Treatment of Red Tide in Ocean Using Hydroxyl Radical

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Abstract—**A pilot-scale experiment for the treatment of red tide in the enclosure was done in sea area of Shandong Province, P. R. China on Aug. 25, 2002. With the method of strong dielectric barrier discharge in microgap, O_2 in air and H_2O in seawater are ionized and dissociated into large numbers of OH· radicals, and then dissolved into a part of seawater to form OH· solution of high concentration. With OH· concentration of 0.68mg/L, the kill efficiencies of 29 kinds of red tide organisms such as *Chaetoceros lorenzianus* and so on reached 99.89%, in which the kill efficiencies of bacterium and vibrio were 100%, and that of *Gonyaulax cysts* and *Prei. Cysts* were up to 100%. At the same time, the content of chlorophyll-a was decreased into the lowest limit of test. DO saturation of seawater was greatly increased to 100% because the residual OH· radical was decomposed into H_2O and O_2 after 20 minutes. Therefore the treatment of red tide using OH· radicals is a kind of advanced oxidation technology, which realizes zero pollution, zero emission and zero residual in the process of the production of OH· radicals and the treatment of red tide.**

I. INTRODUCTION

In 2001, the red tide occurred 77 times in China's ocean and the pollution areas reached 15,000km^2, which increases 49 times and 5,000km^2 areas than that in 2000. In 2002, red tide occurred 79 times in China's ocean and the pollution areas were 10,000km^2. The Red tides occurs mostly in offing of East Sea, Bohai Sea and Yellow Sea of China. The main organism species, the total times and accumulative areas to form red tide are increased greatly year by year [1], which have seriously threatened the ocean environment in china.

At present, many methods for the treatment of red tide are studied in the world [2-8]. However only killing the red tide organisms by $CuSO_4$ medicament and the clay flocculation methods were done in sea areas [2-3]. Some problems are as follows. (1) The superfluous toxicity coagulant or $CuSO_4$ medicament makes the ocean ecosystem to be destroyed, and the coagulant sediments have seriously effect on the benthic of seabed. After a few hours, the red tide organisms flocculated in sea are possible to be dissociated and swum again. (2) Large numbers of residual coagulants and medicament are impossible to be decomposed and disappeared in ocean resulting in the destruction to other organisms for a long time. (3) Killing and coagulation need a long time about 20min~24hours. The concentrations of coagulant and medicament are greatly decreased to the lowest limit to kill the red tide organisms because of diluting and diffusing of sea wave, so that it is impossible to treat a large-scale red tide in ocean. Until now a few tens of methods and thousands of medicaments for the treatment of red tide are still in the stage of laboratory. Only few methods are possible to be used in natural sea [4]. Therefore, A kind of new method for the treatment of red tide is urgently found.

With the method of strong dielectric barrier discharge [9-12], the strong electric field ($E_d \geq 400$Td, 1Td=10^{-17}Vcm^2) is formed with the thinner α-Al_2O_3 dielectric layer at a high pressure ($P \geq 0.1$Mpa or $n=2.6\times10^{19}$/cm^3). The electrons achieve the average energy of above 12eV. The high dissolved concentration OH· radicals are produced using the ionization of O_2 in air and H_2O in seawater. The hydroxyl radicals kill the red tide organisms in ocean belonging to a dissociative radical reaction with a fast reaction rate, which is effective to solve the diluting and diffusing problem of sea wave (Ocean Dynamics). Also there is a broad-spectrum deadly characteristic that is possible to kill organisms meanwhile to bleach and deodorize to seawater.

Hoigne J. et al [13] put forward the concept of Advance Oxidation Technology (AOT) in 1976, meaning the processes that produce the hydroxyl radical (OH·), induce a series of OH· chain reactions, degrade the red tide organisms and other pollutants further decompose their finally residua into CO_2, H_2O and inorganic salts [14-18]. Also the processes accord to the concept of Green Chemistry, Environmental Benign Chemistry [19-20]. Therefore the method for the treatment of red tide using hydroxyl radicals is a kind of AOT, which realizes Zero Emission and Zero Pollution.

II. EXPERIMATNAL METHOD

2.1 Experimental Materials

On Aug. 25, 2002, a pilot-scale experiment for the treatment of red tide was done in the enclosure in sea area of Shandong Province, P. R. China. In this sea area,

the ambient temperature was 32°C, seawater temperature was 24 °C, and pH was 7.13.

