

Short note

# Use of microwave discharge electrodeless lamps (MDEL) II. Photodegradation of acetaldehyde over TiO<sub>2</sub> pellets<sup>☆</sup>

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## Abstract

A microwave discharge electrodeless lamp (MDEL) filled with low pressure mercury gas has been developed for the photocatalytic treatment of organic air pollutants over anatase TiO<sub>2</sub> pellets. The benefit of the combination of MDEL and TiO<sub>2</sub> pellets under microwave radiation was assessed by examining the degradation of acetaldehyde in humidified synthetic air. The effect of microwave irradiation was quantified by the decomposition rate of acetaldehyde and the desorption rate of acetaldehyde on the TiO<sub>2</sub> surface. It is shown that acetaldehyde is readily transformed at the surface of the TiO<sub>2</sub> pellets by the combined action of UV light and microwave irradiation coupling homogeneous and heterogeneous photoreactions. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Microwave discharge electrodeless lamp; Microwave; Acetaldehyde; TiO<sub>2</sub> pellet; Photodegradation

## 1. Introduction

Microwave discharge electrodeless lamps (MDEL) are used for applications such as the drying of paintings and the surface modification of plastics [1]. In recent years, some reports suggested the possibility to use this type of lamps as the light source in photochemical methods for environmental protection [2]. Several studies were published in the last few years on the use of microwave discharge electrodeless lamps, and their effectiveness in photocatalytic wastewater treatment was shown [3]. The efficiency of photo-assisted degradation reactions of organic substrates was enhanced when a combination of UV light and microwave radiation was used for the treatment of wastewaters [4]. In an early study Kataoka et al. reported the photocatalytic degradation of the air pollutant ethylene by using microwave and a UV light irradiated TiO<sub>2</sub>/ZrO<sub>2</sub>-fixed bed reactor [5]. The photocatalytic remediation of air pollutants already finds practical usage in air filters, self-cleaning surfaces and photocatalytic concrete and paints [6].

The aim of this study was to investigate the microwave effect on the degradation of acetaldehyde, which is widely used as a model pollutant to compare the activities of different photocatalysts [7], at the surface of TiO<sub>2</sub> pellets under UV irradiation from a MDEL. It will be shown that the combination of TiO<sub>2</sub> pellets, microwave and MDEL as a new treatment method against air pollutants has definite advantages when compared with other photocatalytic methods.

## 2. Experimental details

### 2.1. Material

TiCat C (Sachtleben Chemie GmbH) was used as photocatalyst. The cylindrical pellets (average length = 7 mm, average diameter = 5.5 mm) were prepared from anatase TiO<sub>2</sub> and calcined at 800 °C. Their BET surface area was approx. 30 m<sup>2</sup>/g. A mixture of acetaldehyde (207 ppm) in nitrogen (Linde) was used as the feed gas for the photocatalytic reactor.

### 2.2. Microwave discharge electrodeless lamp

The microwave discharge electrodeless lamp (length = 130 mm, diameter = 13 mm) was made from super pure quartz,

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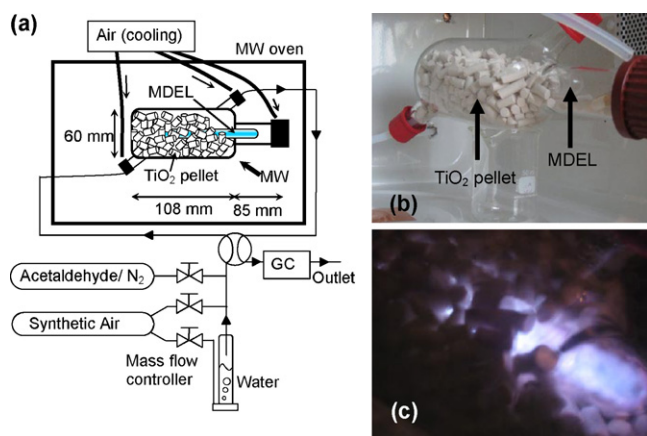


Fig. 1. (a) Schematic presentation of the experimental set-up illustrating some of the details of the reactor; (b) photograph of the experimental set-up showing the microwave Pyrex reactor with the MDEL and the  $\text{TiO}_2$  pellets incorporated into a domestic microwave oven; (c)  $\text{TiO}_2$  pellets irradiated with light emitted from the MDEL.

filled with mercury (approx.  $0.3 \mu\text{g}$ ) and argon ( $0.133 \text{ kPa}$ ). The emission spectrum of the MDEL shows strong emissions at  $185 \text{ nm}$  and  $254 \text{ nm}$  (spectrum not shown) with intensities of  $3 \mu\text{W}/\text{cm}^2$  and  $380 \mu\text{W}/\text{cm}^2$ , respectively. The light intensities were measured in a distance of  $100 \text{ mm}$  from the light source by using ORC UV-06 and UV-M03A light meters. The ozone concentration was measured with a Gemedical OC-300 ozone detector.

