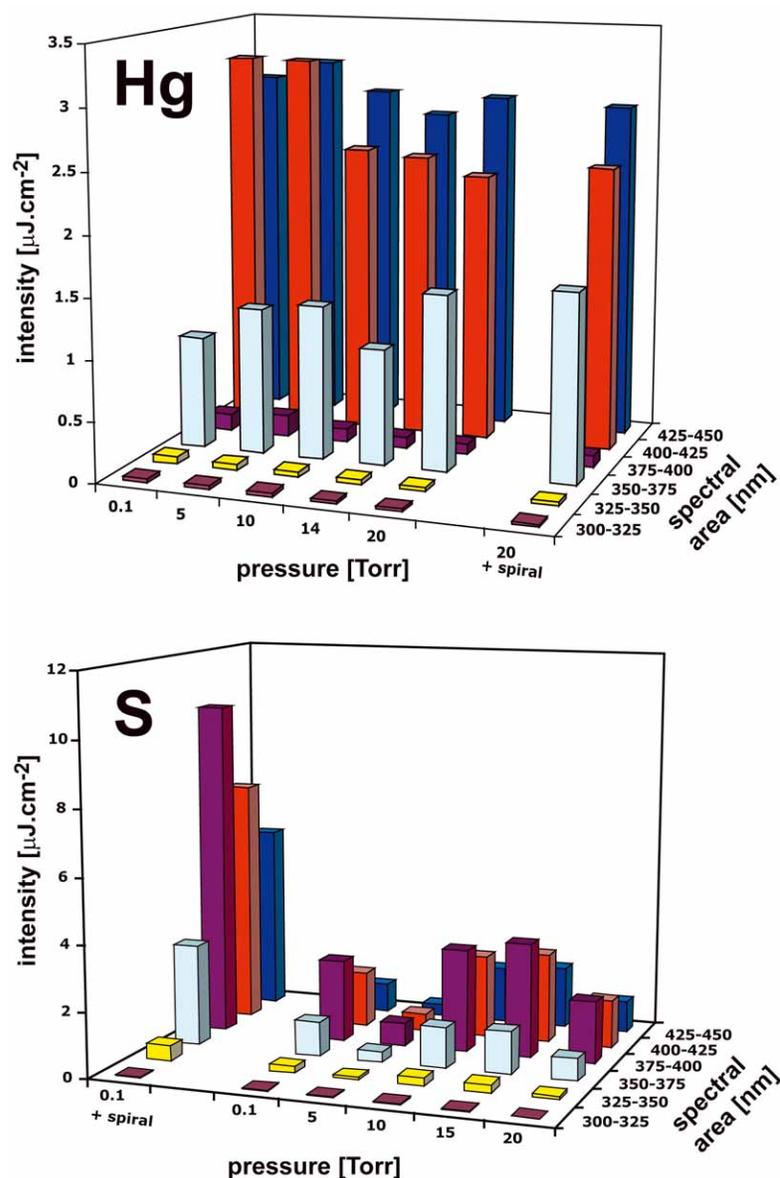


Fig. (10). Dependence of the Hg-EDL and S-EDL intensity on the argon pressure according to spectral area [84].

warm-up time. Ionization is more difficult at higher pressures and it requires a higher input power to establish the discharge.

In general, the pressure of filling gas was recommended to hold between 2-20 Torr (0.266-2.66 kPa), at the operating temperature is usually much higher (10 atm) than that of a conventional electrode lamp. Utilizing argon was considered to be the best compromise between high EDL radiance and long lifetime. Air cannot be used, due to the quenching properties in microwave plasma just like water vapors. To focus the MW field efficiently into EDL, a special Cd low-pressure lamp with a metal antenna (a molybdenum foil) was developed for experiments in MW-absorbing liquids [64].

The emission intensities of Hg-EDLs and S-EDLs have been scaled according to spectral area (300 - 450 nm) in dependence on pressure of argon in the range 0.1-20 Torr (13-2660 Pa) (Fig. 10). Also, the effect of spiral (resistance wire steel, tantalum) on the EDL intensity was studied [84]. The best results were obtained for Hg-EDL with pressure 20 Torr (2.5 μ l Hg, steel spiral) and S-EDL with pressure 0.1 Torr (5 μ g S, tantalum spiral).

The EDLs can be evaluated on photochemical *cis-trans* photoisomerization of *trans*-stilbene (Fig. 11). This method [84] makes possible to compare the various EDL (Hg vs S) at different pressures (5 vs 20 Torr) and it's now under investigation.

d) Temperature of the EDL

Operation at a high power or high temperatures can increase the emission intensity but, at the same time, reduce the lamp lifetime and lead to a broadening of the atomic line profile due to self-absorption and self-reversal effects. It was found that the optimum operating temperature for the mercury filling is 42 °C (for 254 nm line, $6^1S_0-6^3P_1$) [63]. The output is reduced when the temperature is beyond optimum [45].

The relative intensities of the mercury emission peaks in EDL were found [45] to be very dependent on temperature (35-174 °C, in various hydrocarbons); the 254 nm short-wavelength band was suppressed with increasing temperature, however, the 366 nm line was enhanced (Fig. 12).

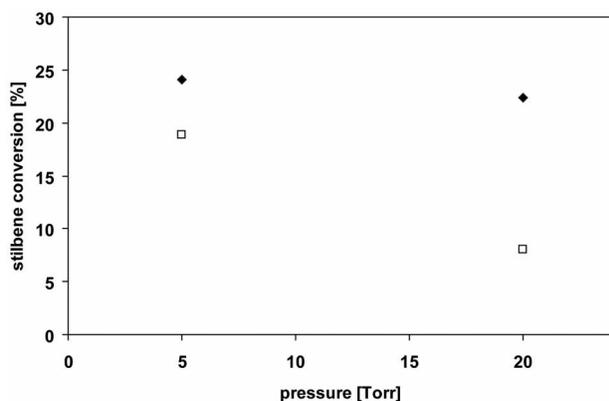


Fig. (11). EDL evaluation on photoisomerization of *trans*-stilbene (♦ Hg-EDL, □ S-EDL) [84].

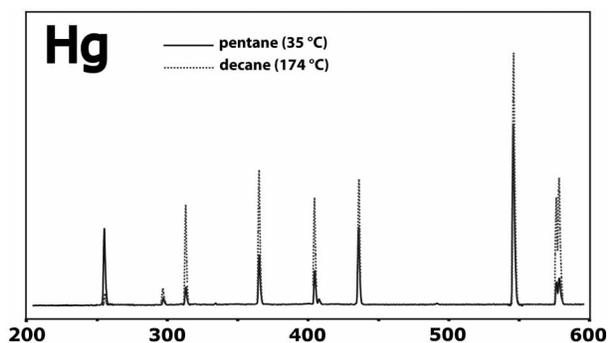


Fig. (12). Emission spectra of quartz Hg-EDL in pentane and decane [45].

e) Effect of the MW Output Power

The frequency and intensity of electromagnetic energy is determined by the type of a device. MW energy is widely used for the excitation of EDL because it is generally more efficient than radio-frequency energy for the generation of intense light. MW radiation for the excitation of gas discharges is usually generated by a fixed frequency (2.45 GHz) magnetron oscillator. The effect of the MW reactor output power on the relative peak intensities was also investigated [45,84] (Fig. 13). It was found that the EDL intensity increased with increasing MW power (30 and 300 W).

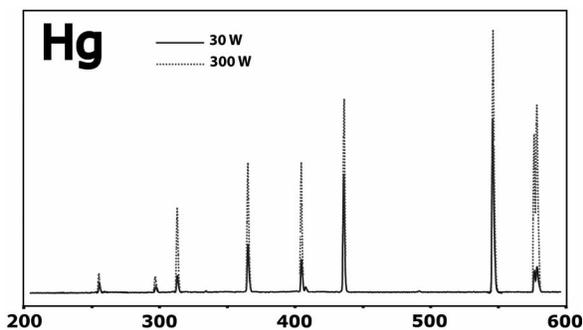


Fig. (13). Emission spectra of quartz Hg-EDL at the 30 and 300 W output power in hexane [45].

f) Solvent Polarity

Solvents absorbing MW radiation significantly reduced the EDL intensities of all emission bands since it reduces the amount of MW energy that powers the lamp [45]. The EDL spectrum in methanol is compared to that in hexane in Fig. (14). Likewise, the

solvent can be also used as an internal UV filter; benzene significantly suppressed the wavelengths below 280 nm. Therefore, hexane is ideal in case a short-wavelength irradiation (254 nm) experiment.

