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Effective utilization of bromine in seawater: Application to water purification technique with supplying ozone minute-bubbles

Salt Production

Keywords: Minute-bubbles, Seawater, Bromine, Ozone, Water purification

Abstract

To create the comprehensive utilization system of seawater resources based on the salt production process, the utilization method of dissolved bromine (Br) in the discharge concentrated brine of salt manufactory in Japan was developed. In the existence process, Br is recovered by a blowout method with Cl_2 gas bubbling from the removed K^+ bittern as the liquid Br_2, which is used to the chemical reagents in fine chemical field so as the catalyst, medicinal drug, inorganic material and pesticide. On the other hand, the oxidation products of Br has the various forms so as the hypobromous acid (HBrO), bromous acid ($HBrO_2$) and bromic acid ($HBrO_3$), and it's application for the water purification process can be expected. For example, HBrO has a highest oxidation potential for the organic compounds, is obtainable by the ozone (O_3) oxidation reaction of dissolved Br in aqueous solution.

In this paper, when ozone/oxygen (O_3/O_2) minute-bubbles were supplied to seawater or NaBr, the influences of the dissolved each salt on the generation of oxygen species (OS) were investigated. The concentration of oxygen species in aqueous solution was determined by colorimetric method. As the results, the solution concentration of total oxygen species (C_{OS}) in modified seawater or 1.0 mmol// NaBr solution during the supplying O_3/O_2 minute-bubbles was increased approximately 1.3-times compared with ion-exchanged water at a reaction time of 120 min. Additionally, when the O_3/O_2 minute-bubbles were supplied into 5.0 mmol// methylene blue (MB) solution, the initial decomposition rate of MB was increased approximately 1.2 times by adding NaBr with concentration of 1.0 mmol//. Consequently, it seems that the improvement of the organic compound decomposition was induced by presence of Br^- ion during O_3/O_2 minute-bubble supply.

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Introduction

In Japan, the development of the recovery and upgrading method for the dissolved inorganic resource from the concentrated seawater discharged is desired in order to improve the process efficiency in the salt industry [1,2]. Especially, because the bromine (Br) in the concentrated brine (bittern) coming from salt manufacture discharge has been enriched to higher than 10 times for seawater, which is effective for raw material of Br. Generally, Br, as Br_2 gas, is recovered by a blowout method from bittern or seawater, which is used to the chemical reagents in fine chemical field so as the catalyst, refrigerant, medicinal drug, inorganic material and pesticide [3,4]. The blowout method is that Br_2 gas is obtained by bubbling chlorine (Cl_2) gas into seawater, and free Br_2 gas obtained is then treated with alkaline or sulfur gas. This method, however, is required Cl_2 gas, which is corrosive and toxic, and thus there have the issues which should be cleared from the viewpoint of safety operation. Alternative utilization method of Br is therefore one of the important topics for not only the salt industry in japan but also fine chemical industry [4].

In this study, we focus the reaction between Br ion and ozone (O_3) in seawater or bittern. The oxidation products of Br such as active species has the various forms so as the hypobromous acid (HBrO), bromous acid ($HBrO_2$) and bromic acid ($HBrO_3$) [5], and it's application for the water purification process can be expected. For example, HBrO has a highest oxidation potential for the organic compounds, is obtainable by the O_3 oxidation reaction of dissolved Br in aqueous solution. Additionally, minute-bubble technique were applied to O_3 oxidation reaction of dissolved Br, because the minimizing the bubble size brings about the acceleration of mass transfer and gas absorption by increasing the gas-liquid interfacial area, an increase in the average residence time of the bubbles by decreasing the buoyancy, and the occurrence of interactions near the gas-liquid interface caused by the electrification of the minute-bubbles [1,6].

In this paper, as fundamental investigation, O_3 solubility behavior was evaluated when O_3 minute-bubbles with different bubble diameter (d_{bbl}) were continuously supplied into water at various solution temperature (T_S) and pH. And then, the effect of O_3 minute-bubble supply on the organic compound decomposition in NaBr solution or artificial seawater was examined.

