

The Effect of High-frequency Ultrasound on the Photocatalytic Decomposition of Organic Compounds in Water

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Access to clean water is necessary for the well-being and economic development of society. Thus, water contamination from human activity such as industry is a serious threat. Recently, the method in which organic contaminants in water are decomposed by photocatalysis has been proposed. However, the rate of decomposition with photocatalysis alone is slow. To enhance the degradation, the authors have developed a process that uses photocatalytic TiO₂ in combination with ultraviolet (UV) light and high-frequency ultrasound (US). High-frequency US irradiation generates mist that contains TiO₂ to increase the reaction area and to overcome the limited light penetration depth. To clarify the effect, the decomposition rate of phenol, known as a representative organic compound in wastewater, is experimentally evaluated. The results support that the proposed process enhances phenol degradation. This technology may be applied to decompose organic gaseous pollutants in waste gas.

1. Introduction

Clean water is essential for the economic development of society. As more countries experience urbanization and industrialization, demand for water usage increases. Global water usage has been increasing at a rate of about 1 % per year (UNESCO, 2020). As water usage increases, more wastewater will be generated. So, the implementation of wastewater treatment is necessary for the sustainable usage of water resources. The traditional biological treatment may not effectively treat refractory organic compounds such as phenolic compounds. However, the removal of phenolic compounds is necessary because they are toxic at low concentrations and classified as priority contaminants (Calace et al., 2002).

Many methods for the removal and degradation of phenol have been proposed and extensively studied. Some methods to remove phenolic compounds from wastewater include distillation, adsorption, chemical oxidation, biological treatment, ozonation, and photochemical treatment (Villegas et al., 2016). The methods that involve the formation of OH radicals are called advanced oxidation processes (AOPs) (Verma et al., 2013). Some examples of AOPs are sonolysis by ultrasound (US) irradiation, photolysis by ultraviolet (UV) irradiation, sonocatalysis (US+TiO₂), photocatalysis (UV+TiO₂), and sonophotocatalysis (UV+US+TiO₂). Although the use of US alone is insufficient for faster removal of the organic compounds, the use of ultrasound together with other processes such as metal, metal oxides, photocatalysis, ozonation, and H₂O₂ exhibits a synergistic effect and can enhance the reaction rate (Anandan et al., 2020). Thus, sonophotocatalysis has gained interest as one of the possible methods for the removal of refractory organics in wastewater.

Previous studies of phenol degradation with sonophotocatalysis using US of lower frequencies have been extensively studied. For example, Khokhawala and Gogate (2010) studied the degradation of phenol via sonophotocatalysis with US irradiation with a frequency of 25 kHz with a pilot-scale reactor. Recently, more studies have investigated sonophotocatalysis using US of higher frequencies that can generate mist particles. Rahimi et al. (2016) investigated the removal of ammonia by sonophotocatalysis and explained that the higher removal of a higher US frequency of 1.7 MHz compared to a lower frequency of 24 kHz is due to atomization and acoustic streaming. Sekiguchi et al. (2010) studied the photocatalytic degradation of gaseous toluene with mist generated by US of 2.4 MHz. The frequency of the ultrasound affects the properties of the mist particles and the degradation by sonophotocatalysis. US irradiation causes atomization, and as the frequency increases,

the concentration of smaller mist increases, and mist diameters decrease (Kudo et al., 2017). Itoh and Kojima (2019) studied the oxidation reaction of potassium iodide with sonophotocatalysis and suggested that photocatalytic reactions were occurring in the mist particles. The usage of both high-frequency US and photocatalysis may have a synergistic effect on the degradation of phenol. However, the degradation of phenol with photocatalysis in conjunction with the high-frequency US that generates mist has not been investigated.

To enhance the degradation of organic compounds, we propose a process that uses photocatalysis and the high-frequency US that generates mist particles. This process provides several advantages compared to photocatalysis alone. For example, TiO_2 particles will be suspended in the mist, so more light may be utilized with the mist particles because of the shorter distance that the UV must penetrate and the increased surface area to receive UV. The efficacy of this process was evaluated through a series of experiments. Additionally, the possible mechanism of the proposed process is suggested. The proposed process can be applied for the treatment of industrial wastewater which can contain refractory organic compounds that are toxic even in low concentrations.

