Improving removal of 4-chlorophenol using a TiO$_2$ photocatalytic system with microwave and ultraviolet radiation

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ABSTRACT

A conventional photocatalytic system is a viable tool to purify wastewaters, whereas poor degradation performance due to diverse pollutants under various conditions still leaves it behind commercial markets. This study aimed to determine the degradation efficiency and mechanism of 4-chlorophenol in a hybrid system integrating a series of unit processes such as a conventional TiO$_2$ photocatalytic reactor as well as microwave and ultraviolet (UV) radiation. The decomposition (rate) of 4-chlorophenol was assessed with respect to the microwave intensity, pH, circulating fluid velocity, hydrogen peroxide level, and oxygen gas injection, along with a mix of individual processes. Results showed that there were favorable conditions for improving the degradation performance within certain limits. However, a significant synergy effect was also observed in the combined processes, which was substantially larger than any single process. Out of them, the best degradation performance was achieved using microwave irradiation and hydrogen peroxide in the photocatalytic reactor. The four intermediates (i.e., benzoquinone, hydroquinone, 4-chlorocatechol, and hydroxyhydroquinone) appeared to be generated through hydroxyl radicals-mediated hydroxylation and dechlorination in the proposed photocatalytic pathway. The present research is expected to provide new insights into designing the high performance photocatalytic system with affordable cost.

1. Introduction

Phenolic compounds, a class of derivatives from aromatic hydrocarbons, are commonly used as active ingredients for herbicides, insecticides, drugs, and dyes as well as preservatives at wood processing in various industrial sectors [1–3]. There has been growing concern over the effect of phenolic chemicals on the human and ecosystem as accident spill and improper disposal increased the occurrence of these toxic chemicals to the environmental media (e.g., surface waters, soils, and ground waters). However, conventional wastewater treatment systems did not eliminate phenolic compounds in an effective manner, specifically for those which became more complex and stable than the original ones through chemical reactions with other pollutants from industrial wastewaters. Chlorophenols generated from the reaction of phenol with chlorine (included in the halogen family) are characterized by extremely toxic, superior stability, and low reactivity, as compared with the parent compound, and even carcinogenic to humans, for example [4]. Primary methods gaining popularity in removing phenolic compounds from wastewaters are physical and biological treatment processes. The physical technique refers to a process that activated carbons serve as a repository for halogen-substituted phenols, whereas the biological technique is a method that phenolics are used as substrates for growth of microorganisms under both aerobic and anaerobic conditions. Currently, by-products as well as associated costs and their derivative removal remain a major hurdle for full-scale applications [5,6].

Advanced oxidation processes (AOPs) have recently showed great promise for removal of non-biodegradable pollutants present in aqueous solutions using reactive radical species (such as hydroxyl and oxygen radicals) harvested directly from the treatment train [7–9]. Ozonation (O$_3$), heterogeneous photocatalysis

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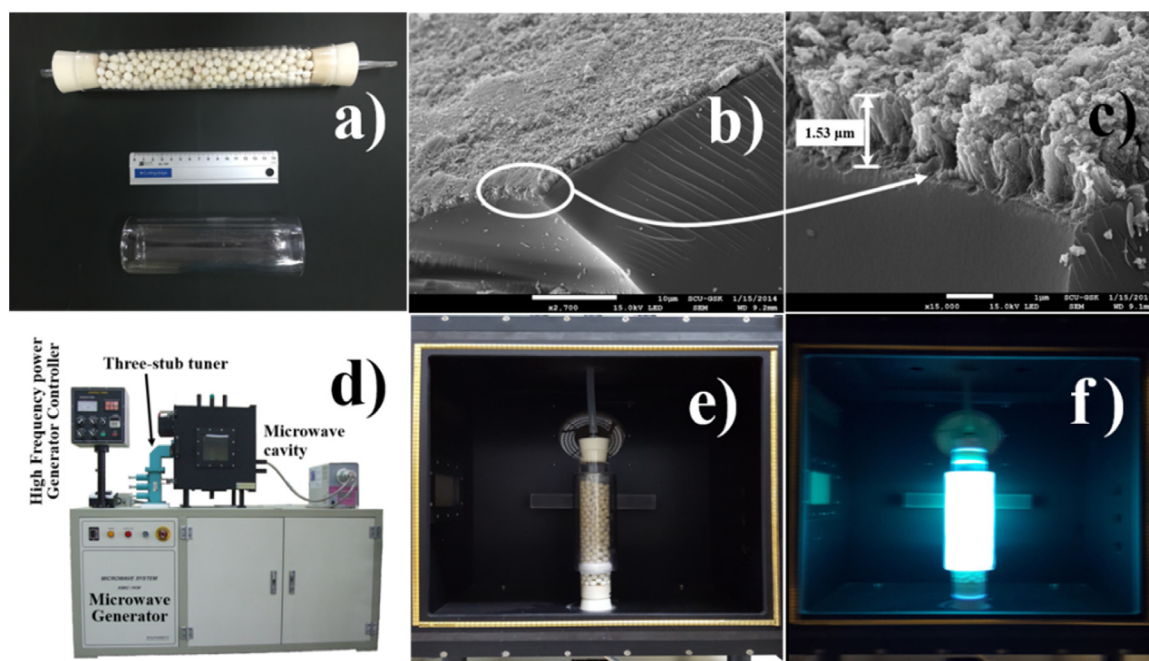E-mail address: jsc@sunchon.ac.kr (S.-C. Jung).

