

# Microwave photocatalysis II: novel continuous-flow microwave photocatalytic experimental set-up with titania-coated mercury electrodeless discharge lamps

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## Abstract

**BACKGROUND:** A continuous-flow microwave photocatalytic reactor was set up consisting of a glass tube equipped with microwave powered mercury electrodeless discharge lamps (EDLs) coated with thin films of nanoporous titanium(IV) oxide. The effect of operational parameters on photocatalytic degradation of aqueous mono-chloroacetic acid (MCAA) by a  $\text{TiO}_2$ /UV/MW process was investigated.

**RESULTS:** Studies were carried out at a relatively high concentration of MCAA ( $0.1 \text{ mol L}^{-1}$ ), and revealed that reaction temperature and light intensity of the EDLs depend inversely on the flow rate, but that the 366 nm line intensity of EDL is directly proportional to the reaction temperature. The photodegradation of MCAA was enhanced by heating and significantly enhanced by air bubbling of the reaction mixture in the glass reservoir at laboratory temperature. The photocatalytic efficiency increased with the number of titania-coated EDLs inserted in the glass tube reactor.

**CONCLUSIONS:** It was found that the operational parameters (i.e. flow rate, reaction temperature, number of titania-coated EDLs, and air bubbling) had important effects on degradation efficiency. The photocatalytic degradation of MCAA on thin films of titanium(IV) oxide in the continuous-flow microwave photoreactor can be enhanced in the  $\text{TiO}_2$ /UV/MW system.

**Keywords:** microwave photocatalysis; continuous-flow photocatalytic reactor; electrodeless discharge lamp; mono-chloroacetic acid; nanoporous titanium oxide thin film

## INTRODUCTION

Microwave radiation has uncovered fascinating effects in chemical engineering, organic synthesis, photochemistry and catalytic processes.<sup>1,2</sup> Some research groups are investigating the enhancement of photodegradation.<sup>3,4</sup>

Recent articles and reviews reported the lab-scale preparation of electrodeless discharge lamps (EDLs),<sup>5,6</sup> their spectral measurements,<sup>7</sup> utilization in photochemistry<sup>8-10</sup> and also in microwave-assisted photocatalytic decomposition of mono-chloroacetic acid.<sup>11</sup>

While some of the physico-chemical principles of photocatalysis are relatively well understood,<sup>12</sup> the reactor engineering of photocatalytic units still requires consideration. Photocatalytic reactor design presents unique challenges due to the requirement that a high surface-area particulate catalyst, a UV illumination source, and contaminant species be kept in close proximity. Typical reactor designs fall into two general classes: batch and continuous-flow. Photochemical degradation processes on a large scale require the construction of continuous-flow photoreactors.

Microwave photocatalysis in continuous-flow reactors can be facilitated by a combination of the following two variables: the type and variation of semiconductor photocatalyst (slurry vs thin film), and external or internal lamp (classical UV lamp vs electrodeless

discharge lamp; EDL). The combination of variables may lead to the following four types of techniques for continuous-flow set-ups in the microwave field:

- (a)  $\text{TiO}_2$  (slurry) + classical UV lamp;<sup>13</sup>
- (b)  $\text{TiO}_2$  (slurry) + EDL;<sup>13-21</sup>
- (c)  $\text{TiO}_2$  (thin film) + classical UV lamp;<sup>22</sup>
- (d)  $\text{TiO}_2$  (thin film) + EDL.<sup>23, present paper</sup>

The enhanced efficiency of photocatalysis in a continuous-flow microwave reactor using a combination of classical UV light and microwave (MW) radiation has been reported in the treatment of aqueous  $\text{TiO}_2$  dispersions (type a) of Rhodamine-B dye.<sup>13</sup>

Recent publications have reported significant advancement in the degradative efficiency of continuous-flow reactors through the coupling of EDLs with MW radiation (type b) to generate UV/Vis irradiation resulting in photocatalytic degradation or

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decomposition of various substrates, e.g. Rhodamine-B,<sup>13,14</sup> 2,4-dichlorophenoxyacetic acid (2,4-D),<sup>15</sup> 4-chlorophenol,<sup>16–19</sup> and azo dye brilliant red X-3B.<sup>20,21</sup>

