Degradation of 4-chlorophenol by a microwave assisted photocatalysis method

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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$_2$O$_2$ 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.
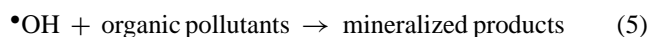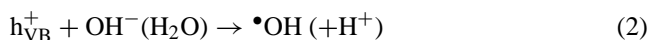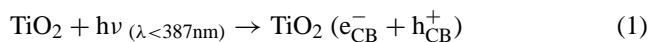© 2005 Elsevier B.V. All rights reserved.

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)).

$$\text{TiO}_2 + h\nu_{(\lambda < 387\text{nm})} \rightarrow \text{TiO}_2\,(e_{CB}^- + h_{CB}^+) \tag{1}$$

$$h_{VB}^+ + \text{OH}^-(\text{H}_2\text{O}) \rightarrow {}^\bullet\text{OH}\,(+\text{H}^+) \tag{2}$$

$$e_{CB}^- + \text{O}_2 \rightarrow {}^\bullet\text{O}_2^- \tag{3}$$

$${}^\bullet\text{O}_2^- + \text{H}^+ \rightarrow {}^\bullet\text{OOH} \tag{4}$$

$${}^\bullet\text{OH} + \text{organic pollutants} \rightarrow \text{mineralized products} \tag{5}$$

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

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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

1—magnetron 2—fan 3—diaphragmatic pump 4—condenser tube
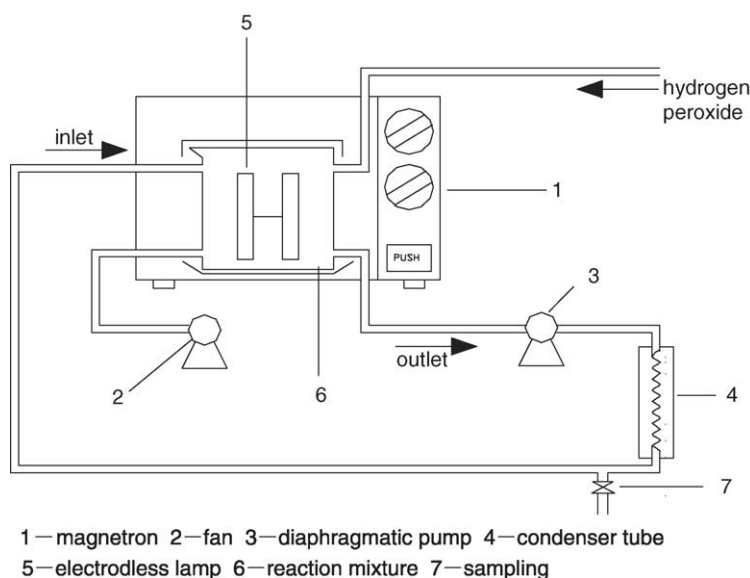5—electrodless lamp 6—reaction mixture 7—sampling

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

the photocatalysis experiments. For reactions carried out in different atmosphere, the required air, pure N_2 gas or pure O_2 gas was bubbled to the reactor through a porous glass tube gas sparger located at the bottom of the reactor throughout the entire reaction period. The solution was circulated at $2\,L\,min^{-1}$ with a pump, and the temperature of 4CP solution in reactor vessel was kept constant at 28–29 °C by a condenser.

The process of UV photocatalysis without microwave was carried out in a continuously aerated stainless steel photochemical reactor (Environmental Science Research Institute of HUST) in batch mode at room temperature, the radiation source was provided with low-pressure mercury vapor lamp which emitted a wavelength around 254 nm as the radiation source. The reactor was filled with 500 mL of an aqueous solution of 4CP (initial concentration of 30 mg/L), the required P25 was added into the reactor and stored in the dark for 15 min for equilibrium before the photocatalysis experiments.

