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Photocatalytic Degradation of Phenol with Ultrasonic Mist and Sunlight

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Due to the toxicity and persistence of the phenolic compounds present in wastewater, their removal is necessary for the prevention of pollution and the recycling of wastewater. Photocatalytic treatment with the utilization of mist droplets generated by ultrasound has been proposed for enhancing the degradation of those compounds by avoiding the limitations such as light irradiation conditions and mass transfer. Previous studies have investigated the degradation of organic pollutants by applying photocatalysts, conventional ultraviolet lamps, and ultrasound with mist generation. For the reduction of energy use, it is of great interest to utilize sunlight as a renewable light source for photocatalytic reactions. In this study, the synergy of sunlight and the presence of the mist droplets on the photocatalytic degradation of phenol is investigated by using a reactor in which titanium oxide is used as the photocatalyst, ultrasound is applied for mist generation, and simulated sunlight is used for illumination. The phenol degradation increased, and the apparent rate constant was 23.5 % higher when the mist droplets were present in the reactor and illuminated with simulated sunlight. In addition, the effect of different irradiance levels was studied. The results of this study demonstrate that ultrasound, mist, and sunlight can be used for the promotion of photocatalytic reactions.

1. Introduction

There is an increasing need for wastewater treatment and the recycling of wastewater with the water demand and the generation of wastewater increasing globally. To reduce water scarcity, advanced water treatment methods including chemical, biological, and physical can be implemented to reduce water pollution and to ensure that the treated water can be reused (Tortajada and van Rensburg, 2020). The use of advanced water treatment techniques becomes crucial, especially for the treatment of toxic and persistent pollutants that are difficult to remove using traditional techniques such as biological treatment. Industrial effluents such as those from the oil refining, petrochemical, and pulp industry contain phenolic compounds that are harmful to aquatic life (Rioja-Cabanillas et al., 2021). However, phenolic compounds inhibit microorganism activity in biological treatment methods (Ahmed et al., 2021).
Advanced Oxidation Processes (AOPs) have been proposed in which radicals are generated for the degradation of those refractory organic compounds (Al-Hamdi et al., 2015). AOPs using Ultraviolet (UV) for the generation of the radicals have been studied, including the UV photocatalysis technique in which semiconductors such as titanium dioxide (TiO_2) and zinc oxide (ZnO) are used (Al-Hamdi et al., 2015). Photocatalytic AOPs are environmentally friendly since they do not require the addition of chemical oxidants and do not produce sludge (Lin et al., 2020), and energy use can be reduced if sunlight is utilized for the photocatalytic reactions. The photocatalytic removal of pollutants may be limited by mass transfer, particle aggregation, and light scattering (Chen et al., 2020). To overcome some of these limitations and to enhance the removal of organic pollutants, hybrid techniques that couple photocatalysis and other technologies to achieve synergistic effects have been studied. For example, the photocatalytic circulating-bed biofilm reactor couples photocatalytic and biological treatment (Marsolek et al., 2008) and sonophotocatalytic reactors that use photocatalytic and sonolytic treatment by the application of ultrasound (US) (Anandan et al., 2020). Sonophotocatalytic reactors exhibit synergistic effects such as the increased generation of cavitation bubbles due to the presence of the catalyst, the improved mass transfer, and the cleaning effect on the photocatalyst by US (Theerthagiri et al., 2021).

