Generation of Radicals using Discharge inside Bubbles in Water for Water Treatment

By
Tomoaki Miichi*, Nobuya Hayashi**, Satoshi Ihara**, Saburoh Satoh** and Chobei Yababe**

Abstract: A new method for a water treatment utilizing radicals produced by a discharge inside bubbles in water is proposed. Radicals with short lifetime (atomic oxygen and OH radical) are used effectively for the water purification because those are generated by discharge inside bubbles in water. OH radical production was confirmed by a light emission of the discharge using the spectroscopic technique. Dissolved ozone concentration of about 0.3 mg/l was obtained when oxygen was used as a bubbling gas. Decolorization process of indigo solution by a discharge inside bubbles in water was investigated.

Key words: Ozone, OH radical, Discharge inside bubbles in water

1. Introduction

Recently, ozone has been utilized for the purification of water because it is a strong oxidizing agent without side effects. However, main disadvantage of the ozonation is the higher technological cost than another purification method. Ozone and radicals such as atomic oxygen and OH radical with the short lifetime have very strong oxidation ability. We have proposed a new type of discharge method “discharge inside bubbles in water”, operating in a bubbled water in order to use not only ozone but also atomic oxygen, OH and the other radicals for water treatment effectively. The principal advantages of this method are as follows:

1. The additional equipment for a radical production is not required.
2. The short-life-time radicals can be effective for the water purification since the conducting tube between the reactor and the radical generator, in which they are decomposed, is not required.

In our previous work, a discharge using plane electrodes was observed in each bubble of nitrogen, helium and air, respectively[1-3]. Generally, polluted water has a small electric resistance, thus, the high voltage pulse with rapid rise time and short time duration is required to avoid the energy loss by a Joule heating of water. For that reason, a pulsed-power generator was set off.

In this report, generation of active radicals such as ozone, OH radicals and hydrogen peroxide was studied using the discharge inside bubbles in water. In order to confirm the fundamental process of purification, decolorization of indigo solution by this method was also studied. The treatment ability of decolorization is clarified by the light absorption method.

Received May 1, 2002
* Venture Business Laboratory
** Department of Electrical and Electronic Engineering, Faculty of Science and Engineering
©Saga University.

2. Experimental apparatus and method

The experimental apparatus, as illustrated in Fig. 1, consists of a pulsed-power generator, a water vessel, a bubbling tube, and plate electrodes. The magnetic pulse compression pulsed-power-generator was employed as a repetitive power supply. This generator can be operated at the maximum pulse repetition rate of 200 pulses per second (pps). A water vessel is filled with pure water (500 ml). The diameter of electrodes with round shape was 75 mm and gap length between them was 7.5 mm. The bubbling tube was located under electrodes. The diameter of the bubbles generated by bubbling tube was approximately 1.5 mm. The number of bubbles increases with the bubbling gas flow rate.

Fig. 1. Schematic diagram of experimental apparatus.

High voltage was applied at the moment when bubbles were passing through the discharge region between electrodes. In this experiment, the dissolved ozone
concentration was measured at discharge period from 5 to 45 min using the ozone monitor (DR/4000: HACH, indigo method).

The emission spectrum from excited OH radicals was measured using a spectroscopic technique, as shown in Fig. 2. The discharge light was taken out from the quartz glass window installed on the side of the water vessel. This light was collected by the lens to a slit of the spectrometer (monochromator). The output of photomultiplier was recorded by an oscilloscope (TDS380: Tektronix) as a light intensity waveform. A light intensity was obtained as the peak value of the output waveform, which was averaged over 256-shots by the oscilloscope.

![Diagram of spectroscopic technique](image)

Fig. 2. Schematic diagram of spectroscopic technique.

The experiment of decolorization was performed using indigo solution (50mg/l). In order to clarify the treatment ability of the method, light absorption spectra of indigo solution after the discharge process were measured by a spectrophotometer (DR/4000: HACH).

Applied voltage between electrodes and circuit current waveforms were measured by the high voltage probe (EP-100K: Pulse Electronic Engineering Co. Ltd.) and the rogowski coil (Model-110: Pearson Electronics Inc.), respectively.

3. Experimental results

3.1 Characteristics of discharge inside bubbles

Figures 3 indicate typical waveforms of applied voltage between electrodes (a) and circuit current (b) during a single operation without gas bubbling. A light emission of discharge did not appear in water. In this case, the discharge system is considered to be an electrical circuit with a capacitor and a resistance, connected in parallel. Therefore, the current waveform shows damping oscillation.

In the case of bubbling, experimental conditions were as follows: the bubbling gas was oxygen and the applied voltage peak was 22 kV. A discharge appeared inside bubbles when the bubbling gas flow rate reached 0.3 l/min, and below this value it was not possible to obtain a discharge.