As an illustration (type c) of the combination of classic UV light and MW radiation in continuous-flow reactors on the thin film layer of the photocatalyst (TiO<sub>2</sub>/ZrO<sub>2</sub> on glass beads) only the gaseous phase photocatalytic oxidation of ethylene has been performed.<sup>22</sup> Photocatalytic reactions in the flowing solution on thin film layers of photocatalyst (type d) with EDLs have been mentioned only in a patent.<sup>23</sup>

Previous work<sup>11</sup> reported the effect of operational parameters (number of coating cycles for EDL, light intensity, initial pH value and H<sub>2</sub>O<sub>2</sub> dosage) on photocatalytic degradation of mono-chloroacetic acid by a UV/MW process in a batch photoreactor. This paper presents a new approach for decomposition of mono-chloroacetic acid in a continuous-flow microwave photocatalytic reactor, together with examination of other operational factors (flow rate, reaction temperature, number of titania-coated EDLs, and air bubbling) influencing the course of photocatalytic reaction.

## MATERIALS AND METHODS

### Chemicals

Mono-chloroacetic acid (Lachema 99%, Prague, Czech Republic), titanium tetraisopropoxide (TIOP, Aldrich, 97% Prague, Czech Republic), cyclohexane (Aldrich, 99%), Triton X-100 (TX-100, Aldrich), and mercury (Aldrich, 99.9999%) were used as obtained. All solutions were prepared using distilled water (conductivity 1 μS cm<sup>-1</sup>). Argon (5.0 grade) was purchased from Linde Technoplyn (Czech Republic).

### Preparation of EDLs and spectral measurements

The vacuum system pattern for the preparation of nanoporous titania-coated EDLs on Pyrex was described previously.<sup>6,11</sup> The lamp length was 50 mm (diameter 20 mm).

Spectral measurements of prepared lamps (light intensity in μW cm<sup>-2</sup> for the 366 nm line of mercury) were carried out using a spectrometer USB2000 with an optical fiber probe and operating software package OOlrrad-C (Ocean Optics, Dunedin, FL, USA).<sup>6,7</sup>

### TiO<sub>2</sub> film preparation and characterization

Thin nanoporous TiO<sub>2</sub> film was prepared by dip-coating the pretreated support into the TiO<sub>2</sub> sol (titanium tetraisopropoxide, Triton X-100, cyclohexane, water) as described previously.<sup>11</sup> Withdrawal rate of the support was 6 cm min<sup>-1</sup> and then the layers were thermally treated at 400 °C. The prepared titania films were characterized by the following techniques: specific surface area, 80 m<sup>2</sup> g<sup>-1</sup> by BET method; crystallographic phase, anatase by X-ray diffraction (XRD); particle size, under 10 nm by XRD; absorption edge, 367 nm by UV/Vis; relative surface roughness, 3.14 nm by atomic force microscopy (AFM).

### Photocatalytic experiments with the continuous-flow set-up

In the continuous-flow set-up mono-chloroacetic acid (MCAA) was chosen as a model water pollutant due to the easy determination of Cl<sup>-</sup> ions (by an ion-selective electrode (ISE)).<sup>11</sup> The oxidative degradation and complete decomposition of MCAA by heterogeneous photocatalysis has been investigated<sup>24–30</sup> and

can be written as follows:



The experimental set-up for the continuous-flow microwave photocatalytic reactor is shown in Fig. 1 and a schematic diagram in Fig. 2. The aqueous mixture of MCAA (total fluid volume 500 mL; 0.1 mol L<sup>-1</sup>) was circulated through the photoreactor system consisting of the glass reservoir (B) (500 mL; fitted with a thermometer (C) and a chloride ion-selective electrode (D)) connected by tubing (ISO Versinic, Saint-Gobain, France) to a PTFE diaphragm pump (F) (Cole-Parmer, Masterflex, Vernon Hills, IL, USA), a glass tube (200 mm (length) × 22 mm (internal diameter)) with titania-coated EDLs (I) inside a modified MW oven (A), and cooling condenser (J). When the constant MW power (900 W) was switched on, the titania-coated EDLs (I) started to emit UV/Vis light. The desired temperature in the continuous-flow photoreactor was achieved by adjustment of the pump flow speed. For reactions carried out in air, the required air (flow 0.03 m<sup>3</sup> h<sup>-1</sup>) was bubbled in via inlet (D) (porous glass tube) located on the neck of reservoir (B).

