



Degradation of marine humic acids by ozone-initiated radical reactions

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ABSTRACT

Degradation of humic acids extracted from seabed sediments, that were collected from two different locations in Japan, was carried out using an ozone treatment technique. Degradation was evaluated by UV₂₅₄ and VIS₄₀₀ absorbance, high performance size exclusion chromatography (HPSEC) and total organic carbon (TOC). Sediment was collected from Ago Bay, Mie prefecture and Ariake Bay, Fukuoka prefecture, Japan. After the ozone treatment, a decrease in absorbance of humic acids was observed over a wide range of pH. The UV₂₅₄ absorbance of all humic acids showed a significant decrease. Furthermore, under neutral pH, more than 80% degradation was achieved for both sediments, with an initial humic acid concentration of 30 mg L⁻¹. The total organic carbon (TOC) content of ozone-dosed solutions showed no significant changes. The decrease in the molecular weight of humic acids was evaluated using the values obtained by high performance size exclusion chromatographic (HPSEC) analysis. Humic acids in extracted solutions were related to the key materials in the sediment, which result from the semi-closed sea environment. Significant environmental improvement can be expected from the use of this technology.

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1. Introduction

In marine ecology, the increased supply of organic matter in seabed sediments causes a phenomenon named eutrophication. As a result, so-called “red tides”, which occur most frequently in summer, have been become a widely recognized problem in coastal areas, and many efforts have been made to combat this problem. Therefore, removal of organic substances that have accumulated due to aquacultural and other industrial purposes in seabed sediments is of great importance in environmental protection. In Ago Bay, Japan, which is the world’s most famous area as the original bay of pearl and oyster culture, more than 10% (by weight) of the sediment is composed of organic substances. Furthermore, humic substances represent between 37% and 51% of these organic substances [1]. Humic substances are not well defined, but are generally divided into three fractions: humin, which represents the insoluble components in aqueous solution at all pH values; humic acids (HA), which are soluble in alkaline to weakly acidic solutions, but deposit at or below pH 2.0; and fulvic acids (FA), which are soluble in aqueous solutions at all pH values [2–5].

Sediments have been recognized as a major repository for persistent toxic substances released in the aquatic environment and frequently contain higher concentrations of pollutants than are found in the water column, because humic substances have the active functions to chelate metal ions and react with toxic organic pollutants [6]. Moreover, humic substances accumulate in the sediment and have the potential to cause adverse effects to indigenous biota and aquatic organisms [7]. Their effects may lead to the fluctuations of significant marine parameters such as pH and salinity. Hence, the degradation techniques of marine humic substances need to be established.

Several techniques have been developed in the field of water purification that use UV-radiation and/or ozonation for the degradation of organic pollutants, which provide high formation rates of hydroxyl radicals. Many studies using ozonation have been carried out with established techniques for the degradation of pollutants in municipal wastewaters, industrial wastewaters, and landfill leachates [8–13]. In the removal of organic substances in water by ozonation processes, an understanding of the effect of humic substances on the degradation reaction of target substances was important in devising effective treatments. Previous studies on the ozone consumption of humic substances during the ozonation process have indicated that humic substances are radical scavengers [14]. Contrary, it has been postulated that the reaction of ozone with humic substances might also generate species that promote

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the conversion of O_3 into OH^\bullet [14,15]. However, to our knowledge, there have been very few evaluative studies of the application of ozonation process into the degradation/removal of humic substances [16,17]. In particular, despite the fact that the contamination of seabed sediments with humic substances provides the potential of serious problems for the environment, few papers dealing with the degradation of marine humic substances by ozonation processes have been presented.

The purpose of the present paper is to report a study of degradation by the ozonation technique of marine humic substances in seabed sediments collected from two different locations in Japan (Ago Bay and Ariake Bay). The experimental data were compared with data obtained using the commercial Aldrich humic acid which was isolated from coal. The degradation process was monitored using a UV/VIS spectrophotometer and total organic carbon (TOC) analyzer. In addition, changes in the molecular weight distribution of HA were clarified by high performance size exclusion chromatography (HPSEC).