2. Experimental

The validity of the proposed process of the degradation of phenol using photocatalysis and high-frequency US that generates mist was evaluated through qualitative and quantitative experiments. First, the presence of the mist particles and the suspension of TiO_2 in the mist were visually identified. The presence of the mist and TiO_2 in it is fundamental in the proposed process which hypothesizes that the mist with TiO_2 suspension improves the degradation. Second, the degradation of phenol was compared for UV+ TiO_2 and UV+US+ TiO_2 to evaluate the extent of the improvement in degradation with the presence of the mist. Third, the degradation of phenol using UV+US+ TiO_2 with different initial concentrations was done to study the behavior of the adsorption and the reaction. The results of these experiments support the capability of the proposed process.

2.1 Materials

Phenol (purity 99 %, FUJIFILM Wako Pure Chemical Corporation) was dissolved in Milli-Q water to the appropriate concentration. Aeroxide TiO_2 P 25 (specific surface area $53 \text{ m}^2/\text{g}$, NIPPON AEROSIL CO., LTD.) was used.

2.2 Apparatus

The experiments varying the reaction conditions include UV+ TiO_2 and UV+US+ TiO_2 . For these experiments, the concentration of the phenol solution was 50 mg/L . 300 mL Pyrex beaker (diameter 77 mm and height 110 mm) was used as the vessel. The vessel was filled with 200 mL of the appropriate mixture of TiO_2 and phenol solution. After filling the vessel, it was covered with a quartz lid (thickness 3 mm). A 4 W UV lamp with the main wavelength at 365 nm (model LUV-4, AS ONE Corporation) was placed directly on top of the quartz lid. The experiments were conducted at room temperature. TiO_2 was added to the phenol solution so that the concentration was 1 g/L . To ensure the adsorption of phenol on TiO_2 , the mixture was left on a magnetic stirrer at 500 rpm for 60 min without UV and US irradiation. 1 min after the TiO_2 was added to the solution, the vessel was placed in a US bath at 44 kHz for 30 seconds. By agitating the mixture with US, the agglomeration of TiO_2 particles can be reduced (Bekkouche et al., 2004). The concentration of phenol was measured every 20 min. For the UV+ TiO_2 experiment, the UV lamp was directly placed on top of the quartz lid, and the mixture was agitated with a magnetic stirrer at 500 rpm. The height of the mixture was 35 mm. The experimental setup for the UV+US+ TiO_2 experiment is shown in Figure 1.

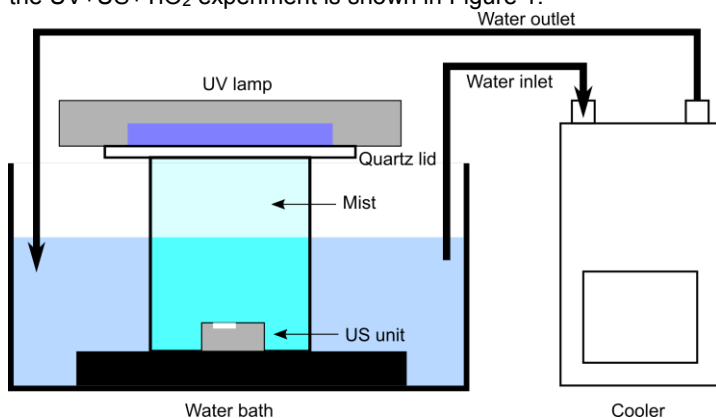


Figure 1: The experimental setup for the UV+US+ TiO_2 experiment

The immersion type ultrasonic atomization unit (about 21.6 W, frequency 1.6-1.7 MHz, model IM1-24, SEIKO GIKEN INC.) was placed inside the vessel. The height of the mixture was 43 mm after placing the US unit in the vessel. The operation of the US unit causes the temperature of the mixture to rise. To keep the temperature of the mixture constant, the vessel was placed inside a water bath, and the cooler was set to 22 °C. US irradiation provided sufficient agitation of the mixture.

The experiments for the degradation of phenol by sonophotocatalysis varying the concentration of phenol were conducted with the same experimental conditions as UV+US+TiO₂.

