Effect of pH on Sonochemical Formation of Hydroxyl Radicals under 20 kHz Ultrasonic Irradiation

Ting-Nien Wu¹, Meng-Chun Shi¹,²

¹. Department of Environmental Engineering, Kun Shan University, 949 Da-Wan Road, Yung-Kang City, Tainan County 71003, Taiwan, R.O.C.  
(E-mail: wutn@imail.ksu.edu.tw)  
². Sustainable Environment Research Center, National Cheng Kung University, 500 Sec. 3 An-Ming Road, Tainan City 709, Taiwan, R.O.C.  
(E-mail: b4890n043@yahoo.com.tw)

Abstract
Advanced oxidation processes have drawn much attention on their application to wastewater treatment recently. However, it is seldom to utilize sonochemical degradation as the tool of environmental remediation. Ultrasonic irradiation may cause acoustic cavitations to concentrate the diffuse energy of sound. The effect of acoustic cavitations can induce the formation, growth, and collapse of bubbles within 10 µs. The hot spot may attain extremely high temperature up to 5000 °C and pressure about 500 atmospheres, which allows the production of hydrogen atoms and hydroxyl radicals through sonolysis. Hydroxyl radicals are very powerful oxidizing agents that are capable of destructing many organic pollutants. This study utilized 20 kHz ultrasonic irradiation as the mechanism of radical production. The production rate of radicals serves as the evaluation tool of sonolysis efficiency under the control of different pHs. Three schemes of detecting radicals were employed, including Fricke measurement, p-CBA probe compound measurement, and hydrogen peroxide indirect measurement. The experiment results were confirmed through different measurement methods. The threshold of ultrasonic intensity was also examined to form radicals under the acidic, neutral, or basic surroundings.

Keywords
Ultrasonic; sonolysis; cavitation; radical; pH

INTRODUCTION
Ultrasound has been applied on physical dispersion process and chemical oxidation reaction for more than a half century. Its broad applications embrace many fields such as emulsification, homogenization, extraction, degreasing, filtration, medical image, cell destruction, surface cleaning, dissolution, drying, degasification, etc. Ultrasound also can generate hydroxyl radicals to destruct or mineralize organic compounds, the so-called sonolysis. Many advanced oxidation processes (AOP) are known able to produce hydroxyl radicals, such as photocatalysis, Fenton reactions, ozone, UV-peroxide, radiolysis, electron beam irradiation and sonolysis. AOPs are highly promising for remediating wastewater because of rapid reaction, easy control, and no secondary pollution. However, ultrasound is not often used as a pollutant remedy in the field of environmental engineering (Ince et al., 2001).

Under an extreme condition, ultrasonic waves can cause the effect of acoustic cavitation through the formation, growth, and implosive collapse of micro-bubbles in a liquid. Cavitation responsible for sonolysis serves as a means of concentrating the diffuse energy of sound. Bubble collapse induced by cavitation procedures intense local heating to roughly 5000 °C and high pressure up to 500 atmospheres, and these hot spots are cooling fast as heating procedures at the rate above 10⁹ K/s (Suslick, 1990). Such an extreme condition is able to break the chemical bonds, induce liquid-phase burning, initiate radical reactions, and degrade most persistent organic pollutants. In other words, sonolysis of organic pollutants is mainly ascribed to the sonochemical generation of radicals and thermal decomposition in the cavitation microbubbles.

A growing number of lab studies have demonstrated that ultrasound irradiation results in a rapid, safe and effective decomposition on aromatics (Visscher, 2003), phenols (Entezari et al., 2003),...
chlorinated compounds (Naffrechoux et al., 2003), and pesticides (David et al., 1997; Gondrexon et al., 1999) in aqueous solution. Several factors including ultrasonic frequency, strength of ultrasounds, solute temperature, cavitation gases, and solute pH may influence the sonochemical degradation of organic contaminants. The pH plays an important role in the sonochemical system because the physical properties of chemicals can be modified depending upon aqueous pH. The sonochemical degradation rate of 4-nitrophenol was reported to decrease with increasing pH, but the disappearance of aniline was found favourable in the alkaline solution by sonolysis (Jiang et al., 2002). The case of hydrazine demonstrated that its degradation was dependent greatly upon pH, but not changing the same trend with pH, under ultrasonic irradiation (Nakui et al., 2007). Previous scientific works didn't provide a consistent result on pH affecting the sonolysis of aqueous contaminants. For that reason, it has raising our interest to understand the effect of pH on the sonochemical generation of radicals. In this study, three radical measurement methods including Fricke measurement, hydrogen peroxide indirect measurement, and probe compound detection were employed to monitor the formation of radicals at different pHs. As a result, the application of ultrasound as the possible remedy alternative of contaminated water is subsequently under progress.

