Original Article

Availability of Seawater as A Chloride Source for UV/electro-chlorine Advanced Oxidation Process

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ABSTRACT

This study reports the availability of seawater as an economical chloride (Cl^-) source for the UV/electro-chlorine process from the viewpoints of advanced oxidation performance and unwanted by-product formation of chlorate ion (ClO_3^-) and bromate ion (BrO_3^-). In the electrochemical oxidant production stage, the oxidant production rate in diluted seawater containing 30 mM Cl^- was 21% lower than that in the NaCl solution due to coexisting electrolytes in the seawater. The ClO_3^- formation during electrolysis was successfully inhibited under acidic conditions and BrO_3^- formation was not detected in the diluted seawater. However, ClO_3^- and BrO_3^- were steadily formed in the undiluted seawater electrolysis, even when the initial pH value was set to 3. The oxidant utilization efficiency for 1,4-dioxane removal during UV irradiation was not deteriorated in the diluted seawater but decreased under basic conditions due to the radical scavenging effect of electrochemically produced free bromine and free chlorine. As a result, the formation of BrO_3^- and ClO_3^- was enhanced under basic conditions, whereas BrO_3^- formation was completely inhibited at an initial $\text{pH} \leq 5$. Consequently, the diluted seawater was thought to be available as a Cl^- source for the UV/electro-chlorine process if an acidic condition was maintained throughout the operation.

Keywords: advanced oxidation process, 1,4-dioxane, free chlorine, seawater electrolysis, UV photolysis

INTRODUCTION

Free chlorine can be photolyzed into a hydroxyl radical ($\text{HO}^\bullet$) and a chlorine radical ($\text{Cl}^\bullet$) by ultraviolet radiation (UV) as follows [1]:

Recently, these photochemical reactions have been applied in the water treatment field as an advanced oxidation process called the “UV/chlorine process”. The number of published papers on UV/chlorine processes has grown rapidly in the last several years [2]. As chlorination and UV treatment are widely used in the water treatment field, technical bases for unit operations constituting UV/chlorine process have been

established. This is an advantage of UV/chlorine process compared to other advanced oxidation processes.

In most UV/chlorine processes, free chlorine is fed as a reagent, such as hypochlorite solution and chlorine gas. However, chlorine reagents are dangerous goods and, for example, classified by the United Nations as corrosive substances (class 8) for hypochlorite solution and toxic gases (class 2.3) for chlorine gas. Therefore, the onsite generation of free chlorine by the anodic oxidation of chloride ions (Cl^-) (reactions (3) and (4)) is an attractive alternative chlorine source for UV/chlorine systems without the stock management of dangerous goods. Studies have demonstrated the efficacy of the UV photolysis of electrochemically generated free chlorine (UV/electro-chlorine) for removing organic contaminants [3–6]. In these studies, UV/electro-chlorine processes were operated at a Cl^- concentration of 15–300 mM, which was almost

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equal to or higher than the Cl^- concentration in concentrated domestic wastewater (14 mM) [7]. Thus, a drawback of the UV/electro-chlorine process is that it requires a chloride addition for electrochemical chlorine production when wastewater does not contain Cl^- sufficiently; however, chlorides, such as industrial grade sodium chloride, are safer and more economical than chlorine reagents.

In the case of wastewater treatment plants constructed in coastal areas, seawater contains ca. 560 mM of Cl^- and is an attractive candidate for an economical Cl^- source [8]. However, seawater contains various anions in addition to Cl^- , such as sulfate, bicarbonate, and bromide (Br^-), some of which act as radical scavengers [9]. Therefore, the use of seawater may have a negative impact on the advanced oxidation performance of the UV/electro-chlorine process, and the inhibition of radical reactions by bicarbonate and Br^- has been reported in several papers on UV/chlorine systems [10,11]. In this paper, the availability of seawater as a Cl^- source for the UV/electro-chlorine process was discussed from the viewpoints of advanced oxidation performance and byproduct formation of chlorate (ClO_3^-) and bromate (BrO_3^-) using artificial and real seawater.