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To further promote the oxidation reaction by photocatalysis, the utilization of the mist generated by US has been studied such as in the oxidation of potassium iodide (Itoh and Kojima, 2019) and the degradation of phenol (Kato et al., 2023). Mist droplets can contain photocatalyst particles and water-soluble pollutants (Sekiguchi et al., 2008). Some of the advantages of the mist droplets for the photocatalytic reactions may include the increased light irradiation area and the shorter light penetration distance.
For applications of photocatalysis, it is of great interest to use sunlight as a renewable source of light energy to convert into chemical energy for benefits such as the reduction in energy usage, reduction of pollution (Sun et al., 2022), and ability to function in remote locations. Thus, many studies have investigated the upgrading of photocatalysts to utilize the full solar spectrum (Barba-Nieto et al., 2020). In addition, the illumination conditions such as the irradiance, wavelength, and distribution affect the photocatalytic reactions (Heredia Deba et al., 2023). Since the intensity of UV is only about 4 % of the overall solar intensity (Barba-Nieto et al., 2020), the degradation of pollutants by the TiO_2 photocatalyst may be less effective when sunlight is used compared when UV lamps are used. In contrast to the wide solar spectrum and the lower proportion of light in the UV range, conventional UV lamps have a narrow spectrum in the UV region effective for photocatalysis by TiO_2. To improve the photocatalytic degradation of pollutants while using sunlight for its benefits, US-generated mist droplets may be utilized to enhance the irradiation condition.
In this study, TiO_2 photocatalyst, simulated sunlight irradiation, and US irradiation were applied in the reactor to investigate the effect and synergy of the US-generated mist and the irradiation of simulated sunlight on the photocatalytic degradation of phenol. Additionally, the effect of the variations in irradiance using the simulated sunlight on phenol degradation was studied. The present work demonstrates the possibility to promote photocatalytic reactions by the utilization of mist droplets and sunlight as a renewable energy source.

2. Experimental

2.1 Materials

As the model pollutant present in many industrial wastewaters, phenol (99 %, Fujifilm Wako Pure Chemical Corporation) was used as is for the degradation reactions. Due to its performance and wide applicability in studies concerning photocatalysis (Ohtani et al., 2010), Aeroxide P25 TiO_2 (Nippon Aerosil Co., Ltd.) was used as the photocatalyst without further modification. Phenol solutions with a concentration of 50 mg/L were prepared using ultrapure water (Millipore Milli-Q, resistivity 18.2 MΩ cm). TiO_2 was added to the phenol solution so that the dosage was 1 g/L. Before starting each trial, the mixture was agitated for 1 min at 500 rpm using a magnetic stirrer, sonicated for 30 s, and agitated again for 1 h for the distribution of the TiO_2 photocatalyst and the adsorption of phenol.

2.2 Reactor setup

Figure 1 shows the reactor used in the study which was irradiated with the simulated sunlight and sonicated for the generation of mist. The reactor was similar to those used in our previous study (Kato et al., 2023) with some modifications. A Pyrex beaker filled with 300 mL of the phenol and TiO_2 mixture was placed in a water bath set to 22 °C. The US unit (1.6–1.7 MHz, 21.6 W, IM1-24, Seiko Giken Inc.) was placed inside the vessel, and a quartz lid was placed on top to contain the mist inside of the vessel.

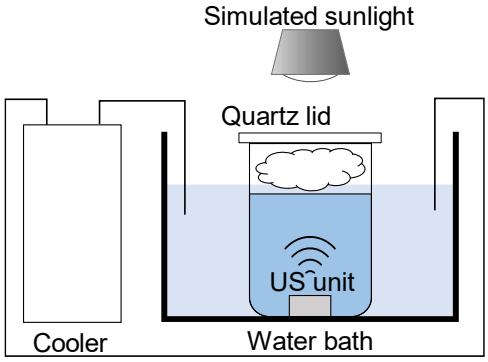

Figure 1: Schematic of the reactor

For the comparison of the effect of the light sources and the different irradiance values on the degradation of phenol with the presence and absence of the mist droplets, a UV lamp with a main wavelength at 365 nm (4 W,

LUV-4, AS ONE Corporation) or a simulated sunlight lamp (500 W Xenon lamp, XC-500EFSS, SERIC Co., Ltd., Japan) that has a spectrum closely resembling the solar spectrum was used to illuminate the mixture. The simulated sunlight provided light with a stable irradiance that can be used to assess the effect of the irradiance. The irradiance of the simulated sunlight was measured using a solar power meter (TM-207, Tenmars Electronics Co., Ltd.), and it was adjusted so that the irradiance was 1,000 W/m^2 or 500 W/m^2 at the top of the vessel.
For experiments that apply US without mist generation, the vessel was filled with glass marbles up to the point where the mixture height reached the quartz lid so that the mist was not generated in the vessel. The US unit was placed on top of the glass marbles so that the marbles did not directly attenuate the US transmission to the liquid phase. The position of the light source was adjusted to account for the change in the height of the mixture.