2. Experimental methods

2.1. Humic acid sample

The HA sample was purchased from Aldrich and was used as received. The chemical information of Aldrich humic acid has been reported as follows [18]: weight-averaged molecular weight: 4100, number-averaged molecular weight: 1630, M_w/M_n : 2.5, polydispersity (ϵ): $919 L^{-1} (\text{mole of OC})^{-1} \text{cm}^{-1}$, the ratio of absorbance (465 nm) to absorbance (665 nm): 7.59. HA (300 mg L^{-1}) was dissolved in 0.1 M NaOH. For experimental use, the pH of the humic acid solution was adjusted using 1 M HCl. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan), resulting in a resistivity $>18 \text{ M}\Omega \text{ cm}$. All chemicals and solvents in this work were of the commercially available purest grade.

For the environmental study, sediment samples were collected from Tategami in Ago Bay (S1) and Kumata in Ariake Bay (S2), Japan, as shown in Fig. 1. A modified process was used to extract humic acids [1]. The sediments collected from the study sites were sieved through a 2 mm mesh in order to remove the large extraneous particles such as bivalve shells and other waste. The samples were then dried at 105°C for 1 day in an electric oven. After drying, the humic acids contained in 50 g of each sediment sample were extracted with 500 mL of 1 M NaOH at 90°C for 4 h on a hot plate. The humic acid solutions were separated from the sediment using a glass fiber filter (Advantec Inc., Tokyo, Japan), then adjusted to the required pH with 1 M HCl and diluted to the required concentration to perform the study. The number-averaged molecular weights of marine HAs (S1 and S2) were almost the same (approximately 10,000 with the calibration using pullulan).

2.2. Ozonation of humic acids

A schematic diagram of the experimental system is shown in Supplementary data Fig. S1. The ozone was produced from dry oxygen gas using an ozonator (Eco-desine Co. Ltd., Model ED-OG-R4), with settings of 0.1 MPa, an ozone flow rate of 1 L min^{-1} , an electric current of 1 A, and an ozone concentration of 10 wt% in a 200 mL reaction solution. In the ozonation system, outlet flows were trapped with a potassium iodide solution to prevent any leakage.

The humic acids, at a concentration of 30 mg L^{-1} , adjusted to pH values of 4, 7 and 12, were ozonated. Following this, different concentrations of the Aldrich HA and the marine humic acids, adjusted