2. Experimental

2.1 Experimental apparatus

Figure 1 shows the experimental apparatus was equipped with a gas flow controller, a dielectric barrier discharge (DBD) reactor, a transformer, a pH meter and a self-supporting bubble generator. Oxygen (O_2) was flowed to the DBD reactor by a mass-flow meter, and a voltage was applied using a transformer to convert to O_3. The gas flow rate of oxygen (F_{O2}) based on unit per volume was controlled at 1.12 mmol/(*l*•min), and incident voltage for DBD device maintained at 80 V. Then, the produced O_3/O_2 mixture was flowed to a bubble generator. The gas flow rate of ozone (F_{O3}) based on unit per volume which measured by using UV ozone monitor (EG-600, EBARA JITSUGYO Co., Ltd.) was 0.14 mmol/(*l*•min). O_3/O_2 minute-bubbles with d_{bbl} of 50 μm were generated using a self-supporting bubble generator by increasing the impeller shear rate under reduced pressure, with the rotation rate maintained at 1500 min^{-1}. For comparison, the bubbles with d_{bbl} of 800 or 2000 μm were obtained using a dispersing-type generator (bore diameter of diffuser plate: 65 - 160 μm).

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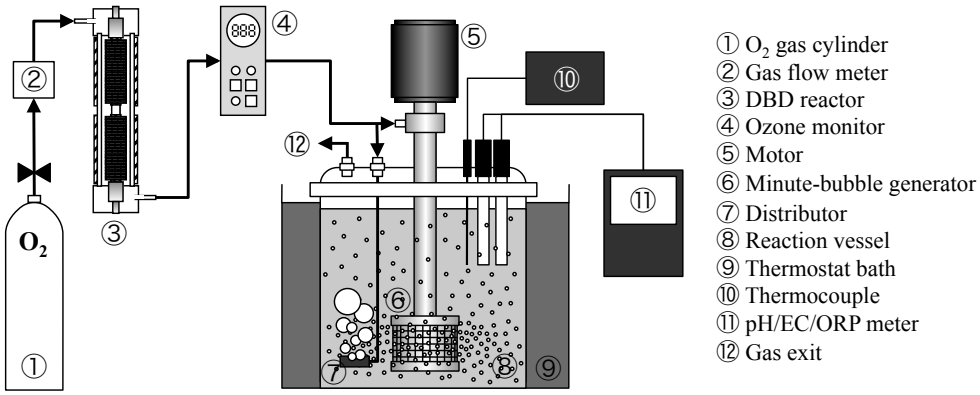

Fig. 1 Experimental apparatus equipped with ozonizer and minute-bubble generator

2.2 Measurement of the concentration of total oxygen species in water

To evaluate the effect of d_{bbl} on the generation of the total active species in water, O_3/O_2 minute-bubbles with d_{bbl} of 50, 800 or 2000 μm were continuously supplied to 800 m*l* of water at various T_S and solution pH. T_S was set at 293 - 323 K, and the solution pH maintained at the range between 3.0 and 11.0 by adding the NaOH or HCl aqueous solution during O_3/O_2 bubble supply. A reaction time (t) was set within 120 min. The concentration of the total oxygen species (C_{OS}) in water was measured by colorimetric method using an ozone meter (O_3-2Z, KASAHARA RIKA Co., Ltd.), because the O_3 test reagent react with both O_3 and other oxygen species such as OH・, HBrO, and BrO^- ion.

2.2 Decomposition of methylene blue

O_3/O_2 bubbles with a d_{bbl} of 50 μm were continuously supplied to 800 m*l* of 5.0 mmol/*l* methylene blue (MB) solution included 5.0 mmol/l NaBr. the concentration of MB was measured using UV-vis spectrophotometer (UV-mini 1240, Shimadzu).