2.3 Sample measurements

The samples were collected from the vessel and filtered using polyethersulfone (PES) syringe filters of pore size 0.1 μm. The filtered samples were analyzed with a UV-vis spectrophotometer (UV-2600i, Shimadzu Corporation). Using the peak absorbance of phenol at 270 nm, the phenol removal was calculated using Eq(1),

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

where C_0 and C_t are the phenol concentrations initially and at time t respectively.

2.4 The analysis of the degradation kinetics of phenol

The Langmuir–Hinshelwood model can be used to analyze the degradation of phenol (Lin et al., 2011). Using the model, the apparent rate constant k_a (min^{-1}) for pseudo-first-order kinetics can be calculated using Eq(2):

$$\ln\left(\frac{C_t}{C_0}\right) = -k_a t \quad (2)$$

3. Results and discussion

3.1 Effect of the mist droplets

To assess the effect of the mist droplets on the degradation of phenol by the photocatalytic reactions, US was applied to the phenol mixture containing the TiO_2 photocatalyst for the generation of mist, and the mixture was irradiated with the light source. Figure 2 shows the phenol removal using the reactor applying US, with and without the generation of mist, while simultaneously irradiating the mixture with the simulated sunlight at 1,000 W/m^2 or with the UV lamp. The simulated sunlight was set to 1,000 W/m^2 to simulate a clear summer day (Kelly and Gibson, 2011). After 180 min with the application of US and the irradiation of simulated sunlight, the phenol removal reached 19.5 % and 17.6 % with and without the mist droplets respectively. With the UV lamp, the phenol removal after 180 min was 14.3 % and 11.1 % with and without mist respectively (Kato et al., 2022).

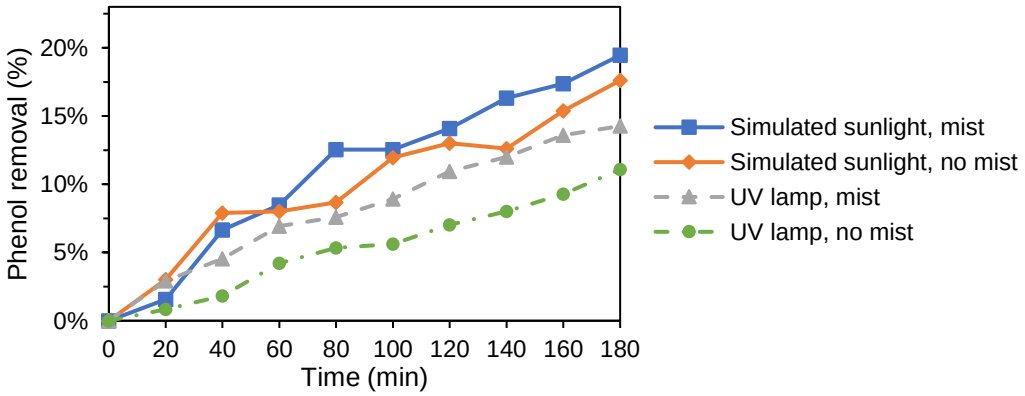

Figure 2: Comparison of the effect of mist under UV and simulated sunlight (1,000 W/m^2)

The results indicate that phenol can be removed with the reactor by applying US and either light source (the simulated sunlight or the UV lamp) to the mixture. Additionally, the presence of the US-generated mist droplets in the reactor increased the phenol removal for both light sources, suggesting that the presence of the mist droplets in the reactor may be involved in the improved removal of phenol.

While UV lamps are often used for laboratory experiments involving photocatalytic reactions to provide stable irradiation, previous studies have also investigated the use of sunlight as an economical and environmentally friendly light source (Ahmed et al., 2010). However, the degradation of pollutants by conventional photocatalytic reactors using TiO_2 slurries can be limited under sunlight irradiation since only a small percentage of the solar intensity is in the UV region that corresponds to the band-gap of the TiO_2 is 2.9–3.0 eV for rutile and 3.1–3.2 eV for anatase (Ozawa et al., 2019). By using the simulated sunlight which can emit light that closely resembles the solar spectrum and by utilizing the synergistic effect of US and the US-generated mist, phenol was degraded more effectively. The reason for this may be the improvement of the irradiation conditions and mass transfer to the active sites of the photocatalyst by the larger specific surface area of the mist droplets in comparison to the bulk mixture. Excessive photocatalyst particles present in the bulk mixture and the mist droplets may lead to light shielding and scattering, resulting in poor irradiation of the photocatalysts as the depth of the mixture increases. Although the mist droplets may introduce light scattering effects, the light may be distributed more evenly inside the reactor, since a more evenly distributed illumination can result in higher degradations by photocatalytic reactions (Heredia Deba et al., 2023). By combining the benefits of the presence of mist droplets and sunlight as a renewable source, the proposed reactor is attractive for enhancing the photocatalytic degradation of phenolic pollutants.