MATERIALS AND METHODS

Materials

1,4-Dioxane (stabilizer free, FUJIFILM Wako Pure Chemical, Osaka, Japan) was selected as a model organic pollutant and is stable against electrolysis, free chlorine, and UV radiation [5]. Thus, 1,4-dioxane acts as a radical probe. The concentration of 1,4-dioxane at the onset of UV irradiation was set to 3.0 mM. Such a high concentration of 1,4-dioxane is sometimes observed in practical industrial wastewaters [12,13].

Artificial seawater was prepared in accordance with "Preparation of Substitute Ocean Water" in ASTM standards D1141-98 [8] using sodium chloride, sodium sulfate, sodium bicarbonate, sodium fluoride, magnesium chloride hexahydrate, calcium chloride, potassium chloride, potassium bromide, strontium chloride hexahydrate, and boric acid. The pH value of the artificial seawater was adjusted to 8.2, by adding 0.1 N sodium hydroxide solution. The artificial seawater contains Na^+ : 480 mM, Mg^{2+} : 54.6 mM, K^+ : 10.2 mM, Ca^{2+} : 10.5 mM, Sr^{2+} : 0.16 mM, Cl^- : 560 mM,

SO_4^{2-} : 28.8 mM, $\text{HCO}_3^- + \text{CO}_3^{2-}$: 2.4 mM, Br^- : 0.85 mM, $\text{B}(\text{OH})_3 + \text{B}(\text{OH})_4^-$: 0.44 mM, and F^- : 0.07 mM. To elucidate the influence of Br^- , Br^- -free artificial seawater was prepared by removing potassium bromide from the artificial seawater. An additive rate of seawater to wastewater should be lowered to avoid an excessive increase in wastewater volume. In this study, a diluted seawater with 30 mM Cl^- was prepared by adding the artificial seawater into distilled and deionized water at an additive rate of 5.36%, because a previous study showed that 30 mM Cl^- was an inflection point of current efficiency of electrochemical chlorine production [5]. All chemicals except 1,4-dioxane were of analytical grade, supplied from Nacalai Tesque (Kyoto, Japan), and used without further purification.

Real seawater was sampled at Suma Beach (NL. 34.6417376, EL. 135.1173584) and the Old Port of Tadaoka (NL. 34.500757, EL. 135.382327) on January 24th and 25th, 2020. The pH values and Cl^- concentrations of the real seawater were 8.12 and 612 mM for the Suma sample and 7.94 and 549 mM for the Tadaoka sample, respectively. The real seawaters were filtered with a glass fiber filter (Whatman GF/B, Cytiva, Tokyo, Japan) before each run.

Equipment

The reactor used in this research was the same as that used in a previous study [14] and consisted of a photochemical reactor with an effective volume of 1.8 L and an undivided electrolytic flow cell with a plate cathode made of stainless steel (SUS 316, Japanese Industrial Standard) and a plate-dimensionally stable anode with a coating based on iridium oxide (JP-330, De Nora Permelec, Fujisawa, Japan) which is designed for chlorine evolution by dilute brine or seawater electrolysis. The effective electrode area was 21.0 cm^2 for each electrode, and the interelectrode gap was 0.11 cm. The photochemical reactor was made of glass (13 cm in diameter and 20 cm in height) and equipped with a low-pressure mercury vapor lamp (UVL20PH-6, Sen Lights, Toyonaka, Japan), which was housed in a quartz jacket with a water jacket and positioned at the center of the reactor. The total UV irradiance at 254 nm outside the jacket was 1.48 ± 0.03 W (average $\pm$ sample standard deviation, $n = 3$). The solution was circulated between the photochemical reactor and the electrolytic flow cell with a peristaltic pump (RP-1000, EYELA, Tokyo, Japan) at a flow rate of 156 mL/min, which is equivalent to a linear velocity of 23.6 cm/s on electrodes. A direct current power supply (AD-8735D, A&D, Tokyo, Japan) was used for the electrolytic flow cell. As it was reported that a current density lower than 30 mA/ cm^2 affected

the current efficiency of electrochemical chlorine production [5,15], the power supply was operated in the galvanostatic mode with an electrolytic current of 1.00 A, which is equivalent to a current density of 47.6 mA/cm².