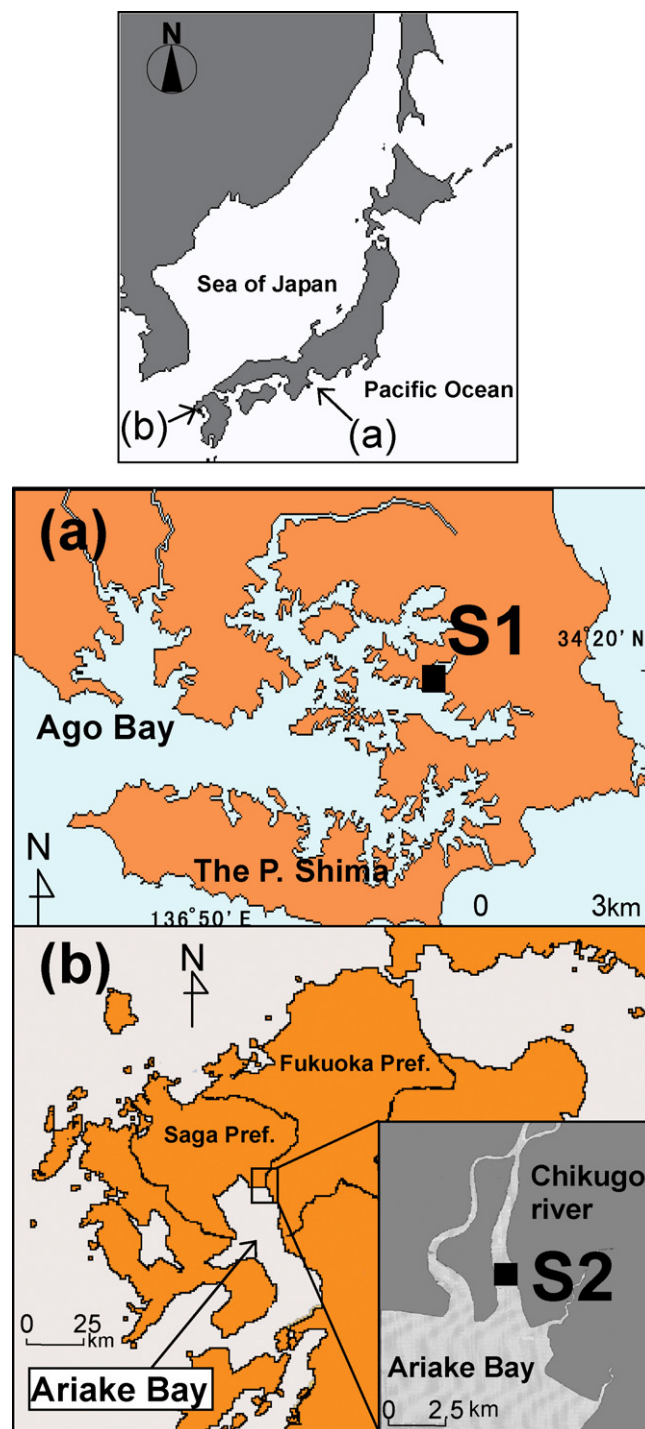


Fig. 1. Location of (a) Ago Bay (S1) in Mie prefecture and (b) Ariake Bay (S2) in Fukuoka prefecture, Japan.

to pH 7, were treated. The O_3 treatment was applied into the humic acid sample solution during 60 min. After ozonation, samples were measured by spectrophotometry to characterize the degradation of marine humic acids.

2.3. Evaluation of the humic acid degradation

The effects of ozonation were determined using a UV/VIS spectrophotometer (Shimadzu Co. Ltd.). Two different wavelengths were evaluated: UV_{254} was used for aromatic compounds, whereas

color was evaluated by the absorbance at VIS₄₀₀. The degradation efficiency was calculated using the following equation,

$$\frac{C}{C_0} = \frac{UV_{254(t)}}{UV_{254(0)}} \quad (1)$$

where C and C_0 are the concentration of HA after and before the reaction, and $UV_{254(0)}$ and $UV_{254(t)}$ are the absorbance at the 254 nm wavelength at the initial time and the reaction time, respectively.

The molecular weight distributions of Aldrich HA and the marine humic acids were evaluated using a high-performance size-exclusion chromatography (HPSEC) system, which comprised a TRI ROTER-V JASCO solvent pump, a UVIDEC-100-V1 JASCO variable wavelength absorbance detector, a TU-100 JASCO thermostat, and a Rheodyne rotary injector valve with a 20 μ L sample loop. A Shodex 805HQ (0.75 cm in diameter, 30 cm in height, Showa Denko KK, Tokyo, Japan) preceded by a guard column was used for separation by size exclusion. The applied flow rate was 1.0 mL min⁻¹. The column packing material (a polymerized diol covalently bonded to a silica support, exclusion limit 4,000,000, permeation limit 100) was selected based upon its low residual hydrophobicity and minimal ion-exchange capacity [19]. The mobile phase consisted of 0.01 M K₂HPO₄–0.01 M KH₂PO₄ solutions buffered to pH 7.0. The HPSEC system was calibrated using pullulan (Shodex STANDARD p-82).