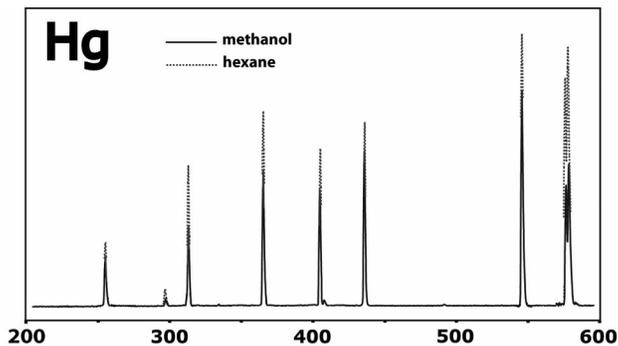


Fig. (14). Emission spectra of quartz Hg-EDL in methanol and hexane [45].

It is concluded that the right choice of the EDL envelope material (quartz, Pyrex) and reaction conditions (temperature, solvent polarity) is essential for an efficient course of a photochemical and photocatalytic processes in this experimental arrangement.

4. MICROWAVE PHOTOCHEMICAL AND PHOTOCATALYTIC REACTORS

Over the past decade, considerable experiences [85-87] have been obtained concerning the construction of the microwave photochemical and photocatalytic reactors [12]. The various lamp configurations in the microwave photoreactors are shown in Fig. (15). Three different arrangements of the lamp (external vs two internal UV/Vis source) and their location in MW field (outside vs inside) are possible, which lead for batch and flow-through mode to six fundamental types of photoreactors, **A1-A3**, **B1-B3**.

The simplest types of microwave photoreactors are a batch flask (Fig. 15, **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 annular, with EDL centered parallel to the axis of the reactor vessel (Fig. 15, **B2**), and into cylindrical photoreactor (**B3**) with a coaxial radiation field that is generated by surrounded EDL. The many microwave photoreactor units are based on these designs.

The microwave photocatalytic reactors can be also divided for batch and flow-through mode to six fundamental types of photoreactors, **A1-A3**, **B1-B3**, Fig. (15), moreover, the type and variation of photocatalyst (slurry vs thin film) needs to be further considered.

4.1. Batch Photochemical Reactors

Chemat *et al.* [88] have proposed the simplest type of microwave photoreactor as a batch flask (Fig. 15, **A1**) in MW field, which is irradiated by a light beam from an external UV/Vis source (classical medium-pressure mercury lamp).

The batch photochemical reactor with internal EDL (Fig. 15, **A2**) used for MW-assisted experiments is an essential tool for experimental work [12]. In this set-up the simultaneous irradiation of the solution with both MW and UV/Vis radiation is utilized. Církva and Hájek [16] have proposed a simple application of a domestic

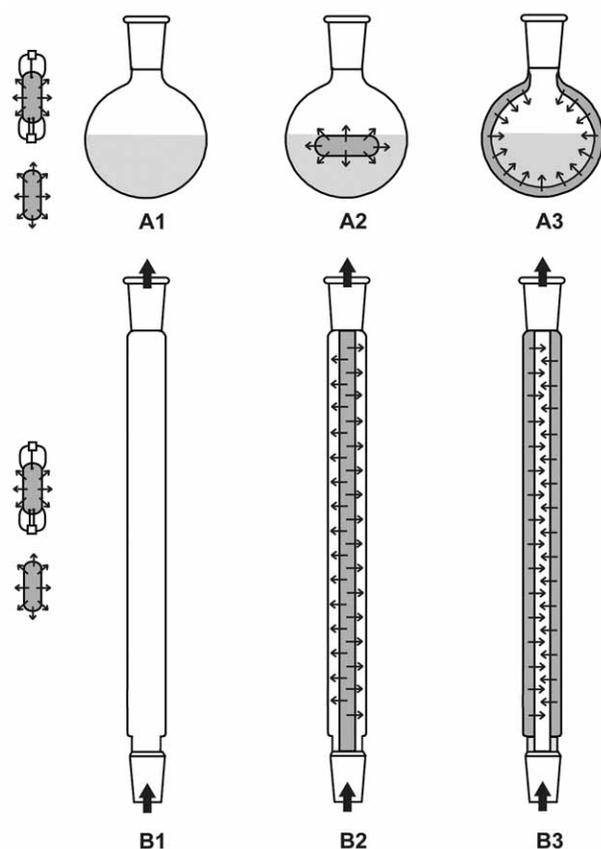


Fig. (15). Cross-sectional view of various microwave photoreactor types with different arrangement of the lamps: (A1) batch with external UV/Vis source (classical lamp or EDL); (A2) batch with internal EDL; (A3) batch with EDL inside of double wall; (B1) flow-through with external UV/Vis source (classical lamp or EDL); (B2) annular flow-through with internal EDL; (B3) cylindrical flow-through surrounded with EDL.

MW oven for MW-assisted photochemical experiments. In this arrangement (Fig. 16), EDL was placed in a reaction vessel located in the cavity of MW oven. The MW field generated a UV/Vis discharge inside the lamp that resulted in simultaneous UV/Vis and MW irradiation of the sample.

Klán, Literák *et al.* published a series of papers that described the scope and limitation of this reactor [48,89-91]. In a typical design (Fig. 16), 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 magnetic stirring. The certain amount of a MW-absorbing solid material (dummy load: basic Al_2O_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.

The MW batch arrangement provided the unique possibility of studying photochemical and photocatalytic reactions under extreme thermal conditions [89]. However, technical difficulties occur when the MW photochemical experiments are to be performed at temperature below the boiling point of the solvent. Therefore a simple low-pressure operating MW photoreactor (Fig. 17) has been constructed and applied [92].

Another novel quartz EDL photochemical reactor has been developed by Ferrari *et al.* [104] using an immersed coaxial dipole

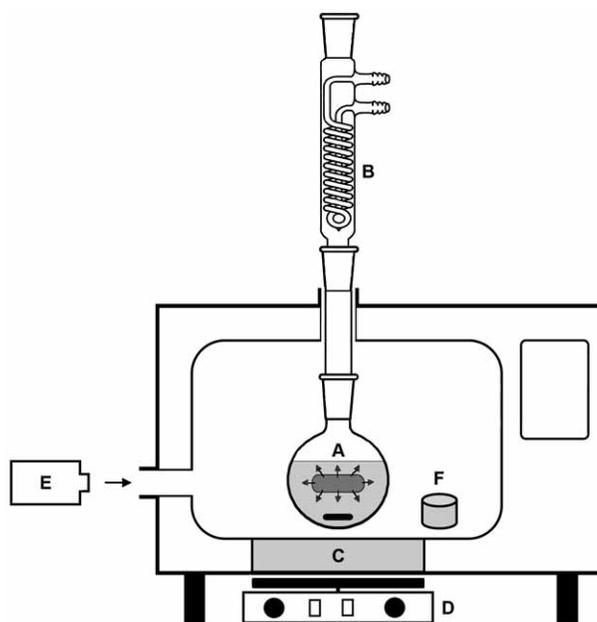


Fig. (16). MW batch photochemical or photocatalytic reactor: (A) reaction mixture with EDL and a magnetic stir bar; (B) Dimroth condenser; (C) aluminum plate; (D) magnetic stirrer; (E) fiber optic spectral probe; (F) dummy load inside the oven cavity [89].