Samples were taken with a 10 mL syringe from the reactor at different pre-determined reaction times. The collected photocatalysis samples were first centrifuged at 4000 rpm for 15 min by using a LG10-2.4 centrifuge (Beijing, China) to remove the TiO_2 prior to chemical analysis. All the samples were analyzed immediately to avoid any further reactions. The concentration of 4CP was quantified by HPLC. Twenty-microliters sample was injected into the D-7000 HPLC system (HITACHI, Japan) equipped with C18 column (Hypersil, China. 250×4.6 mm), which consisted of a L-7100 pump and a L-7420 UV–vis detector. Eighty percent (v/v) aqueous methanol solution was used as mobile phase, its flow rate was fixed at 1 mL/min. The wavelength employed for detecting 4CP was 280 nm. UV–vis spectrophotometer (8500II, Techcomp) was used to measure the UV–vis spectrum of 4CP during degradation. IC (Dx-120, Dionex) equipped with an ASA4-SC column was employed for analysis of chloride-ion concentrations in aqueous solution using sodium chloride solutions as a standard, the mobile phase of a mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ was used at a flow rate of 1.60 mL/min, volume of samples was 20 μL.

Photolyzed solution of 4CP (10 mL) was extracted with chloroform twice (30 ml each), and the organic layers were collected, dried with sodium sulfate, and evaporated to 1 mL for the determination of the intermediates with GC–MS.

Identification of intermediates was performed using a gas chromatography (GC, Varian 3900) with a capillary column (FactorFour^{TM}: VF-5ms, $30\,m \times 0.25\,mm$, 0.25 um) and a mass spectrometer (MS, Saturn 2100T), which were programmed with the Saturn Chemstation software (Saturn WS). Flow rate of helium 99.999% was 1 mL/min. The oven temperature was programmed from 50 (1 min) to 300 (1 min) at a ramp rate of 8 °C/min. The injection volume of extract was 1 μL. All library-matched species exhibited the degree of match better than 80%.

3. Results and discussion

3.1. Effects of TiO_2 dosages on the degradation process

The effects of dosage of TiO_2 on the photocatalytic degradation rates of 4CP were examined. Fig. 2 shows the variation of pseudo-first-order rate constants with different TiO_2 dosages at 0.5, 1.0, 2.0 3.0 and 4.0 mg/L under UV illumination. As shown by Fig. 2, the photocatalytic degradation rate increases with increasing TiO_2 dosages. However, the degradation decreases at higher TiO_2 dosages. The increased degradation is likely due to the increase of the total surface area (or number of active sites) of the photocatalysts available for photocatalytic reaction when increasing the dosage of TiO_2. When TiO_2 was overdosed, the intensity of light penetration attenuated and light scattering increased, which counteracted the positive effect coming from the dosage increment and therefore the overall performance reduced [2].

3.2. Effects of initial pH value of the solution on the degradation process

The effects of initial pH levels on the MW assisted photocatalytic degradation rates of 4CP were investigated. As reported in Fig. 3, the degradation reactions were enhanced in both an alkaline medium and an acid medium. Degradation reactions were enhanced in the alkaline medium may be attributed to two reasons: (1) it is easier for 4CP to absorb UV light as it is present in its anionic state; (2) more hydroxide ions (OH^-) in the solution produced more hydroxyl radicals ($^{\bullet}OH$). Since hydroxyl radical is the dominant oxidizing species in the photocatalytic process, the photodegradation of 4CP is therefore accelerated in an alkaline medium. The reason for the increase of degradation rate at low initial pH value is because more H^+ ions in the solution, more conduction band electrons (e^-) can transfer to the surface of catalyst to react with O_2 to produce more hydroxyl radicals.
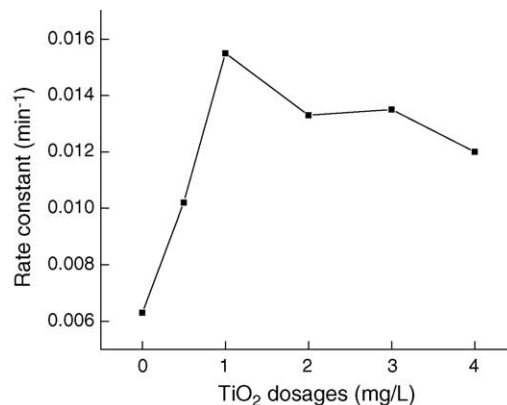

