

Microwave photocatalysis IV: Effects of additional operational parameters on the microwave photocatalytic degradation of mono-chloroacetic acid using titania-coated mercury electrodeless discharge lamps

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Abstract

BACKGROUND: Mercury electrodeless discharge lamps (Hg-EDLs) coated with titania in the form of thin films were used to generate UV/Vis radiation when placed in a microwave field. Effects of additional operational parameters (i.e. initial MCAA concentration, reaction temperature, and the presence of inorganic anions) on the photocatalytic degradation of aqueous mono-chloroacetic acid (MCAA) in a microwave field are discussed.

RESULTS: Studies were carried out in atmospheric or low-pressure batch type microwave photocatalytic reactors. The photocatalytic process was monitored by the change in concentration of Cl^- in the solution. Coupled UV/MW irradiation led to effective photodegradation at higher MCAA concentration at an optimum value of 0.15 mol L^{-1} . Photocatalytic reaction of MCAA was favoured at higher temperature mainly owing to thermal dependence of the Hg-EDL light intensity on the 366 nm line. Inhibition of MCAA photodegradation was observed in the presence of CO_3^{2-} and SO_4^{2-} anions, whereas the effect of NO_3^- was negligible.

CONCLUSIONS: It was found that additional operational parameters had important effects on photocatalytic efficiency in a microwave field. The MCAA photodegradation process with titania-coated Hg-EDLs can be enhanced in the $\text{TiO}_2/\text{UV}/\text{MW}$ system.

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Keywords: Microwave photocatalysis; titania thin film; mercury electrodeless discharge lamp; low-pressure photocatalytic reactor; mono-chloroacetic acid

INTRODUCTION

Coupled activation of photocatalytic reactions by use of two different types of radiation, microwave (MW, $\nu = 2.45 \text{ GHz}$, $E = 0.98 \text{ J mol}^{-1}$) and UV/Vis ($\lambda = 200\text{--}700 \text{ nm}$, $E = 600\text{--}170 \text{ kJ mol}^{-1}$), is covered by the discipline 'microwave photocatalysis'.^{1–3} This combination effect may lead to the enhanced photoassisted degradative efficiency of various substrates.^{4–6} The objective of microwave photocatalysis is frequently, but not necessarily, connected to the use of titania-coated electrodeless discharge lamps (EDLs) as a novel light source which generate UV/Vis radiation when placed into a MW field.⁷

Several studies have noted that photodegradation can be facilitated by the assistance of MW radiation and EDLs to decompose wastewater pollutants, for example Rhodamine B,⁸ 2,4-dichlorophenoxyacetic acid,^{9,10} 4-chlorophenol,¹¹ azo dye red X-3B,¹² methylene blue,¹³ and phenol.¹⁴ Horikoshi *et al.*¹⁵ observed, using ESR techniques that the generation of hydroxyl radicals from the photooxidation of water or surface-bound OH groups in UV irradiated TiO_2 aqueous dispersion increased with the concomitant use of MW radiation.

Titania photocatalytic reactions depend on various parameters that can modify the degradation process. In previous work,⁷ the

effects of initial pH value, light intensity, H_2O_2 dosage, and gas bubbling on the photodegradation of mono-chloroacetic acid (MCAA) over nanoporous titania thin films were studied in detail in a batch type MW reactor. We also reported a new approach for the MCAA degradation in a continuous-flow MW photocatalytic reactor,¹⁶ together with examination of parameters such as flow rate, reaction temperature, number of EDLs, and air bubbling. Additionally, within the scope of our study, we explored the effect of transition metal-doped titania thin films on the photocatalytic degradation of MCAA and Rhodamine B.¹⁷ We also prepared nanocrystalline anatase TiO_2 and V/TiO_2 thin layers efficiently by MW drying and/or MW calcination.¹⁸

This paper represents the continuation of previous studies^{7,16–18} devoted to the investigation of the operational parameter effects in the MCAA photocatalytic reaction in a batch

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type reactor using titania thin films as a photocatalyst. The aim of the present work was to examine the influence of additional operational parameters (i.e. initial MCAA concentration, reaction temperature, and the presence of inorganic anions) on the photocatalytic degradation course of aqueous MCAA in a MW field.

