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Microwave photocatalysis of mono-chloroacetic acid over nanoporous titanium(IV) oxide thin films using mercury electrodeless discharge lamps

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ABSTRACT

The degradation of mono-chloroacetic acid (MCAA) by microwave-assisted photocatalysis has been examined by a new method. A novel electrodeless discharge lamp (EDL) was employed as UV light source generated by microwave irradiation. Titanium(IV) oxide film was used as the photocatalyst due to its superior characteristics. Several factors influencing the degradation of MCAA, such as number of coating cycles, light intensity, initial pH value, gas bubbling, and H_2O_2 dosage have been studied in detail. Mono-chloroacetic acid was efficiently decomposed to HCl, CO_2, and H_2O by the UV irradiated titanium dioxide thin film in a microwave field. The decomposition was enhanced in an alkaline solution and in the presence of H_2O_2, and significantly enhanced by increasing the intensity of UV light.

1. Introduction

Microwave irradiation has found interesting applications in organic synthesis and catalytic processes. Recently, microwave fields have been used to assist photochemical and photocatalytic reactions for the degradation of organic pollutants [1].

Titanium dioxide is widely used as a photocatalyst due to its high activity, large stability to UV light illumination, low price, and non-toxicity [2]. The principle of the photo-catalytic process involves the activation of TiO_2 by UV irradiation of suitable wavelength and the formation of hydroxyl radicals as oxidative species.

Microwave-assisted photocatalysis in a solution can be facilitated by a combination of the following three variables: the type and variation of semiconductor photocatalyst (slurry vs. thin film), external or internal lamp (classical UV lamp vs. electrodeless discharge lamp; EDL), and the frequency of the microwave field (2.45 GHz). The combination of the first two variables (photocatalyst and lamp) may lead to the following four types of techniques:

(a) TiO_2 (slurry) + classical UV lamp + MW field [3–11];
(b) TiO_2 (slurry) + EDL + MW field [12–19];
(c) TiO_2 (thin film) + classical UV lamp + MW field [24];
(d) TiO_2 (thin film) + EDL + MW field [present paper].

Several studies have been reported in the last few years on the enhanced efficiency of the photocatalytic degradation of organic substrates using a combination of classic UV light and microwave radiation in the treatment of aqueous TiO_2 dispersions (type a) of humic acid [3], rhodamine-B dye [4,5], 2,4-dichlorophenoxyacetic acid (2,4-D) [6], phenol [7], bisphenol-A [8,9], 4-chlorophenol [10], and other model compounds [11].

Recent papers have demonstrated outstanding improvement of the degradative efficiency by the coupling of microwave radiation with electrodeless discharge lamps (type b) to the photocatalytic degradation of various substrates, e.g. rhodamine-B [12], 2,4-dichlorophenoxyacetic acid [13,14], phenol [15], 4-chlorophenol [16], azo dye brilliant red X-3B [17], and methylene blue [18]. Some high-temperature/high-pressure microwave/UV digestion procedure [19] of biological samples (serum, urine, and milk) in the aqueous TiO_2 suspension has been accomplished using a cadmium low-pressure EDL. The EDL has been found to generate efficiently UV/vis radiation when placed into a microwave field [20–22]. Comparative studies showed that EDL may provide a high yield of the product in shorter reaction time [23].

As an example (type c) of the combination of classic UV light and microwave radiation on the thin film layer of the photocatalyst (TiO_2/ZrO_2 on glass beads) the gaseous phase photocatalytic oxidation of ethylene has been performed [24] only. The photocatalytic reactions in a solution on some thin film layer of the photocatalyst (type d) have not been published to date.

Microwave radiation provides not only the heat source (as the thermal effect) but also a specific effect [13,14] (the non-thermal effect), as suggested by Marken and co-workers [25], that leads

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to the enhanced photo-assisted degradation of several substrates. Booske et al. [26] have suggested that microwaves can couple into the low microwave frequency elastic lattice oscillations of a crystalline solid, thereby generating a non-thermal distribution that might enhance the ion mobility and thus the diffusion of charge carriers to the surface leading to the increased formation of the surface $^{\bullet}$OH radicals and to the increased concentration of electrons at the surface [6].