Fig. 2. Variation of pseudo-first-order rate constants with TiO_2 dosages, where reaction time is 120 min, the initial pH value is 6, $E = 1450\,lx$, bubbled with air.
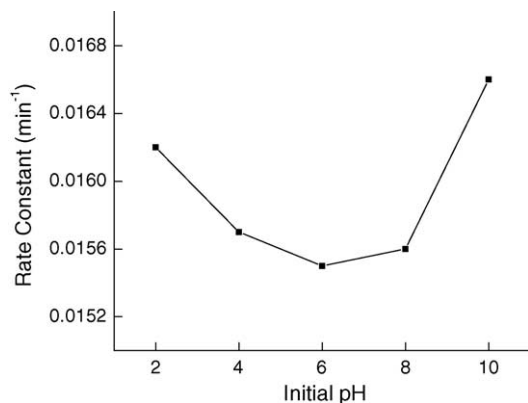
Fig. 3. Variation of pseudo-first-order rate constants with initial pH value, where reaction time is 120 min, the TiO_2 dosage is 1 mg/L, $E = 1450$ lx, bubbled with air.
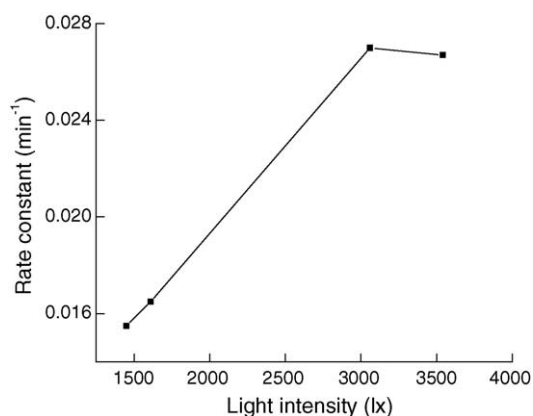

Fig. 4. Variation of pseudo-first-order rate constants with light intensity, where reaction time is 120 min, the TiO_2 dosage is 1 mg/L at an initial pH value of 6, bubbled with air.

3.3. Effects of light intensity of the electrodeless discharge UV lamp on the degradation process

The effects of light intensity E (lux) of the electrodeless discharge UV lamp on the rate constants were shown in Fig. 4. The photocatalysis degradation rate was increased with increasing E because more light energy can be used for degradation of 4CP as the increase in light intensity.

3.4. Effects of gas bubbling on the degradation process

The effects of bubbling the solution or dispersion with a reactive (air, oxygen) or an inert gas (nitrogen) were also examined. Table 1 shows the degradation of 4CP by aeration

Table 1
Effects of gas bubbling on degradation of 4CP in MW/UV/TiO_2[a]

Gas	Nitrogen	Air	Oxygen
Rate constant (min^{-1}) of 4CP degradation	0.0134	0.0155	0.0164

[a] Reaction time is 120 min, TiO_2 dosage is 1 mg/L at an initial pH value of 6, light intensity (E) is 1450 lx.
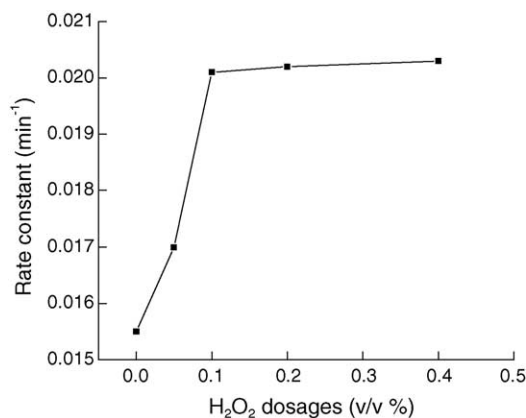

Fig. 5. Variation of pseudo-first-order rate constants with H_2O_2 dosages, reaction time is 120 min, TiO_2 dosage is 1 mg/L at an initial pH value of 6, $E = 1450$ lx, bubbled with air.

air, O_2 or N_2 gas. During the photodegradation process, the recombination of photogenerated valence band holes with conduction band electrons is known to compete with formation of reactive oxygen species ($^{\bullet}OH$), while their formation is influenced by the quantity of oxygen in solution.

3.5. Effects of H_2O_2 dosages on the degradation process

The effects of addition of the H_2O_2 into TiO_2 dispersion were examined (Fig. 5). The degradation of 4CP was increased in the presence of H_2O_2 and influenced by the dosages of H_2O_2. With the addition of H_2O_2, the rate constant was increased abruptly at the low dosages of H_2O_2, but went to a balance after the dosage increases to 0.1%. This is because the addition of H_2O_2 can enhance the formation of $^{\bullet}OH$. H_2O_2 would act as an electron donor to produce hydroxyl radicals by its reduction at the conduction band. The self-decomposition of H_2O_2 by UV illumination would also produce hydroxyl radicals.

