Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 177 (2006) 24–33

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Non-catalytic remediation of aqueous solutions by microwave-assisted photolysis in the presence of H_2O_2

Petr Klán*, Martin Vavrik

Department of Organic Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, 61137 Brno, Czech Republic

Received 9 February 2005; received in revised form 4 May 2005; accepted 11 May 2005

Abstract

Advanced oxidation processes have emerged as potentially powerful methods to transform organic pollutants in aqueous solutions into non-toxic substances. In this work, a comparison of degradation dynamics of five 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 is presented. Relative degradation rate constants have been monitored and the major products were identified. The combined degradation effect of UV and MW radiation was found larger than the sum of isolated effects in all cases studied. It is concluded that such an overall efficiency increase is essentially based on a thermal enhancement of subsequent oxidation reactions of the primary photoreaction intermediates. Optimizations revealed that this effect was particularly significant in samples with a low concentration of H_2O_2, however, a larger excess of H_2O_2 was essential to complete the destruction in most experiments. The absence of heterogeneous catalysts was in no doubt an additional advantage of the technique applied.

Keywords: Photochemistry; Microwave; Remediation; Environmental; Hydrogen peroxide; Aqueous solutions; Aromatic compounds

1. Introduction

Photochemistry in the microwave (MW) field [1] provides an opportunity to combine chemical activation by two distinctive kinds of electromagnetic radiation. While low-energy MW radiation ($E = 0.4$–$40\,\mathrm{J\,mol^{-1}}$; $\nu = 1$–$100\,\mathrm{GHz}$) is typically responsible for dielectric heating causing thermally initiated reactions [2,3], UV–vis radiation ($E = 600$–$170\,\mathrm{kJ\,mol^{-1}}$; $\lambda = 200$–$700\,\mathrm{nm}$) initiates the excited-state transformations. In the past 5 years, we have reported on an original photochemical reactor that takes advantage of an electrodeless discharge lamp (EDL), which generates UV radiation when placed into the MW field inside a reaction mixture [4–7]. There have been first successful attempts to use combined MW/UV irradiation for an efficient degradation of various samples prior to application of a subsequent analytical method. Florian and Knapp proposed a novel MW/UV, high-temperature, high-pressure digestion procedure for the decomposition of interfering dissolved organic carbon as a part of the trace element analysis of industrial or municipal wastewater [8]. Photodegradation [9] and microwave thermolysis [10] of pollutants and toxic agents in wastewater are two important methods for their removal, often in combination with a solid catalyst (e.g., TiO_2). Results from the first environmentally relevant studies already appeared in the scientific literature and the topic is also covered by several patents ([1] and references therein). Campanella et al. [11] reported on minor but positive enhancements of the photodegradation efficiency of *o*- and *p*-chlorophenol aqueous solutions by microwave heating. Those model systems served for extension of the application to other environmentally interesting compounds, such as sodium dodecylbenzenesulfonate or organophosphosphate pesticides. Heterogeneous catalytic degradation of humic acid in aqueous titanium dioxide suspension under MW/UV conditions was studied by Chemat et al. [12] for the first time. An enhancement in this case was

---

* Corresponding author. Tel.: +420 549494856.
E-mail address: klan@sci.muni.cz (P. Klán).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.05.008

reported as higher than a simple addition of both effects. In the past 3 years, Horikoshi, Hidaka, and Serpone have published a series of studies on environmental remediation of various aqueous solutions by simultaneous MW/UV irradiation in the presence of TiO_2 [13–15]. It was proved that this integrated illumination technique is superior in the degradation of various organic compounds than a simple photocatalysis.

In recent years, advanced oxidation processes (AOP) have emerged as potentially powerful methods, which are capable of transforming organic pollutants in aqueous solutions into non-toxic substances. Such a remediation usually relies on the generation of reactive free radicals, especially hydroxyl radicals ($HO^\bullet$) [16]. These radicals react rapidly and usually non-selectively with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from organic molecules, resulting in a series of degradation oxidation reactions ultimately lead to mineralization products, such as CO_2 and H_2O [17]. AOP have been studied in many variation, including UV/H_2O_2, O_3/H_2O_2, $O_3/H_2O_2/UV$, H_2O_2/Fe^{2+} (Fenton reaction); and $UV/H_2O_2/Fe^{2+}$ (Photo-Fenton reaction).

In the present study, we wished to compare 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 techniques in the presence of H_2O_2, where the MW field has been used solely as a simple heating technique. This study focused on (a) examining the effect of MW radiation on the photolytic non-catalytic oxidative degradation under UV irradiation to obtain some evidence for the initial mechanistic steps; (b) on optimizing the degradation process; and (c) on finding whether this simultaneous MW/UV technique is superior in the degradation than a simple photooxidation or MW-assisted oxidation. The combination of the conventional degradation techniques could be promising strategy for drinking water treatment or environmental remediation of polluted wastewaters.

2. Experimental

2.1. Equipment

The experiments were accomplished in a modified MW oven Whirlpool M401 (900 W), operating at 2450-MHz frequency, as described elsewhere [18,19], which had a window for UV irradiation from a conventional high-pressure Hg discharge lamp (400 W). The external irradiation guaranteed identical irradiation conditions for all experiments. The limit on the safe stray leakage of microwave power density was kept below 5 $mW\,cm^{-2}$ at 2450 MHz measured in the 50-mm distance from the equipment. The equipment was checked for leaks especially around the modified area [6]. The experimental system in the microwave oven consisted of a quartz (allowing irradiation at $\lambda > 254$ nm) vessel containing an aqueous solution (50 ml), equipped with a reflux condenser. A typical sample concentration was 10^{-3} $mol\,l^{-1}$ (except pentachlorophenol with $c = 6 \times 10^{-6}$ $mol\,l^{-1}$). All experiments, with MW heating or in its absence, were carried out in this set-up to guarantee the same experimental conditions. The concentration of the solutes was monitored by HPLC during the course of irradiation. The dark controls were done for all chemical systems with the highest H_2O_2 concentrations in the time scale of the experiments at 20 °C;

Table 1
Relative initial pseudo first-order rate constants k_{rel} for phenol ($c = 10^{-3}$ $mol\,l^{-1}$) degradation and the major products

Conditions	H_2O_2 concentration ($mol\,l^{-1}$)	k_{rel} (min^{-1})	Main degradation products[a]
MW; reflux	5×10^{-3}	0.0018 ± 0.0001	Hydroquinone; benzoquinone
MW; reflux	1	0.1021 ± 0.0090	
UV; 20 °C	$5{\times}10^{-3}$	0.0022 ± 0.0001	
UV; 20 °C	1	0.0109 ± 0.0013	
MW/UV; reflux	0	0.0014 ± 0.0001	
MW/UV; reflux	5×10^{-3}	0.0857 ± 0.0032	
MW/UV; reflux	1	0.1489 ± 0.0089	

[a] The products listed were found in all experiments.