Fig. (17). Low-pressure batch microwave photoreactor [92].

antenna and producing a plasma discharge inside the bulb without the need of a MW oven. The advantages over other experimental procedures, like reduced consumption of chemicals, energy saving and simpler setup are highlighted.

In Table 3 are depicted the most important advantages and disadvantages of EDL in photo-applications [12].

Table 3. Advantages and Disadvantages of EDL in Photo-Applications [12]

Advantages
Simultaneous UV/Vis and MW irradiation of the sample
Simplicity of the experimental set-up (use of a commercially MW oven, "wireless" EDL operation)
Low cost of EDL (easy method of EDL preparation in lab)
Possibility of performing photoexperiments at high temperatures
Good photo-efficiency: EDL is "inside" the sample
Choice of the EDL material (Hg, S) might modify its spectral output
Disadvantages
Technical difficulties of performing experiments at temperatures below the solvent b.p.
Intensity of EDLs strongly depends on given experimental conditions:
a) b.p., polarity, and transmittance of solvent
b) output and sort of MW equipment
c) type and intensity of cooling

Microwave photochemistry in a batch reactor has been investigated over the past decade (see Table 4) and can be implemented if external or internal lamps (classical UV lamp vs EDL) are used. The combination of given variables may lead to the following four types of techniques (see Table 4) for batch set-up in a MW field:

- external classical UV lamp (Fig. 15, A1)
- external EDL (Fig. 15, A1)
- internal EDL (Fig. 15, A2)
- internal EDL inside of double wall (Fig. 15, A3)

4.2. Flow-through Photochemical Reactors

The MW flow-through photochemical reactors consisted either of an external UV/Vis source irradiating the sample placed inside the MW field (Fig. 15, B1), or of an internal EDL in the MW field and powered by microwaves. This last type can be subdivided into annular (Fig. 15, B2) and into cylindrical photoreactor (B3).

Horikoshi *et al.* [113] have proposed a flow-through quartz photoreactor for photoremediation of aqueous solutions using either conventional lamp (type B1) or cylindrical EDL (type B3) as sources of UV/Vis radiation.

Table 4. Batch MW Photochemistry

Type	Lamp (envelope)	Reaction	Refs	
A1	class. Hg-MP	$o\text{-CH}_3\text{CO-C}_6\text{H}_4\text{-OCOPh} \rightarrow o\text{-HO-C}_6\text{H}_4\text{-COCH}_2\text{COPh}$	[88]	
		$p\text{-MeO-C}_6\text{H}_4\text{-NO}_2 + \text{OH}^- \rightarrow p\text{-MeO-C}_6\text{H}_4\text{-OH} + p\text{-HO-C}_6\text{H}_4\text{-NO}_2$	[93]	
	class. Hg-HP	$p\text{-R-C}_6\text{H}_4\text{-COCH}_2\text{CH}_2\text{CHR}'$ (R,R' = H,Me; Me,Me; H,C ₇ H ₁₅) \rightarrow $p\text{-R-C}_6\text{H}_4\text{-COCH}_3 + \text{R}'\text{-CH=CH}_2 + \text{cyclobutanols}$	[94]	
		phenol, 4-chlorophenol, PCP, chlorobenzene, nitrobenzene + H ₂ O ₂	[95]	
A2	Hg-EDL (quartz)	$\text{THF} + \text{CH}_2=\text{CH-C}_6\text{F}_{13} \rightarrow \text{THF-CH}_2\text{CH}_2\text{-C}_6\text{F}_{13}$	[16]	
		valerophenone, 4-nitroanisole in high-temperature water	[96]	
		$\text{C}_6\text{H}_{12} + \text{C}_6\text{D}_{12} \rightarrow \text{C}_6\text{H}_{11}\text{-C}_6\text{H}_{11} + \text{C}_6\text{H}_{11}\text{-C}_6\text{D}_{11} + \text{C}_6\text{D}_{11}\text{-C}_6\text{D}_{11}$ $\text{C}_6\text{H}_{12} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{C}_6\text{H}_{11}\text{-C}_6\text{H}_{11} + \text{C}_6\text{H}_{11}\text{-C}(\text{CH}_3)_2\text{OH} + \text{pinacole}$	[97]	
		4-chlorophenol (H ₂ O ₂) \rightarrow 4-chlorocatechol, hydroquinone, benzoquinone	[98,99]	
		$o\text{-tert-butylphenol} \rightarrow \text{C-C dimers}$	[100]	
		$p\text{-tert-butylphenol} \rightarrow \text{C-C and C-O dimers} + o\text{-tert-butylphenol}$	[101]	
		$1,4\text{-dihydropyridines} + \text{O}_2 \rightarrow \text{pyridines}$	[102]	
		acid orange 7 + (H ₂ O ₂) \rightarrow degradation	[104]	
		Hg-EDL (quartz, Pyrex)	valerophenone \rightarrow acetophenone + propene + cyclobutanols PhCOCH ₂ O ₂ CPh + (H-donor) \rightarrow PhCOCH ₃ + PhCOOH PhCl + CH ₃ OH \rightarrow PhOCH ₃ + HCl PhCOCH ₃ + (CH ₃) ₂ CHOH \rightarrow PhCH ₂ C(OH)-C(OH)PhCH ₃ + CH ₃ COCH ₃ PhOCOCH ₃ \rightarrow $o\text{-HO-C}_6\text{H}_4\text{-COCH}_3 + p\text{-HO-C}_6\text{H}_4\text{-COCH}_3 + \text{PhOH}$	[48,91]
			Hg-EDL (Pyrex)	valerophenone \rightarrow acetophenone + propene + cyclobutanols
$p\text{-MeO-C}_6\text{H}_4\text{-NO}_2 + \text{OH}^- \rightarrow p\text{-MeO-C}_6\text{H}_4\text{-OH} + p\text{-HO-C}_6\text{H}_4\text{-NO}_2$	[93]			
bromophenol blue \rightarrow degradation	[103]			
	atrazine \rightarrow degradation	[105]		
Cd-EDL (quartz)	chlorfenvinphos, cypermethrin + photo-Fenton (Fe ²⁺ + H ₂ O ₂)	[106]		
	digestion of skimmed milk	[64]		
	digestion of road dust (determination of Pd)	[107]		
	digestion of serum, urine, milk	[108]		
A3	Hg-EDL (quartz)	polyphosphate/organophosphate \rightarrow orthophosphate (Na ₄ P ₂ O ₇ , 2-glycerophosphate, 4-nitrophenylphosphate, ATP)	[109]	
		$(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2 + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2$	[110]	
		humic acid + H ₂ O ₂ \rightarrow decomposition	[111]	
		water disinfection	[112]	

Církva *et al.* [92] have studied an annular flow-through MW photoreactor (type **B2**), which contained the glass tube with quartz Hg-EDLs (254 nm emission) inside a MW oven (Fig. 18). Photohydrolysis of aqueous mono-chloroacetic acid into hydroxyacetic acid and HCl has been chosen as the model reaction to evaluate photoreactors. The photoreaction course was monitored by the pH change in the solution. The conversion was optimized as a result of a trade-off between the thermal dependence of the quantum yield (which increases with increasing temperature) and the thermal dependence of the EDL light intensity of 254 nm line (which increases with decreasing temperature).

