

Photochemical degradation and toxicity reduction of methyl 1-[(butylamino)carbonyl]-1H-benzimidazol-2-ylcarbamate in agricultural wastewater: Comparative study of photocatalysis and sonophotocatalysis

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ABSTRACT

Photochemical degradation and relative toxicity reduction of agricultural wastewater contaminated with methyl 1-[(butylamino)carbonyl]-1H-benzimidazol-2-ylcarbamate (benomyl) by the sonophotocatalytic system was compared with that of the photocatalytic system. Under the optimal conditions, i.e., initial benomyl concentration was 3.2 mg/L, the concentration of TiO_2 was 2 g/L and H_2O_2 concentration was 1.5 mM, the degradation rates with a sonication/UV/ TiO_2 system was about 1.5 times higher than with a UV/ TiO_2 system and sonication/UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ system was about 1.3 times higher than with a UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ system, respectively. Furthermore, the relative toxicity with a sonophotocatalysis was about 18% lower than with a photocatalysis within a reaction time of 120 min.

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1. Introduction

The widespread usage of pesticides in agriculture poses a potentially serious environmental and health problem, since this may be carcinogenic and/or toxic. Methyl 1-[(butylamino)carbonyl]-1H-benzimidazol-2-ylcarbamate (benomyl) is classified as a possible carcinogen (USEPA) and endocrine disruptors (WWF, World Wildlife Fund). Benomyl is of such a low acute toxicity to mammals. However, benomyl caused adverse health effects (skin irritation, headaches, diarrhoea and sexual dysfunction) to agricultural workers [1,2].

Photocatalysis are commonly used for remediating wastewater contaminated with recalcitrant organic pollutants [3,4].

These methods are attractive because they produce almost no hazardous by-product and can be adjusted for the degree of contaminant removal desired.

Sonophotocatalysis is photocatalysis with ultrasonic irradiation [5]. Sonophotocatalysis degrades pollutants by two different effects, i.e., mechanical effects and chemical effects. Ultrasound effects, such as surface cleaning, particle size reduction and increased mass transfer, are the result of the mechanical effects of ultrasound [6,7]. Cavitation are the process in which micro bubbles, which are formed within a liquid during the rarefaction cycle of the acoustic wave, undergo violent collapse during the compression cycle of the wave [6,8]. This phenomenon is the result of the chemical effect of ultrasonic waves [6,8]. The dissociation of water to radicals is an example of these effects.

The photochemical treatment of pesticides is now at the commercial level. However, the application of sonophotocatalysis on the treatment

of benomyl contaminated wastewater, in particular, was not enough researched.

In this study, it was investigated the feasibility of sonophotocatalysis for treating wastewater contaminated with benomyl by comparing photocatalysis. Also, effluent toxicity to ecosystem was estimated and compared with toxicity of initial wastewater.

2. Materials and methods

2.1. Reagents

As powdered photocatalyst, TiO_2 (P-25; ca. 80% anatase, 20% rutile; BET area, ca. 50 m^2/g) was used without further treatment. Hydrogen peroxide (H_2O_2 , 30%, wt) from Merck was used. The pH was controlled by adding hydrogen chloride (Duksan). Organic solvents were of all pesticide residue analysis grades. All other chemicals were of reagent grades.

2.2. Sonophotocatalytic and photocatalytic reactor

The sonophotocatalytic and photocatalytic reactor has been described in Fig. 1. It consists of an illumination source, sonicator and blower. The light source used two 40 W UV lamps (Sankyo Denki Co). Ultrasonic irradiation was performed from two sides with a reactor. Blower (1 L/min) was used to prevent photocatalyst from settling.

UV intensity was measured with a radiometer (VLX-3W Radiometer 9811-50, Cole Parmer Instrument Co.) at the wastewater surface.

Sonophotocatalysis operation conditions are described in Table 1. Photocatalysis operation conditions are the same as those of sonophotocatalysis except sonication.

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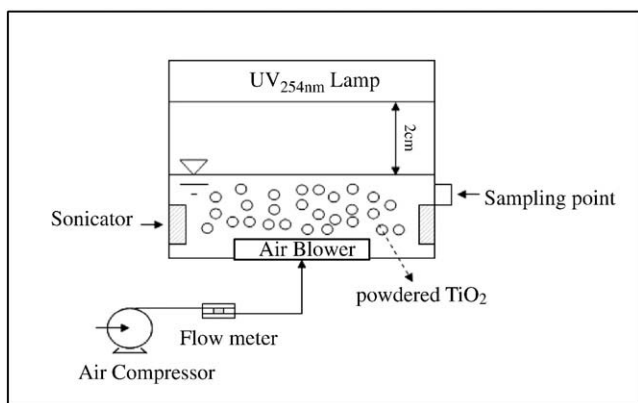


Fig. 1. Schematic diagram of the sonophotocatalytic and photocatalytic system.

2.3. Pretreatment and analysis

Solid phase microextraction (SPME) technology (Supelco) was used for analyzing benomyl and polydimethylsiloxane (PDMS) fiber was used, because it was shown to be ideal for adsorption of benomyl in our previous studies.