Experimental procedure

UV/electro-chlorine treatment

Diluted artificial seawater, diluted real seawater, or sodium chloride (NaCl) solution at a Cl⁻ concentration of 30 mM was poured into the reactor and circulated between the photochemical reactor and the electrolytic flow cell using the peristaltic pump. The direct current power supply was switched on for electrochemical chlorine production without UV irradiation. This step is called “electrolysis stage”. After 60 min of electrolysis, the power supply was turned off, and 1,4-dioxane was added to the solution at a final concentration of 3.0 mM. The solution pH was adjusted to a setting value by adding sulfuric acid or sodium hydroxide, if necessary. Next, UV irradiation was applied without electrolysis for 60 min. This step is called “UV irradiation stage”. The solution in the reactor was sampled every 10 min for chemical analyses.

Electrochemical chlorine production

The effect of pH on electrochemical chlorine production was explored to control the formation of unwanted oxyhalides, such as ClO₃⁻ and BrO₃⁻. Undiluted artificial seawater (560 mM Cl⁻), diluted artificial and real seawater (30 mM Cl⁻), and sodium chloride solution (30 mM Cl⁻) were applied to the electrochemical chlorine production for comparison purposes. The pH of the solution was adjusted to pH 3–9 by adding sulfuric acid or sodium hydroxide. 1.8 L of the pH-adjusted seawater or sodium chloride solution was poured into the reactor and circulated with the peristaltic pump. Then, the direct current power supply was switched on for electrochemical chlorine production. The electrolysis was continued for 60 min, and the solution was sampled from the reactor at 10 min intervals for chemical analyses.

The production rate of ClO₃⁻ during the electrolytic chlorine production was calculated as follows:

$$Pr = (C_{t+\Delta t} - C_t) V / \Delta t \quad (5)$$

Pr: ClO₃⁻ production rate (μmol/min)

C_t: ClO₃⁻ concentration at time *t* (μM)

Δt: sampling interval (min)

V: reactor volume (L)

Chemical analysis

The concentrations of 1,4-dioxane, free chlorine, ClO₃⁻, and BrO₃⁻, and the pH value of the water samples were measured. The concentration of 1,4-dioxane was determined by high-performance liquid chromatography (HPLC), according to Ito *et al.* [16]. The total residual oxidant (TRO) was measured by the DPD (N,N-diethyl-p-phenylenediamin) colorimetric method, which output the sum of free chlorine and free bromine. The concentrations of ClO₃⁻ and BrO₃⁻ were determined using an ion chromatograph (Dionex ICS-1100, Thermo Fisher Scientific, Waltham, USA) with a chemical suppressor (Dionex CES-500, Thermo Fisher Scientific). The analytical conditions were as follows: Dionex Ion Pac AS-23 column (4 × 250 mm, Thermo Fisher Scientific), mobile phase: 4.5 mM Na₂CO₃ + 0.8 mM NaHCO₃, flow rate of 1.00 mL/min, injection volume of 20 μL, and oven temperature of 30°C. The pH value was obtained by the electrometric method using a pH meter (D-53, Horiba, Kyoto, Japan).

RESULTS AND DISCUSSION

UV/electro-chlorine treatment without pH adjustment

Figure 1 shows the time-course changes in pH values and concentrations of TRO and 1,4-dioxane at the UV irradiation stage. The initial TRO concentration in the diluted artificial seawater was 21% lower than that in the NaCl solution. Thus, the coexisting substances in the artificial seawater affected the electrochemical production of the oxidants. The initial pH value in the case using the NaCl electrolyte was pH 9.2, which was higher than that using artificial seawater (pH 8.7). The initial pH value was determined by the electrolysis stage. The following two causations were responsible for the pH difference: (i) higher buffer action of artificial seawater in comparison with the NaCl solution and (ii) the enhancement of electrochemical chlorine production in the NaCl solution. The anodic chlorine production (reactions (3) and (4)) competes with the electrolytic water discharge (reaction (6)). As the stoichiometric ratios of produced protons (H⁺) to consumed electrons are 0.5 for reactions (3) and (4) and 1 for reaction (6), the enhancement of the anodic chlorine production results in a decrease in H⁺ production at the anode, namely a rise in pH value at the electrolysis stage.