Table 2
Relative initial pseudo first-order rate constants k_{rel} for chlorobenzene ($c = 10^{-3}$ $mol\,l^{-1}$) degradation and the major products

Conditions	H_2O_2 concentration ($mol\,l^{-1}$)	k_{rel} (min^{-1})	Main degradation products[a]
MW; reflux	5×10^{-3}	0.0154 ± 0.0005	4-Chlorophenol; 2-chlorophenol; phenol
MW; reflux	0.5	0.0576 ± 0.0044	
UV; 20 °C	0	0.0112 ± 0.0001	
UV; 20 °C	5×10^{-3}	0.0129 ± 0.0002	
UV; 20 °C	0.5	0.1162 ± 0.0060	
MW/UV; reflux	5×10^{-3}	0.1634 ± 0.0004	
MW/UV; reflux	0.5	0.3570 ± 0.0131	

[a] Chlorophenols were identified in all experiments with H_2O_2; phenol was the major photoproduct.

Table 3
Relative initial pseudo first-order rate constants k_{rel} for nitrobenzene ($c = 10^{-3}$ mol l^{-1}) degradation and the major products

Conditions	H_2O_2 concentration (mol l^{-1})	k_{rel} (min^{-1})	Main degradation products[a]
MW; reflux	0.5	0.778 ± 0.023	2-Nitrophenol; 4-nitrophenol
UV; 20 °C	0	0.071 ± 0.003	
UV; 20 °C	0.5	0.195 ± 0.026	
MW/UV; reflux	0.5	1.369 ± 0.072	

[a] The products listed were found in all experiments.

Table 4
Relative initial pseudo first-order rate constants k_{rel} for 4-chlorophenol ($c = 10^{-3}$ mol l^{-1}) degradation and the major products

Conditions	H_2O_2 concentration (mol l^{-1})	k_{rel} (min^{-1})	Main degradation products[a]
MW; reflux	1×10^{-2}	0.00039 ± 0.00001	Phenol; hydroquinone; benzoquinone; coupling products
MW; reflux	1	0.0031 ± 0.0001	
UV; 20 °C	0	0.013 ± 0.001	
UV; 20 °C	1×10^{-2}	0.016 ± 0.001	
UV; 20 °C	1	0.043 ± 0.005	
MW/UV; reflux	1×10^{-2}	0.076 ± 0.004	
MW/UV; reflux	1	0.131 ± 0.006	

[a] Phenol, hydroquinone, and benzoquinone were found in all experiments. The coupling products, such as 5-chlorobiphenyl-2,4′-diol, were formed only by photolysis.

no chemistry was observed in all cases within the error of the measurements.

2.2. *Chemicals*

Water was purified by the reverse osmosis process on an Aqua Osmotic 03 and its quality complied with US Pharmacopaial Standards (USP). Hydrogen peroxide (p.a., 30%) and acetonitrile (HPLC quality) were purchased from Fluka. The exact concentration of H_2O_2 was determined by an iodometric titration. Phenol, chlorobenzene, nitrobenzene, 4-chlorophenol, and pentachlorophenol were purchased from Lachema Co. and they were purified by distillation or recrystallization to a <99% quality. Products listed in Tables 1–4 were identified by HPLC analysis comparing the retention times of the authentic compounds, which were either obtained in our previous studies [20,21] (their identification was based on GC–MS analyses) or purchased from Aldrich.

2.3. *Analysis*

The samples were analyzed on a Shimadzu LC-10AD HPLC apparatus equipped with a UV detector Shimadzu SPD-10A ($\lambda = 220$–300 nm) and columns SGC C-8 or C-18 (150 × 3 mm), with mobile phases for phenol: acetonitrile/water (1:1, v/v), flow rate of 0.8 ml min^{-1}; chlorobenzene: acetonitrile/water (7:3, v/v), flow rate of 1.2 ml min^{-1}; nitrobenzene: acetonitrile/water (1:1, v/v), flow rate of 1.0 ml min^{-1}; 4-chlorophenol: acetonitrile/water (1:1, v/v), flow rate of 0.8 ml min^{-1}; and pentachlorophenol: acetonitrile/water (3:1, v/v), flow rate of 1.0 ml min^{-1}. Methyl benzoate was used as an internal standard. Concentrations of the analyzed compounds were calibrated on authentic samples. The relative standard deviation for triplicate measurements was below 7% in all analyses.

3. Results and discussion

Aqueous solutions of phenol, chlorobenzene, nitrobenzene, 4-chlorophenol, and pentachlorophenol have been subjected to various degradative methods: microwave-assisted destruction (MW), microwave-assisted destruction in the presence of H_2O_2 (MW/H_2O_2), photolysis (UV), photolysis in the presence of H_2O_2 (UV/H_2O_2), microwave-assisted photolysis (MW/UV), and microwave-assisted photolysis in the presence of H_2O_2 (MW/UV/H_2O_2). The degradation dynamics has been monitored to estimate the rate of disappearance of the starting material and, in addition, some photoproducts were identified. All compounds used display strong absorption bands at $\lambda > 254$, therefore, a quartz window and reaction vessel have been employed. The combined MW/UV reactor consisted of a MW cavity, which had a window for an external UV irradiation. The vessel containing the reaction solutions was irradiated always in the same position and distance from the UV source, even in cases that the MW source was off. This guaranteed identical irradiation conditions in all experiments. All samples were analyzed by HPLC during the course of irradiation in the corresponding time intervals. The initial relative rate constants of degradation presented here are valid for the experimental conditions used only.

