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Improving removal of 4-chlorophenol using a TiO_2 photocatalytic system with microwave and ultraviolet radiation

Seo Jin Ki[a], Ki-Joon Jeon[b], Young-Kwon Park[c], Sangmin Jeong[d], Heon Lee[d], Sang-Chul Jung[d,*]

[a] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, 123 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Republic of Korea
[b] Department of Environmental Engineering, Inha University, 100 Inharo, Nam-gu, Incheon 402-751, Republic of Korea
[c] School of Environmental Engineering, University of Seoul, 163 Seoulsiripdaero, Dongdaemun-gu, Seoul 130-743, Republic of Korea
[d] Department of Environmental Engineering, Sunchon National University, 255 Jungang-ro, Sunchon, Jeonnam 540-950, Republic of Korea

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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

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

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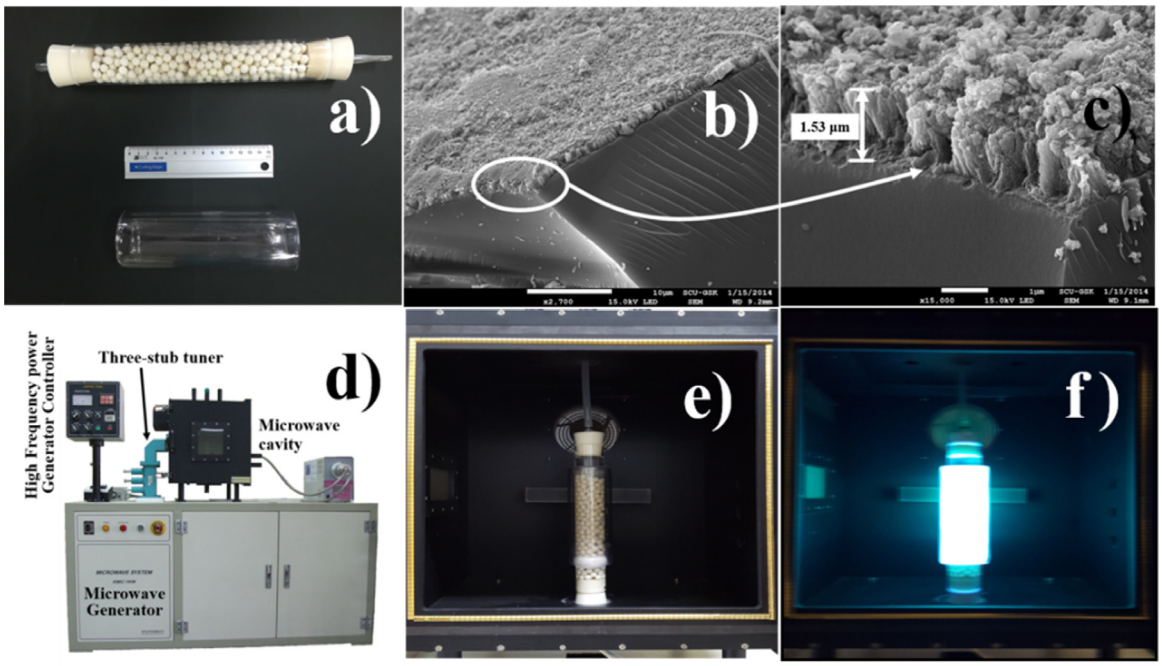

Fig. 1. Photographs of a photocatalytic system used in this study: (a) a photocatalytic reactor packed with TiO_2 alumina balls (top) and microwave discharge electrodeless lamp (MDEL, bottom), (b) medium- and (c) high-resolution images for the developed TiO_2 film on top of the alumina ball surface, 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. TiO_2 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

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