### Analysis

Samples were analyzed every 20 min using a chloride ion-selective electrode (D) (Fig. 2) (Chloride Flow Plus Combination ISE, Sentek, Braintree, UK). ISE was connected to a digital pH/mV meter (inoLab Level 1, WTW, Germany) calibrated with NaCl. Results of the ISE analysis were compared with those obtained by mercurimetry with mercury(II) perchlorate.<sup>31</sup> No organic intermediates from degradation of MCAA (such as formaldehyde or formic acid) were observed.<sup>11,24–26,30</sup>

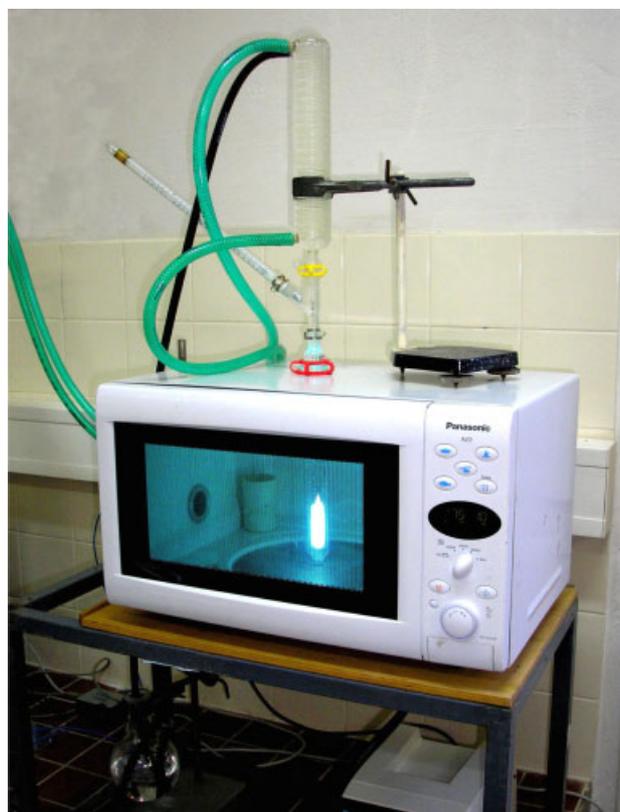
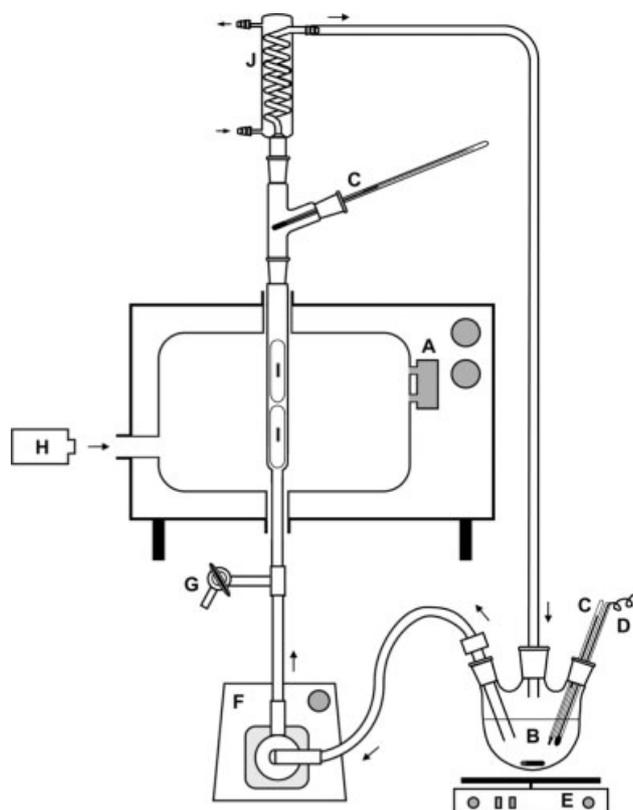


Figure 1. Continuous-flow microwave photocatalytic reactor.