At the UV irradiation stage, UV photolysis of HOCl produces HO[•] and Cl[•] (reaction (1)). These radicals subtract an electron from an electron donor. As a result, HO[•] and Cl[•] are transformed into HO⁻ and Cl⁻, respectively, and the electron

Fig. 1 Time-course changes in pH values and concentrations of total residual oxidant and 1,4-dioxane during the UV irradiation after 60 min electrolysis of the NaCl solution, the diluted artificial seawater, and the Br-free diluted artificial seawater. The initial solution pH was not adjusted. Error bar represents sample standard deviation ($n = 3$).

donor finally produce H^+ . For example, when HOCl acts as an electron donor, the following reactions are established.

Consequently, the overall reaction of reactions (1, 7–10) is as follows:

Thus, the UV photolysis of HOCl finally produces H^+ , which was responsible for the pH decrease during the UV irradiation in **Fig. 1**. In addition, it was reported that 1,4-dioxane attacked by $HO^\bullet$ produced acidic intermediates like glycolic acid and oxalic acid [17,18]. The formation of acidic intermediates was inferred to enhance the pH decrease during the UV irradiation, too.

The removal rate of 1,4-dioxane in the NaCl solution reached 50%, which was higher than that in the diluted artificial seawaters (35% with Br^- and 44% without Br^-). The oxidant utilization efficiency, which is defined as the molar ratio of removed 1,4-dioxane to consumed oxidant during UV irradiation for 60 min, was 0.402 ± 0.022 in the NaCl solution, 0.356 ± 0.023 in the diluted artificial seawater, and 0.416 ± 0.015 in the Br^- -free diluted artificial seawater (average $\pm$ sample standard deviation, $n = 3$). Thus, Br^- lowered the oxidant availability by 11%, whereas coexisting sub-

stances in the artificial seawater except Br^- did not have an inhibitory effect. The difference in initial pH values between the NaCl solution (pH 9.2) and the Br^- -free diluted artificial seawater (pH 8.7) did not influence the oxidant utilization efficiency significantly.

Figure 2 shows the time-course changes in pH values and the concentrations of TRO and 1,4-dioxane in the diluted real seawaters at the UV irradiation stage. The initial TRO concentration and pH in the diluted real seawaters were almost the same as those in the diluted artificial seawater. Thus, the characteristics of electrochemical TRO production did not differ between the artificial and real seawaters. Although 1,4-dioxane removal seems to be enhanced in diluted real seawater during the first 20 min, the changing pattern of the 1,4-dioxane concentration after 30 min did not differ from that in the diluted artificial seawater. Thus, the above discussion on artificial seawater is also true of UV/electro-chlorine treatment in real seawater.

UV/electro-chlorine treatment with pH adjustment

The pH values and concentrations of TRO, 1,4-dioxane, and ClO_3^- during UV irradiation are shown in **Fig. 3**. The changing pattern of pH in the diluted artificial seawater was similar to that in the NaCl solution, although the pH drop in the diluted artificial seawater with initial pH values of 9 and 10 was smaller than that in the NaCl solution because of stronger buffer action derived from carbonate and borate. For initial pH values of no more than 7, the pH value rapidly dropped to approximately 2.5. The initial TRO concentration at initial pH values of 3, 5, and 7 was 3.16 ± 0.06 mM in the diluted artificial seawater and 3.65 ± 0.06 mM in the NaCl

Fig. 2 Time-course changes in pH values and concentrations of total residual oxidant and 1,4-dioxane during the UV irradiation after 60 min electrolysis of the diluted artificial and real seawaters. The initial solution pH was not adjusted.

NaCl solution

Diluted artificial seawater

Fig. 3 Time-course changes in pH values and concentrations of total residual oxidant, 1,4-dioxane, and ClO_3^- during the UV irradiation after 60 min electrolysis of the NaCl solution and the diluted artificial seawater. The solution pH was adjusted just before the UV irradiation.

solution, which were completely photolyzed during the first 20 minutes. The initial TRO is primarily composed of HOCl, because the pK_a of HOCl is 7.44 [19], and the photolysis of HOCl finally produces the same molarity of H^+ such as reaction (11). Accordingly, the production of more than 3 mM of H^+ was responsible for the rapid pH drop.