Due to the high conversion rate of benomyl to carbendazim, it is assumed that most of the benomyl is converted to carbendazim in the samples after comminution. Therefore, benomyl should be converted to carbendazim prior to SPME extraction, otherwise undesired degradation will occur.

After wastewater (50 mL) was contained in a separating type funnel, the pH was adjusted below 2.0 by adding hydrogen chloride (6 N) and shaken. 6 g of the trisodium citrate dehydrate was loaded into the wastewater and the pH was readjusted to 3.5–4.0. After that, 70 g of the sodium chloride and 25 mL of the dichloromethane were loaded into it and shaken for 5 min. After shaking, dichloromethane was separated from the mixture. Iodomethane (50 μ L) and acetone (100 μ L) were added into the separated dichloromethane for derivatization at 90 $^{\circ}$ C for 1 h.

The benomyl was analyzed using a GC (HP-6890II, Hewlett Packard) equipped with a flame ionization detector, an auto-sampler/auto-injector, an integrator and capillary column (HP-5, 5% phenyl methyl siloxane, 50 m \times 0.2 mm, 0.33 μ m). The initial temperature was kept at 40 $^{\circ}$ C for 10 min, then increased by 5 $^{\circ}$ C/min to a final temperature of 80 $^{\circ}$ C, and maintained at this temperature for 12 min in order to ensure the column was clean. The injector and detector temperatures were 280 $^{\circ}$ C and 300 $^{\circ}$ C, respectively. The H_2 gas and air-flow rate of the flame ionization detector were 40 and 400 ml/min, respectively. N_2 carrier gas (99.999%) was delivered at a rate of 1 ml/min.

2.4. Relative toxicity

Microtox $\text{\textcircled{R}}$ Asssay was used for monitoring effluent toxicity. The bioassays for effluent and stock solution were investigated using a Microtox Analyzer Model 500 (Azur Environmental Inc.). The effect of the test compound on the luminescent bacterium *Vibrio fischeri* was evaluated using the Biotox test. Bioluminescence inhibition in the

marine bacterium *V. fischeri* was widely used for toxicity test, it offered greater sensitivity, repeatability and precision [9]. The bacteria were purchased as freeze-dried reagents.

2.5. Mechanism of benomyl degradation

Irradiation of TiO_2 with UV, can create holes and electrons in the valence and conduction bands, respectively (Eq. (1)). Then, the rate of electron/hole recombination, for the production of heat, increases as a function of the UV illumination intensity (Eq. (2)). The resultant holes can react with surface bound hydroxyl groups to generate hydroxyl radicals ($OH\cdot$) (Eq. (3)), and oxygen functions in this role conversion via the superoxide radical ($O_2^{\cdot-}$) (Eq. (4)). Their ($OH\cdot$ or $O_2^{\cdot-}$) radicals can sustain the mineralization process (Eq. (5)) [10].



The photocatalytic oxidation is accelerated by scavenging conduction band electrons [11]. For photocatalytic reactions under ambient conditions, active oxygen species such as hydroxyl radicals ($\cdot OH$), superoxide ions ($\cdot O_2^-$), and hydrogen peroxide (H_2O_2) have been noticed as key species to promote the reaction [12–14]. TiO_2 - H_2O_2 enhanced photocatalytic system is given by the following reaction [15].



Reaction could be more enhanced by the decomposition of liquid water. Activated chemical species, such as radicals proceeded with the chemical reaction by the chemical effect of ultrasonic waves.

The primary process of sonolysis for water was the formation of the hydrogen radical ($H\cdot$) and hydroxyl radical ($OH\cdot$), as shown in Eq. (8). It is thought that both active species react with each other and produce H_2 and H_2O_2 as shown in Eqs. (9) and (10). In other to accomplish overall water splitting, H_2O_2 must be decomposed to O_2 and H_2O , as shown in Eq. (11). But H_2O_2 seldom reacted this way by sonication. Therefore, photocatalytic reaction is another candidate for decomposition of H_2O_2 . In other words, H_2O_2 was decomposed photocatalytically to O_2 continuously and stoichiometrically as shown in Eq. (11). It is possible to decompose water by photocatalytic reaction, however, it is difficult to decompose in practice because of rapid backward reaction, the formation and accumulation of intermediates onto the surface of photocatalyst [16], and other reasons [5]. Therefore, liquid water could be decomposed to hydrogen and oxygen stoichiometrically and continuously by a combined effect of sonolysis and photocatalysis, i.e., sono-photocatalysis (Eq. (12)).



Table 1

Operation conditions of the photocatalysis and sonophotocatalysis.

Volume	5 L
UV wavelength(UV-C)	254 nm
UV intensity	6.525 mW/cm ²
Total UV lamp	2 EA
Sonication (only sonophotocatalysis)	40 kHz, 117 V, 4.1 A, 190 W
TiO_2	1.0, 2.0, 3.0 g/L
Benomyl	3.2, 4.3, 5.2 mg/L
H_2O_2	0.5, 1.0, 1.5, 2.0, 3.0 mM

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