![Waveforms of applied voltage and circuit current](image)

Figs. 3. Waveforms of applied voltage and circuit current without gas bubbling.

Figure 4 illustrates a discharge inside bubbles observed by open-shutter photograph. Most of discharges occur inside bubbles, which faced to electrodes, and a single streamer is formed in the bubble.

![Open-shutter photograph of discharge inside bubbles](image)

Fig. 4. Open-shutter photograph of discharge inside bubbles.

3.2 Ozone generation

Figure 5 shows the dependency of the dissolved ozone concentration in water on the discharge period. The pulse repetition rate, the peak value of applied voltage and the gas flow rate were 100 pps, 22 kV, and 0.3 l/min, respectively. The bubbling gas was oxygen. It can be seen that the ozone concentration is saturated in about 4 min. That saturation value is about 0.3 mg/l. Also the ozone concentration in exhaust gas was 4.3 g/Nm³ in this experimental condition. The detection of ozone proves the generation of atomic oxygen inside bubbles, and suggests that atomic oxygen can be used for water purification using this technique.
3.4 OH radicals detection

Figure 6 indicates the spectrum of light emission from excited OH radicals measured by the monochromator. The pulse repetition rate, the peak value of applied voltage and the gas flow rate were 100 pps, 20 kV, and 0.3 l/min, respectively. The bubbling gas was argon. The emission intensity peak observed at 307 nm and 309 nm confirmed that the transition of OH ($^2\Sigma \rightarrow ^2\Pi$) took place\(^{(4)}\). It is thought that OH radicals were produced by a discharge inside bubbles via the following reaction\(^{(5)}\):

$$e + H_2O \rightarrow e + H + OH.$$  

When the bubbling gas was oxygen, OH band spectrum could not be detected because discharge became unstable in comparison with the case of argon.

By the way, when bubbling gas is oxygen, it is expected that the following reaction occurs, too, in bubbles\(^{(6)}\):

$$O + H_2O \rightarrow 2OH.$$  

However, OH radicals formed by this chemical reaction can't be detected with this spectroscopic technique because this reaction doesn't occur strong light emission.

When the bubbling gas was oxygen, the hydrogen peroxide concentration was measured at discharge period using the test strip (Peroxid-Test: MERCK). Figure 7 illustrates the dependency of the hydrogen peroxide concentration on the discharge period. The pulse repetition rate, the peak value of applied voltage and the gas flow rate were 100 pps, 22 kV, and 0.3 l/min, respectively. The hydrogen peroxide concentration increases with the discharge period. OH radicals recombine to form hydrogen peroxide\(^{(6)}\). Therefore the detection of hydrogen peroxide proves the generation of OH radical inside bubbles.

3.5 Decolorization of indigo solution

In order to confirm the purification process of polluted water including organic compounds, we observed decolorization of indigo solution using discharge inside bubbles in water. Experimental conditions were as follows: the applied voltage peak was 22 kV and the pulse repetition rate was 100 pps. The bubbling gas was oxygen. The discharge period was changed from 5 to 20 min.

Figure 8 shows light absorption spectra of indigo solution, where the flow rate of the bubbling gas was 0.3 l/min. The light absorption peak of indigo was observed at 612 nm. The peak value of the absorption decreases with increase of the discharge period. A change in the color was also confirmed by the visual observation.

Figure 9 indicates the dependency of the light absorption peak on discharge period. The decrease rate of the peak value increased with the bubbling gas flow rate due to the increase of number of bubbles in the discharge region.
Fig. 8. Light absorption spectra of indigo solution for different discharge period.

Fig. 9. Dependency of light absorption peak (612 nm) on discharge period.

The structural formula of indigo is illustrated in Fig. 10. It is known that it has the structure called H-type chromophor. A special optical absorption character is brought by this molecule structure, and indigo solution shows blue. Indigo is decolorized by breaking the chemical structure of this chromophor. In this experiment, ozone and OH radicals were generated by this method and we observed decolorization of indigo solution.

The dissolved ozone concentration in water saturated at about 0.3 mg/l within a few minutes after the discharge treatment started.

The formed OH radicals were directly detected by the spectroscopic technique. The hydrogen peroxide in water concentration increased with the discharge period.

Indigo solution was decolorized by a discharge inside bubbles in water. The peak value of the absorption decreases with increase of the discharge period.

Acknowledgments

This work was partly supported by the Venture Business Laboratory of Saga University. Part of this work was supported by a Grant-in Aid for Scientific Research of the Ministry of Education, Science, Sport and Culture, Japan.

References