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# Degradation of 4-chlorophenol by a microwave assisted photocatalysis method

Zhihui Ai [a,b], Peng Yang [a], Xiaohua Lu [a,*]

[a] *Environmental Science Research Institute, Huazhong University of Science and Technology (HUST), Wuhan 430074, PR China*
[b] *College of Chemistry, Central China Normal University, Wuhan 430079, PR China*

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**Abstract**

In this work, the degradation of 4-chlorophenol (4CP) under simultaneous microwave assisted UV (electrodeless discharge lamp) photocatalysis technique (MW/UV/$TiO_2$) was investigated. Several factors affecting the degradation of 4CP by MW/UV/$TiO_2$ method, such as the dosage of photocatalysts, the initial pH value of the solutions, gas bubbling, light intensity and addition of $H_2O_2$ oxidant, were studied in detail. The synergistic effects between microwave irradiation and $TiO_2$ photocatalysis were also studied. The major intermediates were found to be chlorobenzene, phenol, hydroquinone, benzoquinone and 4-chlorocatechol. Based on the results, a general reaction pathway for the degradation of 4CP was proposed.


*Keywords:* Microwave assisted photocatalysis; Electrodeless discharge lamp; 4-Chlorophenol

## 1. Introduction

The use of semiconductors as photocatalysts for a variety of processes, including the oxidative mineralisation of organic pollutants in water or in the gas phase, destruction of bacteria and reduction of trace metals, continues to be an active field of research [1]. $TiO_2$ is broadly used as a photocatalyst because it is photochemically stable, nontoxic and inexpensive [2]. Photocatalytic degradation using $TiO_2$ under UV light appears to be an effective strategy for degrading and mineralizing chlorinated phenols (CPs) [1,2].

The principles of photocatalysis based on $TiO_2$ have been discussed in several literatures [1–3]. In general, photoinduced electrons ($e^-$) and positive holes ($h^+$) are produced from $TiO_2$ under irradiation of UV light ($\lambda < 387$ nm), which has an energy greater than the band gap (3.2eV) of $TiO_2$ (anatase) (Eq. (1)). These charged species can further generate free radicals ($^\bullet$OH) under appropriate conditions (Eq. (2–4)). The highly oxidizing positive hole has been considered to be the dominant oxidizing species contributing to the mineralization process resulting from the $TiO_2$ photocatalyst (Eq. (5)).

$$TiO_2 + h\nu_{(\lambda<387\text{nm})} \rightarrow TiO_2\,(e^-_{CB} + h^+_{CB}) \quad (1)$$

$$h^+_{VB} + OH^-(H_2O) \rightarrow {}^\bullet OH\,(+H^+) \quad (2)$$

$$e^-_{CB} + O_2 \rightarrow {}^\bullet O_2^- \quad (3)$$

$${}^\bullet O_2^- + H^+ \rightarrow {}^\bullet OOH \quad (4)$$

$$^\bullet OH + \text{organic pollutants} \rightarrow \text{mineralized products} \quad (5)$$

During last two decades, MW irradiation has found its applications in domestic, industrial and medical fields. The applications of microwave energy to enhance chemical reaction have also been growing every now and then [4]. Moreover, microwave irradiation was reported to use for environmental waste treatment [5–7]. However, there are few reports on microwave-assisted photocatalysis. This

* Corresponding author. Tel.: +86 27 67867953; fax: +86 27 67867953.
*E-mail addresses:* lxh@hust-esri.com, jennifer.ai@mail.ccnu.edu.cn (X. Lu).

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might be partially due to microwave chemistry is still a developing field in chemistry, and also due to experimental difficulties that accompany simultaneous application of ultra-violet irradiation and microwave irradiation [8,9].

It has been known for several decades that the electrodeless discharge lamp (microwave lamp; MWL) generates ultraviolet (UV) radiation in the microwave field, i.e. by a wireless way [8]. Low powered and low-pressure electrodeless lamps were utilized in spectroscopy and analytical chemistry four decades ago [10]. Usually light sources such as xenon lamps and mercury lamps were used for studying the $TiO_2$ photocatalysis of 4CP whereas the MWL was seldom used.

