

Ultrasonic enhancement of photo-catalytic oxidation of surfactant

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ABSTRACT. Photo-catalytic oxidation of surfactant (polyoxyethylene-alkyl-ether, C₁₄H₂₉O(CH₂CH₂)₇H, hereinafter referred as SS-70) enhanced by high power ultrasound is examined. The influences of the ultrasonic power and the stirring speed on the degradation rate are investigated. 1000 ml of 100 ppm SS-70 is decomposed totally in about 20 minutes in the photo-catalytic process combined with the ultrasonic irradiation. Without ultrasonic irradiation, the decomposition needs more than 1 hour. The optimum conditions for the hybrid degradation process are discussed. It is found that the stirring speed largely influenced the degradation efficiency. It is considered that the catalyst particles might be localized by ultrasonic standing wave, and caused inhibition to the decomposition in the degradation process. However, by high stirring speed, the inhibition could be overcome.

1. INTRODUCTION

Various types of detergents are contained in home drainage and industrial wastewaters. The main ingredient of detergents is artificial surfactant, which is poorly resolvable and harmful to aquatic microorganisms. Therefore, pretreatment is needed to reduce the surface activity before treating the surfactant containing pollutants. Commonly, the chemical treatment is used, but it is high cost and has a risk of producing other toxic compounds. Instead of the chemical treatment, recently, the applications of both photo-catalytic and ultrasonic oxidation processes have drawn much attention.

In the photo-catalytic oxidation, the light energy causes electron excitation in the semi-conductor particles (TiO₂) to produce unbounded electrons and holes. The photogenerated holes react with water molecules adsorbed on the catalyst surfaces to produce OH radicals as the hydroxylating agent. The photogenerated electrons react with dissolved and adsorbed oxygen molecules to produce OOH radicals as the hydroperoxylating agent. OH radicals and OOH radicals then react consecutively with organic species, and the pollutants are finally decomposed completely.

In the ultrasonic oxidation, the reaction is excited by the so-called cavitation phenomenon [1]. According to this theory, in high power acoustic field, cavities are generated from dissolved gases in the solution, and after repeated pulsation, then collapse. The collapsing cavity produces a micro size field with high temperature and pressure in an extremely short time. This condition leads to subsequent chemical reactions in three phases: internal cavity, interface boundary layer, and liquid bulk. Substance with high hydrophobicity and low boiling point will enter the cavity and be completely decomposed by combustion or pyrolyzation in the cav-

ities. The reactions with OH radicals, which are generated from water sonolysis induced by the high temperature and pressure, occur in the interfacial boundary layer regions, or in the surrounding bulk liquid at normal temperature and pressure.

In our previous studies, it was confirmed that the surfactant was oxidized by both the photo-catalytic reaction [2] and the ultrasonic irradiation [3-5]. However, in the single processes, the decomposition rate is still insufficient, and the surfactant could not be mineralized totally. It is considered that the hydrophilic substances, which are easy to be adsorbed on the catalyst surfaces, can be decomposed efficiently *via* the photo-catalytic reaction. And the hydrophobic substances, which are easily caught in the cavitation bubbles, can be decomposed efficiently by the ultrasonic irradiation. It is hypothesized that by combining the two processes, the decomposition will be more effective as the surfactant has both properties of hydrophilicity and hydrophobicity. In this study, the effect of the ultrasonic irradiation on the photo-catalytic reaction is discussed.

2. MATERIALS AND METHODS

As a surfactant, SS-70 (Sankyo Kasei Co., Japan) is used throughout the experiments. The critical micelle concentration of SS-70 is approximately 0.1 mM (52.2 ppm). Deionized water is used as the solvent. The initial concentration of SS-70 is 100 ppm. The concentrations of SS-70 are measured by a liquid chromatography (HPLC, GL Science #5504, GL Science Corp., Japan). The pH of the solutions is not adjusted.

TiO₂ (P25 JRC-TIO4, Nippon Aerosil, Japan) which has a surface area of *ca.* 50 m²/g is used as photo catalyst. The reaction vessel of cylindrical glass was 100 mm I.D. and 1.0L of volume. TiO₂ particles in the solution are suspended by a shaft driven turbine type stirrer. The

outline of the experimental apparatus is shown in Figure 1. The low-pressure mercury lamp (spectral median wavelength 253.7 nm, 20 W, UVL20PS, Sen Lights Corp., Japan) covered with silica glass cooling tube is installed in the center of the reaction vessel.

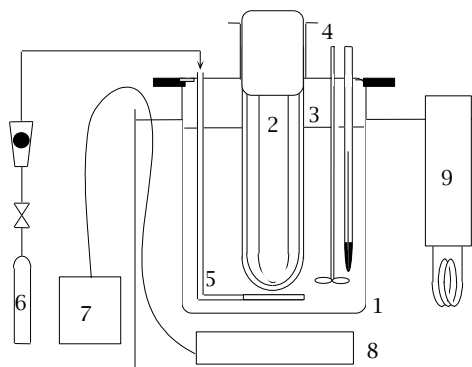


Figure 1. Schematic diagram of experimental apparatus. (1) Photo-catalytic reactor 1.0L, (2) Low pressure mercury lamp, (3) Silica Glass Cooling Tube, (4) Stirrer, (5) Sprayer, (6) Air, (7) Ultrasonic Generator, (8) Ultrasonic Transducer, (9) Heater.