The TOC in the ozonated solutions was measured using a TOC analyzer (TOC-V CPH, TNM-1, SHIMADZU). The ignition loss (IL), total organic carbon (TOC) and total nitrogen (T-N) in the sediments from two places were measured before and after the extraction of humic acids. The IL was measured as the difference in weight between dried (100 °C for 1 h) and combusted (600 °C for 30 min) sediments [20]. An electric oven (Koyo Box Furnace, KBF828N, Nara, Japan) was used for the combustion. The TOC and T-N were measured using a CN corder (VARIO MAX CHS, GmbH) on the dry sediments after treatment with 1N HCl to remove the calcium carbonate derived from bivalves.

3. Results and discussion

3.1. Degradation of Aldrich humic acid

To clarify the degradation characteristics of HA as a result of ozone treatment, spectroscopic data for the ozonated Aldrich HA were compared with data obtained for HA before reaction. The UV–vis absorption spectrum of HA exhibited the same pattern as found in a previous study with the Fenton reaction [21]. As shown in Fig. 2, the absorbance at 220–420 nm decreased with increased reaction time as a result of the ozonation process. Consequently, it was confirmed that the ozonation process is an effective technique for the decomposition of humic acid. Fig. 2 shows that the specific visible absorbance VIS₄₀₀ was completely removed after a reaction time of 15 min, as can also be identified clearly in Supplementary data Fig. S2. However, the absorbance of aromatic moieties at UV₂₅₄ was still present after 15 min. Despite increasing the ozone reaction time to 60 min, no remarkable change in the decomposition of UV₂₅₄ was apparent. Although the treatment with the ozone concentration range of 0.5–3 L min⁻¹ was carried out, the difference was not significant for the one-minute ozonation.

The pH value of a solution is an important parameter in wastewater treatment. The effect of pH on the decomposition of the Aldrich HA was investigated in this study over a pH range from 4 to 12 without the addition of buffer solution. Fig. 3 shows the change in concentration of the Aldrich HA as a function of the reaction time. After 15 min, 71.6, 87.7 and 96.1% of the Aldrich HA had been removed at pH 4, 7 and 12, respectively. Thus, larger decomposition was observed at the higher pH after 15 min. When the initial pH was 7, the pH value decreased down to 5.6 after 15 min ozone treatment.

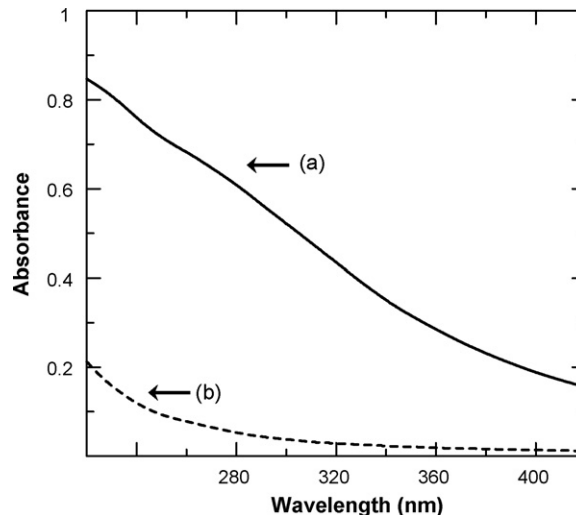


Fig. 2. UV–visible spectral changes for the degradation of the Aldrich HA under the ozonation process. (a) Before reaction; (b) after 15 min. Aldrich HA concentration = 30 mg L⁻¹; O₃ = 10 wt%; flow rate = 1 L min⁻¹.

The phenomena may be able to be explained by a decrease in molecular size due to the formation of formic acid and oxalic acid by the decomposition of humic acid [17,22]. The effect of pH is the result of the relationship between oxidation potential and decomposition behavior of ozone. In acidic region, the ozone is available as molecular ozone and in alkaline region it decomposes into secondary free radicals such as OH[•], HO₂[•] and HO₃[•] [23]. Among the radicals produced, OH[•] radicals are important and have the highest oxidation potential of 2.8 V. Even though hydroxyl radical has a higher oxidation potential than ozone, its selectivity is very less [24]. The oxidizing potential of ozone decreases from 2.08 V in acidic region to 1.4 V in alkaline solutions [25]. This indicates that as the ozone stability decreases with increasing pH it results in the generation of secondary free radicals.