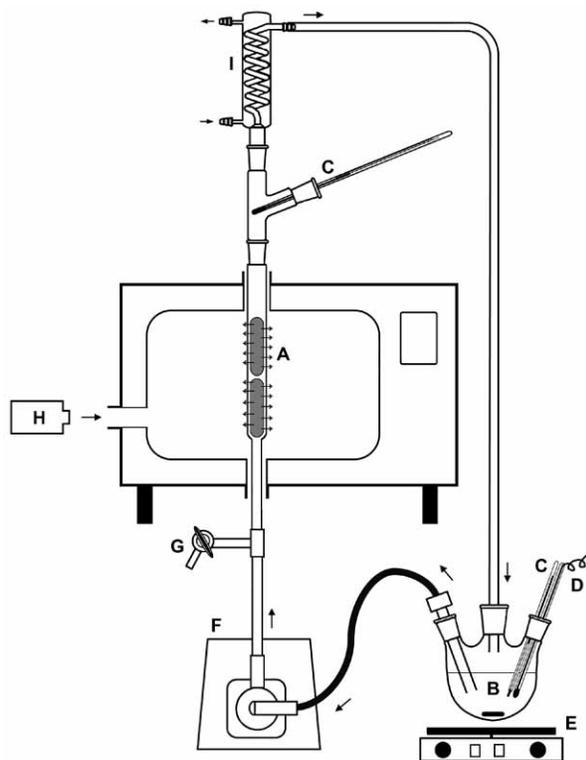


Fig. (18). MW flow-through photochemical or photocatalytic reactor: (A) reaction tube with EDLs; (B) glass reservoir with magnetic stir bar; (C) thermometer; (D) pH/chloride ion-selective electrode and/or tube for air bubbling; (E) magnetic stirrer; (F) PTFE diaphragm pump; (G) outlet; (H) spectrometer with a fiber-optic probe; (I) cooling condenser [92,114].

The experimental set-up for the flow-through MW photoreactor [92] is shown in Fig. 18 and 19). The aqueous mixture has been circulated through the photoreactor system consisting of the glass reservoir (B) (500 mL; fitted with a thermometer (C) and a pH elec-

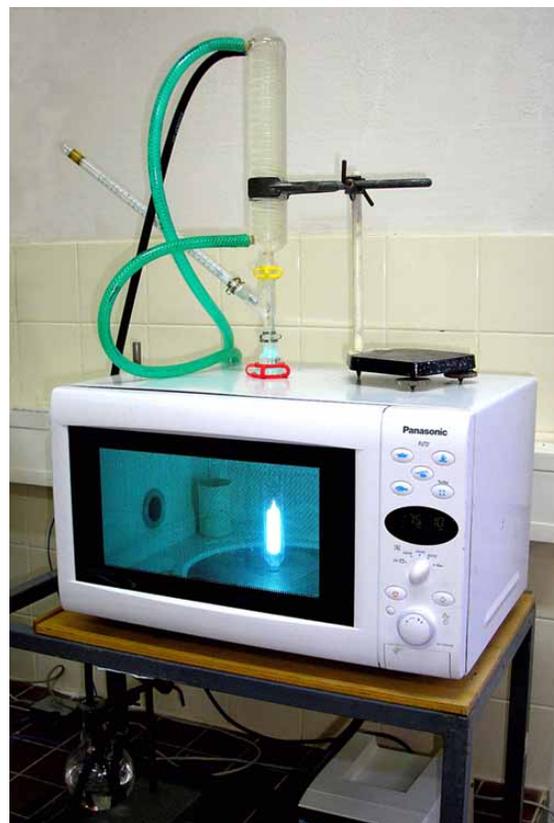


Fig. (19). Flow-through microwave photochemical or photocatalytic reactor [92,114].

trode (D)) connected by tubing (ISO Versinic) to a PTFE diaphragm pump (F), a glass tube (200 x 22 mm) with EDLs (A) inside a modified MW oven, and cooling condenser (I). The EDLs emitted UV/Vis light measured by spectrometer with a fiber-optic probe (H). The desired temperature in the flow-through photoreactor has been achieved by adjustment of the pump flow speed.

Microwave photochemistry in a flow-through reactor has been investigated over the past decade (see Table 5) and can be implemented if external or internal lamps (classical UV lamp vs EDL) are used. The combination of given variables may lead to the following four types of techniques (see Table 5) for flow-through set-up in a MW field:

- external classical UV lamp (Fig. 15, B1)
- external EDL (Fig. 15, B1)
- annular reactor with internal EDL (Fig. 15, B2)
- cylindrical reactor surrounded with EDL (Fig. 15, B3)

Table 5. Flow-through MW Photochemistry

Type	Lamp (envelope)	Reaction	Refs
B2	Hg-EDL (quartz)	$\text{ClCH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{CO}_2\text{H} + \text{HCl}$	[92]
		phenol + $\text{H}_2\text{O}_2 \rightarrow$ decomposition	[115]
		acid orange 7 + (H_2O_2 , O_3) \rightarrow degradation	[104,116,117]
		$\text{H}_2\text{S} \rightarrow \text{SO}_4^{2-}$	[118]
	Hg-EDL (quartz, W wire)	2,4-dichlorophenoxyacetic acid, bisphenol-A	[119]
	I_2 -EDL (Kr, quartz)	$\text{H}_2\text{S} \rightarrow \text{SO}_4^{2-}$	[118]
B3	Hg-EDL (quartz)	water disinfection	[112]

Table 6. Batch MW Photocatalysis

Type	Lamp (envelope)	Catalyst	Reaction	Refs
A1	class. Hg-MP	slurry TiO ₂	rhodamine-B, benzoic acid, pyronin-B	[17,120,121]
			methylene blue	[122]
			DMPO, phenol	[123]
			bisphenol-A	[122,124,125]
			benzoic acid, phthalic acid, <i>o</i> -formylbenzoic acid, phthalaldehyde, succinic acid, dimethyl phthalate, diethyl phthalate, phenol	[126]
			methanol, ethanol, 1-propanol, ethylene glycol, glycerin, acetone, formic acid, acetic acid	[127]
			2,4-dichlorophenoxyacetic acid	[128]
			humic acid	[88]
			4-chlorophenol	[122,129,130]
			ethylene	[131]
A2	Hg-EDL (quartz)	slurry TiO ₂	dimethyl phthalate	[132]
			methylene blue	[133]
			bromophenol	[103]
			malachite green	[134]
				[135]
		slurry TiO ₂ /C	phenol	[136]
		slurry TiO ₂ nanotubes	atrazine	[137,138]
F-Si-comodified TiO ₂	pentachlorophenol			
Hg-EDL (Pyrex)	thin film TiO ₂ , M ⁺ /TiO ₂	CICH ₂ CO ₂ H	[42,44]	
Cd-EDL (quartz)	slurry TiO ₂	digestion of serum, urine, milk	[108]	
A3	Hg-EDL (Ne, quartz)	slurry TiO ₂	2,4-dichlorophenoxyacetic acid	[139]

Table 7. Flow-through MW Photocatalysis

Type	Lamp (envelope)	Catalyst	Reaction	Refs		
B1	class. Hg-MP	slurry TiO ₂	rhodamine-B	[140]		
B2	Hg-EDL (quartz)	slurry TiO ₂	4-chlorophenol	[98,141,142]		
			2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, pentachlorophenol	[99,143]		
			reactive brilliant red X-3B	[144,145]		
			acid orange 7	[146]		
			slurry MnO ₂	cationic blue (X-GRL)	[147]	
			pellets TiO ₂	acetaldehyde	[148]	
			Hg-EDL (Pyrex)	thin film TiO ₂	CICH ₂ CO ₂ H	[114]
			EDL	thin film	fluid remediation	[149]
B3	fluorescent bulb	thin film TiO ₂ /ZrO ₂	ethylene	[131]		
			Hg-EDL (Ne, quartz)	slurry TiO ₂	rhodamine-B	[113,140]
					2,4-dichlorophenoxyacetic acid	[128]

4.3. Batch Photocatalytic Reactors

Microwave photocatalysis in a batch reactor has been investigated over the past decade (see Table 6) and can be implemented if external or internal lamps (classical UV lamp vs EDL) are used. The combination of given variables, i.e. lamps and the type and variation of semiconductor photocatalyst (slurry vs thin film), may lead to the following four types of techniques (see Table 6) for photocatalytic batch set-up in a MW field:

a) external classical UV lamp + slurry/thin film TiO₂ (Fig. 15, A1)

b) external EDL + slurry/thin film TiO₂ (Fig. 15, A1)

c) internal EDL + slurry/thin film TiO₂ (Fig. 15, A2)

d) internal EDL inside of double wall + slurry/thin film TiO₂ (Fig. 15, A3).