MATERIALS AND METHODS

Chemicals

Titanium tetraisopropoxide (97%, Sigma Aldrich, Prague, Czech Republic), cyclohexane (99%, Sigma Aldrich), Triton X-100 (Sigma Aldrich), mono-chloroacetic acid (99%, Lachema, Prague, CR), sodium nitrate (99%, Lachema), sodium carbonate (99%, Lachema), sodium sulfate (99%, Lachema), and mercury (99.9999%, Sigma Aldrich) were used as obtained. All solutions were prepared using distilled water (conductivity $1 \mu\text{S cm}^{-1}$). Argon (5.0 grade) was purchased from Linde Technoplyn (Prague, CR).

Preparation of EDLs and spectral measurements

The vacuum system pattern for the preparation of EDLs on Pyrex glass was described previously.¹⁹ The lamp length was 50 mm (diameter 20 mm).

Spectral measurements of the prepared EDLs (light intensity $5.56 \mu\text{W cm}^{-2}$ for the 366 nm mercury line) were carried out using a USB2000 spectrometer with optic fiber probe and operating software package OOIrrad-C (Ocean Optics, Dunedin, FL, USA).^{19,20}

Titania thin film preparation and characterization

As reported,^{7,16} titanium dioxide precursor was prepared by means of the sol-gel method in the reverse micelles of a non-ionic surfactant, Triton X-100, in cyclohexane. The TiO_2 gels were obtained by hydrolysis of titanium tetraisopropoxide based upon the method of Kluson *et al.*²¹ The molar ratios of initial compounds were 1:1:1 (water /Triton X-100 /titanium tetraisopropoxide) and the volume ratio of surfactant to cyclohexane was kept at 0.45:1 during preparation. Thin films of the TiO_2 precursor on the surface of EDLs were produced by dip coating from prepared gels with a withdrawal rate of 6 cm min^{-1} . The organic content was reduced by thermal treatment at 673 K for 2 h (2°C min^{-1}).

The titania films were characterized (see supplementary data in our previous article⁷) for crystal phase identification by X-ray diffraction using a XRD-7 (Rich. Seifert & Co., Freiberg, Germany) with $\text{Cu K}\alpha$ radiation. Surface pictures in 3D were taken on the AFM Explorer (ThermoMicroscopes, Sunnyvale, USA) and these were then analyzed to estimate the parameter of the relative surface roughness. The absorption edge was determined using absorption data recorded by UV/Vis spectrophotometer (UV-2450, Shimadzu, Japan) in the range 200–800 nm.

Photocatalytic experiments and analysis

Mono-chloroacetic acid (MCAA) was chosen as model compound for the microwave-assisted photocatalytic reactions due to the easy indirect determination of chloride ions by an ion-selective electrode (*vide infra*).⁷ Complete MCAA decomposition by oxidation can be written as follows:



The experimental set-up for the atmospheric-pressure batch microwave photocatalytic reactor was described elsewhere (150 mL of an aqueous solution of MCAA, titania-coated Hg-EDL).⁷ Temperature of the mixture was maintained at reflux (100°C).

The experimental set-up for the low-pressure batch microwave photocatalytic reactor was described elsewhere.²² The lower reaction temperature during MCAA photocatalytic reaction in a MW field was achieved by altering the total pressure of the system with a pump. The measured values of temperature (T in $^\circ\text{C}$) at a given total pressure (p in mbar) were fitted to an exponential growth curve ($R = 0.9999$) and the obtained dependence was used to adjust the required reaction temperature, i.e. 30°C (37 mbar), 40°C (61 mbar), 50°C (114 mbar), 60°C (190 mbar), 70°C (298 mbar), and 80°C (454 mbar).²²

In the case of experiments with inorganic salts (Na_2CO_3 , Na_2SO_4 , NaNO_3), the concentration corresponded to 5 mmol L^{-1} of dissolved salt.