3.6. The synergistic effects between MW irradiation and UV photocatalysis degradation processes

The pre-experimentation in our program showed that the degradation ratio of 4CP was 2.55% after 120 min irradiation in MW system, but there was no change of Cl^- concentration. This result implied that 4CP was not degraded by MW (dechlorination), the loss of 4CP could be because of the microwave superheating effects.

Table 2 summarizes the degradation rate of 4CP and the changes of Cl^- during UV/TiO_2 and MW/UV/TiO_2,

Table 2
Comparison of degradation of 4CP by different methods[b]

Method	MW	UV/TiO_2	MW/UV/TiO_2
Degradation rate (%)	2.25	38.76	82.85
Increase of Cl^- (mg/L)	0	3.79	7.95

[b] Reaction time is 120 min, TiO_2 dosage is 1 mg/L at an initial pH value of 6, light intensity (E) is 1450 lx.
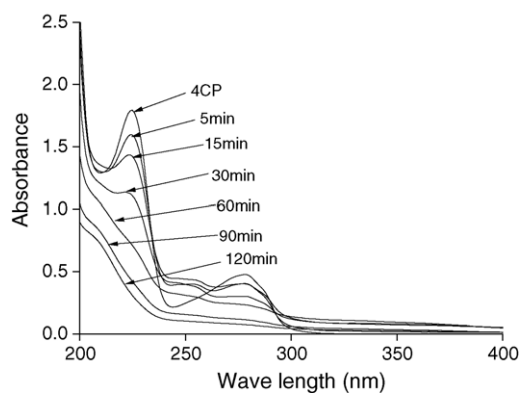
Fig. 6. UV–vis spectra of 4CP in MW/UV/TiO$_2$ process, where the TiO$_2$ dosage is 1 mg/L at an initial pH of 6, light intensity (E) is 1450 lx, bubbled with air.
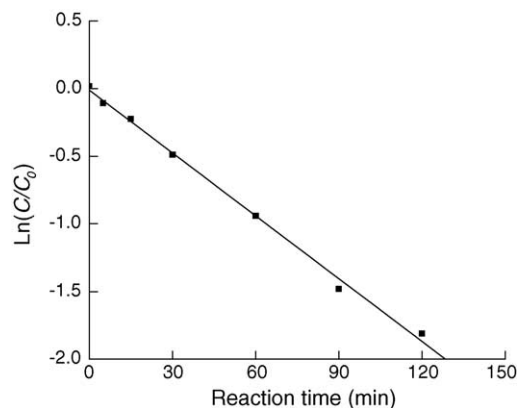

Fig. 7. The pseudo-first-order decay of 4CP in MW/UV/TiO$_2$ system, where the TiO$_2$ dosage is 1 mg/L at an initial pH value of 6, light intensity (E) is 1450 lx, bubbled with air.

respectively. The results shown in Table 2 indicate that the MW/UV/TiO$_2$ is superior to the UV/TiO$_2$. Degradation of 4CP by the MW/UV/TiO$_2$ procedure was nearly complete in contrast to the UV/TiO$_2$. The increase of Cl$^-$ in the degradation of 4CP by the MW/UV/TiO$_2$ process was up to 7.95 mg/L in 120 min, which indicated that chlorine atom left from the radical intermediate completely compared to 8.30 mg/L (theoretic producing amount of Cl$^-$ for 30 mg/L 4CP degradation). The increase of chlorine ion is much more employing MW/UV/TiO$_2$ than that using UV/TiO$_2$. So we think that the synergistic effect between microwave irradiation and the UV/TiO$_2$ method was significant in degradation of 4CP.

The synergistic effect could be attributed to the $^\bullet$OH. That is, microwave irradiation played an important role in enhancing the generation of the $^\bullet$OH in MW/UV/TiO$_2$ system, which increase the degradation rate of 4CP.

As to MW assisted TiO$_2$ photocatalysis procedures, the synergistic effect may be attributed to the following two reasons: (1) the enhanced formation of reactive $^\bullet$OH; (2) the activity of the TiO$_2$ particles surface is somehow affected by microwave irradiation. Titania particles absorb UV light of energy greater than the band gap of 3.2 eV to generate electron/hole pairs. MW likely generated additional defect sites on the TiO$_2$ particles, which inhibited electron/hole recombination, resulting a more efficient photocatalytic process [9].