Specific interactions of microwaves with the UV-illuminated TiO_2 particle surface may give rise to the generation of additional surface defects [27] that can directly increase the concentration of $^{\bullet}$OH radicals, or some other reactive oxygen species, in the aqueous dispersion [6]. The formation of $^{\bullet}$OH radicals was probed by the ESR technique, in which the sample could be irradiated by both UV light and microwave radiation. In this regard, EPR spectroscopic evidence showed that a greater number of $^{\bullet}$OH radicals were produced in the microwave-assisted photocatalytic process in aqueous TiO_2 dispersions [10]. ESR spectra and the photooxidation experiments confirmed that the mixed-phase (P-25) TiO_2 specimen was photocatalytically more active than either of the pure anatase or rutile phases of titania [7]. Horikoshi et al. [4] proved by ESR that about 20% more $^{\bullet}$OH radicals were generated by the photocatalysis with microwave irradiation than by photocatalysis alone.

Blount et al. [28] showed that TiO_2 thin films were more active for photocatalysis of acetaldehyde, acetic acid, and toluene than TiO_2 in the powder form. Also Martyanov and Klabunde [29] described higher activity of prepared sol–gel layers than of the TiO_2 powder. The examination of differences between TiO_2 thin layers and the TiO_2 powder, in the case of the microwave-assisted photocatalysis of chlorinated compounds, is subject of our studies.

In this paper, we present a new method for carrying out photocatalytic reactions with high efficiency in the decomposition of mono-chloroacetic acid (MCAA). This special film arrangement of the photocatalyst form and the microwave source of UV light provides a new form of the TiO_2 utilization.

2. Experimental

2.1. Chemicals

Titanium tetraisopropoxide (TIOP, Aldrich, 97%), cyclohexane (Aldrich, 99%), and Triton X-100 (TX-100, Aldrich) were used as obtained for the photocatalyst sol–gel preparation. Mono-chloroacetic acid (Lachema, 99%) and H_2O_2 (Lach-Ner, 30%, v/v) were used as obtained. All solutions were prepared using distilled water. NaOH (Lach-Ner, pure) was used to adjust the initial pH of solutions to the predetermined levels. Mercury (Aldrich, 99.9999%, electronic grade) was used as obtained. Argon (5.0 grade) was purchased from Linde Technoplyn (Czech Republic).

2.2. Preparation of EDLs and spectral measurements

The vacuum system pattern for the preparation of EDLs was described previously [22]. The EDL blank (Pyrex glass) was cleaned in a water–soap mixture, 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. The dimensions of lamps were 20 mm × 50 mm. This kind of EDL was chosen on the basis of results previously reported by us [30].

Spectral measurements of prepared lamps (light intensity in $\mu W\,cm^{-2}$) 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) [21,22]. The line emission spectra were observed between 250 and 650 nm wavelength.

2.3. TiO_2 film preparation

The TiO_2 sol was prepared by hydrolysis of titanium tetraisopropoxide according to the method described by Kluson et al. [31]. The hydrolysis of TIOP was carried out in the reverse micelles of Triton X-100 in cyclohexane [32]. The molar ratios of initial compounds were 1:1:1 (water: TX-100: TIOP) and volume ratio TX-100: cyclohexane was 0.45.

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 hydrochloric acid ($1\,mol\,l^{-1}$), rinsed with water and ethanol, respectively.

The TiO_2 film was prepared by dip-coating of the pretreated support into the TiO_2 sol with withdrawal rate $6\,cm\,min^{-1}$. The film was finalized by thermal treatment at 673 K after each coating cycle.

2.4. Characterization of thin films

X-ray diffraction (XRD) patterns were recorded on XRD 7 Rich. Seifert Co. and Goniometer HZ63 diffractometer to examine the crystallographic phase and for the estimation of the sample crystallite size (Cu radiation, $\omega = 1.5^{\circ}$, PB geometry).