Fig. 1. Photographs of a photocatalytic system used in this study: (a) a photocatalytic reactor packed with TiO_2 alumina balls (top) and microwave discharge electrodeless lamp (MDEL, bottom), (b) medium- and (c) high-resolution images for the developed TiO_2 film on top of the alumina ball surface, and (d) entire system configuration, and experimental setup (i.e., the reactor and MDEL) inside the microwave cavity (e) in the absence and (f) presence of microwave irradiation.

(TiO_2 and ZnO), and homogeneous photocatalysis (iron metal) are the representative members of AOPs, just to name a few, which are classified based on the sources of radicals [10–12]. Specifically, the system merging photocatalyst TiO_2 and UV irradiation, out of them, was found to provide an excellent performance in effectively breaking down those pollutants into either biodegradable or harmless ones (e.g., water and carbon dioxide) using hydroxyl radicals with extreme reactivity [13–15]. However, this system has not been successfully implemented yet on commercial scale due largely to low degradation performance in response to short residence time and high influent turbidity. Accordingly, this study was motivated to enhance the degradation efficiency in a hybrid system consisting of a conventional TiO_2 photocatalytic reactor with microwave and ultraviolet (UV) radiation 4-chlorophenol, one of phenol-based compounds, was selected as a target degradation chemical. In addition, microwave discharge electrodeless lamp (hereinafter referred to as MDEL) activated by microwave radiation was used to facilitate the degradation performance in the given system. Specific objectives were to investigate the effects of 1) varying operating conditions in a single process and 2) fixed conditions for combining multiple process on the decomposition of 4-chlorophenol as well as 3) to identify its intermediates and pathway involved in the photocatalytic degradation. We believe that the immobilized photocatalyst design improves the overall performance for degradation of the same target chemical than those of heterogeneous suspensions with respect to mass transfer and reusability, thereby reducing system complexity as well as operating cost [16–20].

2. Material and methods

2.1. Experimental materials

All materials used in photocatalytic degradation experiments were purchased from two commercial vendors. For instance, 4-chlorophenol (with a minimum purity of 98%) and hydrogen peroxide (with 30% w/w), which were selected as the target compound and oxidizing agent, respectively, were obtained from Junsei

Chemical Co. In contrast, hydrochloric acid (with concentration of 0.1N) and sodium hydroxide (with concentration of 0.1N), which were used to adjust pH levels in reactant aqueous solutions as well as double distilled water which was used to prepare stock solutions, were provided from Daejung Chemicals & Metals Co. Note that the raw products commercially available are applied directly to the experiments, i.e., without any further purification process.

2.2. TiO2 photocatalyst balls

A low pressure metal organic chemical vapor deposition (LPMOCVD) process was used to synthesize titanium dioxide (TiO_2) coatings on alumina (Al_2O_3) balls. Briefly, titanium tetra isopropoxide ($Ti(OC_3H_7)_4$) served as a precursor for preparation of the TiO_2 film, which were uniformly deposited onto the alumina beads with a diameter of 8 mm at a temperature of 773 K for 1 h. More detailed information on the fabrication technique and experimental conditions employed is described well in our previous papers [21,22]. Fig. 1a displays a quart reactor packed with the TiO_2 photocatalyst balls (see top image), whereas cross-sectional views of the TiO_2 film grown on the alumina ball surface with different resolutions are illustrated in Fig. 1b and c, respectively. The thickness of the TiO_2 film measured through scanning electron microscopy (SEM) analysis was about 1.53 μm. X-ray diffraction analysis showed that the developed film was consistent well with the anatase form of TiO_2 extended along the 112 crystallographic direction (data not shown).