4.4. Flow-through Photocatalytic Reactors

Microwave photocatalysis in a flow-through reactor has been investigated over the past decade (see Table 7) and can be implemented if external or internal lamps (classical UV lamp vs EDL)

are used. The combination of given variables, i.e. lamps and the type and variation of semiconductor photocatalyst (slurry vs thin film), may lead to the following four types of techniques (see Table 7) for photocatalytic flow-through set-up in a MW field:

- a) external classical UV lamp + slurry/thin film TiO₂ (Fig. 15, B1)
- b) external EDL + slurry/thin film TiO₂ (Fig. 15, B1)
- c) annular reactor with internal EDL + slurry/thin film TiO₂ (Fig. 15, B2)
- d) cylindrical reactor surrounded with EDL + slurry/thin film TiO₂ (Fig. 15, B3).

5. CONCLUSION

In this review, we present a new method for carrying out photochemical and photocatalytic reactions with high efficiency in the microwave field. The objective of microwave photochemistry and photocatalysis 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 theory of the microwave discharge in EDLs, their construction, spectral characteristics, preparation of titania-coated films, and their performance. Novel microwave photochemical and photocatalytic reactors with different arrangement of the lamps in the batch and the flow-through experimental set-up are described. The presented photochemical and photocatalytic reactions are indexed into several tables, and their detailed description will be the subject of an upcoming review article.

We have discussed how the concept of MW photochemistry and photocatalysis 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 and photocatalytic synthesis, environmental chemistry, or analysis.

ACKNOWLEDGMENTS

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.

LIST OF ABBREVIATIONS

AOPs	=	advanced oxidation processes
EDLs	=	electrodeless discharge lamps
HP	=	high pressure
MP	=	medium pressure
MW	=	microwave
MWP	=	microwave photochemistry
MWPC	=	microwave photocatalysis
US	=	ultrasound
UV/Vis	=	ultraviolet/visible

REFERENCES

- [1] Klán, P.; Wirz, J. *Photochemistry of Organic Compounds: From Concepts to Practice*; Wiley & Sons: Chichester, UK, 2009.
- [2] Mattay, J.; Griesbeck, A. *Photochemical Key Steps in Organic Synthesis*; VCH: Weinheim, Germany, 1994.
- [3] Griesbeck, A.G.; Mattay, J. *Synthetic Organic Photochemistry*; Marcel Dekker: New York, USA, 2005.
- [4] Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett.*, 1986, 27, 279-282.
- [5] de la Hoz, A.; Diaz-Ortiz, A.; Moreno, A. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chem. Soc. Rev.*, 2005, 34, 164-178.
- [6] Loupy, A. *Microwaves in Organic Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2006.
- [7] Ahluwalia, V.K.; Varma, R.S. *Alternate Energy Processes in Chemical Synthesis. Microwave, Ultrasonic and Photo Activation*; Alpha Science International: Oxford, UK, 2008.
- [8] Bogdal, D. *Microwave-assisted Organic Synthesis. One Hundred Reaction Procedures*; Elsevier: Oxford, UK, 2005.
- [9] Tierney, J.P.; Lidström, P. *Microwave Assisted Organic Synthesis*; Blackwell: Oxford, UK, 2005.
- [10] Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. Microwave assisted organic synthesis—a review. *Tetrahedron*, 2001, 57, 9225-9283.
- [11] Perreux L.; Loupy, A. A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations. *Tetrahedron*, 2001, 57, 9199-9223.
- [12] Klán, P.; Církva, V. *Microwaves in Photochemistry*; In: *Microwaves in Organic Synthesis*; Loupy, A., Ed.; Wiley-WCH: Weinheim, Germany, 2006; Vol. 2, pp. 860-897.
- [13] Chemat, F.; Poux, M.; DiMartino, J.L.; Berlan, J. An original microwave-ultrasound combined reactor suitable for organic synthesis: Application to pyrolysis and esterification. *J. Microw. Power Electromagn. Energy*, 1996, 31, 19-22.
- [14] Cravotto, G.; Beggiano, M.; Penoni, A.; Palmisano, G.; Tollari, S.; Leveque, J. M.; Bonrath, W. High-intensity ultrasound and microwave, alone or combined, promote Pd/C-catalyzed aryl-aryl couplings. *Tetrahedron Lett.*, 2005, 46, 2267-2271.
- [15] Cutress, J.J.; Marken, F.; Compton, R.G. Microwave-Assisted Electroanalysis: A Review. *Electroanalysis*, 2009, 21, 113-123.
- [16] Církva, V.; Hájek, M. Microwave photochemistry. Photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation. *J. Photochem. Photobiol. A*, 1999, 123, 21-23.
- [17] Horikoshi, S.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV-illumination method. I. Microwave-assisted degradation of rhodamine-B dye in aqueous TiO₂ dispersions. *Environ. Sci. Technol.*, 2002, 36, 1357-1366.
- [18] Církva, V.; Zbová, 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, 2009; Chap. 3.
- [19] 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.
- [20] Horikoshi, S.; Serpone, N. Photochemistry with microwaves. Catalysts and environmental applications. *J. Photochem. Photobiol. C*, 2009, 10, 96-110.
- [21] Fehsenfeld, F.C.; Evenson, K.M.; Broida, H.P. Microwave discharge cavities operating at 2450 MHz. *Rev. Sci. Instrum.*, 1965, 36, 294-298.
- [22] Brown, S.C. *Introduction to Electrical Discharges in Gases*; Wiley & Sons: New York, USA, 1966.
- [23] Kazantsev, S.A.; Khutorshchikov, V.I.; Guthöhrlein, G.H.; Windholz, L. *Practical Spectroscopy of High-Frequency Discharges*; Plenum Press: New York, USA, 1998.
- [24] Jackson, D.A. The hyperfine structure of the lines of the arc spectrum of cesium and nuclear spin. *Proc. R. Soc. London A*, 1930, 128, 508-512.
- [25] Meggers, W.F.; Westfall, F.O. Lamps and wavelengths of mercury 198. *J. Res. NBS*, 1950, 44, 447-455.
- [26] Ganeev, A.; Gavare, Z.; Khutorshchikov, V.I.; Khutorshchikov, S.V.; Revalde, G.; Skudra, A.; Smirnova, G.M.; Stankov, N.R. High-frequency electrodeless discharge lamps for atomic absorption spectrometry. *Spectrochim. Acta B*, 2003, 58, 879-889.
- [27] Fridman, A. *Plasma Chemistry*; Cambridge University Press: New York, USA, 2008.
- [28] Wertheimer, M.R.; Fozza, A.C.; Holländer, A. Industrial processing of polymers by low-pressure plasmas: the role of VUV radiation. *Nucl. Instrum. Methods Phys. Res. B*, 1999, 151, 65-75.
- [29] Gleason, W.S.; Pertel, R. High stability EDLs. *Rev. Sci. Instrum.*, 1971, 42, 1638-1643.
- [30] Haarsma, J.P.S.; De Jong, G.J.; Agterdenbos, J. The preparation and operation of EDLs - A critical review. *Spectrochim. Acta B*, 1974, 29, 1-18.
- [31] Sneddon, J.; Browner, R.F.; Keliher, P.N.; Winefordner, J.D.; Butcher, D.J.; Michel, R.G. Electrodeless discharge lamps. *Prog. Anal. Spectrosc.*, 1989, 12, 369-402.
- [32] Církva, V.; Vlková, L.; Relich, S.; Hájek, M. Microwave photochemistry IV: Preparation of the electrodeless discharge lamps for photochemical applications. *J. Photochem. Photobiol. A*, 2006, 179, 229-233.
- [33] 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.
- [34] Herrmann, J.-M. Heterogeneous photocatalysis: state of the art and present applications. In honor of Pr. R.L. Burwell Jr. (1912-2003), Former Head of