Table 1 presents the apparent rate constants k_a of the pseudo-first-order kinetics for the comparison of the presence of mist using the different light sources. Comparing when the mist is or is not present in the reactor, the apparent rate constant was 23.5 % and 31.3 % higher for the simulated sunlight and UV lamp respectively, meaning that the presence of the mist had a larger effect when using the UV lamp. It was observed during the experiments that the generated mist settled in the region above the bulk mixture in the reactor, and both the mist droplets and the bulk mixture were illuminated. The reason for the difference in the apparent rates between the light sources may be due to the UV lamp's larger distribution of the light intensity in the UV-A region for the electron–hole generation of the TiO_2. Thus, the UV lamp had a higher phenol decomposition efficiency because the ratio of the absorbed photons was higher. Although the simulated sunlight has a smaller percentage of irradiance in the UV region, the overall irradiance is higher, resulting in a higher degradation. However, the effect of the mist droplets was greater for the UV lamp because its irradiance in the UV-A region was lower than that of the simulated sunlight, and the mist could receive relatively more light compared to the bulk mixture.

Table 1: The apparent rate constant k_a and correlation coefficient R^2 for the effect of the presence of mist using the simulated sunlight (1,000 W/m^2) and the UV lamp.

Reactor	Simulated sunlight, mist	Simulated sunlight, no mist	UV lamp, mist	UV lamp, no mist
Apparent rate constant, k_a (min^{-1})	0.00118	0.000959	0.000834	0.000636
Correlation coefficient, R^2	0.966	0.948	0.986	0.987

3.2 Effect of the irradiance

To study the effect of variations in irradiances of light with the application of US and the generation of mist on the degradation of phenol, the UV lamp and simulated sunlight with adjusted irradiance levels were used. Figure 3 shows the phenol removal under different light sources and irradiance.

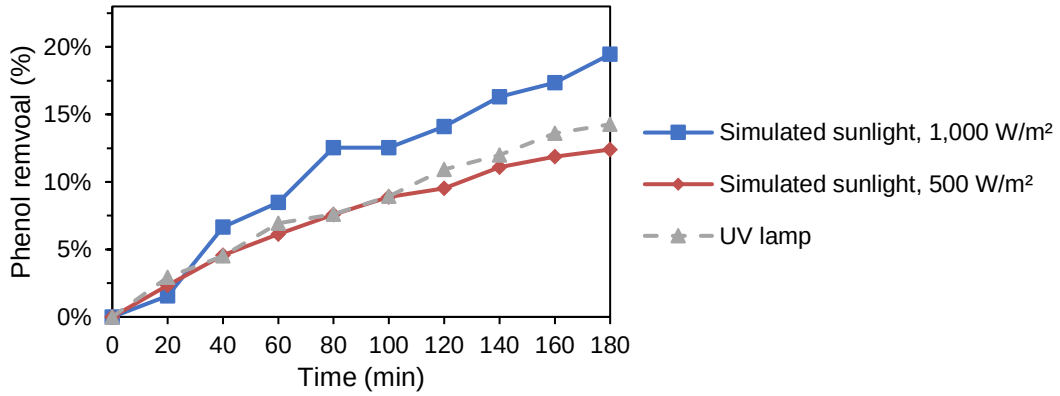

Figure 3: Comparison of the light sources and intensities with the proposed reactor

