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Rapid photocatalytic degradation of nitrobenzene under the simultaneous illumination of UV and microwave radiation fields with a TiO_2 ball catalyst

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ABSTRACT

To use the microwave/ML/TiO_2 hybrid system as an advanced treatment of nitrobenzene (NB), a series of experiments were performed to examine the effects of microwave irradiation and auxiliary oxidants. The degradation of NB was carried out using different combinations of five-unit treatment techniques. The NB degradation rate increased with increasing microwave intensity. The circulation fluid velocity, concentration of H_2O_2, and the rate of O_2 gas injection showed the highest rate of degradation under optimal conditions. A significant synergistic effect was observed when H_2O_2 addition was combined with the microwave/ML/TiO_2 hybrid process.

1. Introduction

Owing to the advances in industry, many organic compounds have been produced as organic solvents, which are contaminating soil and underground water [1,2]. A large portion of these organic compounds are volatile organic solvents and hydrophobic materials, whose specific gravity is larger than water. In addition, they are poisonous and mutagenic derivative materials, and are very difficult to decompose chemically and biologically, giving them significantly long half-life [3]. Nitrobenzene (NB) is used widely in areas, such as aniline synthesis, dyes, rubber making, textile, synthetic resins, pesticide, explosives, cosmetic, and drugs [4,5]. NB, which exists in the environment, is emitted mainly from the manufacturing process of chemical products or the use of products that contain these materials [6,7]. Even at low concentrations, NB can damage the reproductive cells of rodents, and the World Health Organization (WHO) defined NB as an animal carcinogenesis chemical compound [8–10]. For these reasons, this study assessed the decomposition of NB as a model pollutant.

Conventionally, NB in aqueous media is processed using physical, chemical, and biological techniques. The general treatments is composed of adsorption [11,12] and biodegradation [13,14]. These techniques can be effective but it occurs secondary pollution, resulting in high processing cost. Advanced oxidation processes (AOPs) have been shown to be effective in the destruction of aromatic wastewater pollutants [15,16]. Basically, the AOP process uses oxidizing hydroxyl radicals to oxidize pollutants using O_3, H_2O_2, UV, and photocatalysts [17–21]. Among these methods, photocatalysis has been applied frequently for the advanced degradation of aromatic wastewater pollutants [22,23]. In particular, the TiO_2 photocatalytic process has significant advantages, such as available at room temperature, applicable under atmospheric pressure, complete mineralization, and low cost compared to the conventional treatments [24–26].

On the other hand, the use of TiO_2 as a photocatalyst has been limited by its high band gap (3.2 eV), meaning that it can be only activated by ultraviolet (UV) light. In addition, it has a low photo quantum efficiency and a high rate of electron–hole pair recombination [27,28]. Therefore, a method to enhance the processing efficiency is needed to decompose aromatic wastewater pollutants at high speed. Recently the effects of the microwave irradiation on the treatment of non-biodegradable materials in water using TiO_2

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photocatalyst have been investigated [21–23]. Synergistic effects of microwave, leading to considerable increase in the pollutant decomposition efficiency, were observed in those studies [24,25].

In this study, a TiO_2 photocatalytic reaction process with microwave assistance to enhance process efficiency was used to process a non-biodegradable wastewater pollutants with a high decomposition rate. In addition auxiliary oxidants (H_2O_2 and O_2 gas) were added to enhance the response speed. The effects of pH of the reactant aqueous solution and circulating fluid velocity on the decomposition reaction were also examined. Intermediate-products that were produced in the final decomposition reaction were analyzed along with the decomposition reaction mechanism.

2. Experimental

2.1. Chemicals

NB (>99.0%) and a H_2O_2 solution (30 wt.% in H_2O) were purchased from Sigma Aldrich Co. To control the pH, a hydrochloric acid (0.1N) and sodium hydroxide (0.1N) solution obtained from Daejung Chemicals and Metals Co. was used. Double distilled water (Daejung Chemical & Metal Co.) was used to produce the response aqueous solution, and all reagents were used as received.

2.2. TiO_2 photocatalyst ball

TiO_2 photocatalyst balls were used to decompose NB. Chemical vapor deposition (CVD) was performed to coat a TiO_2 film on the surface of the alumina balls (diameter 8 mm, Nikkto, HD-11). Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$) was used as the precursor at a reaction temperature of 773 K for 1 h deposition. Detailed CVD process conditions are reported elsewhere [27,28]. The top of Fig. 1a) shows a cross section scanning electron microscopy (SEM) image of the TiO_2 photocatalyst ball destroyed by a hammer. Fig. 1b) shows a SEM image of a magnified deposit of the TiO_2 film on the surface of the alumina ball. The thickness of the TiO_2 film examined in the TiO_2 photocatalyst ball was approximately 1.2 μm; Fig. 1c) presents the photo-reactor comprised of quartz loaded with TiO_2 photocatalyst balls; d) shows the X-ray diffraction (XRD) pattern of the TiO_2 film prepared by CVD. The TiO_2 film had an anatase crystal structure, which is oriented by the 112 face [27]. 300 TiO_2 photocatalyst balls were used in this study, the total volume of TiO_2 film being 36.19 mm^3.