The nitrogen adsorption and desorption isotherms at 77 K were carried out on ASAP 2010 M (Micromeritics) system following the vacuum-drying of the samples at 378 K for 24 h.

The UV/vis spectrophotometer from Helios Unicam was employed for UV/vis optical spectra measurements and detecting absorption edges of the produced layers.

AFM images of the films were observed with Thericroscopes microscope and then analyzed to estimate the relative surface roughness.

2.5. Photocatalytic experiments

Mono-chloroacetic acid was chosen as a model compound for the microwave-assisted photocatalytic reactions due to the easy determination of chloride ions (ion-selective electrode). Several research groups claim that MCAA does not undergo direct photolysis [33–35]. The complete MCAA decomposition by oxidation can be written as follows:

$$2ClCH_2COOH + 3O_2 \rightarrow 4CO_2 + 2H_2O + 2HCl$$

The experimental equipment consists from a round-bottom flask (500 ml) equipped with the Dimroth condenser. In each experiment, the reactor was filled with 150 ml of an aqueous solution of mono-chloroacetic acid ($0.1\,mol\,l^{-1}$) with predetermined pH value. Then the titania coated mercury EDL (Fig. 1) was placed into the reaction mixture and microwave field (2450 MHz; the domestic MW oven, Whirlpool, 900 W [20]; the laboratory MW oven, Milestone MicroSYNTH Labstation, 1000 W, Fig. 2) was switched on to generate UV/vis radiation. The reaction was carried out below the boiling point of water. For reactions carried out in air, the required air ($0.03\,m^3\,h^{-1}$) was bubbled through a porous glass tube sparger located at the bottom of the reactor.

2.6. Analysis

Samples were taken with a 5 ml syringe from the reactor after every 20 min and immediately analyzed by a chloride ion-selective electrode (Chloride Flow Plus Combination ISE, Sentek, Braintree,

Fig. 1. The titania thin film coated EDL.

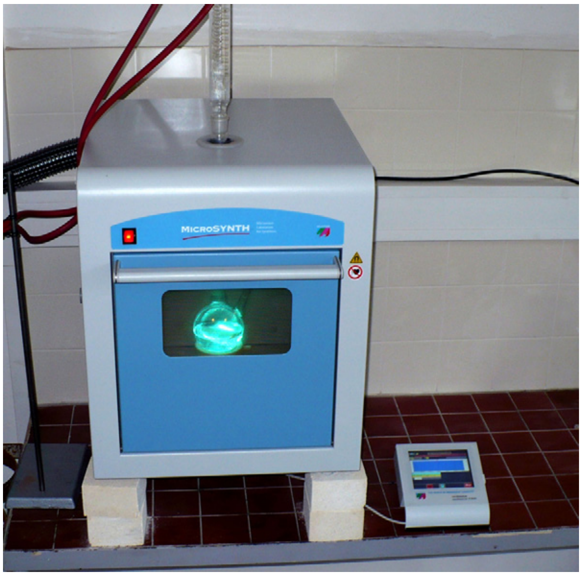

Fig. 2. The microwave photocatalysis arrangement on Milestone's MicroSYNTH Labstation.

UK). ISE was connected to a digital pH/mV meter (inoLab Level 1, WTW, Germany) and it was calibrated (NaCl). Results of the ISE analysis were compared with those obtained by the mercurimetry [36] with mercury(II) perchlorate. For mono-chloroacetic acid no additional reaction intermediate as the formaldehyde [37] was detected (2,4-dinitrophenylhydrazine test) under these thermal reaction conditions.

3. Results and discussion

3.1. Properties of the layers prepared

The crystal phase of titanium dioxide was analyzed by XRD. The observed structure phases revealed anatase as the predominant crystalline phase with a certain amorphous fraction. The crystallite size of the sample was estimated to be less 10 nm.