The ultrasonic transducer (200 kHz 200 W, Kaijo #6633, Kaijo Corp., Japan) is set below the reactor vessel. The reaction vessel and the transducer are placed in a water bath and kept at constant temperature of 298 K. Experimental conditions are shown in Table 1.

Table 1

Concentration of photo-catalyst	0.05 g/1000 mL
UV irradiation power	15 W
Ultrasonic frequency	200 kHz
Powers	80 W or 200 W
Aeration rate	15 mL/min (Air)
Stirring speeds	100, 500 rpm

3. RESULTS AND DISCUSSION

Figure 2 shows the effect of ultrasonic power on the changes of concentration of SS-70 in ultrasonic irradiation and photo-sono-hybrid process, as compared with that in the photo-catalytic reaction. The stirring speed is 100 rpm.

It is seen from the figure that in 1 hour ultrasonic irradiation, only one third (plots A, ultrasonic power is 80 W) or one half (Plots B, the ultrasonic power is 200 W) of SS-70 is decomposed. The decomposition is considered to be brought by OH radicals produced in the acoustic cavitation. Comparing plots A with B, it is found that the decomposition rate is dependent on the ultrasonic power. Higher power of the ultrasound may lead to more extensive acoustic cavitation.

The change of SS-70 concentration under the ultrasonic irradiation in the presence of TiO₂ particles and no ultraviolet irradiation (photo-catalytic process) is

shown by plots C in the figure. It is seen that SS-70 is completely decomposed in 1 hour. Comparing plots A and B with C, there is a significant difference, *i.e.*, in the early stage, the decomposition rate is faster in the presence of TiO₂. The drastic decreases of the concentrations in the early stage of the decomposition under ultrasonic irradiation in the presence of the particles may be caused by the adsorption of SS-70 on the surfaces of TiO₂.

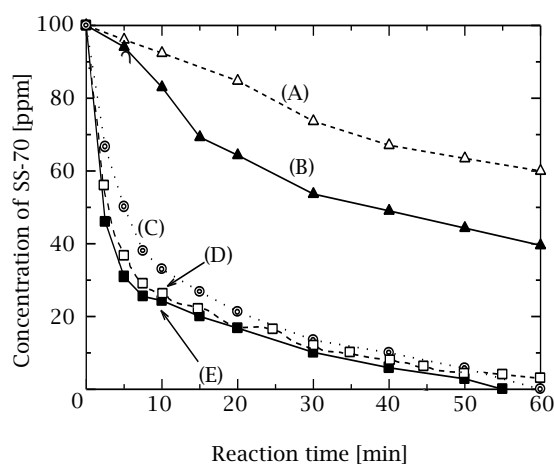


Figure 2. Effect of ultrasonic power on SS-70 degradation. \triangle \blacktriangle : Ultrasonic irradiation; \square \blacksquare : Hybrid process, open keys are for 80 W, solid keys are for 200 W. \odot : Photo-catalysed reaction.

Plots D shows the changes of SS-70 concentration in the photo-catalytic reaction combined with the ultrasonic irradiation. Comparing plots C with D, there are two significant differences, *i.e.*, in the early stage the decomposition rates are faster in the presence of TiO₂, and in the latter stage, the decomposition rate is slower in the presence of TiO₂. The slow decrease in the concentration in the latter stage of the decomposition may be due to the attenuation of the ultrasonic energy caused by the catalyst particles. The decrease of the concentration in the early stage of the decomposition under ultrasonic irradiation in the presence of the particles may be caused by the following three reasons.

Firstly, the TiO₂ particle surfaces may be eroded by collapsing cavities induced by the power ultrasound. This will increase the activity of the catalyst. However, the particle size after the irradiation have been not measured. Secondly, the diffusion layer thickness around the solid catalysts may be decreased by the acoustic pressure or by the ejecting flow from the collapsing cavities. This will enhance the mass transfer to the solid catalyst surface. And thirdly, the ultrasonic irradiation may cause a different scheme of the decomposition path as compared with the photo-catalytic reaction.