The time-course change in TRO concentration in Fig.

3 was classified into two groups: (a) the neutral and acidic initial pH group and (b) the basic initial pH group. In group (a), TRO was rapidly photolyzed and completely consumed during the first 20 min but persisted for 30 or 40 min in group (b). The principal species of TRO were HOCl in group (a) and ClO_3^- in group (b), judging from the pK_a of HOCl [19]. As the quantum yield of HOCl at 254 nm is higher than

that of ClO^- [20], HOCl is photolyzed more easily than ClO^- . Thereby, TRO in group (a) was consumed more rapidly than that in group (b).

The behavior of 1,4-dioxane concentration was also divided into the same two groups as the pH change, namely the (a) neutral and acidic initial pH group and (b) basic initial pH group. In the former, the 1,4-dioxane concentration dropped to ca. 1 mM within 20 min and reached a plateau thereafter. In the latter, the 1,4-dioxane concentration decreased slowly and reached a plateau after 30–40 min. As the plateau of 1,4-dioxane concentration agreed well with the time range of the complete consumption of TRO, reactive radicals produced by UV photolysis of TRO were thought to primarily contribute to 1,4-dioxane degradation. The oxidant utilization efficiencies are shown in Fig. 4. The oxidant utilization efficiency decreased under basic initial pH values. HOCl and ClO^- can contribute to reactive radical production but also act as radical scavengers as follows [9,21,22]:

The higher rate constants of ClO^- than of HOCl indicate that the radical scavenging effect of ClO^- is stronger than that of HOCl . Thus, the high reactivity of ClO^- with $\text{HO}^\bullet$ and $\text{Cl}^\bullet$ resulted in low oxidant utilization efficiency at the basic initial pH values. In addition, the radical scavenging effect of carbonate was also inferred to contribute to deteriorating the oxidant utilization efficiency at the basic initial pH values, because carbonate ion has higher rate constants with $\text{HO}^\bullet$ and $\text{Cl}^\bullet$ than bicarbonate ion [9,23].

An inhibition effect of the artificial seawater against the NaCl solution was observed at an initial pH of 9 and 10 (Fig. 4). As is discussed in the section “UV/electro-chlorine treatment without pH adjustment”, the inhibition effect of the artificial seawater was caused by Br^- . It is well known that Br^- scavenges $\text{HO}^\bullet$ as follows [9]:

However, the reaction (16) does not depend on a pH value, and thereby the scavenging effect of Br^- was not a main causation of the inhibition effect at an initial pH of 9 and 10. The reaction rate constant of Br^- with HOCl is higher than that with ClO^- [19]. Thus, the inhibition effect of Br^- on

Fig. 4 Oxidant utilization efficiencies in the NaCl solution and the diluted artificial seawater under various initial pH values. The oxidant utilization efficiency is defined as a molar ratio of removed 1,4-dioxane to consumed total residual oxidant during the UV irradiation.

1,4-dioxane degradation is expected to be enhanced under neutral or acidic conditions, judging from the pK_a of HOCl [19]. However, our experimental results (Fig. 4) contradict this expectation. Two possible factors were responsible for this discrepancy: (i) very low initial concentration of Br^- and (ii) difference in reactivities of bromine species with $\text{HO}^\bullet$. In factor (i), the initial Br^- concentration was only 0.046 mM in this study, whereas the initial TRO concentration ranged from 3–4 mM. Accordingly, the vain consumption of free chlorine by Br^- was less than 2% of the TRO consumption, even if all the Br^- reacted with oxidants. Thus, the TRO consumption by Br^- was thought to have an insignificant impact on 1,4-dioxane degradation in this study. In factor (ii), electrolysis of the diluted artificial seawater produces free bromine in addition to free chlorine, and chemical species of free bromine changes among Br_2 , hypobromous acid (HOBr), and hypobromite ion (BrO^-) depending on the solution pH value as follows [24,25]:

The molar fraction of each bromine species in this study is depicted in Fig. 5, which clearly shows that BrO^- exists in the basic region and is predominant at pH values higher than

Fig. 5 The molar fraction of free bromine species calculated from reactions (17) and (18). The Br^- concentration is $53 \mu\text{M}$.