3. Experimental results and Discussion

3.1 Effects of minimization bubble diameter on concentration of total oxygen species in water

In order to clarify the influence of minimizing the bubble diameter on the generation of oxygen species (OS) in water, the O_3/O_2 bubbles at a d_{bbl} of 50 - 2000 μm were continuously supplied to ion-exchanged water. **Fig. 1** shows the time changes in C_{OS}, when O_3/O_2 bubbles with d_{bbl} values of 50, 800 and 2000 μm were supplied to the ion-exchanged water at T_S of 298 K. In either d_{bbl}, C_{OS} increase with increasing t, and C_{OS} at d_{bbl} of 40 μm was higher than that of 2000 μm at all values of t. This result causes because the gas absorption and OH・ generation with hydration of dissolved O_3 were accelerated by the minimization of O_3/O_2 bubble diameter [7]. Moreover, in the range of over 60 min, C_{OS} was maintained a constant value, which value increased with decreasing d_{bbl}. It seems that O_3 gas solubility for the water as the apparent steady-state value

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was increased by the increase in the inner pressure and residence number of O_3/O_2 minute-bubbles.

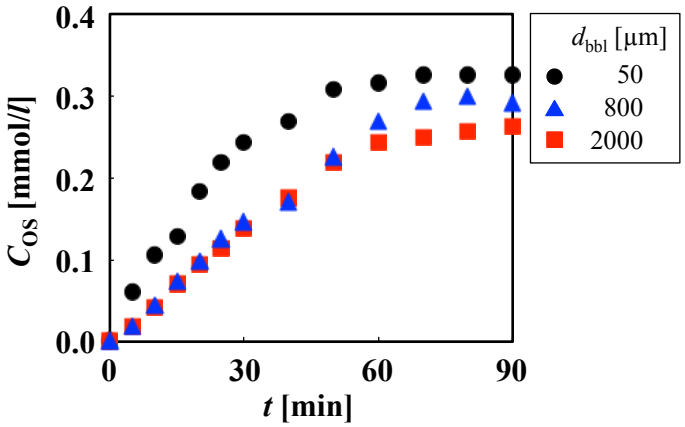

Fig. 1 Comparison of the time changes in the total concentration of the oxygen active species

3.2 Effects of solution temperature and pH on concentration of total oxygen species in water

When O_3/O_2 minute-bubbles were supplied to HCl and NaOH aqueous solutions with different solution pH at T_S of 298 K, the time changes in C_{OS} is shown in **Fig.2 a)**. C_{OS} showed higher value with decreasing solution pH at a solution pH at all values of t, and the initial increasing rates for C_{OS} (r_{OS}) at solution pH of 3.0, 6.0 or 11.0 were 15.4, 12.1 and 0.02 μmol/(l・min), respectively. A higher solution pH enhance to the reaction of the dissolved ozone molecule and OH^- ion near the minute gas-liquid interfaces around O_3/O_2 minute-bubbles, and C_{OS} reduction was induced by radical chain reaction from O_3 [8].