The effect of initial HA concentration was studied using Aldrich HA at a range of concentrations from 15 to 150 mg L⁻¹ at pH 7 (Fig. 4). With increasing the original HA concentrations from 15 to 150 mg L⁻¹, the degradation efficiencies decreased gradually from 88.9% to 77.8%. For all of the HA concentrations, the degradation

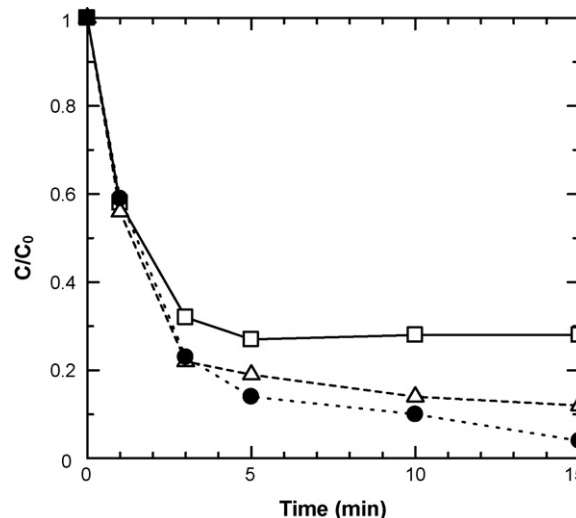


Fig. 3. Degradation of the Aldrich HA at different pH values. Aldrich HA concentration = 30 mg L⁻¹; O₃ = 10 wt%; flow rate = 1 L min⁻¹. □: pH 4, △: pH 7, ●: pH 12.

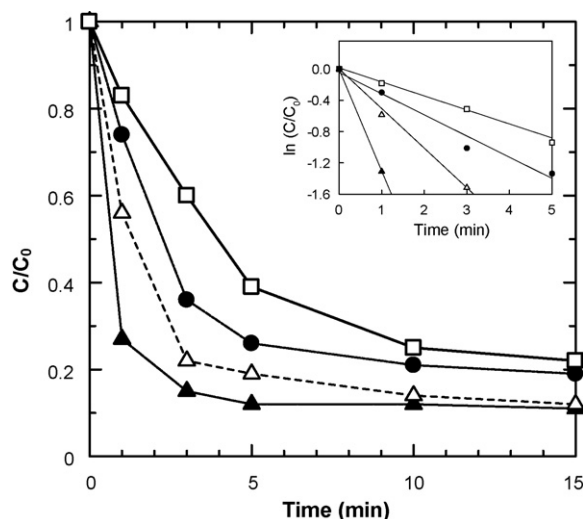


Fig. 4. Degradation of the Aldrich HA at different concentrations. $O_3 = 10$ wt%; flow rate = 1 L min^{-1} ; pH 7. \square : 150 mg L^{-1} ; \bullet : 75 mg L^{-1} ; \triangle : 30 mg L^{-1} ; \blacktriangle : 15 mg L^{-1} . The insert figure shows $\ln(C/C_0)$ versus the ozonation time.

efficiency decreased sharply until 5 min, and then the efficiency decreased gradually in the treatment time range of 5–15 min. The reason for the phenomena could not be clarified. Maybe, the phenomena may be associated with the fact that the total organic carbon in the sample could not decrease for the ozone degradation of humic acids (as described later).