The specific surface area (S_{BET}, BET: Brunauer–Emmett–Teller) from the nitrogen adsorption was determined as $85.1 \pm 0.3\,m^2\,g^{-1}$.

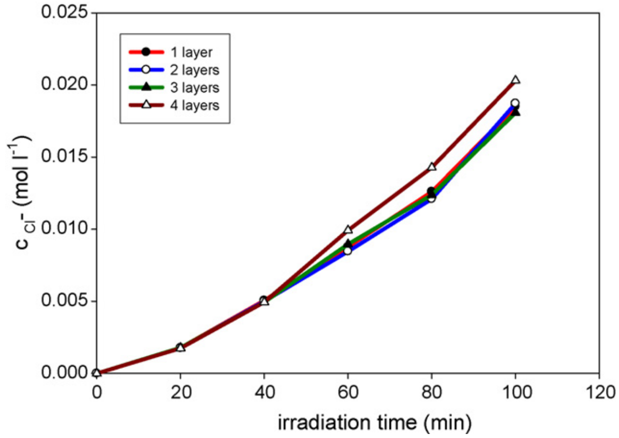

Fig. 3. The effect of the number of coating cycles on the concentration of chloride ions in time (the EDL intensity: $5.56\,\mu W\,cm^{-2}$).

Optical absorbance spectrum of TiO_2 film sample was measured. The absorption edge was detected at the wavelength of about 364 nm (3.41 eV). This illustrated that the absorption in TiO_2 started at that wavelength.

From AFM images, the film of TiO_2 was homogeneous with approximately uniform crystallite size. The relative surface roughness was 1.79 nm.

All spectra (XRD, absorption) and AFM images obtained in this work are available as supplementary data alongside the electronic version of this article as published in Elsevier Web Products.

3.2. Effect of the number of coating cycles

The effect of the number of coating cycles on the photocatalytic degradation of MCAA was examined. Fig. 3 shows that there were no significant differences between numbers of coating cycles on the formation of chloride ions because the reaction takes place on the photocatalyst surface. Generally, it is not possible to prepare a layer of appropriate properties during one coating cycle. Thinner layers are usually difficult to activate, whereas thicker layers do not have some of the important properties, such as high transparency, good mechanical strength, or excellent adhesion to various supports. For these reasons all of the TiO_2 film samples employed herein were coated in four layers.

The complete decomposition of MCAA ($0.1\,mol\,l^{-1}$) to HCl, CO_2, and H_2O was accomplished in 490 min (the EDL intensity: $5.56\,\mu W\,cm^{-2}$; EDL: 2 layers), when the concentration of chloride ions was $0.0997\,mol\,l^{-1}$.

3.3. Effect of light intensity

The light intensity effect was investigated in the reaction mixture amounting 150 ml and at the initial MCAA concentration of $0.1\,mol\,l^{-1}$. The light intensity was varied from 3.9 to $8.7\,\mu W\,cm^{-2}$. Fig. 4 shows the change in the chloride ion concentration with light intensity. The photocatalytic reaction efficiency increased with increasing light intensity presumably because more active sites can be formed on the catalyst surface. The influence of light intensity depends on the reaction conditions, such as the reaction mixture amount and, of course, the dissolved pollutant amount. Under lower light intensity an insufficient number of active sites for the degradation of the pollutant in low concentration can be formed. In such cases, the photocatalytic reaction proceeds more slowly and the higher light intensity does not have any influence on the photocatalytic efficiency.

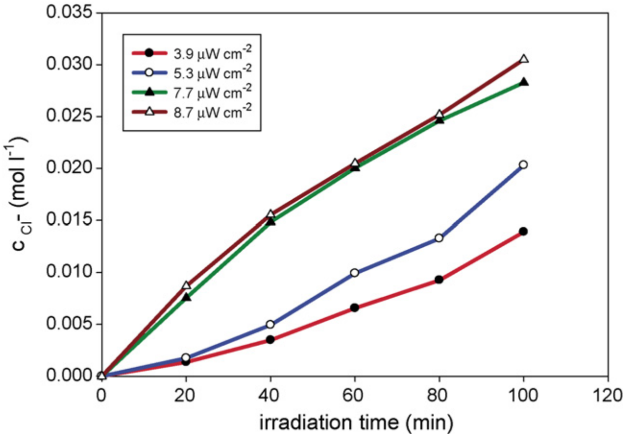

Fig. 4. The time dependence of c_{Cl^-} at various intensity of light (EDL: 1 layer).