Chlorophenols (CPs) are common organic contaminants, which show low biodegradability, and therefore are persistent pollutants, posing serious risks to the environment once mixed into natural water [11,12]. These compounds are carcinogenic, mutagenic and have a tendency to accumulate in fatty tissue [13]. Many efforts have been dedicated to the study of alternative technologies that are able to minimize the deleterious effect caused by this anthropic material. Using conventional technique to eliminate this kind of compounds may be difficult as they are usually present at low concentrations in water or they are especially refractory to the oxidants. Therefore, it has been necessary to develop more effective processes for the destruction of such contaminants [12].

Based on the above considerations, a research program on integrating MW and UV light for degradation hazardous organic pollutants was performed. In this program 4CP was chosen as a model compound and the photocatalytic degradation process using a MW assisted electrodeless discharge UV lamps system in the presence of $TiO_2$ was investigated.

## 2. Materials and methods

### 2.1. Chemicals

Standard material 4CP was obtained from Sigma Chemical Co., and the initial concentration of 4CP in all experiments was 30 mg/L. $TiO_2$ Degussa P25 (particle size of 20–30 nm; composition, 83% anatase and 17% rutile; BET surface area of 50 $m^2/g$) made in Germany was used as the photocatalyst in this study. Analytical $H_2O_2$ (30% v/v) was employed as the oxidant. All solutions were prepared using distilled deionized water (18 mΩ) by an EASY-pure ultrapure water system. $H_2SO_4$ (AR grade) and NaOH (AR grade) were used to adjust the initial pH of solutions to the predetermined levels. Oxygen or nitrogen (99.99%) was used for deaeration of solutions. Analytical grade chloroform was used to extract the samples for GC/MS analysis.

### 2.2. Methods

All microwave assisted photocatalysis experiments were conducted using a MW assisted electrodeless discharge UV lamp system, which was modified, from a domestic MW oven (2450 MHz, power 750 W). The schematic experimental details of reactor are shown in Fig. 1. It consisted of a cylindrical glass reactor (1 L) provided with the required elements for the development of the different processes. In each experiment, the reactor was filled with 500 mL of an aqueous solution of 4CP with predetermined pH value. The electrodeless discharge lamp containing mercury vapor with a peak emission at 254 nm was placed into the reactor vessel so that the MW field induced UV irradiation interacted with the reaction mixture. The required amounts of $TiO_2$ were added to the reactor and stored in the dark for 15 min for equilibrium before

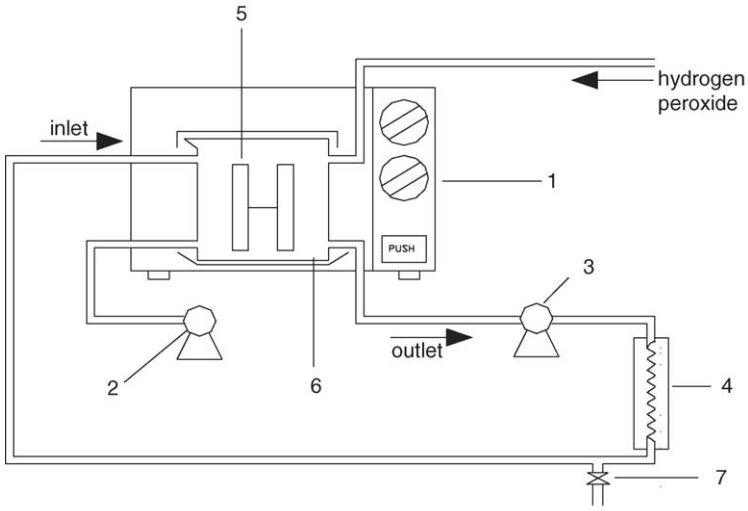


Fig. 1. Schematic diagram of MW/MWL system.