2.3. Microwave-assisted photocatalytic system

Fig. 1d exhibits an entire photocatalytic system which is applied to the degradation experiments of 4-chlorophenol. The experimental apparatus consisted of four essential components, (1) a microwave generator at 2.45 GHz (with a maximum power of 1 kW), (2) a three-stub tuner that effectively transferred energy from the generator to the cavity, (3) a power controller which constantly maintained and altered the intensity of the microwave

radiation during the experiments, and (4) a microwave cavity (with dimensions of $470 \times 550 \times 235$ in mm) in which the photocatalytic reaction took place. Fig. 1e and f also show two snapshots of experimental configuration inside the microwave cavity when the MDEL (see bottom image in Fig. 1a) installed outside of the photocatalytic reactor (see top image in Fig. 1a) was idle and activated by the microwave radiation, respectively. Note that the MDEL is used instead of conventional UV lamps to provide an UV radiation to the reactor. This is because traditional lamps have metal electrodes that cannot emit the UV light inside the cavity. The MDEL which was made of quartz had a double tube structure with a vacuum between the two sides of the glass, where an extremely small amount of mercury was contained. Specifically, the MDEL with an inside diameter of 36 mm, an outside diameter of 55 mm, and a length of 170 m was used in the degradation experiments.

2.4. Experimental procedure

Below is a detailed description of the experimental procedure employed for the photocatalytic degradation of 4-chlorophenol. A 0.15 mM aqueous solution of 4-chlorophenol was prepared by dissolving 4-chlorophenol in 500 mL mL of distilled water. The reactant aqueous solution was then transferred to a stainless steel beaker in a constant temperature water bath and passed through the photocatalytic reactor at flow rates of 200–600 mL/min using a roller pump. Note that the water bath which keeps the solution at 298 K is used to eliminate the thermal effects of the microwave radiation on the degradation of 4-chlorophenol. Before starting the designed experiments, the UV light which was emitted from the MDEL was provided to the reactor in 15 s and the reactant aqueous solution was also circulated for 10 min to maintain a constant solute concentration in the reactor. During the experiments, the microwave power delivered to the cavity varied from 0.2 to 0.6 kW, which was evenly distributed throughout the reactor using a stirrer on the rear side of the cavity. Samples were taken from the stainless steel beaker at various time intervals to estimate the decomposition rate of 4-chlorophenol under different experimental conditions. The concentrations of 4-chlorophenol in the samples were quantified by UV–vis (UV–vis) spectrophotometer (UV-1801, Shimadzu Co. Ltd.) with the absorption maximum at 225 nm. Gas chromatography mass spectrometry equipped with a headspace auto sampler (GC/MS, QP2000, Shimadzu Co. Ltd.) was also used to identify a degradation mechanism of a parent compound (i.e., 4-chlorophenol) and its intermediates produced during a series of photocatalytic experiments. The capillary column was a HP-5 MS with dimensions of 30 m (in length) × 0.25 mm (in internal diameter) × 0.25 μm (in film thickness), which was operated initially at 323 K for 30 s and then maintained at 553 K for 5 min after increasing its temperature at a rate of 10 K/min.

3. Results and discussion

3.1. Photocatalytic degradation of 4-chlorophenol

Fig. 2 illustrates the change of the absorption spectrum in different times (from 0 to 100 min) when the reactant solution circulated through the photocatalytic reactor is exposed to both microwave and UV radiation. The experiments were conducted under the following operating conditions: the microwave intensity of 0.4 kW and the circulating fluid velocity of 400 mL/min. In fact, the reactant aqueous solution of 4-chlorophenol was found to have strong absorbance at 225 and 280 nm [23,24]. From the figure, it was determined that the absorbance at wavelengths of around 225 and 280 nm decreased considerably, as the reaction time increased. However, a slight increase in absorbance was also observed at
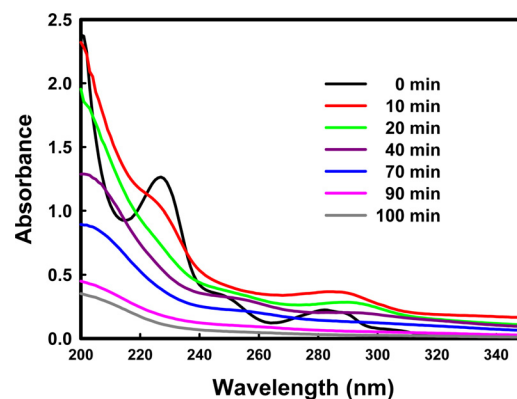

Fig. 2. The absorption spectra of the reactant solution monitored at selected time intervals (0, 10, 20, 40, 70, 90, and 100 min), obtained using ultraviolet-visible spectrophotometer.

about 280 nm for exposure times of 10 and 20 min. The intermediates generated during the photocatalytic process probably caused a temporary increase of absorbance at around 280 nm. Nonetheless, the absorbance at both 225 and 280 nm decreased progressively during the long exposure times [25,26].