**Figure 2.** Schematic diagram for the continuous-flow microwave photocatalytic experiments: (A) modified microwave oven with magnetron; (B) glass reservoir with magnetic stir bar; (C) thermometer; (D) 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) glass tube with titania-coated EDLs; (J) cooling condenser.

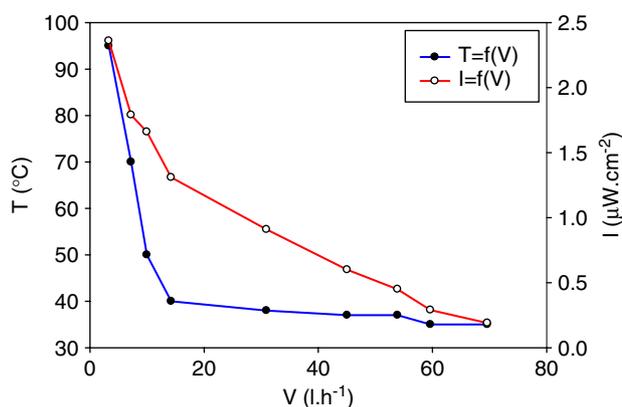
## RESULTS AND DISCUSSION

### Effect of flow rate and reaction temperature

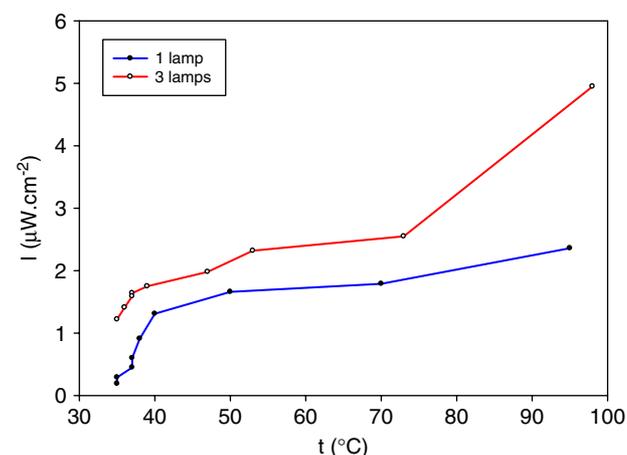
It was not easy to carry out MW assisted photoreactions at different temperatures. The reaction temperature was mostly assigned as the boiling point of the solvent and some superheating may have occurred. The influence of superheating on reaction behaviour is well known. Superheating can increase reaction temperature and consequently, the reaction rate.

The effect of volumetric flow rate on the reaction temperature ( $T = f(V)$ ) is summarized in Fig. 3. The results indicate that increasing the flow rate from 5 to 15 L h<sup>-1</sup> led to a rapid decrease in reaction temperature (from 95 °C to 40 °C), however, at higher flow rate from 15 to 70 L h<sup>-1</sup>, the reaction temperature decreased minimally (from 40 °C to 35 °C) and was almost independent of the volumetric flow rate. These results are logical, because with increasing flow rate (15–70 L h<sup>-1</sup>) the residence time of the reactant (aqueous MCAA) decreases in the microwave photocatalytic reactor and the reaction mixture is warmed up by hot EDLs. In the case of a low flow rate (5 L h<sup>-1</sup>) the highly MW absorbing water was heated mainly by MW radiation.

The effect of volumetric flow rate on the light intensity of EDLs (for the 366 nm line) ( $I = f(V)$ ) is also plotted in Fig. 3. The results indicate that with increasing flow rate from 5 to 70 L h<sup>-1</sup>, the light intensity of EDLs decreases continuously (from 2.4 μW cm<sup>-2</sup> to 0.2 μW cm<sup>-2</sup>). Therefore too high a volumetric flow rate is inconvenient, giving low EDL light intensity and low reaction temperature (*vide infra*).