Figure 3 shows the effect of the stirring speed on the changes of the concentration of SS-70 with time. Plots A and B show the decomposition under the ultrasonic irradiation with stirring speeds of 100 rpm and

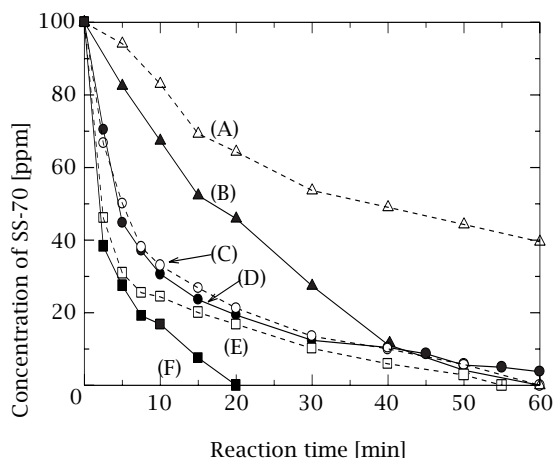


Figure 3. Effect of stirring speed on SS-70 degradation \triangle : Ultrasonic irradiation; \square : Hybrid process, \circ : Photo-catalytic reaction, open keys are for 100 rpm, solid keys are for 500 rpm.

500 rpm, respectively. Comparing plots A with B, there is a significant difference, even the ultrasonic power is the same (200 W). The decomposition rate is higher, as the stirring speed increases. It may be considered that the generation of the cavitation increases by stirring. The reasons are described as follows.

Firstly, the aeration bubble is disintegrated by the stirring, producing micro size bubbles to enhance the acoustic cavitation. Secondly, it is considered that the hydrodynamic cavitation [6] around the turbine is generated from the dissolved gas. The bubbles from the hydrodynamic cavitation become nuclei of the acoustic cavitation as well as the disintegrated aeration bubble. Neppiras [7] had investigated the cavitation threshold as functions of initial bubble radius R_0 , the ratio between acoustic pressure P_A and the gas pressure, and the operating frequency. There are two thresholds of the cavitation: the transient cavitation threshold, which determines the bubble collapse that leads to the chemical reaction, and the rectified diffusion threshold, determining the stability of the bubble. Bubbles with sufficiently small radius than the resonance one will be expanded by the ultrasound, and finally collapse after reaching the transient cavitation threshold. Bubbles with radius near the resonance radius will pulsate dynamically, but never collapse. Bubbles with radius under the boundary condition (rectified diffusion threshold) will be stable and neither expanded nor compressed. From Neppiras's theory, the bubble will collapse easily under ultrasonic irradiation, when the bubble diameter is much smaller than the resonance radius. The resonance radius corresponding to ultrasonic frequency of 200 kHz is approximately 10 μm .

Plots C and D in Figure 3 show the indicated degradation of SS-70 in the photo-catalytic reaction with stirring speeds of 100 rpm and 500 rpm, respectively. There is no significant difference between plots C and D. It is considered that the photo oxidation is less affected by the stirring, since reaction occurs on the sur-

face of TiO_2 particles.

The degradations of SS-70 in the hybrid process are shown in plots E (100 rpm) and F (500 rpm). It is clear that the degradation rate with stirring speed of 500 rpm is approximately three times faster than that of 100 rpm.

The effect of the stirring speed is discussed as follows. Under the ultrasonic irradiation, a standing wave with stationary nodes and bellies of the sound pressure fields are created in the reactor [8]. The particles may be localized in the nodes, causing inhibition on the photo-catalytic reaction. By an intensive stirring, the dispersion of the localized particles may be promoted, and the inhibition can be eliminated.

4. CONCLUSIONS

Photo-catalytic oxidation of surfactant enhanced by high power ultrasound was examined. The influences of ultrasonic power and stirring speed on the degradation rate were investigated. 1000 mL 100 ppm SS-70 was decomposed totally in 20 min, three times faster than that without ultrasound.

Besides of that the ultrasound has potential to decompose the surfactant, it was also considered that the enhancement were also caused by increasing in the activity of the catalyst and mass transfer to the catalyst surface under ultrasonic irradiation. The activity of catalyst increased by the destruction of TiO_2 surface due to ejecting flow from the collapsing cavities. The mass transfer enhancement is due to the decrease in the diffusion layer thickness around the TiO_2 surface caused by the acoustic pressure and the ejecting flow from the collapsing cavities.

The influence of the stirring speed was also investigated. It was considered that the aeration bubble is disintegrated by the stirring to produce micro size bubbles to enhance the acoustic cavitation. The stirring was also caused the hydrodynamic cavitation to produce small bubbles from the dissolved gas around the stirring turbine that become nuclei of the acoustic cavitation as well as the disintegrated aeration bubble.

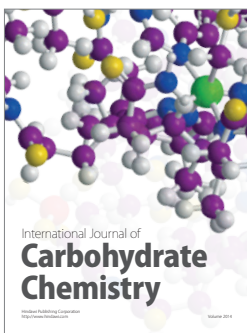
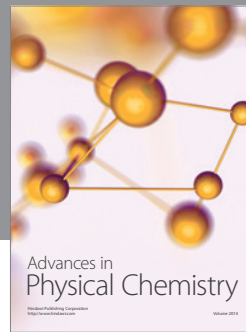
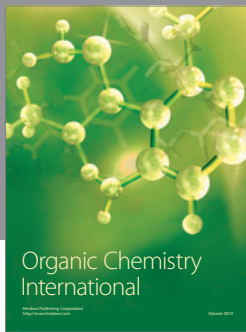
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