- Ipatieff Laboratories, Northwestern University, Evanston (Ill). *Top. Catal.*, **2005**, *34*, 49-65.
- [35] Zhao, J.; Yang, X. Photocatalytic oxidation for indoor air purification: a literature review. *Buill. Environ.*, **2003**, *38*, 645-654.
- [36] Rajeshwar, K.; Osugi, M.E.; Chanmanee, W.; Chenthamarakshan, C.R.; Zaroni, M.V.B.; Kajitvichyanukul, P.; Krishnan-Ayer, R. Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. *J. Photochem. Photobiol. C*, **2008**, *9*, 171-192.
- [37] Pérez-Hernández, R.; Mendoza-Anaya, D.; Fernández, M.E.; Gómez-Cortés, A. Synthesis of mixed ZrO₂-TiO₂ oxides by sol-gel: Microstructural characterization and infrared spectroscopy studies of NO_x. *J. Mol. Catal. A*, **2008**, *281*, 200-206.
- [38] Yuan, Z.F.; Li, B.; Zhang, J.L.; Xu, C.; Ke, J.J. Synthesis of TiO₂ thin film by a modified sol-gel method and properties of the prepared films for photocatalyst. *J. Sol-Gel Sci. Techn.*, **2006**, *39*, 249-253.
- [39] Gelover, S.; Mondragón, P.; Jiménez, A. Titanium dioxide sol-gel deposited over glass and its application as a photocatalyst for water decontamination. *J. Photochem. Photobiol. A*, **2004**, *165*, 241-246.
- [40] Kluson, P.; Kacer, P.; Cajthaml, T.; Kalaji, M. Preparation of titania mesoporous materials using a surfactant-mediated sol-gel method. *J. Mater. Chem.*, **2001**, *11*, 644-651.
- [41] Kluson, P.; Kacer, P.; Cajthaml, T.; Kalaji, M. Titania thin films and supported nanostructured membranes prepared by the surfactant assisted sol-gel method. *Chem. Biochem. Eng. Q.*, **2003**, *17*, 183-190.
- [42] Čírkva, V.; Žabová, H.; Hájek, M. Microwave photocatalysis of monochloroacetic acid over nanoporous titanium(IV) oxide thin films using mercury electrodeless discharge lamps. *J. Photochem. Photobiol. A*, **2008**, *198*, 13-17.
- [43] Kluson, P.; Luskova, H.; Cajthaml, T.; Solcova, O. Non thermal preparation of photoactive titanium(IV) oxide thin layers. *Thin Solid Films*, **2006**, *495*, 18-23.
- [44] Žabová, H.; Čírkva, V. Microwave photocatalysis III. Transition metal ion-doped TiO₂ thin films on mercury electrodeless discharge lamps: preparation, characterization and their effect on the photocatalytic degradation of monochloroacetic acid and Rhodamine B. *J. Chem. Technol. Biotechnol.*, **2009**, *84*, 1624-1630.
- [45] Müller, P.; Klán, P.; Čírkva, 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.
- [46] Müller, P.; Klán, P.; Čírkva, V. The electrodeless discharge lamp: a prospective tool for photochemistry. Part 5. Fill material-dependent emission characteristics. *J. Photochem. Photobiol. A*, **2005**, *171*, 51-57.
- [47] Phillips, R. *Sources and Applications of Ultraviolet Radiation*; Academic Press: London, UK, **1983**.
- [48] 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.
- [49] Ury, M.G.; Wood, C.H. Deep UV lamp bulb with improved fill. U.S. Patent 4,859,906, August 22, 1989.
- [50] Dolan, J.T.; Ury, M.G.; Turner, B.P.; Waymouth, J.F.; Wood, C.H. Lamp having controllable characteristics. WO Patent 93,21655, October 28, 1993.
- [51] Dolan, J.T.; Turner, B.P.; Ury, M.G.; Wood, C.H. Method and apparatus for igniting electrodeless lamp discharge. U.S. Patent 5,682,080, October 28, 1997.
- [52] Dolan, J.T.; Ury, M.G.; Wood, C.H. Lamp including sulfur. U.S. Patent 5,404,076, April 04, 1995.
- [53] Johnson, P.D.; Dakin, J.T.; Anderson, J.M. High efficacy electrodeless high intensity discharge lamp. U.S. Patent 4,810,938, March 07, 1989.
- [54] Dakin, J.T.; Berry, T.; Duffy, M.E.; Russell, T.D. Low mercury arc discharge lamp containing praseodymium. U.S. Patent 5,363,015, November 08, 1994.
- [55] Shea, A.J.; Feuersanger, A.E.; Keeffe, W.M.; Struck, C.W. Electrodeless lamp bulb. Eur. Patent 06,03014, June 22, 1994.
- [56] Russell, T.D.; Berry, T.; Dakin, J.T.; Duffy, M.E. Arc chamber for a lamp containing an essentially mercury-free fill. Eur. Patent 05,42467, May 19, 1993.
- [57] Marshall, G.B.; West, T.S. Multi-element atomic fluorescence spectroscopy. I. Stimulation of atomic fluorescence of mixtures of bismuth, mercury, selenium and tellurium – cadmium and zinc – gallium and indium by means of multi-element microwave-excited electrodeless discharge tubes. *Anal. Chim. Acta*, **1970**, *51*, 179-190.
- [58] Patel, B.M.; Browner, R.F.; Winefordner, J.D. Design and operation of temperature-controlled multiple element electrodeless discharge lamps for atomic fluorescence spectrometry. *Anal. Chem.*, **1972**, *44*, 2272-2277.
- [59] Lapatovich, W.P.; Gibbs, G.R.; Proud, J.M. Compact mercury-free fluorescent lamp. U.S. Patent 4,647,821, March 03, 1987.
- [60] Lapatovich, W.P.; Gibbs, G.R.; Proud, J.M. Compact mercury-free fluorescent lamp. U.S. Patent 4,480,213, October 30, 1984.
- [61] Lapatovich, W.P.; Gibbs, G.R. Mercury-free discharge lamp. U.S. Patent 4,492,898, August 08, 1985.
- [62] Kogelschatz, U.; Esrom, H.; Zhang, J.Y.; Boyd, I.W. High-intensity sources of incoherent UV and VUV excimer radiation for low-temperature materials processing. *Appl. Surf. Sci.*, **2000**, *168*, 29-36.