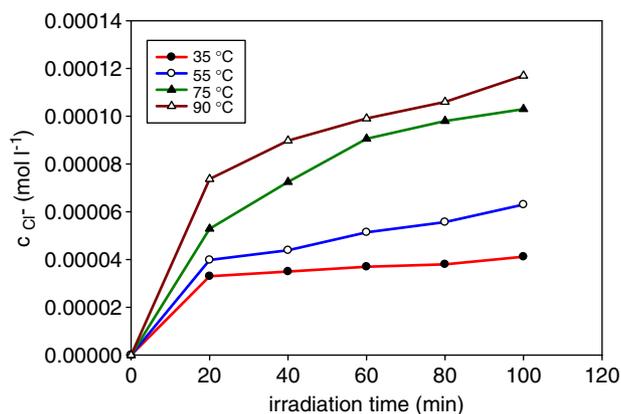
**Figure 3.** Effect of volumetric flow rate on reaction temperature ( $T = f(V)$ ) and on the light intensity of EDLs (366 nm line) ( $I = f(V)$ ) (EDL: two layers).



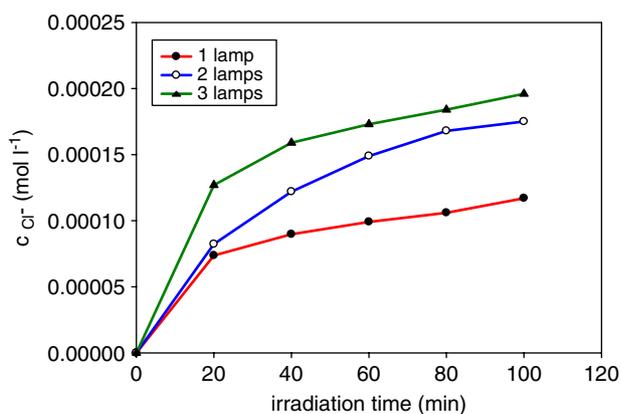
**Figure 4.** Effect of reaction temperature on the light intensity of EDLs (EDL: two layers).

The temperature of the MCAA aqueous medium affects the EDL envelope (Pyrex) temperature and therefore the plasma lighting properties.<sup>5</sup> The relative intensities of the individual emission peaks in Hg-EDL were found to be very dependent on temperature;<sup>7</sup> the 254 nm line was suppressed with increasing temperature, however, the 366 nm line (the titania-coated Hg-EDL on Pyrex) was enhanced. This phenomenon was disclosed in a previous report<sup>7</sup> and Fig. 4 shows the effect of reaction temperature on EDLs light intensity for one and three EDLs. The results show that the highest intensity values ( $I$  (μW cm<sup>-2</sup>)) were obtained at higher temperatures.

The study involving the influence of temperature on photocatalytic MCAA reaction was made in the range 35 to 90 °C when the reaction temperature was altered by changing feed flow rate. Figure 5 shows the dependence of chloride ion concentration on the reaction temperature over time. The Cl<sup>-</sup> concentration was maximum at 90 °C indicating that intensive heating is required for degradation of the MCAA in the photocatalytic reaction. Therefore, the photoreactor flow rate significantly affects the apparent photodegradation rate of MCAA. A very small amount of chloride ions (0.00012 mol L<sup>-1</sup>) were generated to ensure an ultra-short contact time of reaction mixture with one EDL. For practical purposes it would be necessary to use more EDLs.



**Figure 5.** Dependence of chloride ion concentration on the reaction temperature over time (EDL: two layers).

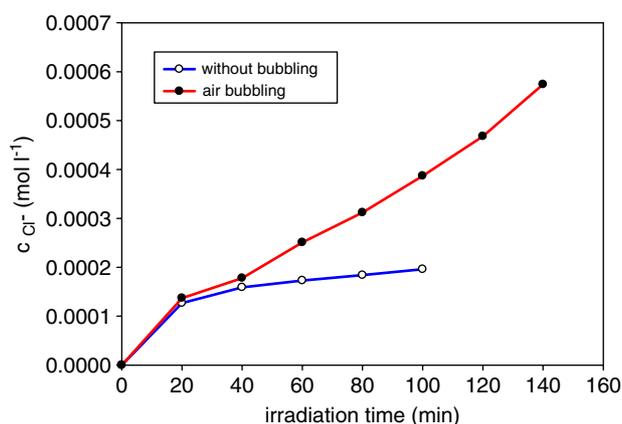


**Figure 6.** Effect of number of titania-coated EDLs on MCAA photodegradation (EDL: two layers; reaction temperature 90 °C).