### 2.3. Experimental set-up

The experimental set-up (Fig. 1a) was in accordance with the photodegradation method for  $\text{NO}_x$  given by the Japanese Industrial Standard JIS R 1701-1:2004. Dry air ( $500 \text{ ml}/\text{min}$ ), wet air ( $500 \text{ ml}/\text{min}$ ), and the acetaldehyde/nitrogen gas mixture ( $5 \text{ ml}/\text{min}$ ) were accurately controlled employing mass flow controllers (Brooks Smart Service (TMF); Models 5860S). The concentration of acetaldehyde in the feed gas mixture was adjusted to  $1 \text{ ppm}$ . The gas mixture was introduced into a cylindrical Pyrex reactor, containing the  $\text{TiO}_2$  pellets ( $213 \text{ g}$ ) and the MDEL, through a Teflon tube. The Pyrex reactor was placed inside a domestic microwave-cooking oven (SEVERIN 700, power consumption set at  $700 \text{ W}$ ).

The possible melting of the three plastic caps of the microwave Pyrex reactor by the heating of the microwave was prevented by cooling the entire oven inside with an air stream. The acetaldehyde concentration in the gas stream exiting the microwave Pyrex reactor was measured with a Syntech Spectras GC955 system employing a photoionisation detector (PID).

### 2.4. Adsorption process of acetaldehyde on the $\text{TiO}_2$ surface

When the acetaldehyde containing gas stream was introduced into the microwave Pyrex reactor in the dark, it was observed that more than  $90\%$  of the incoming acetaldehyde concentration was adsorbed by the  $\text{TiO}_2$  pellet's surface initially (see Fig. 2). Sub-

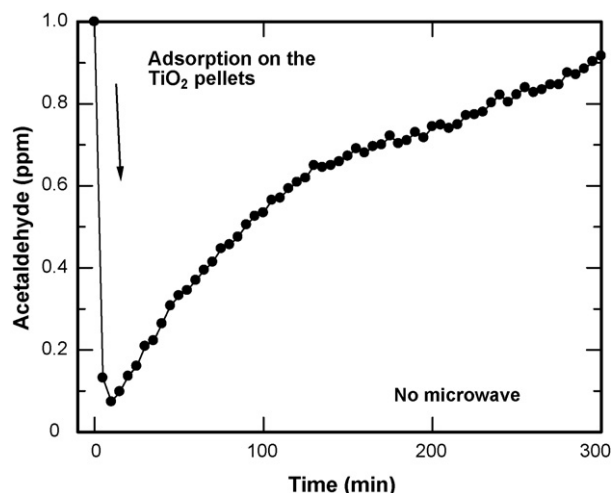


Fig. 2. Temporal profile showing the adsorption of acetaldehyde on the  $\text{TiO}_2$  pellet's surface in the dark.

sequently, the surface of the  $\text{TiO}_2$  pellets was slowly saturated by further flushing with the acetaldehyde containing gas mixture. It was confirmed that more than  $90\%$  of the initial acetaldehyde concentration was detected in the exhaust gas stream after  $300 \text{ min}$  ( $5 \text{ h}$ ) continuous adsorption in the dark. The irradiation and the microwave excitation were only started after this initial adsorption equilibration phase.

## 3. Results and discussion

In a first experimental run the transformation of acetaldehyde in the humidified air stream over  $\text{TiO}_2$  pellets under the combined action of microwave excitation and UV light irradiation emitted from a MDEL was examined. The change of the acetaldehyde concentration is shown in Fig. 3a as a function of the reaction time. Immediately after the microwave irradiation was switched on, the concentration of acetaldehyde in the outlet gas stream increased and reached a maximum value of  $8.7 \text{ ppm}$  after  $6 \text{ min}$ . This indicates that acetaldehyde is desorbed from the  $\text{TiO}_2$  surface under these experimental conditions. An increase of the temperature of the  $\text{TiO}_2$  pellets under the microwave irradiation alone, favoring the thermal desorption of the organic compound was observed (Table 1). After only  $60 \text{ s}$  of microwave excitation a surface temperature of the  $\text{TiO}_2$  pellets of approx.  $84 \text{ }^\circ\text{C}$  was measured. Moreover, the temperature increased up to approx.  $207 \text{ }^\circ\text{C}$  within  $5 \text{ min}$  of microwave irradiation. Therefore, it was concluded that the acetaldehyde initially adsorbed at the  $\text{TiO}_2$  surface is removed by thermal desorption resulting from the heating of the  $\text{TiO}_2$  pellets.