8.55. von Gunten and Oliveras [26] reported the following reactions:

These reactions indicate that free bromine consumes $\text{HO}^\bullet$ repeatedly through radical chain reactions and produces BrO_3^- . Furthermore, the initiation reaction with BrO^- (reaction (20)) is faster than that with HOBr (reaction (19)). Accordingly, the radical scavenging effect of free bromine is expected to intensify under basic conditions. In addition to the reaction rates, HOBr is more easily photolyzed by UV light at 254 nm than BrO^- [14]. As a result, the lifetime of BrO^- in the photochemical reactor was longer than that of HOBr , which also increased the opportunity for scavenging radicals by BrO^- . The observed BrO_3^- concentrations in the diluted artificial seawater after 60 min of UV irradiation were 42, 50, 46, and $48 \mu\text{M}$ at initial pH values of 7, 8, 9, and 10, respectively; whereas BrO_3^- was not detected at initial pH values of 3 and 5 (detection limit: $2.6 \mu\text{M}$). These results

indicate that the radical scavenging mechanism of reactions (19–24) was active and that acidification was useful for avoiding BrO_3^- formation.

ClO_3^- is produced through the self-decomposition of free chlorine (reactions (25) and (26)) and radical reactions initiated by $\text{ClO}^\bullet$ [2]. The optimal pH for reaction (25) was reported to be 7.24, and reaction (26) is favorable in basic conditions [27]. Additionally, the formation of $\text{ClO}^\bullet$ is enhanced by ClO^- rather than HOCl (reactions (12–15)). Therefore, ClO_3^- formation is expected to be enhanced in neutral or basic conditions. Such a situation was also observed in this study (**Fig. 3**). The ClO_3^- concentration was elevated during the first 10–20 min and reached a plateau, which was inversely related to the TRO concentration.

The UV/electro-chlorine process using the diluted real seawaters was also performed at an initial pH of 3. The experimental results are described in the Supplementary material. The pH values and concentrations of 1,4-dioxane and TRO in the diluted real seawater (**Fig. S1**) were almost the same as those in the diluted artificial seawater. The formation of BrO_3^- was not observed during UV irradiation, whereas ClO_3^- concentration was slightly elevated by ca. $10 \mu\text{M}$. Thus, acidification before UV irradiation was effective for preventing BrO_3^- and ClO_3^- formation at the UV irradiation stage and enhancing 1,4-dioxane degradation in the UV/electro-chlorine process.

Effect of pH on electrochemical oxidant production

ClO_3^- was detected in both the NaCl solution and the diluted seawater before UV irradiation (**Fig. 3**), which was generated at the electrolysis stage. To control ClO_3^- and BrO_3^- formation during electrolysis, the effect of pH adjustment before electrolysis on the production of TRO, ClO_3^- , and BrO_3^- was discussed. **Fig. 6** shows the time-course changes in pH values and concentrations of TRO and ClO_3^- at the electrochemical oxidant production stage. In all runs, BrO_3^- formation was not observed (detection limit: $2.6 \mu\text{M}$). The essential starting material of BrO_3^- formation in advanced oxidation processes is free bromine (reactions (19) and (20)). In addition, the BrO_3^- formation process involves reactions among bromine-containing chemicals like $\text{BrO}^\bullet$ and BrO_2^- (reactions (21) and (22)). As the Br^- concentration in the diluted seawater was only $46 \mu\text{M}$, such a low Br^- concentration might result in the unobservable BrO_3^- formation.

NaCl solution Diluted artificial seawater

Fig. 6 Time-course changes in pH and concentrations of total residual oxidant and ClO_3^- during electrolysis of the NaCl solution and the diluted artificial seawater.