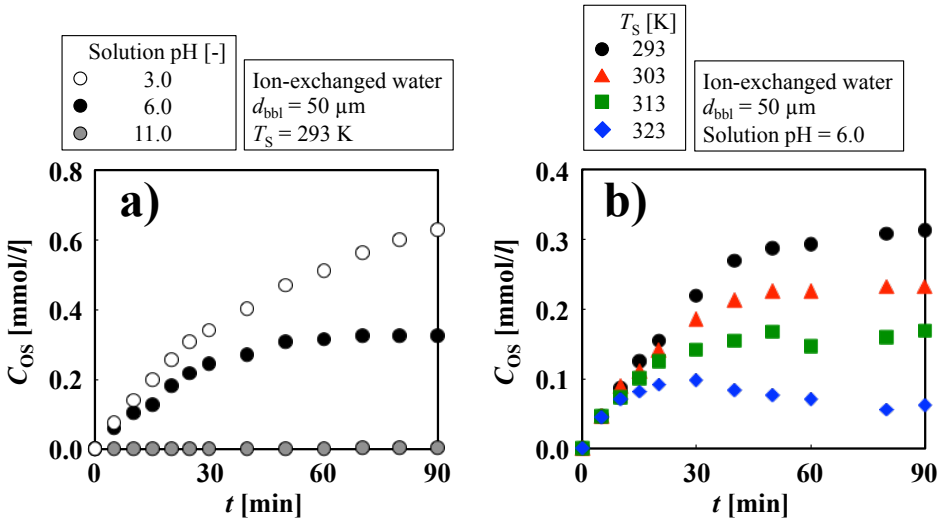

Fig. 2 Comparison of the time changes in the total concentration of the oxygen active species under different conditions of a) solution pH and b) temperature.

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Fig.2 b) shows the time changes in C_{OS} in the temperature range of 298 - 323 K at a constant solution pH of 6.0. A constant value of C_{OS} was higher at a lower temperature, because the temperature rising was reduced the gas solubility of O_3 for water. This tendency of O_3 is consistent with general knowledge about gas dissolution to a liquid [9].

3.3 Evaluation of concentration of total oxygen species in seawater

To evaluate the generation of OS in aqueous solution including the numerous ions, O_3/O_2 minute-bubbles with d_{bbl} of 50 μm were continuously supplied to the modified seawater. For comparison, O_3/O_2 minute-bubbles were supplied also to ion-exchanged water or 1.0 mmol// NaBr solution. **Fig. 3 a)** shows the time changes in C_{OS} in each aqueous solution. Both the constant values of C_{OS} in the modified seawater and 0.1 mol// NaBr solution reached to 0.43 mol//, which were higher than the case of ion-exchanged water. Then, the time change in solution pH during O_3/O_2 bubble supply in each aqueous solution is shown in **Fig. 3 b)**. When O_3/O_2 minute-bubbles were supplied into each aqueous solution, the solution pH in the modified seawater or 0.1 mol// NaBr solution was increased rapidly from 5.5 to approximately 9.0, although the solution pH in ion-exchanged water was reduced rapidly to approximately 5.0. Generally, in the case where the organic compounds in waste water included Br are oxidative decomposed using O_3 bubbling method, the solution pH shift to alkaline region by the generation of oxoacid as a by-products (hypobromous acid, bromic acid etc.) [10,11]. Therefore, the increase of C_{OS} was caused by oxidative reaction of the dissolved Br- ion in the modified seawater or 0.1 mol// NaBr solution. However, the contribution ratio of Cl^- and Na^+ ions for C_{OS} increase was comparatively low, because the increase of C_{OS} by O_3/O_2 minute-bubble supply was not confirmed in NaCl solution.

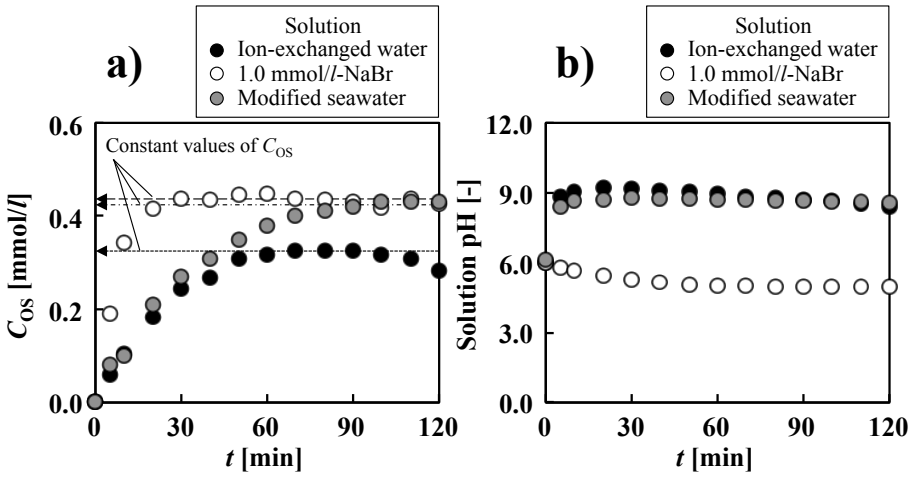

Fig. 4 Comparison of the time changes in the total concentration of the oxygen active species in each aqueous solution.