Hydrogen peroxide is a safe, efficient, and easy-to-use chemical oxidant suitable for wide usage on contamination prevention. It was first used to reduce odor in wastewater, and from then on, it became widely employed. However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants, it must be combined with UV light, salts of particular metals, or ozone to produce the desired degradation results [16]. Photolysis in the presence of H_2O_2 is based on the formation of $HO^\bullet$ radicals by means of the O–O bond cleavage ($H_2O_2 + h\nu \rightarrow 2HO^\bullet$) and the subsequent propa-

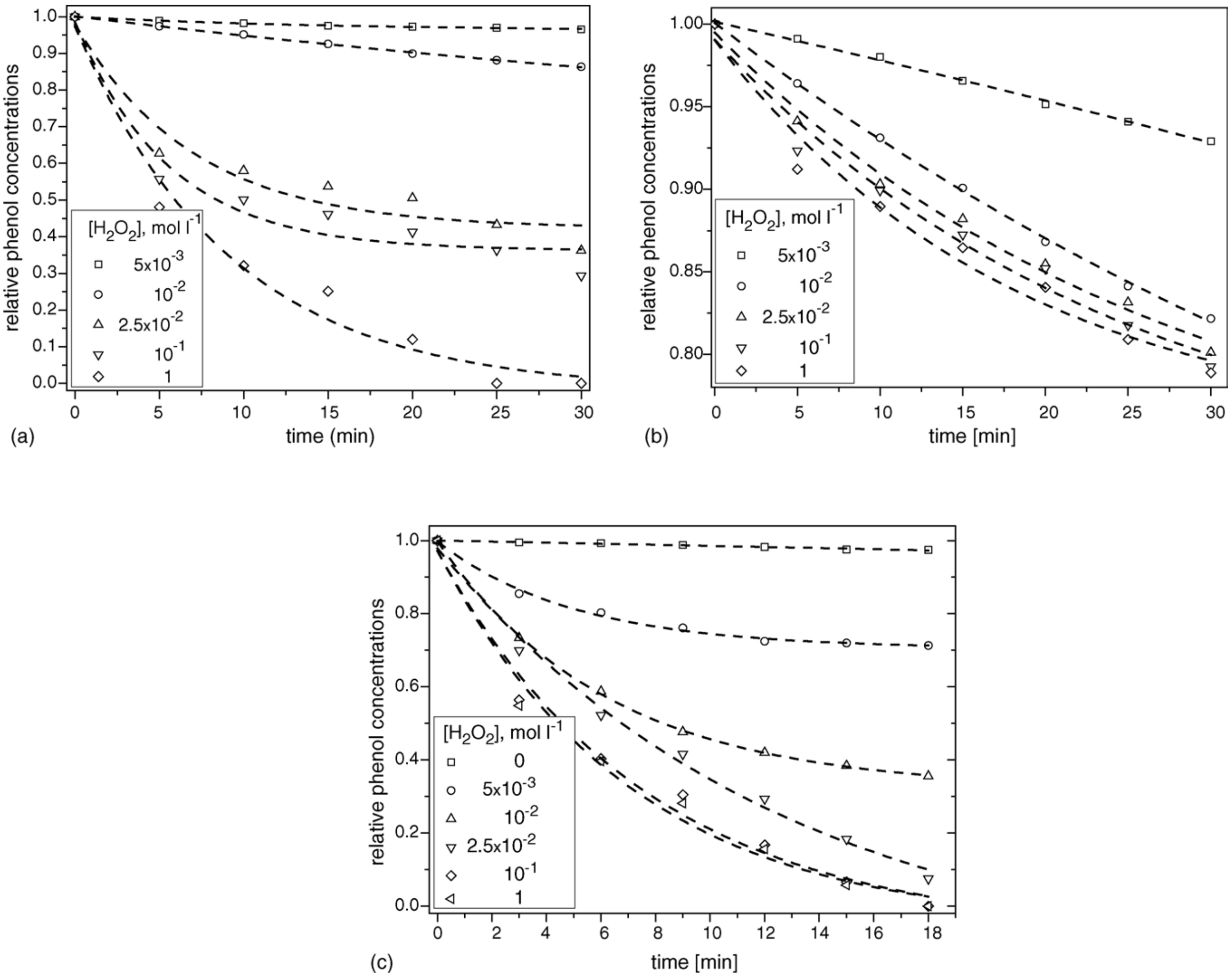


Fig. 1. (a) Microwave-assisted degradation of phenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (b) Photolysis of phenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water at 20 °C. (c) MW-assisted photolysis of phenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water.

gation reactions [22]. The molar absorptivity of hydrogen peroxide at 253.7 nm is low (∼20 M^{-1} cm^{-1}) and HO$^\bullet$ radicals are formed per incident photon absorbed. If there are other strong UV absorbers different than hydrogen peroxide, such as organic aromatic compounds, an internal filter effect is observed. In addition, the degradation of organic chromophores can simultaneously proceed by direct photolysis, and if MW heating is introduced, thermal effects on all chemical processes are anticipated. The combined MW/UV/H_2O_2 treatment of the solutions must thus reveal a complex chemistry.

3.1. Phenol

Phenol aqueous solutions ($c = 10^{-3}$ mol l^{-1}) containing hydrogen peroxide were subjected to MW heating and the degradation profiles were fitted to monoexponential curves (Fig. 1a). A high concentration of H_2O_2 was essential: only a large excess ($c = 1$ mol l^{-1}) enabled an efficient destruction of the starting compound and lower concentrations left a large portion of the starting compound unreacted. A MW/H_2O_2 destruction was very responsive to [H_2O_2]—raising the concentration from 5×10^{-3} to 1 mol l^{-1} corresponded to the initial pseudo-first-order reaction rate constants (k_{rel}) equal to 0.0018 and 0.1021 min^{-1}, respectively, that is an increase by a factor of 55 (Table 1). Photolysis (UV/H_2O_2) of the same solutions at 20 °C revealed that the phenol consumption is significantly less sensitive to [H_2O_2] compared to thermal degradation (Fig. 1b; Table 1). The photodegradation curves were also fitted to a first-order reaction law as was also observed elsewhere [23]. A combined remediation technique (MW/UV/H_2O_2) proved to be very successful (Fig. 1c); samples with a very low peroxide concentration ($c = 5 \times 10^{-3}$ mol l^{-1}) were degraded with the same reaction efficiency as those using MW/H_2O_2 at high peroxide concentrations (Table 1). Further addition of peroxide had only minor effect on the rate constants. It is apparent from the table that such an enhancement is higher than a simple addition of both effects by factors of 21 and 1.3 at 5×10^{-3} and $1\,\mathrm{mol\,l^{-1}}$ peroxide concentrations, respectively. Phenol was not expected to provide any efficient photochemical degradation other than oxidation by H_2O_2 or oxygen. The internal filter effect of phenol ($\lambda_{max} = 270$) will definitely become substantial when only small amount of H_2O_2 molecules are present in the samples. The oxidation products identified, hydroquinone and benzoquinone, represent typical primary adducts of the hydroxyl radicals with phenol.