The TRO production did not depend on the initial pH, although the production rate in the NaCl solution was higher than that in the diluted artificial seawater. The observed current efficiency was $30.7 \pm 1.1\%$ in the diluted seawater and $38.4 \pm 0.4\%$ in the NaCl solution. A similar current efficiency in diluted seawater electrolysis was observed by other researchers [28]. The solution pH rose steadily and approached pH 9. Judging from the pK_a of HOCl , 97% of the electrochemically generated free chlorine was dissociated into $\text{ClO}^- + \text{H}^+$ at pH 9. Thus, the rise in the solution pH was stopped around pH 9 by H^+ supply through the dissociation of HOCl . The elevation rate of the pH value in the diluted artificial seawater was slightly lower than that in the NaCl solution because of the stronger buffer action of artificial seawater. ClO_3^- formation was observed in all runs. The formation rate of ClO_3^- in the NaCl solution was higher than that in the diluted artificial seawater. As discussed in “UV/electro-chlorine treatment with pH adjustment” section, a

higher pH is favorable for ClO_3^- formation. Therefore, the rapid rise in pH value in the NaCl solution was thought to enhance ClO_3^- formation.

For a deeper understanding of electrochemical oxidant production, runs using diluted real seawaters and undiluted artificial seawater were performed. The results are shown in **Fig. S2** and **Fig. S3** of the Supplementary material, respectively. In the diluted real seawater with an initial pH of 3 (**Fig. S2**), the elevation of pH was delayed due to the stronger buffer action. However, the change in TRO concentration over time was almost the same as that in the diluted artificial seawater. The change in ClO_3^- concentration over time was also similar to that in the diluted artificial seawater, although its concentration in the real seawater at Tadaoka point was slightly lower. The longer lag time for pH elevation in the Tadaoka sample might be responsible for the lower ClO_3^- formation. BrO_3^- formation was not observed in either the diluted real or artificial seawaters. Thus, the abovementioned

discussion on the diluted artificial seawater was thought to be true for the diluted real seawater.

In the undiluted artificial seawater (Fig. S3), the TRO concentration reached 6.06–6.15 mM, which was 1.9 times higher than that in diluted seawater (3.20–3.22 mM). Thus, the use of undiluted seawater effectively saved electrical energy for oxidant production. However, ClO_3^- formation was also enhanced because of the high TRO concentration. Moreover, ca. 0.3 mM of BrO_3^- formation was observed due to the elevation of Br^- concentration from 0.046 to 0.85 mM. Such ClO_3^- and BrO_3^- formation in seawater electrolysis has also been observed by other researchers [29]. Therefore, the use of undiluted seawater is not recommended for electrochemical TRO production.

In conclusion, the diluted seawater was thought to be available as a Cl^- source for the UV/electro-chlorine process. The acidification of the solution is recommended to diminish the unfavorable ClO_3^- and BrO_3^- formation. The use of a pH controller will be a better option for keeping an acidic pH throughout electrolysis, whereas it will not be required in the UV irradiation stage, owing to self-acidification by photolysis of free chlorine (Fig. 3).

CONCLUSIONS

The availability of seawater as a Cl^- source for the UV/electro-chlorine process was discussed from the viewpoints of advanced oxidation performance and the byproduct formation of ClO_3^- and BrO_3^- using artificial and real seawater. The conclusions are summarized as follows:

- (1) The electrochemical TRO production rate in the diluted seawater was 21% lower than that in the NaCl solution due to coexisting electrolytes in the seawater. The pH value did not influence the electrochemical oxidant production.
- (2) The formation of ClO_3^- at the electrolysis stage was successfully inhibited under acidic conditions and BrO_3^- formation was not detected in the diluted seawater. However, both ClO_3^- and BrO_3^- were steadily formed in the undiluted seawater electrolysis, even when the initial pH value was set to 3. Consequently, the use of undiluted seawater is not recommended.
- (3) The oxidant utilization efficiency for 1,4-dioxane removal during UV irradiation was decreased under basic conditions due to the radical scavenging effects of carbonates and electrochemically produced TRO. As the NaCl solution was free from free bromine, the deterioration of oxidant utilization efficiency in the NaCl

solution under basic conditions was milder than that in the seawater. As a result of scavenging radicals by free bromine and free chlorine, the formation of BrO_3^- and ClO_3^- was enhanced under basic conditions. Consequently, the diluted seawater was thought to be available as a Cl^- source for the UV/electro-chlorine process when an acidic condition is maintained throughout the operation.

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SUPPLEMENTARY MATERIALS

Supplementary Materials file for this article is available at the link below.

https://www.jstage.jst.go.jp/article/jwet/19/6/19_21-080/_supplement/_download/19_21-080_1.pdf

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