The degradation of HA has been explained using a pseudo-first order degradation equation model [26,27]. Ozone reacts with organic matter via two pathways [28]. Thus, its kinetic at different operational pH can be represented by:

$$\frac{d[\text{HA}]}{dt} = -k_1[\text{HA}][\text{O}_3] - k_2[\text{HA}][\bullet\text{OH}] \quad (2)$$

where $[\text{O}_3]$ is concentration of ozone at time t , $[\bullet\text{OH}]$ is concentration of hydroxyl radical at time t . $[\text{HA}]$ is concentration of humic acid, k_1 and k_2 are kinetic rate constants for direct molecular ozone oxidation and radicals oxidation, respectively. Eq. (2) can be reduced to:

$$\frac{d[\text{HA}]}{dt} = (-k_1[\text{O}_3] - k_2[\bullet\text{OH}])[\text{HA}] \quad (3)$$

The terms could be replaced by an apparent pseudo first-order rate constant, k_{oz} (min^{-1}).

$$\frac{d[\text{HA}]}{dt} = -k_{oz}[\text{HA}] \quad (4)$$

From this equation, as shown in the insert of Fig. 4, the decomposition rate (k_{oz}) was calculated to be 1.8×10^{-1} , 2.9×10^{-1} , 5.1×10^{-1} and $13 \times 10^{-1} \text{ min}^{-1}$, for ozonation at concentrations of 150, 75, 30 and 15 mg L^{-1} , respectively. The data, obtained by the same method, on the humic acid degradation rate using ozonation, based on UV_{254} and VIS_{400} parameters, are presented in Table 1. The rate constants calculated in this study were higher than those reported from previous studies [17]. This can be explained by the structural differences in the humic acids used in the experiments, and by the alterations in the humic acid molecules as an effect of preozonation [17,27]. Conversely, the calculated rate constant of VIS_{400} was observed to be faster than that of UV_{254} , which represents the carbon double bonds and aromatic structure within the humic acid molecule. Rapid decoloration with ozonation may be attributed to rapid attack by the ozone molecule on the chromophoric functional groups in the outer regions of the humic acid molecule. Thus, these

Table 1

Degradation rate constant for different humic acid samples under ozonation treatment.

Humic acid (mg L^{-1})	Wavelength			
	254 nm		400 nm	
	k_{oz} (min^{-1})	$t_{1/2}$ (min)	k_{oz} (min^{-1})	$t_{1/2}$ (min)
15	1.31	0.50	1.98	0.35
30	5.14×10^{-1}	1.3	7.38×10^{-1}	0.90
75	2.87×10^{-1}	2.4	4.36×10^{-1}	1.6
150	1.84×10^{-1}	3.8	2.94×10^{-1}	2.4

results suggest that the humic acid dosage is correlated with the rate of decomposition of humic substances.

3.2. Degradation of marine humic acid

Fig. 5 depicts the decomposition of the marine humic acids, extracted from the Ago Bay and Ariake Bay sediments, respectively. The concentration of marine humic acids (S1 and S2) was 30 mg L^{-1} , and the pH of HA sample solution was adjusted to be 7. The decomposition efficiencies reached 80% during 10 min' ozonation. Previously, we have investigated the photo-Fenton degradation of marine humic acids, which were extracted from the Ago Bay sediments. Because it took 5 h to achieve the efficiency of 80% in the photo-Fenton process of marine HA, it was found that the present O_3 treatment was very superior to the photo-Fenton technique for the degradation of marine humic acid. The pseudo first-order rate constants (k_{oz}) for the ozone-driven degradation of humic acids from S1 and S2 were 0.40 and 0.36 min^{-1} on the basis of the calculation with UV_{254} , respectively. Hence, the rate constants for the degradation of humic acid with relatively large molecular weight ranges (S1 and S2) were smaller compared with those obtained for the humic acid degradation with relatively small molecular weight ranges (Aldrich chemicals).