3.2. Effect of microwave intensity

Fig. 3a shows the variation in the decomposition rate of 4-chlorophenol as a function of the microwave intensity, from 0.2 to 0.6 kW. As shown in the figure, the pseudo first-order kinetic model was shown to successfully describe the experimental data on the photocatalytic degradation of 4-chlorophenol obtained under different conditions. The first-order kinetic model can be expressed as:

$$C/C_0 = \exp(-kt) \quad (1)$$

where C_0 and C are the concentrations of 4-chlorophenol at $t = 0$ and time t (in units of M/L^3), respectively. k indicates the overall decomposition rate constant (in unit of $1/T$). Note that the non-thermal effects produced from the microwave radiation are only involved in this photocatalytic process as we constantly maintain the reactant solution at a particular temperature using the water bath, as discussed earlier. It was shown from the figure that the degradation rate of 4-chlorophenol increased significantly with increasing the microwave intensity from 0.2 to 0.5 kW. Beyond this limit, the degradation of 4-chlorophenol was, however, accelerated slightly by the microwave intensity. In fact, the MDEL was found to emit three types of UV radiation, namely UV-A, UV-B, and UV-C. According to our previous study [27], the emission level of UV-C which was remarkably higher than those of UV-A and UV-B was increased sharply up to 0.4 kW and then very slowly after that. It should be noted that the higher the intensity of the UV radiation, the more reactive radical species (e.g., hydroxyl radical) are available for the photocatalytic reaction, and vice versa. Accordingly, we observed with the microwave intensity kept above 0.4 kW a slow increase in the decomposition rate of 4-chlorophenol.

3.3. Effect of pH

Fig. 3b describes the effect of pH levels (between 2 and 10) on the decomposition rate of 4-chlorophenol. The same operating conditions, as described in Section 3.1, were applied to these experiments, but the degradation of the parent compound was determined for pH levels of 2, 4, 7, and 10. As can be seen in the figure, as pH values extends from 2 to 10, the degradation rate of 4-chlorophenol declines quite rapidly. The decomposition
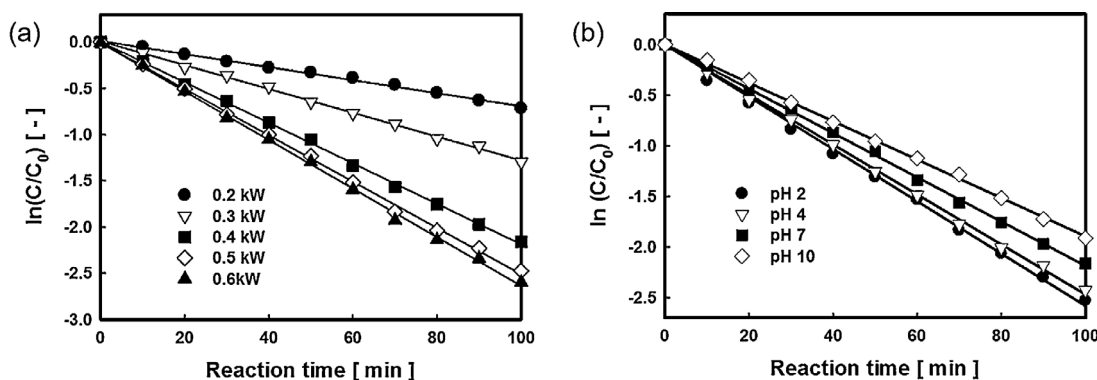
Fig. 3. The photocatalytic degradation of 4-chlorophenol conducted under different levels of (a) microwave intensity (0.2, 0.3 0.4, 0.5, and 0.6 kW) and (b) pH (2, 4, 7, and 10).

rate constants of 4-chlorophenol estimated from the first-order kinetic model were 2.582×10^{-2} (for pH 2), 2.470×10^{-2} (for pH 4), 2.192×10^{-2} (for pH 7), and 1.895×10^{-2} min^{-1} (for pH 10). These results were consistent well with the findings of previous studies that high pH values (i.e., alkaline conditions) lowered the overall degradation efficiency of 4-chlorophenol [28–30]. This is attributed to the decrease of reactive radical species (e.g., hydroxyl radical) at high pH levels. By the way, the decomposition rate of 4-chlorophenol was only improved slightly in pH 2 than in pH 4. The main reason is that the surface of TiO$_2$ photocatalyst balls is positively charged at very low pH based on its point of zero charge, so strong competition between the chloride ion and the target compound occurs near the adsorbent surface [31,32].