3.2. Chlorobenzene

Chlorobenzene solutions ($c = 10^{-3}\,\mathrm{mol\,l^{-1}}$) were exposed to the same degradation techniques as those of phenol. While thermal degradation of the phenol solutions was more efficient than that of photolysis, chlorobenzene was more sensitive to the UV irradiation comparing to phenol. The molar absorption coefficient of chlorobenzene at $\lambda_{max} = 264$ is about one order or magnitude lower than that of phenol ($\lambda_{max} = 270$). The rationalization must be in efficient photoreductive dechlorination and aryl free radical coupling reactions commonly observed in all H-donating solvents [24], in addition to photosubstitution, the major pathway in methanol or aqueous solutions [25]. The main product of hydrolysis was phenol, identified in all irradiated samples, but formation of 4-chlorophenol and 2-chlorophenol was also relatively efficient in samples containing H_2O_2. Fig. 2a and Table 2 show that chlorobenzene is destroyed by MW/H_2O_2 with the pseudo-first-order reaction rate constants (k_{rel}) equal to 0.0154 and $0.0576\,\mathrm{min^{-1}}$, for H_2O_2 concentrations 10^{-2} and $0.5\,\mathrm{mol\,l^{-1}}$, respectively. Degradation of chlorobenzene using various photoinduced oxidation processes, such as direct ultraviolet light-induced photolysis, has been investigated under aerobic and anaerobic conditions by Dilmeghani and Zahir, and a UV/H_2O_2 process was found superior to simple photolysis [26]. The same findings were apparent in our experiments, in which photolysis (UV/H_2O_2) of the solutions (Fig. 2b) displayed an efficient and complete degradation only at higher peroxide concentrations, with curves fitted

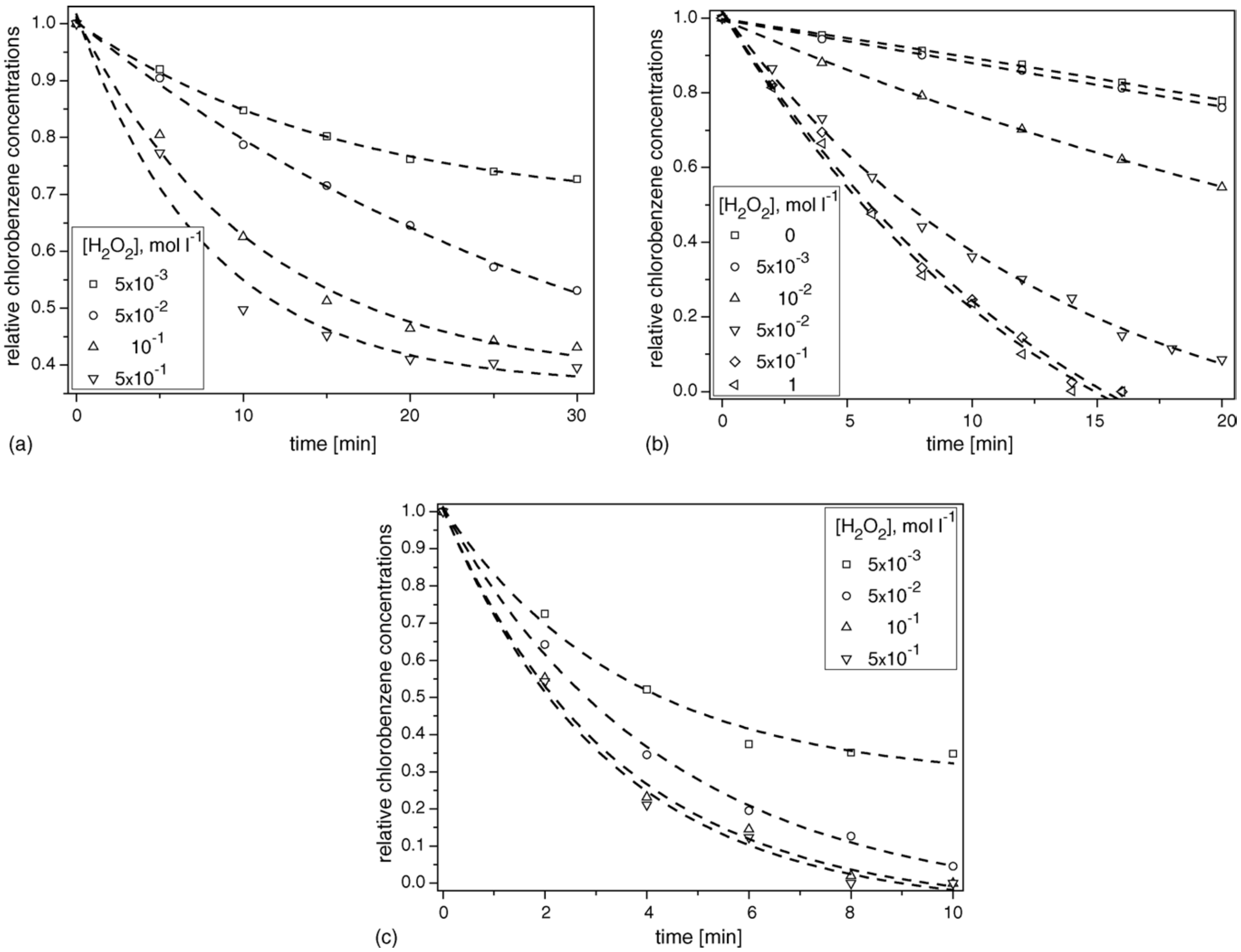


Fig. 2. (a) Microwave-assisted degradation of chlorobenzene ($c = 10^{-3}\,\mathrm{mol\,l^{-1}}$) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (b) Photolysis of chlorobenzene ($c = 10^{-3}\,\mathrm{mol\,l^{-1}}$) in the presence of H_2O_2 (the concentrations are shown in the inset) in water at 20 °C. (c) MW-assisted photolysis of chlorobenzene ($c = 10^{-3}\,\mathrm{mol\,l^{-1}}$) in the presence of H_2O_2 (the concentrations are shown in the inset) in water.

to a first-order reaction law again. A combined technique (MW/UV/H_2O_2) proved to be very successful (Fig. 2c). The process efficiency, expressed by the relative rate constants (Table 2), at [H_2O_2] equal to 5×10^{-3} mol l^{-1} was ∼6 times higher than the sum of those of UV/H_2O_2 or MW/H_2O_2, while only by a factor of 2 at a higher peroxide concentration ($c = 0.5$ mol l^{-1}).