Similar results, which gave a decomposition efficiency of between 80 and 90%, were also obtained in a 60 min reaction time. Since the humic acid sample was applied into the HPSEC analysis, the results were compared with those obtained before the treatment (Fig. 6). It was found from a result of the HPSEC that

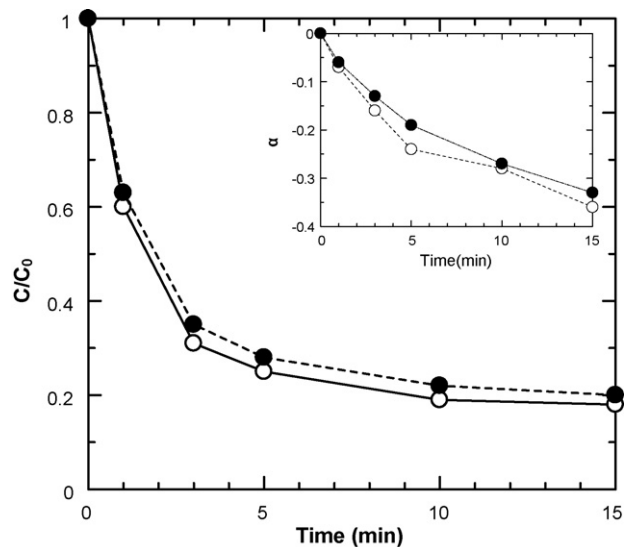


Fig. 5. Degradation of S1 (Ago Bay) and S2 (Ariake Bay). S1 and S2 HA concentration = 30 mg L^{-1} , $O_3 = 10$ wt%, flow rate = 1 L min^{-1} , pH 7. \circ : Ago Bay; \bullet : Ariake Bay. The α value in insert figure was defined as the rate of change of pH compared with the initial pH.

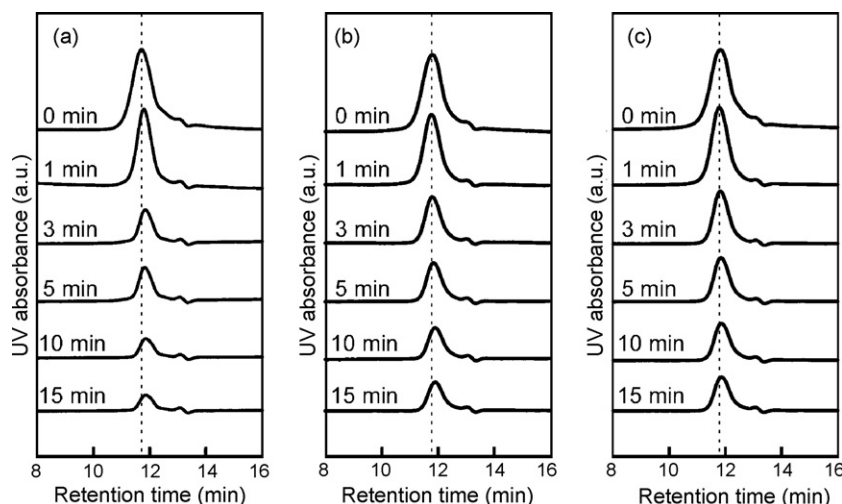


Fig. 6. Analysis of HPSEC chromatograms under ozonation. (a) Aldrich HA, (b) S1, (c) S2. HA concentration of Aldrich, S1, and S2 = 30 mg L⁻¹; O₃ = 10 wt%; flow rate = 1 L min⁻¹; pH 7.

the ozone treatment made the molecular weight of humic acid very extremely low in an instant because the HPSEC of marine humic acids proved the larger retention time of peak and lower peak height with increasing the treatment time. The insert in Fig. 5 shows α , which was defined as the rate of change of pH compared to the initial pH, versus the ozonation time, which also describes this phenomenon. These results suggest that the molecular weight decreased during decomposition of the humic acid. In this study, the humic substances in the seabed sediments were able to be resolved using ozone-initiated radical reactions. In the future, these solidified sediments, following purification by ozone treatment, could be used with future advanced technology as natural ecosystem recovery materials [29].