MATERIALS AND METHODS

Chemicals
Reagent grade of ferrous sulphate from Shimakyu’s Chemical Co. (Japan), sulphuric acid from Nihon Shiyaku Reagent Co. (Japan), and sodium chloride from Wako Pure Chemical Industries, Ltd. (Japan) were used in the Fricke measurement. Reagent grade of sodium hydroxide, monopotassium phosphate, and potassium iodide from Shimakuyu’s Chemical Co. (Japan) as well as ammoniumheptamolybdat-4-hydrate from Sigma-Aldrich Chemicals Co. (U.S.A.) were used in hydrogen peroxide indirect measurement. Analytical grade of 4-chlorobenzoic acid (p-CBA) from Fluka Chemicals Co. (Switzerland) was used in probe compound detection. All reagents were prepared with de-ionized water, which was made by Mili-Q system (Millipore TK-10, USA). Analytical grade of methanol (99%) purchased from Merck Ltd. (Taiwan, ROC) was utilized as a mobile-phase elute in the analysis of high performance liquid chromatography (HPLC).

Experimental Setup
Ultrasonic irradiation experiments were conducted in a bench-scale continuously recycling reactor system, which is comprised with an ultrasonic processer, a reactor cell, a thermostatic water bath, a recycling water reservoir, and a pH meter. Ultrasound source was supplied by the Branson Sonifier 450 ultrasonic processor equipped with a 450 W power supply and a 1.3 cm diameter of titanium probe operating at 20 kHz. The reactor cell is 50 ml cylindrical glassware that is connected to the thermostatic water bath at the outlet and the recycling water reservoir at the inlet. The recycling water was cooled to $5 \pm 2 \, ^\circ C$ in the thermostatic water bath and purged with air to oxygen saturation in the recycling water reservoir. The ultrasonic power was controlled by the panel setting, and the sonication probe was dipped 1 cm below the water surface. During the irradiation, the pH of recycling water was monitored at the water reservoir, and the samples were taken every 90 seconds at the outlet of the reactor cell.

Radical Measurement
The number of the radicals formed in sonochemical reactions is an important measure of the sonolysis efficiency. Although the free radicals can be directly detected by electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spin trapping technique, the expensive apparatus and the intricate spin adduct treatment make the spin trapping technique unpopular. In this study, three simple and reliable methods of radical measurements are introduced as the following.
**Fricke dosimeter.** The Fricke dosimeter was first proposed to quantify the generated radicals in radiation chemistry (Fricke and Hart, 1966), and then it was applied for ultrasound dosimetry (Jana and Chatterjee, 1995). The Fricke solution was prepared with 1 mM Fe(NH₄)₃(SO₄)₂·6H₂O, 0.8 N H₂SO₄, and 1 mM NaCl. The formation of OH radicals can be estimated based on the oxidation of Fe²⁺ to Fe³⁺ in the acidic Fricke solution. As shown in eq. (1), water can be dissociated to OH radicals and H atoms by ultrasound. The conversion of Fe²⁺ to Fe³⁺ is not only due to OH radicals but also to the H atoms. The chemical reactions in the Fricke solution are given eq. (2) through (6). Accordingly, the oxidizing agents involved in the reaction with Fe²⁺ include OH radicals, HO₂ radicals, and H₂O₂. Based on the stoichiometric calculation, the number of OH radicals produced in Fricke solution is theoretically equal to one quarter the amount of Fe³⁺ generation. The produced Fe³⁺ concentration in Fricke solution through ultrasonic irradiation was measured by Hitachi U3010 UV spectrometer at the wavelength of 304 nm, and the concentration of OH radicals can be calculated accordingly.