3.4. Effect of circulating fluid velocity

The influence of the circulating fluid velocity on the decomposition rate of 4-chlorophenol is displayed in Fig. 4a. The degradation experiments were performed at pH 7 under the microwave intensity of 0.4 kW with the velocity range from 200 to 600 mL/min. From the figure, it was found that increasing the circulating fluid velocity as high as 400 mL/min contributed remarkably to improving the degradation of the parent compound. However, above this limit, the degradation rate of 4-chlorophenol subsequently leveled off (for 500 mL/min) or even decreased slightly (for 600 mL/min). This implied that there existed an optimal velocity which expedited the (photocatalytic) degradation process of 4-chlorophenol. In fact, we observed that gas bubbles occurred in the reactor when the circulating fluid velocity started to exceed 500 mL/min. Hence, those bubbles appeared to lessen the degradation rate of the parent compound by modifying flow regimes at the pore level (in the reactor). The decomposition rate constants of 4-chlorophenol calculated for 200, 300, 400, 500, and 600 mL/min were 1.318×10^{-2}, 1.759×10^{-2}, 2.192×10^{-2}, 2.291×10^{-2}, and 2.059×10^{-2} min^{-1}, respectively.

3.5. Effect of H$_2$O$_2$ addition

Fig. 4b depicts how the decomposition rate of 4-chlorophenol is modulated by the concentration of hydrogen peroxide. The decomposition rate constant of the parent compound was determined at pH 7 in the circulating fluid velocity of 400 mL/min under the microwave intensity of 0.4 kW, where hydrogen peroxide was dosed separately at concentrations of 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and 10^0 M. The decomposition rate of 4-chlorophenol was accelerated steadily between 10^{-4} and 10^{-1} M concentrations of hydrogen peroxide and then was decreased abruptly at 10^0 M, as illustrated in the figure. The degradation rate constants of 4-chlorophenol were esti-

mated to be 2.254×10^{-2}, 2.379×10^{-2}, 2.697×10^{-2}, 3.003×10^{-2}, and 1.869×10^{-2} min^{-1} in ascending order of concentration (of hydrogen peroxide). When hydrogen peroxide was added to the reactant solution, the number of electrons exited on the TiO$_2$ surface was reduced while the formation of hydroxyl radical was correspondingly increased due to its reaction with superoxide radical anion [33,34]. The balanced equation for this chemical reaction can be written as:

$$H_2O_2 + O_2^{\bullet -} \rightarrow OH^\bullet + OH^- + O_2 \qquad (2)$$
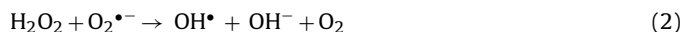
Eq. (2) indicates that the larger the addition of hydrogen peroxide, the more hydroxyl radicals are available for the photocatalytic reaction, which in turn encourages the rapid decomposition of 4-chlorophenol. However, excessive addition of hydrogen peroxide to the reactant solution was found to slow down (rather than speed up) the degradation of the parent compound. This is because in such a condition, it acts as scavenger of hydroxyl radicals as well as inhibitor which blocks active sites in the TiO$_2$ surface [13].

