Generation of OH Radical by Ultrasonic Irradiation in Batch and Circulatory Reactor

Yu Fang, Sayaka Shimizu, Takuya Yamamoto and Sergey Komarov

1 Graduate school of environmental studies, Tohoku University, Sendai, Miyagi Prefecture 980-8579, Japan
2 Komatsu Ltd., Komatsu, Ishikawa Prefecture 923-0392, Japan
E-mail: fang.yu.p7@dc.tohoku.ac.jp

Abstract. Ultrasonic technology has been widely investigated in the past as one of the advance oxidation processes to treat wastewater, in this process acoustic cavitation causes generation of OH radical, which play a vital role in improving the treatment efficiency. In this study, OH radical formation rate was measured in batch and circulatory reactor by using Weissler reaction at various ultrasound output power. It is found that the generation rate in batch reactor is higher than that in circulatory reactor at the same output power. The generation rate tended to be slower when output power exceeds 137W. The optimum condition for circulatory reactor was found to be 137W output and 4L/min flow rate. Results of aluminum foil erosion test revealed a strong dependence of cavitation zone length on the ultrasound output power. This is assumed to be one of the reasons why the generation rate of HO radicals becomes slower at higher output power in circulatory reactor.

1. Introduction

1.1. Advanced oxidation processes in water treatment
With the expansion of urban city and modern industry, demand of water is phenomenally growing. Meanwhile, wastewater treatment and recycling has becoming an important issue, especially for recalcitrant organic wastewater, which mainly contains polycyclic aromatic hydrocarbon, halogenated hydrocarbon, heterocyclic compounds, organic pesticide and so on [1]. Advanced Oxidation Processes (AOPs), as a promising water treatment technology, has been investigated widely in recent years. By supplying energy and adding matters, such as ozone and H2O2, OH radicals can be produced in water, which attack the organic pollutants to promote their degradation into CO2, H2O, and inorganic salts [2], [3].

According to the mechanism of OH radical generation, various advanced oxidation processes have been widely investigated. Examples are Fenton process, ozone, ultrasound and plasma. Many hybrid processes have been also developed [4]-[15]. Some of them have already been industrialized for treating small amount of wastewater [16], [17]. Among these techniques, ultrasound water treatment has shown great potential. The main effect of ultrasound is related to the phenomenon called cavitation.

1.2. Cavitation
Cavitation is produced as a result of rupturing a liquid during the negative pressure half cycle of ultrasound wave [18]. Cavitation also can be defined as a process of generation, subsequent growth and collapse of the cavities (or cavitation bubbles) releasing large amounts of energy over a very small location providing very high-energy densities [19]. In this process, hot spots are generated in the
vicinity of cavities, which creates conditions of high temperature and pressures, usually up to few thousand Kelvins and few thousand atmospheres [20]. As a result, highly reactive free radicals, mainly OH radicals, are generated. There are four types of cavitation. Acoustic cavitation, hydrodynamic cavitation, optic cavitation, and particle cavitation. Among these, only acoustic and hydrodynamic cavitation can generate cavitation field of high enough intensity for water treatment [19].

1.3. Acoustic cavitation
Power ultrasound is capable of producing both chemical and physical effects in liquid. A typical frequency range for ultrasound is 20 ~100 kHz. In the case of acoustic cavitation, tiny bubbles are generated by the ultrasound wave, which is transmitted in liquids following compression and rarefaction cycles. When the negative pressure of rarefaction cycle exceeds attractive forces between the molecules of liquid, a void is formed. This void, or so-called cavity, is filled with solvent vapor or dissolved gas. In the compression cycle, the cavity does not totally collapse but continues to grow to form larger acoustic cavitation bubbles. When some bubbles expand to an unstable size, they violently collapse and generate high temperature zone (hot spots) and shock waves. Volatile and hydrophobic pollutants are degraded by thermal reaction in the hot spots of cavitation bubbles. Compounds which are more hydrophilic are decomposed in the bulk liquid by OH radicals generated in the cavitation bubble [21].

1.4. Acoustic streaming
Apart from generation of cavitation bubbles and hot spots, ultrasonic waves may also cause a steady flow in fluids, which is known as acoustic streaming [22]. Acoustic streaming is a kind of macroscopic flow caused by attenuation of ultrasound waves due to viscosity, thermal conductivity and interaction with cavitation bubbles [23]–[26].

Acoustic streaming is very important for wastewater ultrasonic treatment. The OH radicals, which have quite short life, are mainly generated in a small volume near the ultrasonic sonotrode tip, usually called cavitation zone. Therefore, targeted compounds should pass through the cavitation zone to be treated with OH radicals. Hence, to design an efficient ultrasonic wastewater treatment reactor, an optimized flow pattern inside the reactor is needed, especially for continuous reactors, adapted to application in industry. Thus, in this study, generation of OH radicals in batch and circulatory reactors was investigated under various acoustic powers using a Weissler model reaction. Besides an aluminum foil erosion test was conducted to investigate intensity and dimension of cavitation zone under the sonotrode tip.