Samples of MCAA were analyzed at regular intervals (20 min) using a chloride ion-selective electrode (ISE; Chloride Flow Plus Combination, Sentek, Braintree, UK) assuming a stoichiometry of 1 mol Cl^- produced per 1 mol of MCAA converted. ISE was connected to a digital pH/mV meter (inoLab Level 1; WTW, Weilheim, Germany) calibrated with NaCl .⁷ The measured results of ISE analysis were compared with those obtained by the mercurimetry with mercury(II) perchlorate. For MCAA no additional reaction intermediates (produced by partial mineralization) as the formaldehyde, formic acid and chloromethane were detected (2,4-dinitrophenylhydrazine test, GC/MS analysis, NMR spectroscopy) under these thermal reaction conditions.

RESULTS AND DISCUSSION

Properties of titania thin films

Diffractions that are attributable to anatase crystal phase are clearly detectable in the XRD spectrum of the thermally treated titania thin film. The AFM image can provide some quantitative data about the surface roughness and also grain size of the titania thin film. The surface of the films appears uniform and homogeneous. The root mean square roughness value of the titania thin film surface is 0.48 nm and the absorption edge of titania was detected at the wavelength of about 365 nm.⁷

Effect of initial MCAA concentration

In wastewater treatment systems, the pollutant concentration plays an important role in determining the kinetics of the photocatalytic reaction. It is generally known that the degradation rate increases with increase in initial substrate concentration until a certain level. Further increase in initial substrate concentration leads to a decrease in the degradation rate.^{23,24} Degradation of MCAA at the various initial concentrations (0.01, 0.025, 0.05, 0.10, 0.15, and 0.20 mol L^{-1}) as a function of exposure time, is shown in Fig. 1. According to previous investigations, the influence of the initial MCAA concentration on the photodegradation efficiency can be described by pseudo-first-order kinetics.¹⁷ The apparent rate constants (k_{app}) for the MCAA photodegradation were determined from the slope of $\ln(c_0/c) = k_{app} t$ plots (see Table 1).

For initial concentrations of 0.010 and 0.025 mol L^{-1} the photodegradation was almost complete after 100 min and 140 min, respectively. This trend may be due to the availability of sufficient catalyst surface for the MCAA degradation. For higher initial MCAA concentrations ($0.05\text{--}0.20 \text{ mol L}^{-1}$) the photocatalytic efficiency was lower, but better results could be obtained by extending the reaction time. As the initial concentration (c_0) increased, the requirement of photocatalyst surface needed for the degradation also increased. This apparently led to a decrease in the rate

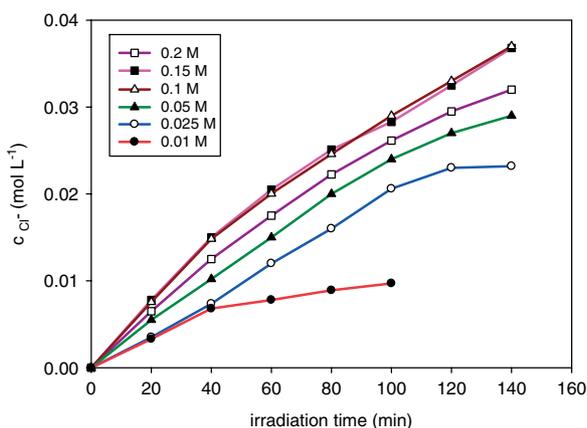


Figure 1. Effect of initial concentration on MCAA photodegradation (Hg-EDL intensity: $5.56 \mu\text{W cm}^{-2}$; EDL: two layers; reaction temperature 100°C).

Table 1. Kinetic parameters for MCAA photodegradation at various initial concentrations (reaction temperature 100°C)

Initial concentration c_0 (mol L ⁻¹)	Apparent rate constant k_{app} ($R^2 \geq 0.98$) (min ⁻¹)
0.010	0.0271
0.025	0.0116
0.050	0.0062
0.100	0.0037
0.150	0.0024
0.200	0.0014

constant (k_{app}), i.e. from 0.0271 to 0.0014 min^{-1} (Table 1), as the initial concentration was increased from 0.01 to 0.20 mol L^{-1} . However, when the concentration was increased from 0.01 to 0.10 mol L^{-1} , there was a sharp decrease in the rate constant values (7.3 times), while further increase to 0.20 mol L^{-1} did not significantly affect the rate constant.