3.6. Effect of O$_2$ gas injection

The decomposition of 4-chlorophenol is also investigated as a function of oxygen levels (Fig. 4c). This is because that auxiliary oxidants such as oxygen have been found to assist the photocatalytic degradation process [13,35,36]. Specifically, oxygen gas injected enhanced the photocatalytic activity of TiO$_2$ balls not only by restricting the recombination between electrons and holes through reaction with electrons in conduction band, but also by promoting generation of hydroxyl and hydroperoxyl radicals. The same operating conditions, as explained in Section 3.5, were applied to these experiments, but the velocity of oxygen gas further varied between 50 and 200 mL/min on behalf of dose of hydrogen peroxide. The effect of oxygen gas on the decomposition of 4-chlorophenol, as shown in the figure, was quite similar to that of hydrogen peroxide in terms of its pattern and magnitude. In other words, the degradation rate of 4-chlorophenol was improved up to 150 mL/min and then decreased at 200 mL/min. The estimated decomposition rate constants of 4-chlorophenol ranged from 2.192×10^{-2} to 2.819×10^{-2} min^{-1} depending on the velocity of oxygen gas. In accordance with previous studies [13,35,36], these results signified that while increasing oxygen levels helped speed up the degradation of 4-chlorophenol, overdose of oxygen gas rather reduced the degradation performance due to excessive bubbles generated in the reactor.
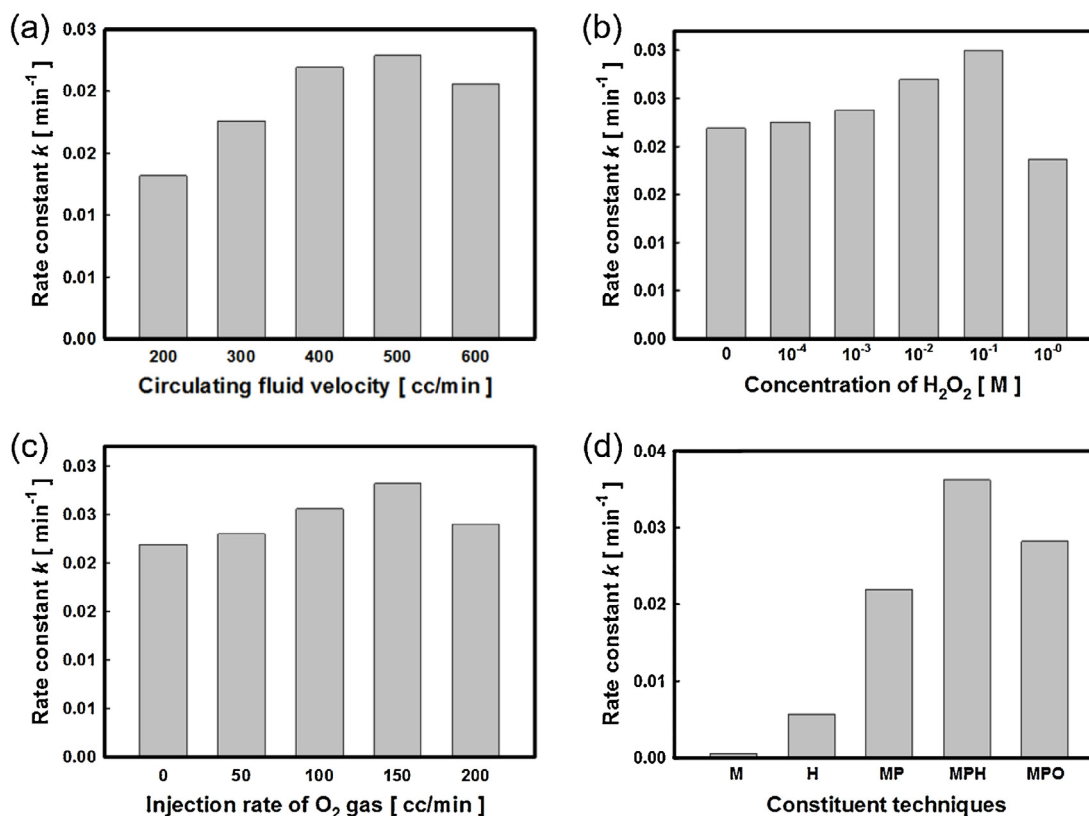
Fig. 4. The decomposition rate constants estimated using the pseudo first-order kinetic model based on the data obtained under varying experimental conditions: (a) circulating fluid velocity (from 200 to 600 mL/min), (b) concentration of hydrogen peroxide (from 10^{-4} to 10^{0}), (c) injection rate of oxygen gas (from 0 to 200 mL/min), and (d) a single process (M: microwave radiation and H: hydrogen peroxide) versus combined processes (MP: microwave radiation and photocatalytic reactor, MPH: MP plus hydrogen peroxide, and MPO: MP plus oxygen gas).
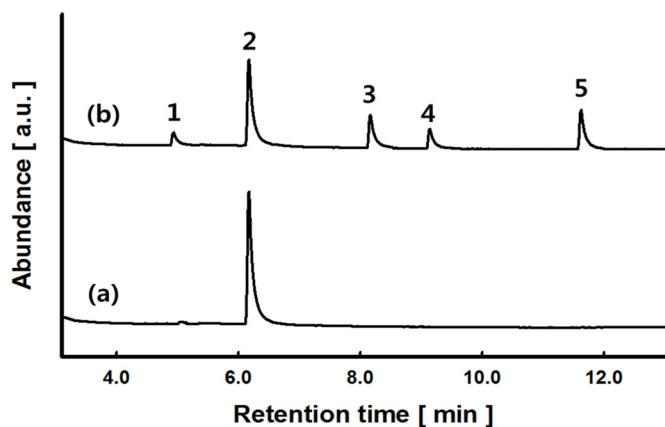

Fig. 5. Chromatograms of the reactant solution monitored at different sampling times, (a) 0 and (b) 20 min, characterized by gas chromatography.