3.7. The UV–vis spectrum of 4CP samples during degradation

The changes in the absorption spectra of 4CP degraded by the MW/UV/TiO$_2$ photocatalysis process are shown in the Fig. 6. The spectrum of 4CP in the UV region exhibits a band with a peak absorbance at 225 nm. The de-
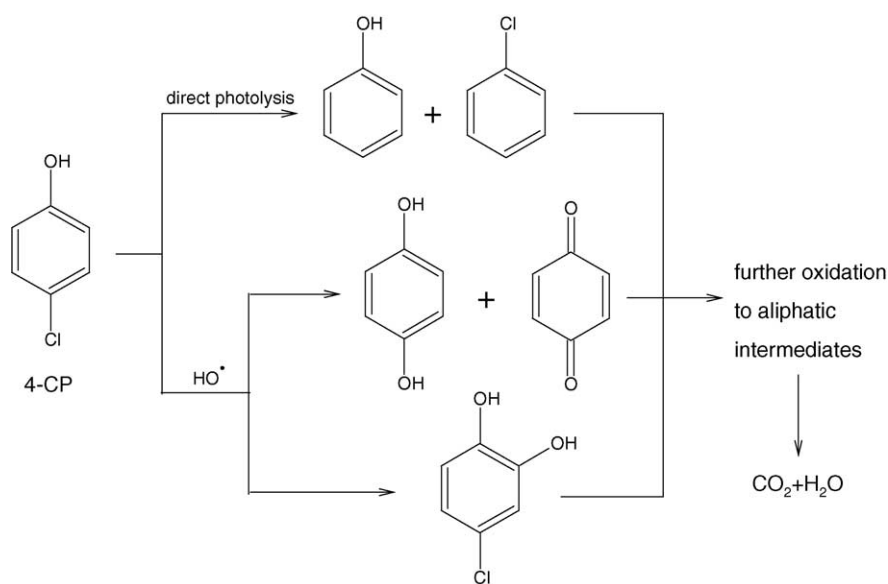

Fig. 8. Reaction intermediates and the possible mechanistic pathway of 4CP degraded in microwave assisted UV system, where the reaction time is 120 min, TiO$_2$ dosage is 1 mg/L at an initial pH value of 6, $E = 1450$ lx, bubbled with air.

crease of at 225 nm in this figure indicates a rapid degradation of 4CP. Disappearance of the spectral features in the UV–vis spectrum of 4CP after a 60 min irradiation period agrees with the change of the solution color. The color of the solution changed from colorless to brown within 5 min during the photocatalysis process, and then changed to colorless after 60 min. Oligomers, hydroquinone, benzoquinone, were potential intermediates for degradation of 4CP [1,13,14].

The microwave assisted UV photocatalytic degradation of 4CP was found to follow pseudo-first-order decay kinetics, as shown in Fig. 7. The rate constant is 0.0155 min^{-1}.

3.8. Reaction intermediates and the possible mechanistic pathway

A detailed study on TiO_2 photocatalytic degradation of 4CP reveals the formation of several intermediates shown in Fig. 8. The intermediates identified were chlorobenzene, phenol, hydroquinone, benzoquinone and 4-chlorocatechol. Identification was performed with Nist database of GC–MS. Key reactions involved in the photodegradation of 4CP by TiO_2 photocatalysis assisted by microwave are: (a) direct photolysis by UV light, (b) hydroxylation of the aromatic ring, (c) substitution of chlorine by $^\bullet$OH and (d) oxidation of chlorinated hydroquinone to the corresponding quinone, (e) further oxidation to aliphatic intermediations, and (f) mineralization into carbon dioxide and water.

4. Conclusions

(1) The pseudo-first-order degradation kinetics was observed for degradation of 4CP by MW/UV/TiO_2.
(2) MW assisted UV photocatalytic degradation rate increases with dosage of TiO_2, but decreases when TiO_2 overdoses. The degradation was slightly enhanced in either acid solutions or alkaline solutions, but significantly enhanced by increasing the irradiation intensity, purging oxygen or adding H_2O_2 to the solution or dispersions.
(3) The synergistic effects between MW irradiation and UV photocatalysis method are significant because of the enhanced formation of reactive $^\bullet$OH in MW/UV/TiO_2.
(4) The principal intermediates during the MW/UV/TiO_2 degradation of 4CP were chlorobenzene, phenol, hydroquinone, benzoquinone and 4-chlorocatechol.

Acknowledgements

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