At longer reaction times the acetaldehyde concentration decreased to values lower than the inlet concentration, clearly indicating that acetaldehyde is transformed under the experimental conditions (cf. Fig. 3a). Besides the possible photocatalytic degradation of acetaldehyde at the UV irradiated  $\text{TiO}_2$  surface other transformation mechanisms, *i.e.* (a) the thermal reaction of the aldehyde [8] at the  $\text{TiO}_2$  pellets heated by microwave excitation, (b) the direct photolysis of acetaldehyde [9] by the  $185 \text{ nm}$  UV light emitted from the MDEL, and (c)

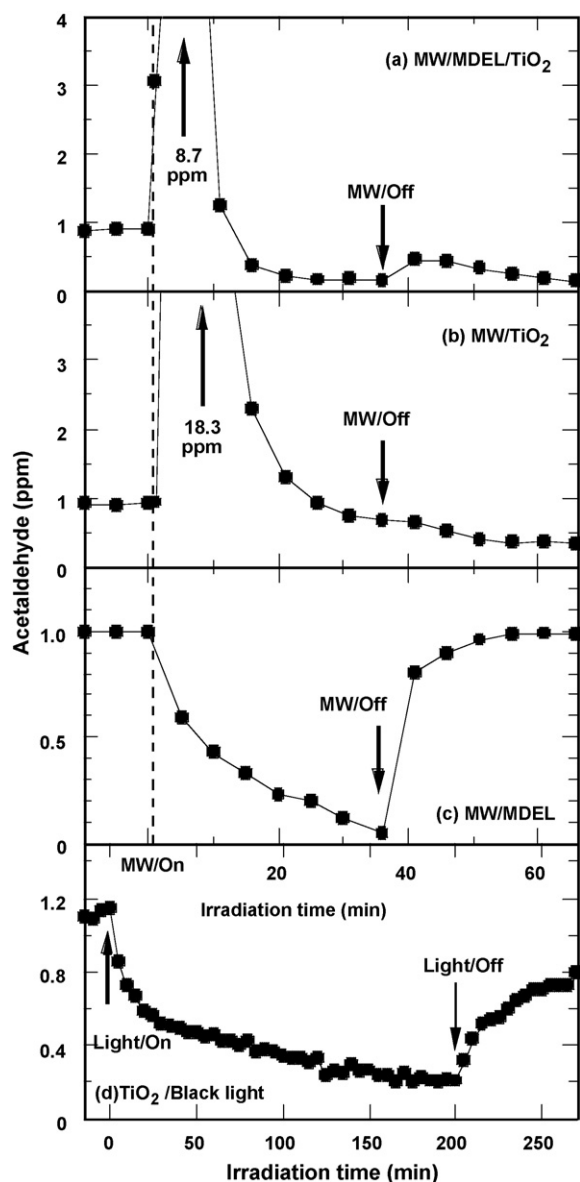


Fig. 3. Change of concentration of acetaldehyde as a function of the reaction time observed by using (a) MW/MDEL/TiO<sub>2</sub>, (b) MW/TiO<sub>2</sub>, (c) MW/MDEL, and (d) TiO<sub>2</sub>/Black light methods.

Table 1  
Temperatures measured at the surface of the TiO<sub>2</sub> pellets under microwave irradiation

MW radiation time (s)	Temperature (°C)
0	26
20	38
30	64
60	84
90	102
120	146
180	172
240	193
300	207

Average of 10 measurements with a thermo-couple at different positions inside the TiO<sub>2</sub>-containing pellet reactor (error about 10%).

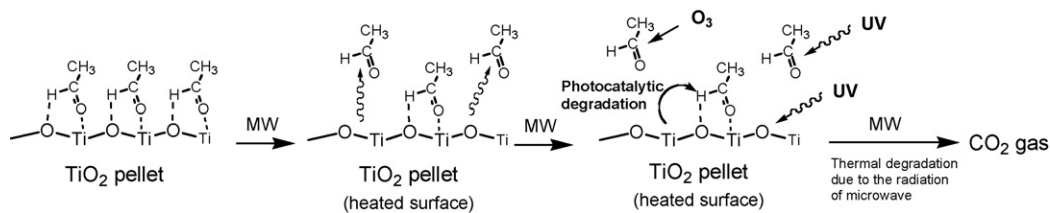
gas phase reactions between acetaldehyde and reactive oxygen species including O<sub>3</sub>, O(1D), and •OH, which are known to be formed photochemically from O<sub>2</sub> and H<sub>2</sub>O contained in the gas stream by the 185 nm UV light [10] emitted from the MDEL, have to be considered.