3.3. Nitrobenzene

Nitrobenzene solutions ($c = 10^{-3}$ mol l^{-1}) containing hydrogen peroxide were found to be thermally very unstable. Fig. 3a shows that all MW/H_2O_2 degradation processes at the peroxide concentrations in the interval of 2×10^{-2} and 0.5 mol l^{-1} underwent with nearly same k_{rel} equal to ∼0.78 (Table 3). In contrast, photolysis was relatively less efficient (Fig. 3b), although nitrobenzene has a significant absorption in the region of 250–400 nm ($\lambda_{\max} = 280$), but still reaching a 100% conversion. Nitroaromatic compounds are known to be photoreactive, for instance, via photoinduced nucleophilic substitution [7], thus subsequent oxidation by the hydroxyl radicals [27,28] produced photochemically should not be the exclusive degradation pathway, despite the fact that 4-nitrophenol and 2-nitrophenol were found to be exclusive oxidation products at low conversions (Table 3). A combined effect of MW and UV did barely increase the degradation efficiency ($k_{\mathrm{rel}} = \sim 1.4$) but still the total degradation rate constant for the MW/UV/H_2O_2 technique was higher than a simple addition of those of MW/H_2O_2 and UV/H_2O_2.

3.4. 4-Chlorophenol

Chlorophenols belong among the most widely studied organic micropollutants. 4-Chlorophenol is used in paper, herbicide, and pesticide industries, and it has been identified in aquatic and soil environment [29,30]. Monochlorophenols in neutral aqueous solutions absorb significantly in the region of 250–290 nm; the absorption maximum of the para derivative is at 278 nm [31]. In the present study, a MW/H_2O_2

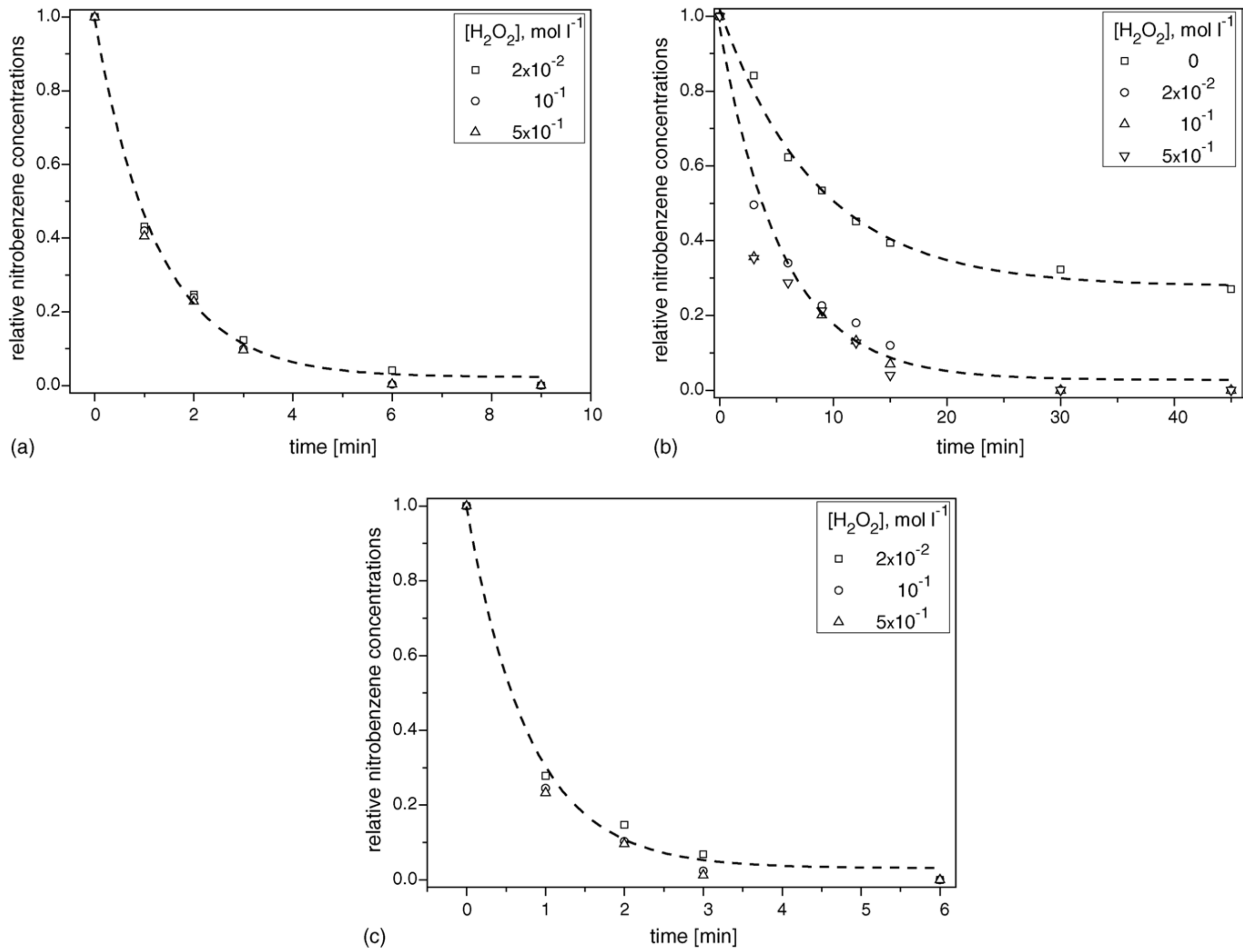


Fig. 3. (a) Microwave-assisted degradation of nitrobenzene ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (b) Photolysis of nitrobenzene ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water at 20 °C. (c) MW-assisted photolysis of nitrobenzene ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water.

technique was found to be significantly less efficient than that of UV/H_2O_2 (Fig. 4a and b; Table 4) and again, a modest enhancement in the combined technique was observed (Fig. 4c, Table 4). The degradation profiles of chlorophenol photolysis at low H_2O_2 concentrations were practically linear, following nearly zero-order kinetics, which suggests that a direct not-assisted photolysis was a dominant process. Fig. 4d displays a comparison of the degradation profiles of the corresponding techniques used, showing an optimal condition for complete chlorophenol destruction. Photolysis of this compound in aqueous solution is known to give a mixture of primary products; the major products in degassed solutions are known to be hydroquinone via the photosolvolysis mechanism and 5-chlorobiphenyl-2,4′-diol [32]. Table 4 lists the products, form which a coupling product (chlorobiphenyldiol) was formed only by UV irradiation. Hydroquinone and benzoquinone were found in significant amounts in all experiments, which means that oxidation by the hydroxyl radicals prevails in heated solutions over bimolecular coupling reactions of the radical intermediates produced by photolysis.