2. Experimental setup and instrumentation

2.1. Ultrasonic equipment and sonotrode characteristics
In this study, In this study, two kinds of ultrasonic system were applied. The first one was made by NIPPON SEIKI, for the sake of convenience, referred as to device A, and the other was made by TELSONIC, referred as to device B. Output frequency ranges for device A and B were 17~23kHz and 18.9~21.2kHz respectively. In these experiments, there was a need to know acoustic power transmitted into water. For this purpose, calorimetric measurements were performed using both devices. The main dimension of sonotrodes is showed in Table 1. Both sonotrodes were made of Ti-4V-6Al alloy.

| Table 1. Dimension of sonotrodes |
|-------------------------------|
| Device | Length / mm | Tip diameter / mm |
|-------|-------------|-------------------|
| A     | 122         | 26                |
| B     | 255         | 47                |
2.2. Calorimetric measurement
The calorimetric measurements were performed in an acrylic cylinder vessel, filled with 500ml distilled water. The vessel had a 100mm diameter, 146mm height and 10mm wall thickness. Temperature variation was measured with a thermocouple fixed at the centreline of sonotrode at a distance of 20, 40 and 60 mm from the vessel bottom. The vessel was wrapped with a heat insulating material to prevent heat loss. Immersion depth of sonotrode was 30mm.
Assuming that all the ultrasound energy is converted to heat, the heat increase of water bath can be considered equal to the acoustic energy transmitted into the liquid. The measurements were performed at 150°C. Ultrasound irradiation time for device A and B were 1200s and 160s respectively. Calorimetric measurements results showed that the lowest and the highest acoustic power for device A were 12W and 24W, and those for device B were 137W and 301W.

2.3. Reactor set up
In this study, a batch model reactor and circulatory model reactor were investigated respectively. Schematic drawings of both the reactors are showed in Fig. 1. For the batch experiment, a 2L beaker was used as the reactor filled with 1L of 0.1mol/L KI solution. To keep the solution temperature constant at a level of 15°C a water-cooled coil was immersed in the beaker. Sonotrode immersion depth was 30mm. Ultrasound frequency was set in 20 kHz for both devices. Irradiation time was 60 minutes and 15 minutes, respectively. Solution samples were taken every 10 mins for device A and 3 mins for device B.

In circulatory experiments, a 1L acrylic cylinder of 100mm in diameter and 200mm in height was used as a reactor equipped with inlet and outlet tubes as shown in Fig.2(b). The tubes were connected to a temperature-controllable fluid circulator filled with 6L of 0.1mol/L KI solution. The solution temperature was kept at the level of 15±2°C. Ultrasound irradiation time was set to 120 min and 15 min for device A and B, respectively. Solution samples were taken every 20 min for device A and 3 min for device B. These experiments were carried out at three flow rates, 2, 4 and 6 L/min measured by a flow meter.

2.4. Weissler reaction
In this study, Weissler reaction was applied to evaluate the formation rate of OH radicals. Weissler reaction has been widely used as a test reaction to investigate ultrasonic and hydrodynamic cavitation. The OH radicals, which generated in cavitation zone have a very short lifetime and react soon with iodide ion through a series of intermediate steps, to form tri-iodide complex I3-. The key reactions are assumed to be as follows [27]:

\[ H_2O \rightarrow H^- + OH^- \]  

(1)
\[ \text{OH} \cdot + I^- \rightarrow \text{OH}^- + I \]  \hspace{1cm} (2)

\[ I + I^- \rightarrow I_2^- \]  \hspace{1cm} (3)

\[ I_2^- \rightarrow I_2 + 2I^- \]  \hspace{1cm} (4)

\[ I_2 + I^- \rightarrow I_3^- \]  \hspace{1cm} (5)

Concentration of tri-iodide complex \( I_3^- \) was measured by an ultraviolet visual spectrophotometer (Shimadzu Co., Ltd, Japan), based on the maximum absorption peak of \( I_3^- \) at a wavelength for 353nm. Then, the rate of \( I_3^- \) ion formation was determined and used as a quantitative measurement of OH radical generation. As can be readily seen from the above reactions, two OH radicals must react with two \( I^- \) ions to produce one \( I_3^- \) ion. Therefore, the rate of OH radical formation can be obtained simply by multiplying the rate of \( I_3^- \) ion formation by 2.

3. Experimental results and discussion

3.1. Weissler reaction

In the batch type reactor, spectrophotometer measurements revealed that concentration of \( I_3^- \) ion increases linearly with treatment time when the other parameters are kept constant. This suggests that generation of OH radicals occurs at a constant rate at a fixed acoustic power. Based on these data, OH radical generation rate was determined at various values of acoustic powers. The results are shown in Fig. 2. It is clearly that OH radical generation rate increases significantly with increasing the acoustic power. However, this increase becomes slower when acoustic power exceeds 137W.