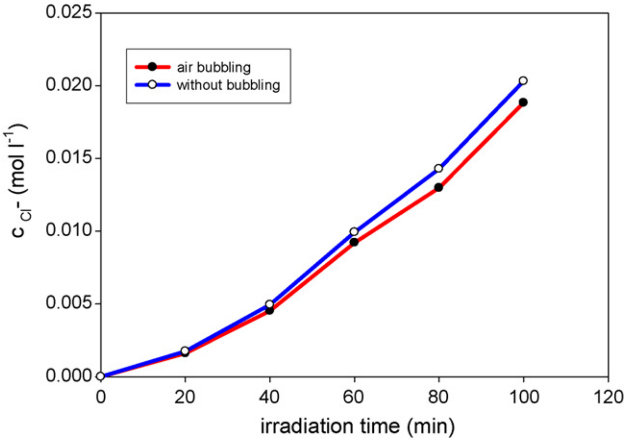

Fig. 6. The time dependence of c_{Cl^-} on an air bubbling of the reaction mixture (the EDL intensity: 5.56 μW cm^{-2}; EDL: 2 layers).

3.4. Effect of initial pH

The pH has a complex effect on the rates of photocatalytic reaction and the observed effect generally depends on the type of the pollutant and semiconductor. It is also known [17] that pH has an effect on the electrostatic charge of the TiO_2 surface, which determines the density of $TiOH_2{}^+$ groups.

In this experiment, the pH was adjusted before photocatalytic reaction by addition of the corresponding amount of NaOH to the solution. As presented in Fig. 5, the reaction was enhanced in an alkaline medium. The reason for the increase to the high initial pH is having more hydroxide ions present that may produce more hydroxyl radicals ($h^+{}_{vb} + OH^- \rightarrow OH^\bullet$). The presence of anions, e.g. chloride anion, can affect the degradation process. These anions can react with hydroxyl radicals and consume them ($OH^\bullet + Cl^- \rightarrow Cl^\bullet + OH^-$) and they can absorb UV radiation as well.

The pH value may affect the surface charge of the catalyst. At lower initial pH the degradation rate decreases in the presence of chloride ions. It is because of the adsorption on the positively charged catalyst surface. However, at high initial pH, there is no significant influence of chloride ions [38].

3.5. Effect of gas bubbling

The presence of oxygen as the electron acceptor is recommended so as to prevent the recombination between the generated positive holes and electrons. Horikoshi [6] found that under a low oxygen concentration (nitrogen-purging) the photodegradation rate in the presence of microwaves was higher than that in the absence of microwave irradiation. As mentioned above, specific interactions of microwaves with the UV-illuminated TiO_2 particle surface give rise to the generation of additional surface defects that can prohibit the recombination of holes with electrons. In EDL/TiO_2 the high transference rate decreases the need of dissolved oxygen concentration in the solution.

In these preliminary experiments the effect of air gas bubbling was also checked. As can be seen in Fig. 6, the presence of air does not influence the photodecomposition of MCAA. More to the contrary, we can see a mild decrease because this reaction is carried out at 100 °C. Temperature affects the amount of oxygen that can be dissolved in water. When fresh water is heated up, air bubbles start to form. If the water is cooled down and then again reheated, bubbles will not appear until the water starts to boil (water is deaerated). 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 [39].