Beyond a certain level, 0.15 mol L^{-1} , increasing initial concentration did not further enhance the MCAA degradation. Presumably, at high MCAA concentration the active sites of titania are covered by MCAA ions and the generation of hydroxyl radicals is then reduced. Because of good photochemical efficiency of EDLs that utilized more light energy, the photodegradation of high MCAA concentration became more effective in a MW field. The optical path is shortened by the use of titania coated EDL because it is immersed in the reaction mixture and thus the direct contact between reaction mixture, thin film of titania, and UV/Vis light is ensured.

The MCAA concentration (0.10 mol L^{-1}) used in this study was quite high. However, the MW photocatalysis of such a high MCAA concentration did not result in decrease of reaction efficiency. This indicates that photocatalysis in a MW field can repress the negative effect of high initial substrate concentration. This observation can be explained on the basis of the following two possible aspects. First, it was well established by Horikoshi *et al.*¹⁵ that specific interactions of microwaves with the illuminated surface of titania may invoke the generation of additional surface defects that directly lead to the higher concentration of hydroxyl radicals or some other reactive species. Another possible cause for such results is that chemical reactions under MW radiation are closely

associated with existence of superheating, formation of hot spots, polarization, rotation, and dielectric properties.^{25–28}

Effect of reaction temperature

The microwave photocatalytic experiments in the batch set-up were carried out in a round-bottomed flask equipped with a titania coated Hg-EDL.^{7,16,17} The temperature of the reaction mixture increased rapidly and was maintained at reflux (about 100°C). Investigations of the effect of temperature on the MCAA photocatalytic reaction course were therefore carried out in the low-pressure batch microwave photocatalytic reactor.²² Changes of reaction temperature during photocatalysis in a MW field could be achieved by altering the total pressure of the system using a pump (*vide supra*).

The reaction temperature has a strong effect on the MCAA photodegradation in a MW field. This fact is related to the temperature dependence of the EDLs light intensity.²⁰ Effect of temperature on the titania-coated EDL envelope is closely associated with the fill gas pressure and has already been investigated.²² The temperature dependent emission spectra of Hg-EDL demonstrated that the 254 nm line was suppressed with increasing temperature, while the 366 nm line (which is fundamental to photocatalysis) was enhanced. Nevertheless, the total light intensity of EDL increased with increasing temperature.

Fox and Dulay²⁹ have stated that compared with most photoreactions, photocatalytic reactions are not dramatically sensitive to small variations in temperature. The enhanced temperature at photocatalysis probably increases the collision frequency of molecules. Zeltner *et al.*³⁰ indicated that increasing the reaction temperature increased the rates of all reactions, except for the photogeneration of e^-/h^+ pairs. On the other hand, increasing the reaction temperature lowers the solubility of oxygen in the solution. The strong effect of solution temperature on photodegradation of the azo dye reactive brilliant red X-3B in MW/TiO₂ system with quartz Hg-EDL has been also found.²⁸

The dependence of chloride ion concentration on reaction temperature over time is shown in Fig. 2. In the range 30 – 60°C there is no significant effect on the degradation of MCAA, the rate constants (k_{app} , Table 2) are within the range 0.0001 to 0.0004 min^{-1} . However, from 70 to 80°C there is a strong increase in rate constants from 0.0007 to 0.0020 min^{-1} (Table 2), the consequence of the increasing EDL light intensity. Therefore, it is obvious that microwave photocatalysis is sensitive to temperature. The effect of light intensity of the EDL on the degradation of MCAA was also described in our previous study.⁷ The degradation rate was increased with increasing light intensity because more light energy can be used for MCAA degradation and thus more active sites can be formed on the catalyst surface.