In the circulatory type reactor, concentration of \( I_3^- \) ion increased also linearly with treatment time. Two typical sets of data are plotted in Fig. 3 or the minimal (a) and maximal (b) acoustic powers examined in this study. In both cases, the time variations of \( I_3^- \) ion concentration was dependent on liquid flow rate, although this dependence appears to be different when device A and B were used. Based on these data, the rate of OH radical generation for the circulatory reactor was calculated. The results are presented in Fig.4 for different flow rates. It is seen that the OH generation rate increases in the range of acoustic power from 0 to 137 W. After that, the generation rate is decreased with acoustic power or remains almost unchanged. Under the present experimental conditions, the maximal rate of OH radical generation was obtained at acoustic power of 137 W and flow rate of 4 L/min.

Comparison of the OH radical generations rates for batch and circular reactors reveal that the batch reactor provides a more efficient ultrasonic treatment than circulatory one. For example, the maximal rate in the circulatory reactor treatment is equal \( 14.8\times10^{-9} \) mol/sec, while in the batch reactor this value reached \( 23.6\times10^{-9} \) mol/sec at the same acoustic power.

In order to find out the reason for this difference, additional experiments were performed. The goal of these experiments was to measure the level of cavitation under the sonotrode tip. All these measurements were done using device B only.

3.2. Cavitation intensity test

It is well known from the relevant literature that cavitation level (or intensity) can be measured using aluminum foil test [28]-[30]. In this test, a piece of thin aluminum foil is fixed at a certain location in the cavitation zone. Cavitation bubbles, when collapse near the foil, poke tiny holes in the aluminum foil removing a part of aluminum from the foil. Obviously, the higher the cavitation intensity, the more holes are poked in the foil and the greater is the loss of foil weight. Thus, the cavitation intensity can be estimated from the rate of foil weight loss.
Fig. 2 Effects of output power on OH radical generation rate in batch reactor experiments

Fig. 3 Time variation of I$_3^-$ concentration at various flow rates acoustic power (a)12W and (b)301W

Fig. 4 Effects of output power on OH radical generation rate in circulatory reactor experiments
In these experiments, a piece of foil was fixed in a steel frame of 20×20 mm in size. The frame was positioned in water at a fixed distance Z from the sonotrode tip and parallel to its surface. Ultrasound waves were introduced in water to produce cavitation for the time interval of 20~600 sec, depending on distance Z. Then, the loss in foil weight was measured using a precision balance.

Figure 5 presents variation in the rate of foil weight loss \( U_e \) with the distance from the sonotrode tip for two acoustic powers, \( P = 137 \text{W} \) and \( 301 \text{W} \). Notice that the plot is made using a base 10 logarithmic scale for the y-axis because of a very strong dependence of \( U_e \) on \( Z \). It is readily seen that at the higher acoustic power, a high-intense cavitation zone is formed under the sonotrode tip, however the intensity is drastically decreased with distance. At \( Z = 20 \text{ mm} \), the intensity is reduced by 100 times relative to that at \( Z = 5 \text{ mm} \). On the other hand, at \( P = 137 \text{ W} \), reduction of \( U_e \) with \( Z \) is not so significant. At distances more that 20 mm, the cavitation intensity at \( P = 137 \text{ W} \) is approximately one order of magnitude higher than that at \( P = 301 \text{ W} \). Local peaks, observed in both the curves, are conceivably due to formation of standing wave between sonotrode tip and aluminum foil. Thus, too high acoustic power results in formation of a very intense but short cavitation zone in liquid. Alternatively, ultrasound waves of relatively low intensity produce a more uniform and longer cavitation field. This can be one of the reasons allowing us to explain the dependence of OH radical generation rate on acoustic power. As mentioned above, OH radicals can be produced in cavitation zone. In the batch-type reactor, liquid is involved in circulatory flow generated in the beaker by acoustic streaming. In this case, KI solution can pass through the cavitation zone many times. However, in the case of circulatory reactor, the residence time of liquid in the beaker is much shorter compared to the batch reactor case. That is why the above-mentioned decrease in the size of cavitation zone with acoustic power can lead to a situation where progressively smaller fraction of KI solution would be able to pass through cavitation zone.

Maikel M. van Iersel [31] has also claimed that shielding of the acoustic wave is more pronounced at higher cavity fractions. Accordingly, a large amount of the supplied energy is attenuated in the immediate vicinity of sonotrode tip and thus experimentally determined OH radical generation rate may tend to increase relatively little, or even decrease, with increasing the acoustic power.

4. Conclusion
In this study, effects of acoustic power on generations of OH radical in batch and circulatory reactor were investigated.
- In the case of batch reactor, OH generation rate increased with output power growth; reaction efficiency was much higher than in circulatory reactor at same output.
In the case of circulatory reactor, the best reaction condition was obtained in 137W output and 4L/min flow rate; with the growth of output power, OH generation rate grewed firstly, and then decreased after 137W output.

- Aluminum foil erosion test clarified that high acoustic power resulted in an intense but very short cavitation zone, which may suppress the generation of OH radicals.

Further research on flow pattern in circulatory reactor is need, especially on the coupling effects of acoustic streaming and bumped circulation flow.

5. References
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