3.6. Effect of H_2O_2 dosages

One effective strategy for inhibiting e^-/h^+ recombination is to add another electron acceptor to the reaction system. The use of H_2O_2 [40] has been demonstrated to enhance the rates of Brilliant

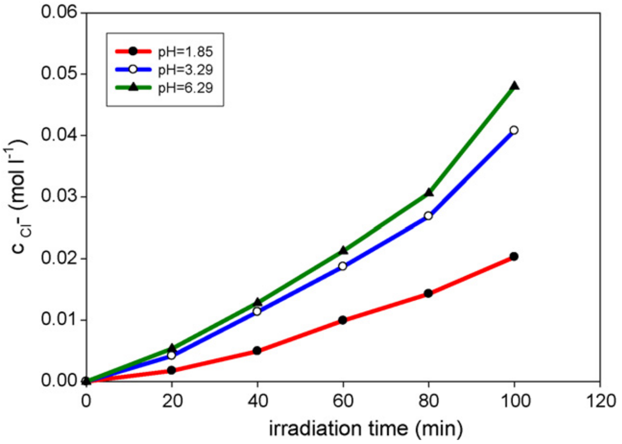

Fig. 5. The effect of initial pH on the photocatalytic decomposition of MCAA (the EDL intensity: 5.56 μW cm^{-2}; EDL: 2 layers).

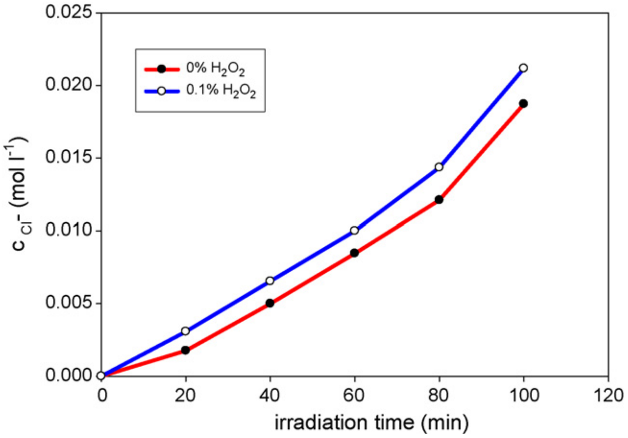

Fig. 7. The effect of adding H_2O_2 on photocatalytic decomposition of MCAA (the EDL intensity: 5.60 μW cm^{-2}; EDL: 2 layers).

Red X-3B degradation remarkably because it traps the photogenerated electrons more efficiently than molecular oxygen. Secondly, the application of H_2O_2 produces $^{\bullet}OH$ radicals (at the conduction band [16]) which can again degrade some pollutants.

The photocatalytic decomposition of MCAA was increased, when H_2O_2 was present in the solution. The effect of H_2O_2 was enhanced by increasing the H_2O_2 dose from 0 to 0.3% (v/v). At the initial stage, the reaction rate was increased abruptly, then went to a balance after the H_2O_2 dosage was 0.1% (v/v) (Cl^- concentration 0.021175 mol l^{-1}; reaction time: 100 min; the EDL intensity: 5.60 $\mu W\,cm^{-2}$; EDL: 2 layers).

The effect of optimal H_2O_2 dosage 0.1% (v/v) on photocatalytic degradation of MCAA was shown in Fig. 7. It has been observed that H_2O_2 dosage has only a slight effect on the reaction enhancement.

4. Conclusions

Mono-chloroacetic acid was totally decomposed to HCl, CO_2, and H_2O over the irradiated titanium dioxide film in microwave field. Thin titanium films were prepared by the sol–gel process and defined by several characterization techniques. This study revealed that the reaction efficiency depends on the intensity of light and initial pH value of the solution. Moreover, the degradation of mono-chloroacetic acid was enhanced in an alkaline solution and in the presence of H_2O_2, and significantly enhanced by increasing the intensity of light. Furthermore, this paper also discloses that efficiency of UV irradiation is not influenced by the number of coating cycles or by air bubbling. MCAA also yielded no observed organic intermediates under these thermal reaction conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.02.009.

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