Effect of inorganic anions

Many anions such as CO_3^{2-} , SO_4^{2-} , and NO_3^- , widely present in natural waters, industrial wastewaters, and agriculture, have significant influence on the photocatalytic degradation of various organic compounds.^{28,31} The presence of inorganic salts decreases more or less the photocatalytic efficiency depending on their nature, concentration, and the solution pH. Added ions can inhibit the photodegradation of organic compounds in several ways: (i) trapping of holes at the surface; (ii) trapping of hydroxyl radicals or other oxidizing species; and (iii) competitive adsorption with the reactant on the catalyst surface.³² In the literature, the inhibition

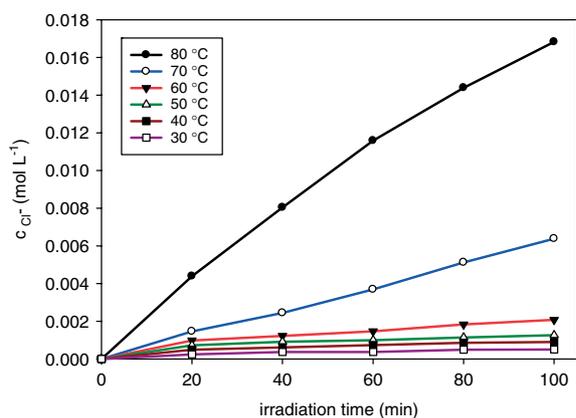


Figure 2. Effect of reaction temperature on MCAA photodegradation in the low-pressure set-up ($c_{\text{MCAA}} = 0.10 \text{ mol L}^{-1}$; Hg-EDL intensity: $5.56 \mu\text{W cm}^{-2}$; EDL: two layers).

Table 2. Kinetic parameters for MCAA photodegradation at various reaction temperatures ($c_{\text{MCAA}} = 0.100 \text{ mol L}^{-1}$)

Reaction temperature (°C)	Apparent rate constant k_{app} ($R^2 \geq 0.98$) (min^{-1})
100	0.0037
80	0.0020
70	0.0007
60	0.0004
50	0.0003
40	0.0002
30	0.0001

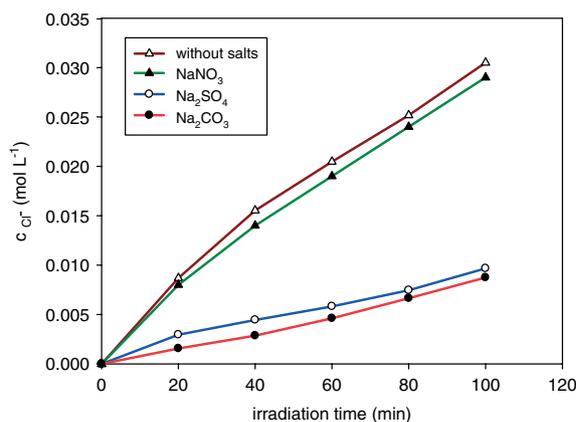


Figure 3. Effect of inorganic anions on MCAA photodegradation ($c_{\text{MCAA}} = 0.10 \text{ mol L}^{-1}$; Hg-EDL intensity: $5.56 \mu\text{W cm}^{-2}$; EDL: two layers; reaction temperature 100°C).

of photocatalytic efficiency in the presence of inorganic ions is often explained by the scavenging of hydroxyl radicals by ions.³¹

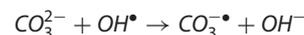
In order to study the effect of inorganic anions, Na_2CO_3 , Na_2SO_4 , and NaNO_3 were added separately to the MCAA solution. The concentration of the anions of those salts was 5 mmol L^{-1} . Figure 3 shows the time change of the Cl^- concentration during photocatalytic reaction of MCAA with different anions.