3.5. Pentachlorophenol

Due to a low pentachlorophenol solubility in water, 6×10^{-6} mol l^{-1} solutions were prepared for the present studies. Table 5 and Fig. 5a and b clearly show that both MW/H_2O_2 and UV/H_2O_2 remediation techniques gave comparable results at the corresponding peroxide concentrations, which in addition had only moderate effect on the relative rates. The MW/UV/H_2O_2 treatment exhibited a rate enhancement higher than a simple addition of both effects by factors of 2.4 and 1.6 at 10^{-2} and 1 mol l^{-1} peroxide concentrations, respectively. Degradation of pentachlorophenol by some advance oxidation techniques has been studied before, showing that octachlorodibenzo-*p*-dioxin or

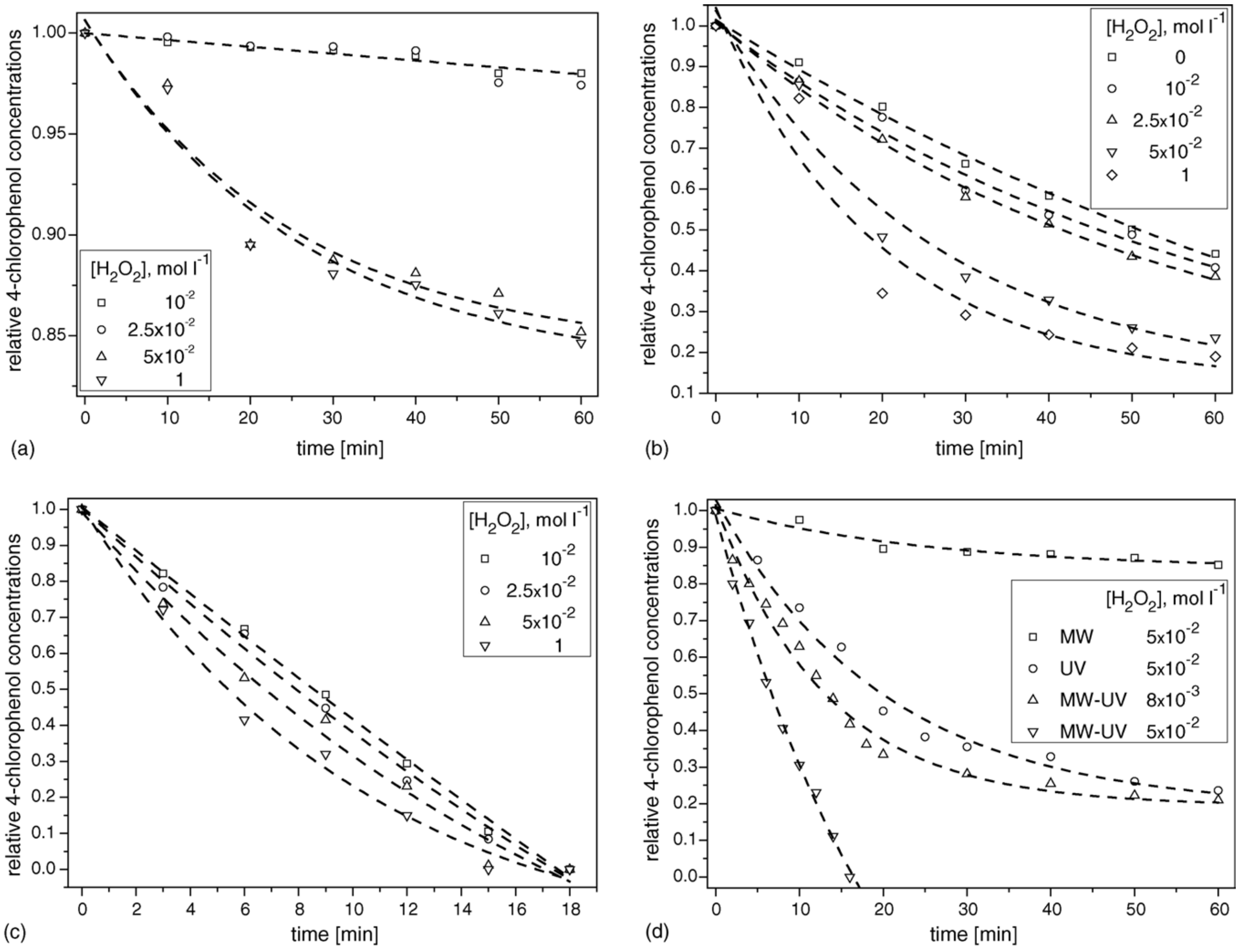


Fig. 4. (a) Microwave-assisted degradation of 4-chlorophenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (b) Photolysis of 4-chlorophenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water at 20 °C. (c) MW-assisted photolysis of 4-chlorophenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (d) Degradation of 4-chlorophenol ($c = 10^{-3}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water under given conditions: microwave heating (MW), photolysis at 20 °C (UV), and MW-assisted photolysis (MW-UV).

Table 5
Relative initial pseudo first-order rate constants k_{rel} for pentachlorophenol ($c = 6 \times 10^{-6}$ mol l^{-1}) degradation

Conditions	H_2O_2 concentration (mol l^{-1})	k_{rel} (min^{-1})
MW; reflux	2×10^{-2}	0.065 ± 0.002
MW; reflux	0.5	0.130 ± 0.015
UV; 20 °C	0	0.058 ± 0.002
UV; 20 °C	2×10^{-2}	0.067 ± 0.004
UV; 20 °C	0.5	0.110 ± 0.014
MW/UV; reflux	2×10^{-2}	0.514 ± 0.044
MW/UV; reflux	0.5	0.549 ± 0.067

2-hydroxy nonachlorodiphenyl ether were formed as primary products [33]. Several products detected by HPLC in this work, however, remained unidentified due to their very low concentrations.