2.3 Analysis

Samples (3 mL) were taken from the vessel every 20 min up until 180 min using syringes. The samples were filtered using PES syringe filters of pore size 0.1 μm to remove TiO₂ particles. The absorbance of the samples was measured with a UV-vis spectrophotometer (model ASUV-1100, AS ONE Corporation) at 270 nm, which is the absorbance peak of phenol. The phenol removal was calculated by the following equation:

$$\text{Phenol removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C₀ and C_t is the concentration of phenol at time 0 and at time t respectively.

3. Results and discussion

3.1 Observation of the mist particles

The visual examination of the mist and the presence of the TiO₂ in the dried mist suggests that TiO₂ is suspended in the mist particles and the possibility that degradation is enhanced in the proposed process. For the US+UV+TiO₂ experiment, mist particles were observed inside the vessel. The mist generation by the high-frequency US unit is shown in Figure 2a. The mist particles were sampled and dried to visually examine the presence of TiO₂ in the mist. Figure 2b shows the sampled and dried mist particles, and the white spots in the image suggest that TiO₂ was suspended in the mist. Because this is a visual observation of the mist particles, the amount of mist generated and TiO₂ present in the mist is not quantified. Consequentially, the exact reaction mechanism of the proposed process is unknown. In the future, experiments to quantitatively analyze the mist is necessary to clarify the mechanism. At the current state, the observation of the mist with TiO₂ suspension is enough to support the proposed process and the inferred mechanism that is shown in Figure 5.

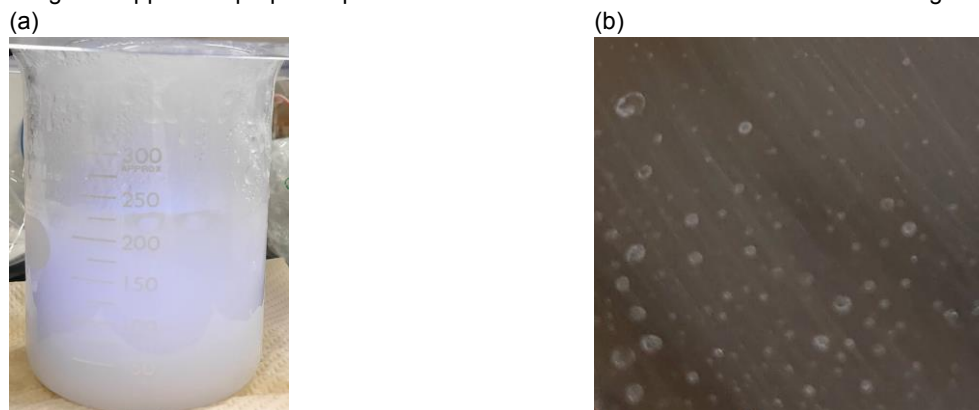


Figure 2: (a) The reaction vessel with the generated mist particles (b) The observation of TiO₂ in the mist particles from the reaction vessel

3.2 Comparison of the degradation of phenol for UV+TiO₂ and UV+US+TiO₂

The degradation of phenol for UV+TiO₂ and UV+US+TiO₂ was compared to quantify the extent of the improvement due to the use of high-frequency US that generates mist. Figure 3a shows the phenol concentration (mg/L) against time (min) for UV+TiO₂ and UV+US+TiO₂. For both reaction conditions, the same amount of adsorption was expected, and about 8 % of the initial amount of phenol at 50 mg/L was adsorbed by TiO₂ particles. The adsorption was much faster than the rate of degradation for both reaction conditions. The UV irradiation or UV+US irradiation was started after the initial adsorption. Figure 3b shows the phenol removal for UV+TiO₂ and UV+US+TiO₂. The concentration after adsorption was used as the initial concentration. After 180 min, the phenol removal was 8.42 % for UV+TiO₂ and 18.1 % for UV+US+TiO₂. Phenol removal for

UV+US+TiO₂ was 2.15 times that of UV+TiO₂. The results suggest that the degradation improved by the proposed process and that the improvement may be due to the generated mist particles with TiO₂ suspension. Van de Moortel et al. (2020) investigated the effect of using US on the photocatalytic reaction of phenol. Their research cannot be directly compared with this research because of the different initial concentrations of phenol (their research used 10 ppm phenol while our research used 100 ppm phenol), the different frequency and power of the US unit (their research used 24 kHz while our research used 1.6-1.7 MHz), and the different peak wavelength and power of the UV lamp. Also, a difference in the results is expected because of the mist produced by the high-frequency US. Despite the differences, we also find that using US with UV photocatalysis can increase the phenol degradation rate.