2.3. Microwave lamp

TiO_2 is activated by ultraviolet-rays and can conduct photocatalysis reaction. On the other hand, the UV-lamps ordinarily used cannot be used in microwave field because of the adhered metal electrodes. Therefore, in this study, a microwave investigation was conducted and a UV emitting electrodeless microwave lamp (ML, 36 mm ID, 55 mm OD, and 170 mm length) was used. The ML was prepared from double-tube type quartz and a minimal amount of mercury was charged within the vacuumed ML tube. Fig. 2a) presents a photograph of the cavity with non-irradiated microwave; Fig. 2b) shows a photograph of ML inside the microwave cavity that is emitting UV and microwave radiation.

2.4. Experimental set-up

The NB decomposition reaction was conducted using a microwave/ML/TiO_2 ball hybrid photocatalyst system. The hybrid experimental system was composed the following elements: generator producing 2.45 GHz microwave (maximal power 1 kW); a three-stub tuner for impedance matching, which was used to maximize the transfer of electromagnetic waves energy; a power monitor to control the microwave intensity; and a microwave cavity (470 × 550 × 235 mm), where photocatalysis reaction occurs. The decomposition reaction experiment using the aforementioned equipment is as follows. NB was dissolved in 500 mL of DI water; thus, a 2 mM NB reactant aqueous solution was prepared. The NB reactant solution was contained in a stainless steel beaker installed in a constant temperature water bath and a roller pump was used to circulate the photocatalyst reactor in the microwave cavity at 200–500 cc/min fluid. When microwaves were irradiated in the reactant aqueous solution, the temperature increased continuously. To exclude the thermal effects of microwaves, the reactant aqueous solution was cooled to 298 K using a constant temperature water bath. Before the decomposition reaction, the TiO_2 catalyst balls was activated by ML for 30 s. In addition, before the decomposition reaction, it was circulated for 5 min to maintain the concentration of the NB reactant aqueous solution. Through a wave-guide, the NB reactant aqueous solution was decomposed when it was circulated in the microwave cavity with the existing microwaves with an actual power of 0.2–0.6 kW. A three-stub tuner was used to minimize the reflected microwaves and the intensity was maintained using a power monitor. To evenly transfer the microwaves within the microwave cavity, a stirrer was installed inside the cavity.

2.5. Analysis

The morphology of the TiO_2 photocatalyst ball was examined by field emission scanning electron microscopy (FESEM, JEOL-JSM-7100F), the crystal structure was characterized by XRD (Max Science, MPX3). The pH of the NB reactant aqueous solution, which was controlled using HCl and NaOH, was measured using a pH-meter (HM-30R, TOADKK). To measure the decomposition rate according to the reaction time, samples of the NB reactant solution inside the stainless steel beaker were collected and the concentration of NB was measured using UV–vis spectrometer (UV-1801, Shimadzu Co.) at the maximum wavelength (λ_{max} = 268 nm). A gas chromatography mass spectrometer/headspace (GS/MS, QP2000, SHIMADZU Co. Ltd) auto sampler was used to examine the NB decomposition mechanism according to the microwave/ML/TiO_2 ball hybrid photocatalyst system and to review the intermediate-products. At this time, the column used a HP-5 ms (30 m × 0.25 μm × 0.25 mm) and reaction was continued from the initial temperature of 323 K for 30 s, and increased to 553 K at 10 K/min speed and then held at 553 K for 5 min.

3. Results and discussion

3.1. Photocatalytic degradation of NB

Fig. 3 presents the change in the UV–vis spectrum according to the reaction time of the NB reactant solution, which was decomposed using the microwave/ML/TiO_2 hybrid system. This decomposition reaction was conducted under the condition that the microwave intensity is a circulating reaction aqueous solution at 0.5 kW with a 400 cc/min rate. The UV–vis spectrum shows that the characteristic band can be observed in the NB reactant solution in wavelength at 268 nm [29]. Under increasing decomposition reaction time, it clearly demonstrates decreased NB concentration in the wavelength ranges at around 268 nm and approximately 99% of them was decomposed at 100 min. The absorbance of the NB reactant solution (0 min) that did underwent the photocatalysis decomposition reaction at a wavelength 400 nm was 0. On the other hand, when microwave/ML/TiO_2 hybrid system was used to conduct photo catalysis decompose reaction, absorbance increased

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