\[
\begin{align*}
H_2O & \rightarrow H\cdot + \cdot OH \\
Fe^{2+} + \cdot OH & \rightarrow Fe^{3+} + OH^- \\
H\cdot + O_2 & \rightarrow HO_2\cdot \\
Fe^{2+} + HO_2\cdot & \rightarrow Fe^{3+} + HO_2^- \\
HO_2\cdot + H^+ & \rightarrow H_2O_2 \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + \cdot OH + OH^- \\
Fe^{2+} + \cdot OH & \rightarrow Fe^{3+} + OH^- 
\end{align*}
\]

**H₂O₂ indirect measurement.** As illustrated in eq (1), the formation of OH radicals and H atoms is expected by ultrasonic irradiation. The occurrence of recombining OH radicals may form H₂O₂ as eq. (7). The active H atom may react with oxygen to produce HO₂ radical, and the further coalescence of HO₂ radicals generates H₂O₂ given in eq. (8). The concentration of H₂O₂ was indirectly measured by the iodide method (Hua and Hoffmann, 1997). Ultrasonic irradiation experiments were carried out in the presence of a pH buffer solution that contains 4.8 × 10⁻³ M NaOH and 8.3 × 10⁻³ M KH₂PO₄. The sampled liquor of 2 ml was mixed with 1 ml of 0.1 M potassium biphthalate and 0.75 ml of the iodide indicator solution containing 0.4 M potassium iodide, 0.06 M sodium hydroxide, and 2 × 10⁻⁴ ammonium molybdate. The treated sample stood still 2 min and subsequently analyzed its absorbance by Hitachi U3010 UV spectrometer at the wavelength of 351 nm.

\[
\begin{align*}
H_2O & \rightarrow H\cdot + \cdot OH \\
\cdot OH + \cdot OH & \rightarrow H_2O_2 \\
H\cdot + O_2 & \rightarrow HO_2\cdot \\
HO_2\cdot + HO_2\cdot & \rightarrow H_2O_2 + O_2 
\end{align*}
\]

**p-CBA probe compound detection.** Another indirect measurement of OH radicals is to quantify the probe compound reacted with radicals, and p-CBA is the most widely used compound because of its stability in reaction and analysis (Kao and Su, 2009). During ultrasonic irradiation experiments, the concentration of p-CBA in the reactor cell were measured by a Hitachi L-7100 HPLC system equipped with a Hitachi L-7420 diode array UV-Vis detector and fitted with a reverse phase RP-18, 5 μm, 4.6 × 250 mm column. The operative condition of HPLC analysis was set at isocratic mode and eluted with a mobile phase composed of methanol and water at a 65:35 ratio. The flow rate of elution was 1 ml min⁻¹, and UV detection was performed at 234 nm. The peak of p-CBA occurs at 8.5 min on the HPLC chromatograph.
RESULTS AND DISCUSSION

Quantification of Fricke Dosimeter

Figure 1 displays the growth of ferric concentration in a Fricke solution during the ultrasonic irradiation experiments. As illustrated in eq.(1) through (6), the Fricke mechanisms did convert Fe$^{2+}$ to Fe$^{3+}$ as expected. The concentration of ferric ions in the Fricke solution was linearly increasing with ultrasonic irradiation time in Fig. 1, and all experiments showed the R-square values greater than 0.9. Based on the stoichiometry of the Fricke mechanisms, the growth of ferric ions in the Fricke solution is equivalent to four times of OH radicals produced. The production rate of OH radicals was accordingly calculated as one quarter the slope of the ferric growth in Fig.1. As can be seen in Fig. 2, the production rate of OH radicals slightly lessens with increasing pH in the Fricke solution. The higher level of ferric ions promoted the production of OH radicals in the Fricke solution, and it may be ascribed to the participation of ferric ions in Fenton reactions to enhance the catalytic effect. In Fig.3, the downgrade trend of OH radical production with increasing pH was observed, but this trend became vague as ultrasonic strength less than 0.32 watt/cm$^2$-cm$^3$.

![Figure 1](image1.png)

(a) The growth of Fe$^{3+}$ concentration in a Fricke solution with (a) a low initial ferric level, and (b) a high initial ferric level under 0.47 watt/cm$^2$-cm$^3$ ultrasonic irradiation.