Carbonate anions significantly decreased the MCAA photocatalytic rate constant (k_{app} , Table 3) from 0.0037 to 0.0008

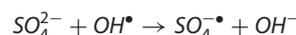
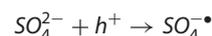
Table 3. Kinetic parameters for MCAA photodegradation in the presence of inorganic salts

Salt	Apparent rate constant k_{app} ($R^2 \geq 0.98$) (min^{-1})
Without	0.0037
NaNO_3	0.0035
Na_2SO_4	0.0010
Na_2CO_3	0.0008

min^{-1} , as shown in Fig. 3 (solid circles). Zhang *et al.*³³ studied photocatalytic degradation of the reactive dye Brilliant Orange K-R, and noted that CO_3^{2-} or HCO_3^- anions activated pH changes. In our experiments, the addition of carbonate changed the pH of MCAA from 1.85 to 1.95. This weak increase of pH cannot make the surface of titania negatively charged and cause weaker adsorption of MCAA on the TiO_2 surface. This fact is accepted at pH value of 6.25 and more. However, as we reported in our previous study,⁷ increase of pH by adding NaOH led to the increase of MCAA degradation efficiency. It stands to reason that the pH changes cannot be the primary reason for the inhibiting effect of carbonate ions, even though the pH changes were larger. These ions mainly act as hydroxyl ion scavengers (produce the carbonate radical anions, $\text{CO}_3^{\bullet-}$, as a weak oxidizing agent) and may also affect the adsorption of the degrading species.

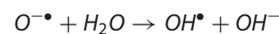
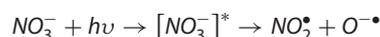


Sulfate ions were found to decrease the photocatalytic efficiency and photocatalytic rate constant (k_{app} , Table 3) from 0.0037 to 0.0010 min^{-1} (Fig. 3, open circles), and were adsorbed on the positively charged TiO_2 surface. The reaction of adsorbed SO_4^{2-} with positive holes (h^+) and hydroxyl radicals inhibit²⁸ the MCAA photodegradation.



However, the inhibiting effect of sulfate ions was lower than that of carbonate ions. Radical $\text{SO}_4^{\bullet-}$ is also a strong oxidizing agent, but it is less reactive than OH^\bullet and h^+ . Consequently, these radicals were present in the reaction mixture as an oxidizing agent and may compensate the MCAA photodegradation in a way.

Inhibition of the MCAA photodegradation by nitrate ions presented in the reaction mixture was very low (Fig. 3, solid triangles), lower than expected, as has also been reported elsewhere.³⁴ The photocatalytic rate constant (k_{app} , Table 3) was 0.0035 min^{-1} , i.e. almost the same as that without salts. The NO_3^- can absorb UV light and produce hydroxyl radicals which have a positive effect on the MCAA photodegradation. The negative effect resulted from decreased adsorption counteracts²⁸. Therefore, overall, the nitrate ions had a negligible effect on the MCAA photocatalytic reaction.



CONCLUSION

Heterogeneous photocatalysis on thin titania films proved to be a very effective method for water pollution remediation. The titania-coated mercury electrodeless discharge lamps (EDLs) are used

to generate UV/Vis radiation when placed in a microwave field. Degradation of aqueous mono-chloroacetic acid (MCAA) depends on several operational parameters, i.e. initial MCAA concentration, reaction temperature, and the presence of inorganic anions. Coupled UV/MW irradiation in atmospheric or low-pressure batch type microwave photocatalytic reactors leads to effective photodegradation at higher MCAA concentrations at an optimum value of 0.15 mol L^{-1} . The photocatalytic reaction of MCAA is favoured with higher temperature mainly owing to thermal dependence of the Hg-EDL light intensity for the 366 nm line. Inhibition of the MCAA photodegradation is observed in the presence of CO_3^{2-} and SO_4^{2-} anions, whereas the effect of NO_3^- is negligible. This should be of great importance for the optimization of the experimental conditions for technological applications such as scale up of photocatalytic reactors and taking into account the role of the different parameters.

ACKNOWLEDGEMENTS

The authors thank the Grant Agency of the Czech Republic (104/07/1212) for funding this research. HŽ thanks the Grant Agency of the Czech Republic for part funding her PhD studentship (Doctoral Grant No. 203/08/H032).

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