- [63] Browner, R.F.; Winefordner, J.D.; Glenn, T.H. Temperature stabilized spectral source. U.S. Patent 3,786,308, January 15, 1974.
- [64] 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.
- [65] Ono, T.; Murayama, S. Flat microwave-powered ultraviolet source. *Appl. Optics*, **1990**, *29*, 3934-3937.
- [66] Yoshizawa, K.; Kodama, H.; Minowa, Y.; Komura, H.; Ito, H. Microwave generated plasma light source apparatus. U.S. Patent 4,498,029, February 05, 1985.
- [67] Hochi, A.; Horii, S.; Takeda, M.; Matsuoka, T. Electrodeless HID lamp and electrodeless HID lamp system using the same. Eur. Patent 07,62476, March 12, 1997.
- [68] Haugsjaa, P.O.; Nelson, W.F.; Regan, R.J.; McNeil, W.H. Electrodeless light source having improved arc shaping capability. U.S. Patent 3,942,058, March 02, 1976.
- [69] Kramer, J.M.; McNeil, W.H.; Haugsjaa, P.O. Electrodeless light source having rare earth molecular continua. U.S. Patent 4,206,387, June 03, 1980.
- [70] Mueller, P.; Ury, M.G.; Wood, C.H. Deep UV lamp bulb. U.S. Patent 4,501,993, February 26, 1985.
- [71] Uekawa, S.; Gallagher, C. Metal hydrides lamp and fill for the same. U.S. Patent 6,121,730, September 19, 2000.
- [72] Dakin, J.T. Electrodeless high pressure sodium iodide arc lamp. U.S. Patent 4,783,615, November 08, 1988.
- [73] Witting, H.L. High efficacy electrodeless high intensity discharge lamp exhibiting easy starting. U.S. Patent 4,890,042, December 26, 1989.
- [74] Kirkpatrick, D.A.; Dolan, J.T.; MacLennan, D.A.; Turner, B.P.; Simpson, J.E. High brightness microwave lamp. WO Patent 00,70651, November 23, 2000.
- [75] Kamarehi, M.; Levine, L.; Ury, M.G.; Turner, B.P. Electrodeless lamp with improved efficacy. U.S. Patent 5,831,386, November 03, 1998.
- [76] Kirkpatrick, D.A.; MacLennan, D.A.; Petrova, T.; Roberts, V.D.; Turner, B.P. Electrodeless discharge lamps and bulb containing sulfur, selenium or tellurium. WO Patent 02,082501, October 17, 2002.
- [77] Dolan, J.T.; Ury, M.G.; Waymouth, J.F.; Wood, C.H. High power lamp. WO Patent 92,08240, May 14, 1992.
- [78] Turner, B.P. Tellurium lamp. U.S. Patent 5,661,365, August 26, 1997.
- [79] Kim, H.-S.; Choi, J.-S.; Kang, H.-J.; Jeon, Y.-S.; Jeon, H.-S. Electrodeless lamp using tin iodide. Eur. Patent 10,93152, April 18, 2001.
- [80] Kim, H.-S.; Choi, J.-S.; Kang, H.-J.; Jeon, Y.-S.; Jeon, H.-S. Electrodeless lamp using SnI₂. U.S. Patent 6,633,111, October 14, 2003.
- [81] Xia, L.-Y.; Gu, D.-H.; Tan, J.; Dong, W.-B.; Hou, H.-Q. Photolysis of low concentration H₂S under UV/VUV irradiation emitted from microwave discharge electrodeless lamps. *Chemosphere*, **2008**, *71*, 1774-1780.
- [82] Voronov, A.; Reber, S. Device for treating fluids, especially water sterilization, comprising an electrodeless gas discharge lamp. U.S. Patent Appl. 2009,120882, May 14, 2009.
- [83] Dakin, J.T.; Berry, T.; Duffy, M.E.; Russell, T.D. Low mercury arc discharge lamp containing praseodymium. U.S. Patent 5,363,015, November 08, 1994.
- [84] Relich, S.; Čírkva, V.; Vlková, L.; Hájek, M. *Photochemistry in the Microwave Oven: Preparation, Evaluation and Applications of the Electrodeless Discharge Lamps*. Proceedings of the 3rd International Conference on Microwave Chemistry, Brno, Czech Republic, September 03-07, **2006**; Potáček, M.; Janků, S.; Dostál, J.; Táborská, E.; Mazal, C.; Pálková, A.; Šibor, J.; Moravec, Z.; Urbánková, M.; Mikulášek, J.; Kareš, R., Eds.; Masaryk University: Brno, Czech Republic, **2006**; pp. PO-21.
- [85] Braun, A.M.; Maurette M.-T.; Oliveros, E. *Photochemical Technology*; Wiley & Sons: Chichester, UK, **1991**.
- [86] De Lasa, H.; Serrano, B.; Salas, M. *Photocatalytic Reaction Engineering*; Springer: New York, USA, **2005**.
- [87] Oppenländer, T. *Photochemical Purification of Water and Air*; Wiley-VCH: Weinheim, Germany, **2003**.
- [88] 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. Microwave Power E. R.*, **1999**, *34*, 55-60.
- [89] Klán, P.; Hájek, M.; Čírkva, V. The electrodeless discharge lamp: a prospective tool for photochemistry: Part 3. The microwave photochemistry reactor. *J. Photochem. Photobiol. A*, **2001**, *140*, 185-189.
- [90] Klán, P.; Literák, J.; Hájek, M. The electrodeless discharge lamp: a prospective tool for photochemistry. *J. Photochem. Photobiol. A*, **1999**, *128*, 145-149.
- [91] 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.
- [92] Čírkva, V.; Relich, S.; Hájek, M. Microwave photochemistry V: Low-pressure batch and continuous-flow microwave photoreactors with quartz mercury electrodeless discharge lamps. Photohydrolysis of monochloroacetic acid. *J. Chem. Technol. Biotechnol.*, **2010**, *85*, 185-191.
- [93] Klán, P.; Růžička, R.; Heger, D.; Literák, J.; Kulhánek, P.; Loupy, A. Temperature-sensitive photochemical aromatic substitution on 4-nitroanisole. *Photochem. Photobiol. Sci.*, **2002**, *1*, 1012-1016.
- [94] 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.
- [95] Klán, P.; Pavrik, M. Non-catalytic remediation of aqueous solutions by microwave-assisted photolysis in the presence of H₂O₂. *J. Photochem. Photobiol. A*, **2006**, *177*, 24-33.