![Figure 2](image2.png)

(b) The dependence of pH on the formation of ultrasound-induced OH radicals at different initial ferric levels by the measurement of Fricke dosimeter.
**H$_2$O$_2$ Indirect Measurement**

Under ultrasonic irradiation at 0.4 ± 0.05 watt/cm$^2$cm$^{-3}$, there exists a linear relationship between the produced H$_2$O$_2$ concentration and the irradiation time. All experiments showed the R-square values greater than 0.9, and the regression slope corresponded to the production rate of H$_2$O$_2$ by the iodide method. Figure 4 showed the production rate of H$_2$O$_2$ oscillating between 0.74 and 1.47 µM/min at different solution pHs. The H$_2$O$_2$ indirect measurement was repeated at least twice at each solution pH, and the highest and the lowest values also presented in Fig. 4. Based on the result of H$_2$O$_2$ indirect measurement, there is no upgrade or downgrade trend of H$_2$O$_2$ production changing with the solution pH. However, the moving curve in Fig. 4 indicated that the strong basic (pH > 11) environment seems to be unfavourable for the production of ultrasound-induced H$_2$O$_2$.

![Graph of pH dependence on ultrasound-induced OH radicals production rate](image-url)

**Figure 3.** The dependence of pH on the formation of ultrasound-induced OH radicals at different ultrasonic strengths by the measurement of Fricke dosimeter.

![Graph of pH dependence on H$_2$O$_2$ production rate](image-url)

**Figure 4.** The dependence of pH on the formation of ultrasound-induced H$_2$O$_2$ by the iodide method.
Figure 5. The pseudo first-order kinetic plot of p-CBA probe compound at different pH.

Figure 6. The dependence of pH on the formation of ultrasound-induced OH radicals by the measurement of p-CBA probe compound.

Figure 7. The influence of ultrasonic strength on the production of OH radicals by the measurement of Fricke dosimeter.
**p-CBA Probe Compound Detection**

As using p-CBA as probe compound to detect the production of OH radicals, the concentration of OH radicals in solution is assumed reaching steady-state. The production rate of OH radicals can be obtained according to eq. (9).

\[
-d[p\text{-CBA}] / dt = k \ [p\text{-CBA}] \ [OH^*] 
\]  

(9)

Figure 5 provided the pseudo first-order kinetic plot that experimental data did not fit the regression line well. The regression slope corresponded to the production rate of OH radicals by the p-CBA probe compound detection method. Figure 6 showed the production rate of OH radicals oscillating between 0.048 and 0.0122 min\(^{-1}\) at different solution pHs. The p-CBA probe compound detection was repeated at least twice at each solution pH, and the highest and the lowest values also presented in Fig. 6. Based on the result of p-CBA probe compound detection, there is no upgrade or downgrade trend of OH production rate changing with the solution pH. The possible explanation is that the measured production rate of OH radicals in solution is dynamically varied due to not reaching the steady-state condition. Another clarification was regarding to the low dissolubility that the homogeneous solution did not achieved affecting the contact of the p-CBA molecule and the cavitation microbubbles.

**CONCLUSIONS**

In this study, all three methods of radical detection have confirmed the generation of OH radicals by ultrasonic irradiation. Among three employed methods, Fricke dosimeter detection and hydrogen peroxide indirect measurement are more reliable due to their R-square values of linear regression greater than 0.9. The application of Fricke dosimeter detection is limited to the acidic solution (pH < 4). The strong acidic condition and a high level of initial ferric concentration can improve the generation of ultrasound-induced OH radicals. In the Fricke solution, the production rate of OH radicals was increased with the strength of ultrasonic irradiation. Figure 7 illustrated that the threshold of ultrasonic strength is 0.16 watt/cm\(^2\)-cm\(^3\) in order to initiate the radical-forming mechanisms. Comparatively, hydrogen peroxide indirect measurement can be applied in a wide pH range. However, the production of H\(_2\)O\(_2\) by ultrasonic irradiation might be inhibited as the solution pH reaching 11. It is implicated that the favourable pH condition is varied for the production of OH radicals and H\(_2\)O\(_2\). By using p-CBA probe compound detection, the reliability of measurement is poor because of its worse R-square values of linear regression. Thus, the deduction of pH affecting the production rate of OH radicals is not persuasive according to p-CBA probe compound detection.

**ACKNOWLEDGEMENTS**

This work was partially supported by the National Science Council (NSC), Taiwan, R.O.C. under Grant No. NSC-94-2211-E-168-008. The financial support on the establishment of analytical instruments from Department of Environmental Engineering, Kun Shan University was especially thanked.

**REFERENCES**