Conventional methods such as adsorption and distillation have low efficiencies and high operational costs (Villegas et al., 2016). Combining biological treatment with AOPs is effective for treating refractory organic compounds that are difficult to remove using conventional methods, and it may reduce the cost of the treatment of water (Oller et al., 2011). Thus, using the proposed method combined with biological treatment may be efficient and economical for the complete mineralization of organic compounds in wastewater.

The use of the US unit results in more energy consumption, but it can be offset by the reduced time for the degradation. To reduce energy consumption, sunlight may be used as the light source. Additionally, optimizing the process such as the phenol concentration, TiO₂ dosage, and US frequency may result in lower energy consumption and an improvement in the degradation rate.

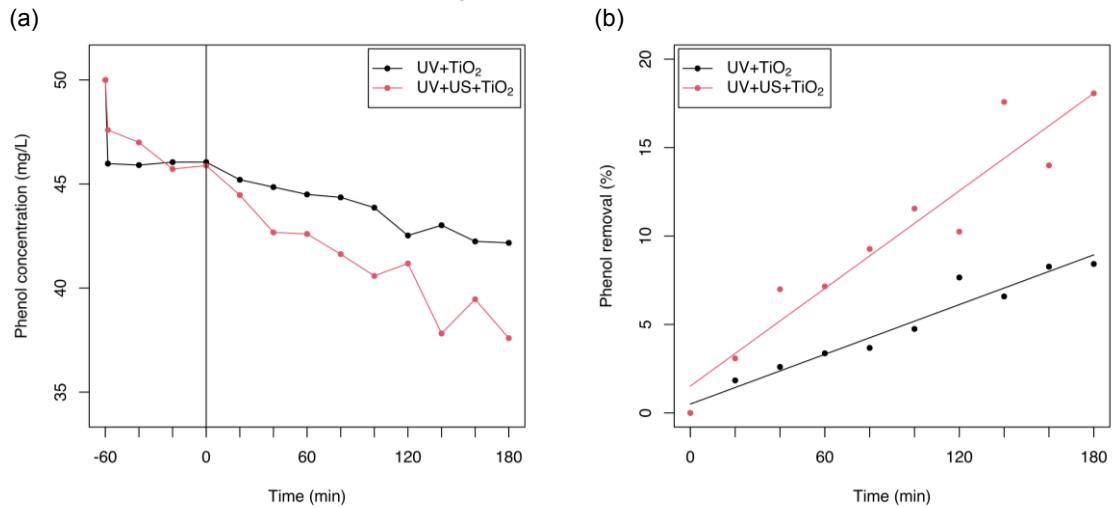


Figure 3: Degradation of phenol under different reaction conditions (50 mg/L phenol, 1 g/L TiO₂) for (a) phenol concentration and (b) for phenol removal

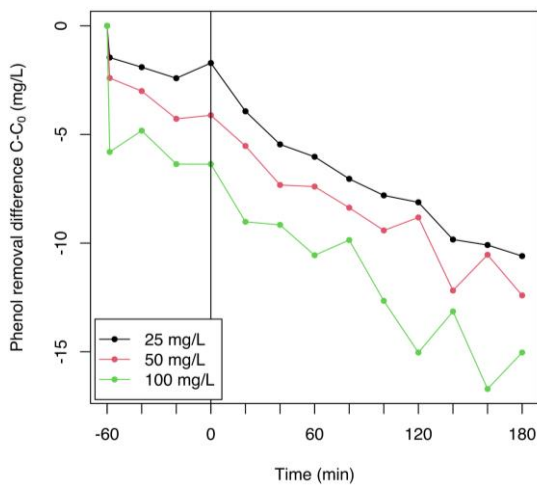


Figure 4: Degradation of phenol for different concentrations (UV+US+TiO₂, 1 g/L TiO₂)

3.3 Degradation of phenol for different concentrations using UV+US+TiO₂

To study the behavior of the adsorption and the reaction in the proposed process, the degradation of phenol with different initial concentrations was evaluated. Figure 4 shows the degradation of phenol for different concentrations using UV+US+TiO₂ where the phenol removal difference $C-C_0$ is shown on the vertical axis with C and C_0 as the concentration and initial concentration respectively. As the concentration of phenol increased, more phenol was adsorbed onto the TiO₂ particles. Similar to the results in Figure 3a, the adsorption was faster than the rate of degradation for the different initial concentrations. For higher concentrations, the adsorption may be saturated. Additionally, the phenol removal may be limited by the light intensity for higher concentrations. This implies that the proposed process may be effective for higher concentrations with increased light intensity.