In a second experimental run the change of the acetaldehyde concentration was measured by using the TiO<sub>2</sub> pellets under irradiation with microwaves alone, i.e. without the MDEL (see Fig. 3b). The initial amount of desorbed acetaldehyde under microwave excitation in the absence of the MDEL was higher compared with the values measured in the experiment under additional irradiation with UV light emitted from the MDEL. The difference in the maximum acetaldehyde concentrations measured during the desorption step of both experimental runs was about 10 ppm. This can be explained assuming a photochemical and/or a photocatalytic transformation of acetaldehyde at the TiO<sub>2</sub> surface induced by the UV light emitted from the MDEL. Subsequently, a further decrease of the acetaldehyde concentration to values lower than the feed concentration of 1 ppm was observed under continuous excitation with the microwave alone (cf. Fig. 3b). However, the measured concentrations (1.29 ppm after 21 min) were always higher than in the corresponding experiment performed in the presence of the MDEL (0.23 ppm after 21 min; see Fig. 3a). It is evident from this experimental observation that the thermal transformation contributes only to a certain extent to the overall degradation of acetaldehyde under the combined action of UV light and microwave excitation.

In a third experimental run, the acetaldehyde containing gas was irradiated with microwave and UV light from the MDEL in an empty (i.e. TiO<sub>2</sub>-free) reactor. Also under this experimental condition a decrease of the acetaldehyde concentration was observed (Fig. 3c). The final acetaldehyde concentration (0.05 ppm after 36 min) was even lower than in the experimental run performed in presence of TiO<sub>2</sub> (Fig. 3a), indicating that direct photolysis and/or gas phase reactions with photogenerated reactive oxygen species contribute significantly to the overall reaction observed in the photocatalytic experiment described above.

The transformation of acetaldehyde under the combined microwave MDEL irradiation was compared with the standard photocatalytic degradation under conditions similar to those described for the NO degradation by JIS R 1701-1:2004. The experimental conditions and the load of TiO<sub>2</sub> pellets (213 g) were adjusted to the conditions employed during the microwave experiments. The source of UV light was a UV-A Phillips lamp (1.0 mW/cm<sup>2</sup> at around 350 nm). Under these experimental conditions the initial acetaldehyde concentration was photocatalytically reduced by about 80% after an irradiation time of 200 min (see Fig. 3d).

The experimental results shown above can be interpreted as follows: (1) acetaldehyde is photocatalytically degraded by the action of UV-A light alone at the surface of the TiO<sub>2</sub> pellets employed in this study (Fig. 3d); (2) the combined action of microwave and UV light from the MDEL in absence of TiO<sub>2</sub> also results in a significant decrease of the acetaldehyde concentration, most likely due to a homogeneous photochemical



Scheme 1. Proposed mechanism of the microwave desorption process of acetaldehyde on the  $\text{TiO}_2$  surface and the degradation of acetaldehyde at the  $\text{TiO}_2$  pellets under UV irradiation by the MDEL.

transformation of the organic compound (Fig. 3c); (3) the thermal degradation of acetaldehyde at the  $\text{TiO}_2$  pellets heated by microwave irradiation alone is smaller importance than the photochemical and/or photocatalytic reactions of this compound (compare Fig. 3a–c); (4) acetaldehyde is readily transformed under the combined action of  $\text{TiO}_2$ , UV light, and microwave irradiation (Fig. 3a) coupling homogeneous and heterogeneous photoreactions.

A schematic presentation of the different reaction steps proposed for the degradation of acetaldehyde under the experimental conditions of Fig. 3a is given in Scheme 1. The initially adsorbed acetaldehyde is removed from the surface of the  $\text{TiO}_2$  pellets by the microwave heating. Photodegradation of acetaldehyde is subsequently initiated by the ultraviolet light (185 nm and 254 nm) emitted from the MDEL, possibly mediated by the action of photogenerated reactive oxygen species such as  $\text{O}_3$ , which was already detected within 1 min of irradiation. Adsorbed acetaldehyde at the surface of the  $\text{TiO}_2$  pellets is transformed by the  $\text{TiO}_2$  mediated photocatalytic reaction and to a minor extend by thermal reactions.

#### 4. Conclusion

The following observations have been made when the degradation of acetaldehyde was measured in a system combining microwave excitation and UV-illumination initiated by a MDEL. The microwave energy leads to a rapid heating of the  $\text{TiO}_2$  pellets and to the generation of ultraviolet light by the MDEL. Desorption of acetaldehyde from the  $\text{TiO}_2$  surface results from the heating of the  $\text{TiO}_2$  pellets. Transformation processes of acetaldehyde are initiated by direct photolysis of the organic compound as well as indirectly by the photochemical formation of reactive oxygen species. On the other hand, adsorbed acetaldehyde on the  $\text{TiO}_2$  surface is transformed by photocatalysis and to a minor extend by thermal reactions. The effect of the microwave excitation for the combination of MDEL and  $\text{TiO}_2$  pellets can thus be explained by desorption, pyrolysis and photodegradation. The proposed novel method suggests that microwave energy can be used effectively for the degradation of organic compounds in polluted air.

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