3.7. Synergy effect of combined processes

Fig. 4d highlights the effect of combining multiple processes on the decomposition (rate) of 4-chlorophenol. In the figure, the experimental results conducted under the microwave radiation of 0.4 kW (indicated as a capital letter M) and 0.1 M hydrogen peroxide (indicated as H) separately were included as the reference for comparison purposes. Also, the multiple processes combining the microwave radiation and TiO2 photocatalyst balls are represented as MP. MPH and MPO signify the experimental results involving additional unit process of 0.1 M hydrogen peroxide and the velocity of oxygen gas with 150 mL/min on top of the mul-

tiple processes MP, respectively. The results showed that the degradation rate of 4-chlorophenol was considerably slower in M ($k = 0.052 \times 10^{-2}$ min^{-1}) than in P ($k = 0.563 \times 10^{-2}$ min^{-1}) when considering a single process only. However, all multiple processes MP, MPH, and MPO exhibited a faster degradation than any single process. Out of them, MPH showed the highest rise in the decomposition rate. More specifically, the degradation rate constants of 4-chlorophenol in MPH and MPO was shown to increase by 64 and 28%, respectively, as compared to that of MP. The degradation rate in MPH ($k = 3.605 \times 10^{-2}$ min^{-1}) was even greater than the sum of its parts, MP and H ($k = 2.755 \times 10^{-2}$ min^{-1}). These results confirmed that 1) there was a clear synergy effect when various processes were combined together and 2) more auxiliary oxidants were generated in the presence of the microwave radiation plus hydrogen peroxide in the photocatalytic reactor.

3.8. Degradation mechanism

Fig. 5a and b illustrate GC chromatograms of the reactant solution obtained at different times, 0 and 20 min, respectively. The samples were taken from the experiments conducted at pH 7 in the circulating fluid velocity of 400 mL/min under the microwave intensity of 0.4 kW. As shown in both figures, two chromatograms showed the difference in terms of the number of peaks and their heights. The largest peak at a retention time of 6.18 min (labeled with an Arabic numeral 2) observed in the initial sample represented 4-chlorophenol (see Fig. 5a). In the next sample, this peak was reduced slightly while four peaks at 4.93 (labeled with 1), 8.16 (labeled with 3), 9.14 (labeled with 4), and 11.6 min (labeled with 5) were newly detected (see Fig. 5b). Those minor peaks appeared to be associated with intermediates which were generated during
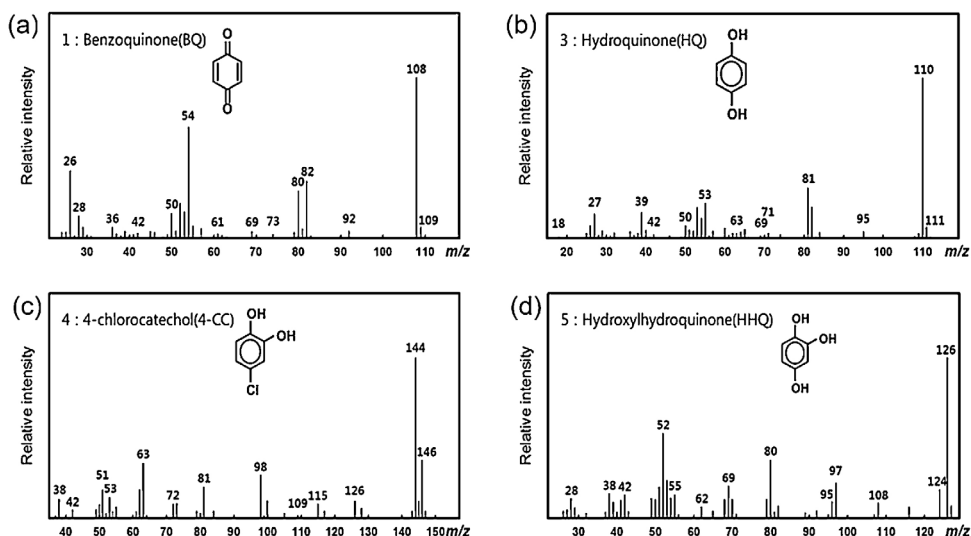
Fig. 6. The mass spectra of representative intermediates detected during the course of the photocatalytic degradation of 4-chlorophenol (at 20 min, see Fig. 5b), analyzed from gas chromatography mass spectrometry.
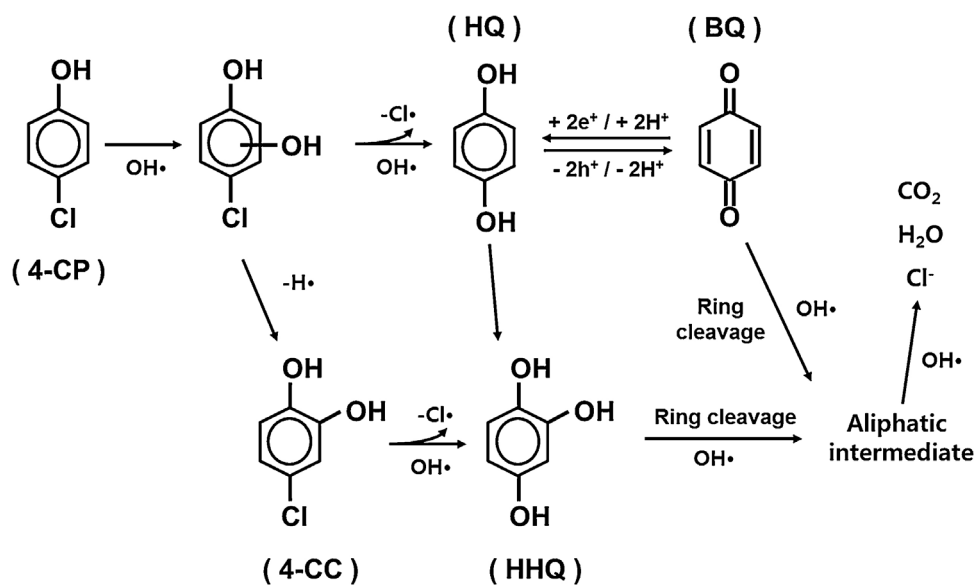