The phenol removal after 180 min was higher when the irradiance of the simulated sunlight was set to 1,000 W/m^2 compared to when it was 500 W/m^2. If enough phenol is present in comparison to the TiO_2 dosage, doubling the irradiance from 500 W/m^2 to 1,000 W/m^2 would result in doubling the phenol degradation. However, the phenol degradation of 1,000 W/m^2 compared to 500 W/m^2 was only 1.57 times the degradation. Thus, enough UV was provided in the case of 1,000 W/m^2 while phenol degradation can be improved further in the case of 500 W/m^2 by increasing the irradiance. Additionally, this ratio suggests that while enough phenol was present in the reactor, the mist droplets improved the phenol degradation even under a lower light intensity.
There may be variations in solar irradiation depending on factors such as the location, season, time of day, and weather, resulting in the different degradation performances of photocatalytic reactors. Although the current reactor utilizing the US-generated mist droplets can promote the degradation of phenol, the degradation is lower when the irradiation of the simulated sunlight was lower. To further promote the degradation of pollutants using sunlight at lower irradiances, the mist droplets can be utilized further to improve the irradiance conditions.

3.3 The photocatalytic degradation of phenol in the reactor with simulated sunlight and US-generated mist

Figure 4 shows the UV spectra of the phenol degradation in the reactor using TiO_2, US to generate mist, and simulated sunlight irradiation. The degradation of phenol involves the oxidation of phenol to aromatic intermediates, the ring-opening reactions of those intermediates, and further oxidation for the complete mineralization into carbon dioxide and water (Xu et al., 2013). It can be seen that the peak of phenol at 270 nm is decreasing, and no clear peaks of the intermediates were observed, indicating that phenol and its intermediates can be degraded in the reactor which involves the bulk mixture and the US-generated mist droplets that receive the simulated sunlight irradiation. Thus, phenol and its intermediates can degrade with sunlight and UV lamp irradiation.

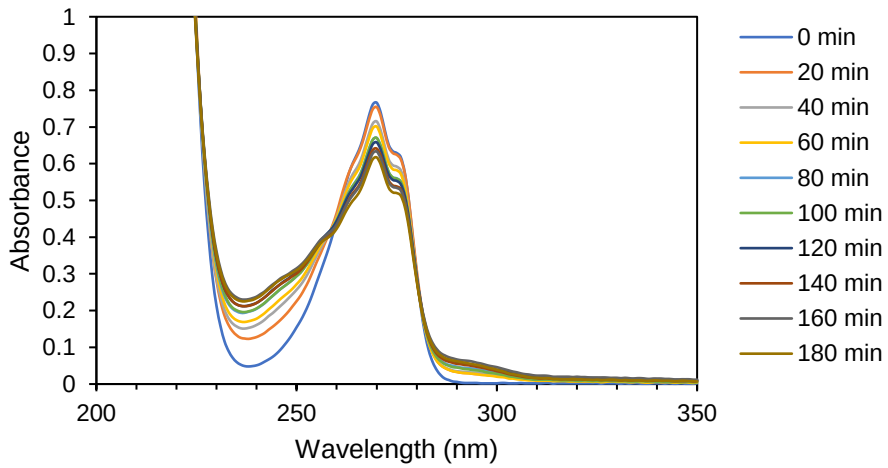

Figure 4: UV spectra of the degradation of phenol with simulated sunlight (1,000 W/m^2)

4. Conclusions

In this study, the effect of the US-generated mist simultaneous application of TiO_2 photocatalyst, simulated sunlight, and US to investigate the presence of the mist droplets on the photocatalytic degradation of phenol using simulated sunlight was investigated. Phenol was successfully degraded using the reactor with the presence of the mist droplets, and the apparent rate constant was 23.5 % higher when the reactor was irradiated with the simulated sunlight and the presence of the US-generated mist compared to when no mist was generated. However, the improvement in the phenol removal by the presence of the mist was less pronounced for the simulated lamp at 1,000 W/m^2 compared to the UV lamp. In addition, a higher irradiance resulted in a higher phenol removal rate, but the mist droplets could be utilized at lower intensities for the removal of phenol. The results and the analysis of the UV spectra indicate that phenol and its intermediates are degraded. These results suggest that the photocatalytic degradation of phenol can be improved by utilizing US-generated mist and sunlight as a renewable light source. To improve the reactor design utilizing the mist droplets and sunlight, further research should be done to clarify the reaction mechanism of the photocatalytic degradation of organic pollutants exclusively in the mist droplets.

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