### Effect of number of the coated EDLs

The number of titania-coated EDLs has an effect on the light intensity, which has been investigated in a batch type photoreactor.<sup>11</sup> The photocatalytic MCAA reaction efficiency increased proportionally with increasing light intensity (radiant flux  $\Phi$ ) of the EDLs.<sup>32</sup> This confirms the photo-induced nature of the activation of the catalytic process, with the participation of photo-induced electrical charges (electrons and holes) in the reaction mechanism.<sup>32</sup> However, above a certain value ( $25 \text{ mW cm}^{-2}$ ),<sup>32</sup> the reaction rate becomes proportional to  $\Phi^{1/2}$ . It can be demonstrated that the rate of electron-hole formation becomes greater than the photocatalytic rate, which favours electron-hole recombination. Another report stated that at high intensities,<sup>33</sup> the expected rate-limiting factor is mass transfer, i.e. the rate of photodegradation becomes independent of light intensity.

Figure 6 shows the influence of the number of the titania-coated EDLs on MCAA photodegradation at a reaction temperature 90 °C. The light intensity of one EDL at 90 °C is only about  $2 \mu\text{W cm}^{-2}$  (for the 366 nm mercury line) which is much less than  $25 \text{ mW cm}^{-2}$  (for all lines present). An increase in the number of lamps (from 1 to 3 lamps) increased the concentration of chloride ions in time during irradiation. This finding corresponds with literature results where higher light intensity and amount of photocatalyst led to higher degradation rate.<sup>26</sup>



**Figure 7.** Time dependence of  $c_{Cl^-}$  with and without air bubbling through the reaction mixture (three EDLs: two layers; reaction temperature 90 °C).

### Effect of air bubbling

Air bubbling is the simplest way to supply the appropriate amount of oxygen to the reaction mixture. In the case of MCAA photocatalytic reactions,<sup>25</sup> it is well known that oxygen bubbling through the reaction mixture provides higher conversion of the pollutant. The dioxygen seems to participate in the degradation process from the initial stages of the MCAA photocatalysis by reacting rapidly with the intermediate radicals formed.<sup>27</sup>

The amount of dissolved oxygen is an important parameter due to its limited concentration in the solution. The significant role of air in the photocatalytic reaction is to prevent the recombination of electron-hole pairs and moreover the air bubbling rate provides turbulence in the solution. Horikoshi found that under nitrogen purging the photo-degradation rate in the presence of MW was higher than that in the absence of MW irradiation.<sup>15</sup>

As reported previously,<sup>11</sup> in a batch type photoreactor the presence of air does not significantly influence the decomposition of MCAA. This is attributable to the low solubility of air in water at a higher temperature (100 °C). The solubility of oxygen in water at 101.325 kPa pressure decreases from 8.06 ppm at 25 °C to 0.87 ppm at 95 °C.<sup>34</sup>

In this study, a photocatalytic continuous reactor with recirculation was used for investigation of the air bubbling effect on microwave assisted MCAA photocatalysis. The reaction mixture was bubbled via inlet (D) in the glass reservoir (B, Fig. 2) at the laboratory temperature and then circulated through the photoreactor at 90 °C. The differences in performance between air bubbled through the mixture and no air bubbled through the mixture are presented in Fig. 7. These results indicate the important role of oxygen in the photocatalytic reaction of MCAA, as was presented in previous papers.<sup>25–28</sup>

## CONCLUSION

The decomposition of mono-chloroacetic acid by microwave assisted photocatalysis over nanoporous titanium dioxide thin films was examined. The study focused upon a novel continuous-flow microwave photocatalytic experimental set-up. It revealed that reaction temperature and light intensity of the EDLs depend inversely on the flow rate, but that the 366 nm line intensity of the EDL is directly proportional to the reaction temperature. Moreover, the photodegradation of mono-chloroacetic acid was enhanced by heating and significantly enhanced by bubbling air through the

reaction mixture in the glass reservoir at laboratory temperature. Furthermore, the photocatalytic efficiency was increased with the number of the titania-coated EDLs inserted in the glass tube reactor.

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