Fig. 7. Proposed pathway for the photocatalytic degradation of 4-chlorophenol.

the photocatalytic degradation process. Note that no significant difference is observed in the number of peaks between the samples collected during the initial 20 min of reaction time, even though the heights of individual peaks vary slightly from sample to sample (data not shown). Fig. 6 also shows the mass spectrum of four intermediates (i.e., individual peaks observed in Fig. 5b). Those corresponded to benzoquinone (BQ, for label 1), hydroquinone (HQ, for label 3), 4-chlorocatechol (4-CC, for label 4), and hydroxyhydroquinone (HHQ, for label 5), all of which were known as intermediate products typically generated during the photocatalytic decomposition of the parent compound [16,37–40]. Based on these results, we proposed two preferred routes involved in the photocatalytic degradation of 4-chlorophenol (see Fig. 7). The first step was to generate HQ using hydroxylation (which was mediated by hydroxyl radicals) and dechlorination reactions, which was in turn converted to either BQ through oxidation reaction or HHQ

through a second round of hydroxylation reaction. The other route included hydroxylation of 4-chlorophenol at the ortho-position to yield 4-CC, followed by dechlorination of 4-CC to yield HHQ. In the proposed pathway, two intermediates BQ and HHQ were then transformed to aliphatic intermediate through ring cleavage, which was eventually converted into carbon dioxide (CO_2), water (H_2O), or chloride ion (Cl^-) by repeated hydroxylation. In fact, the concentration of 4-chlorophenol was sharply reduced in the early stage of the photocatalytic reaction, specifically dropping to 61.5% of its initial level at 20 min (see Fig. 2). Approximately 70% of 4-chlorophenol which disappeared during the first 20 min of reaction time was converted to a series of intermediates such as HHQ (38.3% in terms of percent composition by concentration), HQ (31.6%), 4-CC (19.2%), and BQ (10.9%), as illustrated in Fig. 5. Based on this quantitative information, our degradation scheme for the photocatalytic reaction of 4-chlorophenol was designed to have two primary

forms of yields, the highest level of HHQ from the second and third highest levels of HQ and 4-CC as well as the lowest level of BQ from the second highest level of HQ only. Chromatographic analysis of the samples collected after 20 min also showed that the heights of individual peaks for 4-chlorophenol and all intermediate compounds declined progressively during the remaining period of the experiments (data not shown). This indicated that our photocatalytic system initially contributed to converting 4-chlorophenol into the proposed intermediates, but more actively participated in further reactions such as the complete degradation of the intermediate compounds through low molecular weight organic acids to non-toxic end products after 20 min, as shown in Fig. 7. From all these results, we found that hydroxyl radicals generated during the photocatalytic process played an important role in the degradation of 4-chlorophenol and the decomposition rate could be enhanced by an effective combination of individual processes.

4. Conclusions

In this study, the degradation of 4-chlorophenol was investigated using the photocatalytic reactor under the microwave and UV radiation. The decomposition rate of 4-chlorophenol was assessed under varied operating conditions for a single process (i.e., the microwave intensity, pH, circulating fluid velocity, and concentrations of hydrogen peroxide and oxygen) as well as under given conditions for combined processes. In general, the degradation performance was improved with increasing the microwave intensity, circulating fluid velocity, and concentrations of hydrogen peroxide and oxygen as well as with lowering the pH level. However, the decomposition rate of 4-chlorophenol often decreased beyond certain thresholds, indicating there would be optimal conditions for accelerating the degradation performance. The degradation of 4-chlorophenol was faster for the photocatalytic system which combined multiple processes than that of any single process. In fact, the degradation performance was highest for the system assisted with both microwave irradiation and hydrogen peroxide and low to negligible for individual processes. Two preferred degradation routes involving hydroxyl radicals-mediated hydroxylation and dechlorination were proposed based on four intermediates identified during the course of experiments.

Acknowledgements

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