3.4 Inference of the reaction mechanism

From the observation of the mist particles in Figure 2a and Figure 2b, it is presumed that the TiO₂ particles are suspended along with the phenol solution in the mist generated by the high-frequency US. Based on the results shown in Figure 3 and Figure 4, the TiO₂ particles adsorb phenol, and the rate of adsorption is much faster than the rate of degradation. In addition to the adsorption of phenol, the intermediates may also be adsorbed by TiO₂. The intermediates include aromatic compounds such as catechol, hydroquinone, and benzoquinone and opening compounds such as resorcinol and various acids (Sun and Smirniotis, 2003). US irradiation may remove some of the adsorbed chemicals on TiO₂ (Chen and Smirniotis, 2002). The TiO₂ particles which are deagglomerated and cleaned may be present in the mist particles, and those may utilize more UV light.

The irradiation of US causes acoustic cavitation which includes the formation, growth, and collapse of bubbles; when the bubble collapses, the local temperature is around 5000 °C, and the pressure is about 500 atm (Suslick, 1990). In the case of US irradiation, water is directly decomposed into H and OH radicals, and in the case of US+TiO₂, water is decomposed indirectly with TiO₂ in addition to direct decomposition (Kubo et al., 2005). Additionally, US irradiation deagglomerates the TiO₂ particles (Anju et al., 2012), so more light may be absorbed. The generation of the mist particles by high-frequency US may improve the degradation rate of phenol with the combination of photocatalysis. The inferred reaction mechanism in the mist particles is shown in Figure 5. For photocatalysis, consideration of the optical penetration length is important for the utilization of the available light (Chen and Ray, 1999). The diameter of the mist particles is much less than the height of the mixture in the vessel (Kudo et al., 2017). Thus, more light may be utilized with the generation of the mist particles. The deagglomerated TiO₂ may absorb more UV light once in the mist.

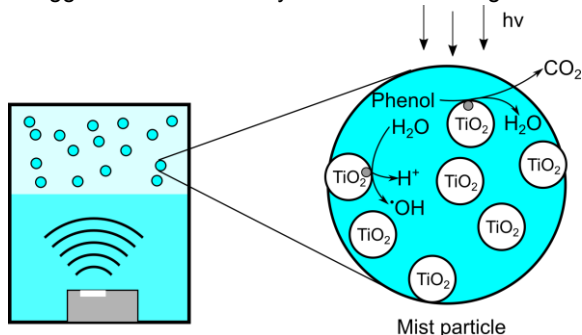


Figure 5: The inferred mechanism for the degradation of phenol in the mist particles

H and OH radicals may be formed in the mist through photocatalytic water decomposition. The highly reactive OH radicals oxidize phenol and its intermediates. The final products after the reactions are H₂O and CO₂.

In addition to the application of sonophotocatalysis with high-frequency US that generates mist particles in the liquid phase, the technology may be applied to decompose volatile compounds in the gas phase. Sekiguchi et al. (2010) has studied the photocatalytic degradation of gaseous toluene with mist.

4. Conclusion

In this study, we propose a process that uses photocatalytic TiO₂ in combination with ultraviolet (UV) light and high-frequency ultrasound (US). Experiments were conducted to evaluate the capability of the process. First, the presence of the mist particles with TiO₂ suspension was visually identified to support the proposed process. Second, to quantify the improvement by using US irradiation that generates mist, the degradation of phenol was compared for UV+TiO₂ and UV+US+TiO₂, and the removal rate for UV+US+TiO₂ was 2.15 times that of UV+US+TiO₂. Third, to study the adsorption and the reaction of the process, the degradation of phenol for

different initial concentrations using UV+US+TiO₂ was assessed. More phenol was adsorbed by TiO₂ for higher concentrations, and the adsorption was faster than the phenol degradation.

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