A simultaneous UV irradiation and MW heating of molecules may affect the course of reactions by various mechanisms at each step of the transformation [1]. From many possibilities, one is a bimolecular photoreaction starting with a ground state molecule, which is electronically excited, transformed into an intermediate (or a transition state), and finally yields a product. Virtually each step may be complicated by a parallel microwave-assisted reaction offering a different chemical history. Microwave radiation in MW-transparent media may affect electronically excited molecules or short-lived transition states, however, the lifetime of the species must be long enough to provide a sufficient time for the interaction with this low-frequency radiation. Another pathway becomes important when MW dielectric heating initiates "dark" (thermal) chemical reactions, especially in polar solvents, competitive or exclusive to a photochemical pathway and yielding same or different products. The efficiency of photoreaction can be also altered by microwave induction when the excitation energy of the starting ground state molecule is temperature dependent (e.g., [4,5]). In such a case, individual effects of both types of electromagnetic radiation simultaneously influence a single chemical step, in

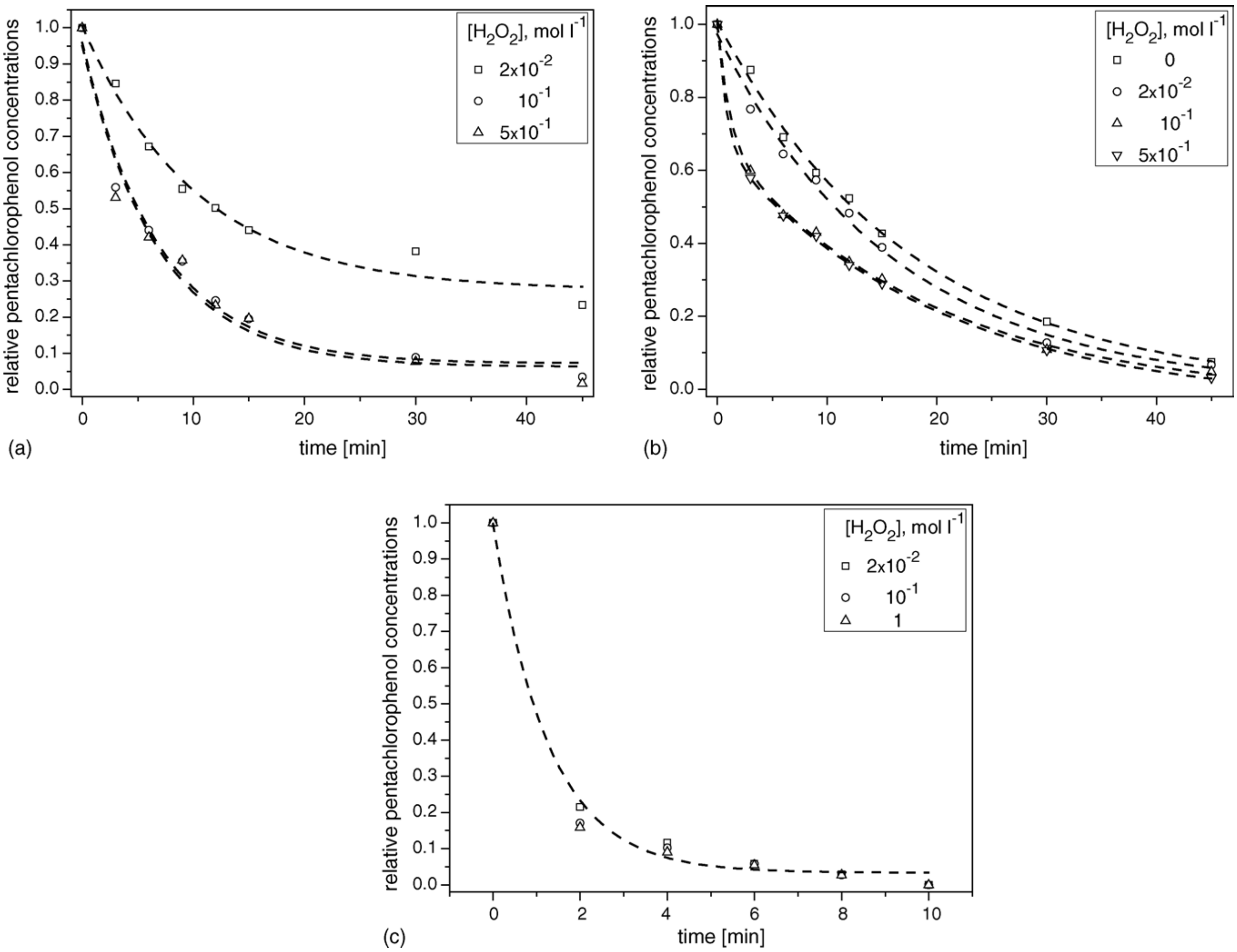
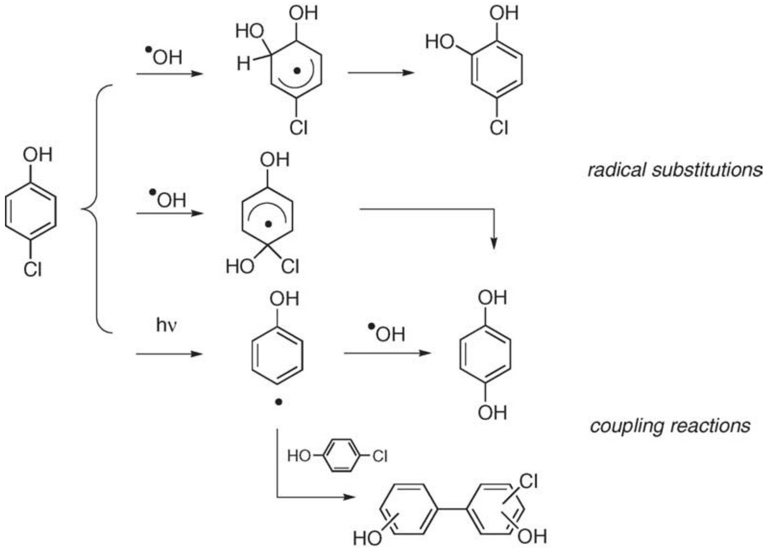


Fig. 5. (a) Microwave-assisted degradation of pentachlorophenol ($c = 6 \times 10^{-6}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water. (b) Photolysis of pentachlorophenol ($c = 6 \times 10^{-6}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water at 20 °C. (c) MW-assisted photolysis of pentachlorophenol ($c = 6 \times 10^{-6}$ mol l^{-1}) in the presence of H_2O_2 (the concentrations are shown in the inset) in water.



Scheme 1.

which the ground state molecules (MW-heated molecules) are being excited. Naturally, if the intermediates react with different rate constants, the total observed rate constant of the reaction is proportional to the sum of all individual rate constants.