3.3. Total organic carbon

Fig. 7 shows the degradation of TOC in the ozone treatment solution during a 15-min reaction. Our expectation was that TOC reduction might occur after the ozonation; however, no remarkable change in S1 and S2 was observed with the dosed solutions. In the dosed solution containing HA, the TOC decreased (a 20% decrement) over 3 min for 15–75 mg L⁻¹ of humic acid. When the 150 mg L⁻¹ initial concentration was studied, the degradation occurred later in the initial stage. After 15 min, the TOC became constant. Therefore, these results reflect that organic carbon could not be mineralized into carbon dioxide by the ozone treatment. How-

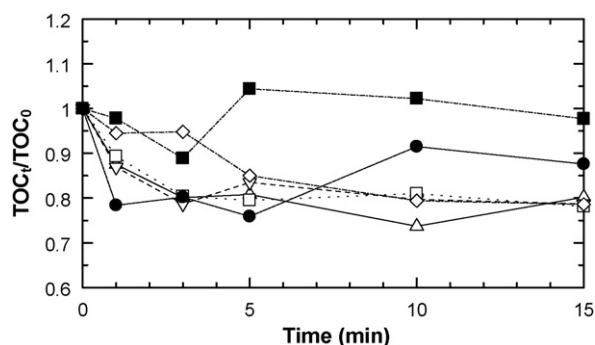


Fig. 7. Changes in TOC during degradation of Aldrich HA, S1 and S2. HA concentration of Aldrich, S1, and S2 = 30 mg L⁻¹, pH 7, O₃ = 10 wt%, flow rate = 1 L min⁻¹. Δ : 15 mg L⁻¹; ∇ : 30 mg L⁻¹; \square : 75 mg L⁻¹; \diamond : 150 mg L⁻¹; \bullet : Ago Bay; \blacksquare : Ariake Bay.

Table 2

The IL, TOC and T-N in the seabed sediments from Ago Bay (S1) and Ariake Bay (S2).

Sampling station		IL (%)	TOC (mg/g)	T-N (mg/g)
S1	Before ^a	11.2	38.6	3.48
	After ^b	6.7	15.5	1.50
S2	Before ^a	10.6	16.6	1.47
	After ^b	8.0	7.63	0.51

^a Before extraction of humic acids.

^b After extraction of humic acids.

ever, the load environment of marine humic acids could be considered to be lowered with the ozone treatment, since the molecular weight of organic substances became very extremely low [30].

Table 2 shows the IL, TOC and T-N in the sediments before and after extraction with the humic substances from S1 and S2. Overall, the data for S1 were higher than those from S2. These data indicated that the organic substances were equivalent to those that are resolved rather easily: the depletion rates for IL following extraction relative to before extraction were 0.40 and 0.25 for S1 and S2, respectively. This might be attributed to a difference in the degradation efficiency, which was 30% larger for S1. As shown in Fig. 5, a higher degradation efficiency was generally observed for S1. In general, in Ago Bay (S1), sediments have accumulated that consist of fine particles originating from eutrophication. In contrast, the sediments from Ariake Bay (S2) accumulate in the mouth of the Chikugo River, and therefore might be consistent with an origin on land [31]. These results suggest that the organic materials originating from these organic particles were equivalent to easily resolved organic materials.

4. Conclusion

Ozonation was demonstrated to be a very efficient technique, and was able to produce a clear color in samples contaminated with marine humic acid within approximately 15 min. Ozone may react with marine humic acids in water via two pathways: with a direct attack of molecular ozone into them, or through a variety of derived oxygen radicals especially hydroxyl radical, which can act as secondary oxidants. The degradation rate of humic acid was strongly accelerated by the O₃ processes. High molecular weight substances were degraded into low molecular weight substances; however, complete removal was impossible. Degradation of humic

acids could be helpful in the restoration of the marine ecosystem in seabed sediments. Moreover, this technique could be used to treat other high molecular weight substances from different wastes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.09.013.

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