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3.4 Effects of Br- ion on methylene blue decomposition with O_3/O_2 minute-bubble supply

In order to confirm the improvement effects of organic compound decomposition by the acceleration of OS generation in solution with Br ion, O_3/O_2 minute-bubbles were continuously supplied into methylene blue solution with NaBr addition. The time changes in the decomposition ratio of methylene blue ($C_{MB}/(C_{MB})_0$) in MB solution and MB/NaBr solution are shown in **Fig. 5**. $C_{MB}/(C_{MB})_0$ represents from MB concentration at each time against the initial MB concentration. $C_{MB}/(C_{MB})_0$ was decreased with progress the reaction time regardless NaBr addition. Additionally, the initial decreasing rates of C_{MB} in 0.0 mmol/*l* and 5.0 mmol/*l* NaBr solution were 31 μmol/(*l*・min) and 26 μmol/(*l*・min), respectively. These results indicate the generation of oxoacid such as hypobromous acid by oxidative reaction of Br- ion with O_3/O_2 minute-bubble supply was enhanced the organic compound decomposition. Consequently, when O_3/O_2 minute-bubble were supplied into seawater, the organic compound decomposition can be improved by not only the acceleration of O_3 dissolution and OS generation with minimizing bubble diameter, but also the generation of oxoacid from Br ion.

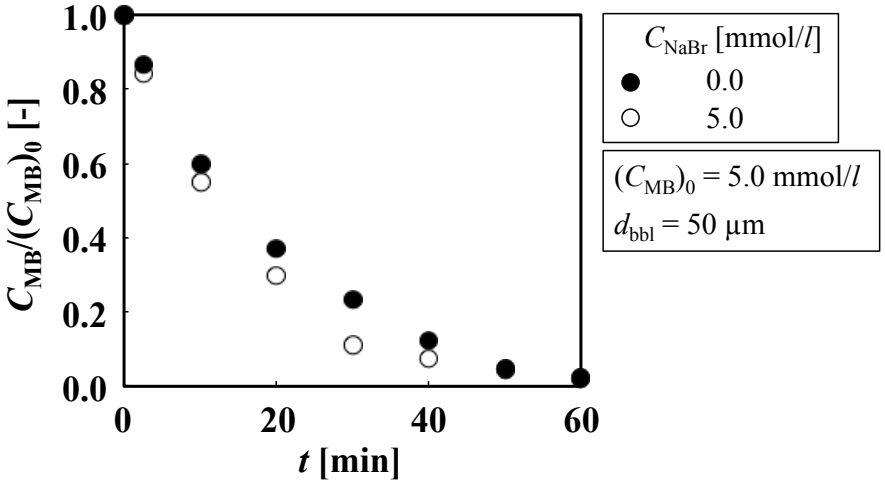

Fig. 5 Comparison of the time changes in methylene blue concentration in MB solution and MB/NaBr solution.

Conclusions

For the effective utilization of bromine in seawater, the improvement technique of organic compound decomposition by the acceleration of oxygen species generation using O_3/O_2 minute-bubble injection into seawater was investigated. This investigation revealed the following;

1) O_3 gas solubility for the water increased with decreasing d_{bbl} and solution temperature.

2) At a higher solution pH, the concentration of oxygen species was reduced by radical chain reaction from O_3.

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3) The increase of C_{OS} was caused by oxidative reaction of the dissolved Br- ion in the modified seawater or 0.1 mol// NaBr solution.

4) The generation of oxoacid such as hypobromous acid by oxidative reaction of Br- ion with O_3/O_2 minute-bubble supply enhanced the organic compound decomposition.

Acknowledgements

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