For example, we can assume that 4-chlorophenol undergoes two basic reactions when its aqueous solution containing H_2O_2 is simultaneously irradiated by MW and UV: radical substitutions and a coupling reaction (Scheme 1). Thus, a competition between the reaction of the OH radicals created either photochemically or thermally from H_2O_2 [16,28,34,35] and other photoreactions in their absence must be observed. The electrophilic OH radicals can cause continuing oxidation of all intermediates present, which eventually leads to the formation of benign final products. In addition, photochemically formed intermediates may react with $HO^\bullet$ to form more complex side-products. A homolytic C–Cl bond cleavage producing free phenolic radicals may lead to the dimer formation due to radical electrophilic-like or electrophilic (when electron transfers from $Ar^\bullet$ to $Cl^\bullet$) substitution [20]. A higher temperature must influence kinetic barriers of all elemental steps. Therefore, we should not be surprised that the combined effect of UV and MW radiation is larger than the sum of both. It is apparent that if the same thermal reactions proceed in the UV irradiated samples, only equally or more efficient photochemical reactions can significantly compete. The overall efficiency enhancement is then based exclusively on an enhancement of reaction successive to a photochemical step (e.g., that of the phenol radical, which is the only primary photoproduct shown in Scheme 1) as well as on a larger production of the hydroxyl radicals by MW-assisted photolysis of H_2O_2. Finally, an internal filter effect due to absorption capabilities of the organic substrates must play an imperative role in optimization procedures as well.

4. Conclusion

Oxidation of organic pollutants dissolved in water is an attractive method of treatment resulting in the conversion of organic compounds into innocuous materials, such as carbon dioxide and water. The results presented in this work show that the 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 catalysts is in no doubt an important advantage of this technique. Non-catalytic remediation of aqueous solutions by MW-assisted photolysis in the presence of H_2O_2, which takes advantage of thermal enhancement of the processes initiated or followed by absorption of light, was found to be very efficient. Optimization revealed that the simultaneous effect is particularly significant in samples with a low concentration of H_2O_2, however, a large excess of H_2O_2 may be essential to complete the destruction. It was realized that each system requires a specific approach to find ideal destruction conditions and that the partition between the photochemical and thermal pathways is dependent on the ratio of the degradation rates and initial reaction conditions. A remarkable increase in the degradation efficiency under a simultaneous MW/UV/H_2O_2 treatment than would be expected from a simple addition of the reaction efficiencies was observed to be specific for a given substrate, caused presumably by an enhancing the probability of subsequent thermal reactions of the primary photoreaction intermediates.

Acknowledgements

This work was supported in part by the Czech Ministry of Education, Youth and Sport (MSM 0021622413) and the COST D32/04 program.

References

[1] P. Klan, V. Cirkva, Microwave photochemistry, in: A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley-WCH, Weinheim, 2002, p. 463.
[2] R.A. Abramovitch, Org. Prep. Proc. Int. 23 (1991) 685.
[3] C. Gabriel, S. Gabriel, E.H. Grant, B.S.J. Halstead, D.M.P. Mingos, Chem. Soc. Rev. 27 (1998) 213.
[4] P. Klan, J. Literak, Collect. Czech Chem. Commun. 64 (1999) 2007.
[5] P. Klan, J. Literak, S. Relich, J. Photochem. Photobiol. A: Chem. 143 (2001) 49.
[6] P. Klan, M. Hajek, V. Cirkva, J. Photochem. Photobiol. A: Chem. 140 (2001) 185.
[7] P. Klan, R. Ruzicka, D. Heger, J. Literak, P. Kulhanek, A. Loupy, Photochem. Photobiol. Sci. 1 (2002) 1012.
[8] D. Florian, G. Knapp, Anal. Chem. 73 (2001) 1515.
[9] J.P. Scott, D.F. Ollis, Environ. Prog. 14 (1995) 88.
[10] G. Windgasse, L. Dauerman, J. Microw. Power Electromagn. Energy 27 (1992) 23.
[11] L. Campanella, R. Cresti, M.P. Sammartino, V.G., in: SPIE Conference on Environmental Monitoring and Remediation Technologies, Boston, 1998, p. 105.
[12] S. Chemat, A. Aouabed, P.V. Bartels, D.C. Esveld, F. Chemat, J. Microw. Power Electromagn. Energy 34 (1999) 55.
[13] S. Horikoshi, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 5229.
[14] S. Horikoshi, H. Hidaka, N. Serpone, J. Photochem. Photobiol. A: Chem. 153 (2002) 185.
[15] S. Horikoshi, H. Hidaka, N. Serpone, J. Photochem. Photobiol. A: Chem. 161 (2004) 221.
[16] O. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[17] O. Legrini, E. Oliveros, A.M. Braun, Photochemical Processes for Water Treatment, McGraw-Hill, New York, 1994.
[18] J. Literak, P. Klan, J. Photochem. Photobiol. A: Chem. 137 (2000) 29.
[19] P. Muller, P. Klan, V. Cirkva, J. Photochem. Photobiol. A: Chem. 158 (2003) 1.
[20] J. Klanova, P. Klan, J. Nosek, I. Holoubek, Environ. Sci. Technol. 37 (2003) 1568.
[21] P. Klan, J. Klanova, I. Holoubek, P. Cupr, Geophys. Res. Lett. 30 (2003), Art. No. 1313.
[22] W.H. Glaze, J.W. Kang, D.H. Chapin, Ozone Sci. Eng. 9 (1987) 335.
[23] U. Bali, E.C. Catalkaya, F. Sengul, J. Environ. Sci. Health A: Toxic/Hazard. Subst. Environ. Eng. 38 (2003) 2259.
[24] N.J. Bunce, J.P. Bergsma, M.D. Bergsma, W. Degraaf, Y. Kumar, L. Ravanal, J. Org. Chem. 45 (1980) 3708.
[25] G.G. Choudhry, G.R.B. Webster, O. Hutzinger, Toxicol. Environ. Chem. 13 (1986) 27.
[26] M. Dilmeghani, K.O. Zahir, J. Environ. Qual. 30 (2001) 2062.
[27] F.S.G. Einschlag, L. Carlos, A.L. Capparelli, Chemosphere 53 (2003) 1.
[28] F.S.G. Einschlag, L. Carlos, A.L. Capparelli, A.M. Braun, E. Oliveros, Photochem. Photobiol. Sci. 1 (2002) 520.
[29] L.R. Suntio, W.Y. Shiu, D. Mackay, Chemosphere 17 (1988) 1249.
[30] A.J. Beck, S.C. Wilson, R.E. Alcock, K.C. Jones, Crit. Rev. Environ. Sci. Technol. 25 (1995) 1.
[31] P. Boule, C. Guyon, J. Lemaire, Chemosphere 11 (1982) 1179.
[32] K. Oudiehani, P. Boule, J. Photochem. Photobiol. A: Chem. 68 (1992) 363.
[33] M. Fukushima, K. Tatsumi, Environ. Sci. Technol. 35 (2001) 1771.
[34] A. Goi, M. Trapido, Chemosphere 46 (2002) 913.
[35] A. Kunz, P. Peralta-Zamora, N. Duran, Adv. Environ. Res. 7 (2002) 197.