- [96] 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.
- [97] Nüchter, M.; Ondruschka, B.; Jungnickel, A.; Müller, U. Organic processes initiated by non-classical energy sources. *J. Phys. Org. Chem.*, **2000**, *13*, 579-586.
- [98] Ai, Z.; Yang, P.; Lu, X. Degradation of 4-chlorophenol by microwave irradiation enhanced advanced oxidation processes. *Chemosphere*, **2005**, *60*, 824-827.
- [99] 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.
- [100] Církva, V.; Kurfürstová, J.; Karban, J.; Hájek, M. Microwave photochemistry II. Photochemistry of 2-tert-butylphenol. *J. Photochem. Photobiol. A*, **2004**, *168*, 197-204.
- [101] Církva, V.; Kurfürstová, J.; Karban, J.; Hájek, M. Microwave photochemistry III. Photochemistry of 4-tert-butylphenol. *J. Photochem. Photobiol. A*, **2005**, *174*, 38-44.
- [102] 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.
- [103] 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.
- [104] 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/H₂O₂ process. *J. Photochem. Photobiol. A*, **2009**, *204*, 115-121.
- [105] 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.
- [106] 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.
- [107] Limbeck, A. Microwave-assisted UV-digestion procedure for the accurate determination of Pd in natural waters. *Anal. Chim. Acta*, **2006**, *575*, 114-119.
- [108] Matusiewicz, H.; Stanis, E. Characteristics of a novel UV-TiO₂-microwave integrated irradiation device in decomposition processes. *Microchem. J.*, **2007**, *86*, 9-16.
- [109] Howard, A.G.; Labonne, L.; Rousay, E. Microwave driven ultraviolet photodecomposition of organophosphate species. *Analyst*, **2001**, *126*, 141-143.
- [110] Kunz, A.; Peralta-Zamora, P.; Durán, N. Hydrogen peroxide assisted photochemical degradation of ethylenediaminetetraacetic acid. *Adv. Environ. Res.*, **2002**, *7*, 197-202.
- [111] 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.
- [112] Bergmann, H.; Iourtchouk, T.; Schöps, K.; Bouzek, K. New UV irradiation and direct electrolysis-promising methods for water disinfection. *Chem. Eng. J.*, **2002**, *85*, 111-117.
- [113] 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.
- [114] Žabová, H.; Církva, V.; Hájek, M. Microwave photocatalysis II. Novel continuous-flow microwave photocatalytic experimental set-up with titanium-coated mercury electrodeless discharge lamps. *J. Chem. Technol. Biotechnol.*, **2009**, *84*, 1125-1129.
- [115] Han, D.-H.; Cha, S.-Y.; Yang, H.-Y. Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/H₂O₂ process and kinetic study. *Water Res.*, **2004**, *38*, 2782-2790.
- [116] 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 H₂O₂. *J. Hazard. Mater. B*, **2006**, *134*, 183-189.
- [117] 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.
- [118] Xia, L.-Y.; Gu, D.-H.; Tan, J.; Dong, W.-B.; Hou, H.-Q. Photolysis of low concentration H₂S under UV/VUV irradiation emitted from microwave discharge electrodeless lamps. *Chemosphere*, **2008**, *71*, 1774-1780.
- [119] 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.
- [120] Horikoshi, S.; Saitou, A.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination method. V. Thermal and nonthermal effects of microwave radiation on the photocatalyst and on the photodegradation of rhodamine-B under UV/Vis radiation. *Environ. Sci. Technol.*, **2003**, *37*, 5813-5822.
- [121] Horikoshi, S.; Kajitani, M.; Hidaka, H.; Serpone, N. Investigation of factors that influence TiO₂ photoassisted degradations under simultaneous illumination by UV and microwave radiation fields. *J. Photochem. Photobiol. A*, **2008**, *196*, 159-164.
- [122] Horikoshi, S.; Sakai, F.; Kajitani, M.; Abe, M.; Serpone, N. Microwave frequency effects on the photoactivity of TiO₂: Dielectric properties and the degradation of 4-chlorophenol, bisphenol A and methylene blue. *Chem. Phys. Lett.*, **2009**, *470*, 304-307.
- [123] Horikoshi, S.; Hidaka, H.; Serpone, N. Hydroxyl radicals in microwave photocatalysis. Enhanced formation of OH radicals probed by ESR techniques in microwave-assisted photocatalysis in aqueous TiO₂ dispersions. *Chem. Phys. Lett.*, **2003**, *376*, 475-480.
- [124] Horikoshi, S.; Tokunaga, A.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination method. VII. Thermal/non-thermal effects in the microwave-assisted photocatalyzed mineralization of bisphenol-A. *J. Photochem. Photobiol. A*, **2004**, *162*, 33-40.
- [125] Horikoshi, S.; Kajitani, M.; Serpone, N. The microwave/photo-assisted degradation of bisphenol-A in aqueous TiO₂ dispersions revisited. Re-assessment of the microwave non-thermal effect. *J. Photochem. Photobiol. A*, **2007**, *188*, 1-4.
- [126] Horikoshi, S.; Hojo, F.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination technique. 8. Fate of carboxylic acids, aldehydes, alkoxy carbonyl and phenolic substrates in a microwave radiation field in the presence of TiO₂ particles under UV irradiation. *Environ. Sci. Technol.*, **2004**, *38*, 2198-2208.
- [127] Horikoshi, S.; Abe, M.; Serpone, N. Influence of alcoholic and carbonyl functions in microwave-assisted and photo-assisted oxidative mineralization. *Appl. Catal. B*, **2009**, *89*, 284-287.
- [128] Horikoshi, S.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV-illumination technique IV. Non-thermal effects in the microwave-assisted degradation of 2,4-dichlorophenoxyacetic acid in UV-irradiated TiO₂/H₂O dispersions. *J. Photochem. Photobiol. A*, **2003**, *159*, 289-300.
- [129] Horikoshi, S.; Tokunaga, A.; Watanabe, N.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination technique 9. Peculiar hydrolytic and co-catalytic effects of platinum on the TiO₂ photocatalyzed degradation of the 4-chlorophenol toxin in a microwave radiation field. *J. Photochem. Photobiol. A*, **2006**, *177*, 129-143.
- [130] Horikoshi, S.; Sakai, F.; Horikoshi, S.; Abe, M.; Emeline, A.V.; Serpone, N. Microwave-specific effects in various TiO₂ specimens. Dielectric properties and degradation of 4-chlorophenol. *J. Phys. Chem. C*, **2009**, *113*, 5649-5657.
- [131] Kataoka, S.; Tompkins, D.T.; Zeltner, W.A.; Anderson, M.A. Photocatalytic oxidation in the presence of microwave irradiation: observations with ethylene and water. *J. Photochem. Photobiol. A*, **2002**, *148*, 323-330.
- [132] Liao, W.; Wang, P. Microwave-assisted photocatalytic degradation of dimethyl phthalate using a microwave discharged electrodeless lamp. *J. Braz. Chem. Soc.*, **2009**, *20*, 866-872.
- [133] Hong, J.; Sun, C.; Yang, S.-G.; Liu, Y.-Z. Photocatalytic degradation of methylene blue in TiO₂ aqueous suspensions using microwave powered electrodeless discharge lamps. *J. Hazard. Mater.*, **2006**, *133*, 162-166.
- [134] Ju, Y.; Yang, S.; Ding, Y.; Sun, C.; Zhang, A.; Wang, L. Microwave-assisted rapid photocatalytic degradation of malachite green in TiO₂ suspensions: mechanism and pathways. *J. Phys. Chem.*, **2008**, *112*, 11172-11177.
- [135] Liu, Y.; Yang, S.; Hong, J.; Sun, C. Low-temperature preparation and microwave photocatalytic activity study of TiO₂-mounted activated carbon. *J. Hazard. Mater.*, **2007**, *142*, 208-215.
- [136] Gao, Z.; Yang, S.; Ta, N.; Sun, C. Microwave assisted rapid and complete degradation of atrazine using TiO₂ nanotube photocatalyst suspensions. *J. Hazard. Mater.*, **2007**, *145*, 424-430.
- [137] Gao, Z.; Yang, S.; Sun, C.; Hong, J. Microwave assisted photocatalytic degradation of pentachlorophenol in aqueous TiO₂ nanotubes suspension. *Sep. Purif. Technol.*, **2007**, *58*, 24-31.
- [138] Yang, S.; Fu, H.; Sun, C.; Gao, Z. Rapid photocatalytic destruction of pentachlorophenol in F-Si-commodified TiO₂ suspensions under microwave irradiation. *J. Hazard. Mater.*, **2009**, *161*, 1281-1287.
- [139] Horikoshi, S.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination technique VI. A simple modified domestic microwave oven integrating an electrodeless UV-Vis lamp to photodegrade environmental pollutants in aqueous media. *J. Photochem. Photobiol. A*, **2004**, *161*, 221-225.
- [140] Horikoshi, S.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination technique. 3. A microwave-powered plasma light source and photoreactor to degrade pollutants in aqueous dispersions of TiO₂ illuminated by the emitted UV/Visible radiation. *Environ. Sci. Technol.*, **2002**, *36*, 5229-5237.
- [141] 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.
- [142] Ai, Z.; Yang, P.; Lu, X. Degradation of 4-chlorophenol by a microwave assisted photocatalytic method. *J. Hazard. Mater. B*, **2005**, *124*, 147-152.
- [143] Li, F.; Lu, X.; Ai, Z.; Yuan, S.; Mei, P. Study on the relationship between structural parameters and photocatalytic activity of chlorophenols. *Fresenius Environ. Bull.*, **2007**, *16*, 1345-1350.
- [144] Zhang, X.; Wang, Y.; Li, G. Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO₂ catalyst. *J. Mol. Catal. A*, **2005**, *237*, 199-205.
- [145] Zhang, X.; Li, G.; Wang, Y. Microwave assisted photocatalytic degradation of high concentration azo dye Reactive Brilliant Red X-3B with microwave electrodeless lamp as light source. *Dyes Pigm.*, **2007**, *74*, 536-544.

- [146] Zhang, X.; Sun, D.D.; Li, G.; Wang, Y. Investigation of the roles of active oxygen species in photodegradation of azo dye AO7 in TiO₂ photocatalysis illuminated by microwave electrodeless lamp. *J. Photochem. Photobiol. A*, **2008**, *199*, 311-315.
- [147] Liu, R.; Wang, H.; Zhao, X.; Xiao, S.; Qu, J. Microwave electrodeless lamp assisted catalytic degradation of X-GRL with manganese dioxides: Adsorption and manganese(IV) reductive dissolution effects. *Catal. Today*, **2008**, *139*, 119-124.
- [148] Horikoshi, S.; Kajitani, M.; Horikoshi, N.; Dillert, R.; Bahnemann, D.W. Use of microwave discharge electrodeless lamps (MDEL). II. Photodegradation of acetaldehyde over TiO₂ pellets. *J. Photochem. Photobiol. A*, **2008**, *193*, 284-287.
- [149] Obee, T.N.; Hay, S.O.; Sangiovanni, J.J.; Hertzberg, J.B. Electrodeless ultraviolet discharge fluid remediation. WO Patent 03,094982, November 20, 2003.

Received: 15 November, 2009

Revised: 17 December, 2009

Accepted: 17 December, 2009