The red tide organisms were cultivated in the enclosure by The First Institute of National Ocean Bureau in Qing Dao. The red tide organisms cultured are as follows:

Chaetoceros lorenzianus, Ch. curvisetus, Ch. decipien, Ch. terres, Ch. didymus, Ch. compressus, Ch. sp., Ch. affinis, Nitzschia sp, Nitzschia closterium, Asterionella japonica, Amphiprora sp, Thalassiosira sp., Skeletonema costatum, Streptotheca thamesis, Eucampia zoodianus, Biddulphia sinensis, Rhiz. stolterfothii, Hemiaulus sinensis, Thalassionema nitzschioides, Licmophora sp., Scrippsiella trochiodea, Peridinium pellucidum, peri. Pallidum, Peri. Bipes, Peri. Steinii, Peri. spp., Peri. Quiquecorne, Gonyaulax polygramme, Prorocentrum tristinum, Gymmnodinium sp., Gyrodinium sp., Dinoflagellates, Gonyaulax cysts, Prei. Cysts, Alexandrium sp, bacterium and vibrio.

2.2. Experimental System

The experimental system for killing the red tide organisms in sea enclosure is shown in Fig.1. A part of seawater is pumped into the pipe passing the filter 1. High concentration OH· radicals are injected into the dissolver 5 with a part of seawater to produce the dissolved hydroxyl radicals, which the mass transfer efficiency is 98.8%. Hydroxyl is dissolved further through the gas/liquid separator 6 and the residual OH· is removed by eliminator 7. The dissolved OH· concentration reaches 4.2mg/L in pipe and is sprayed in the sea enclosed 10 through the shower nozzle 9. The unicorn-form enclosure was made of polyethylene film with the dimensions of 1.1m diameter and 2.3m depths. Three samples in three sections, the surface, 1.0m and 2.0m depth of enclosure are taken respectively. The average values of three samples in same section are the experimental results.

Before applying the DBD discharge, O_2 with the purity of 98.5 % enrich by air and H_2O at gas state were introduced into the plasma reactor 14. The concentration of H_2O in the mixed gases is 3.5% (v/v). The hydroxyl radicals and other activated particles such as HO_2^-, HO_3·, O_3^{-}·, O_3, H_2O_2 and so on are produced by a series of plasma reactions.

2.3. Test Methods

The total numbers of bacterium are counted with the ocean 2216E culture medium plate. The numbers of vibrio are counted on the spreading plate of TCBS culture medium. The numbers of ocean microalgae are counted directly with haemacytometer under microscope after fixed by iodine solution. Three samples are done in every test. The experimental error in measurements of cell counting is less than 5%.

The chlorophyll-a of red tide organism and DO of seawater are monitored in line with YSI-6600-M Environmental Monitoring System. The gas flow rate is measured using a Type-LZJ10 Flow Meter. The flow rate of seawater is monitored with Model 8035 Burkert Flow meter 7 (Burkert Co. in France).

The ratio concentration of OH· is tested using electrochemistry method and revised by Fluorescence method of benzoic acid. The concentration of other activated particles is converted into the OH· concentration according to their oxidation potential.

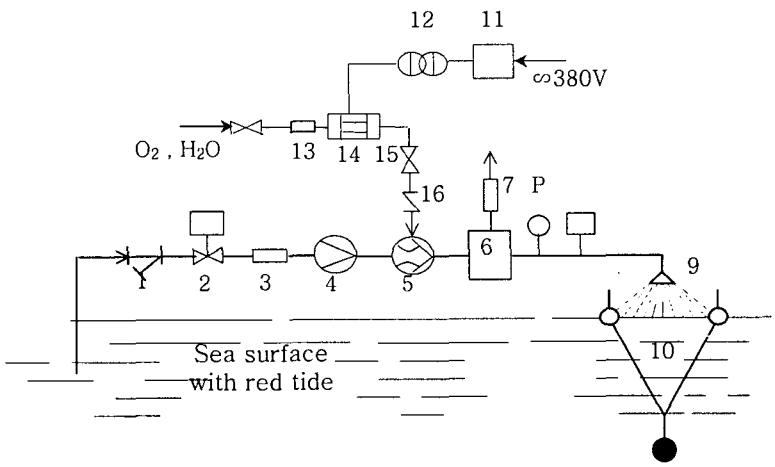

Fig.1. System for Killing Red Tide Organisms in Sea Enclosure

1. Filter; 2. Electric valve; 3. Liquid flowmeter; 4. Pump; 5. Gas/liquid dissolver; 6. Gas/liquid separator; 7. Eliminator of residual OH·; 8. Monitor of electrochemistry; 9. Shower nozzle; 10. Sea enclosure; 11. Controller; 12. Transformer; 13. Gas flowmeter; 14. OH· plasma reactor; 15. Valve; 16. Check valve.

III. RESULTS AND DISCUSSION

3.1. Killing the Red Tide Organisms

The nutrition salt was put in the enclosure to culture the red tide organisms with the content of 1.74×10^6/mL. The hydroxyl solution of 4.2 mg/L was sprayed into the enclosure in which the ratio concentration of OH· was 0.68 mg/L. The experimental results of OH· killing organisms such as *Chaetoceros lorenzianus* etc is shown in table 1, which the tests were done after 24h. The total numbers of red tide organism were decreased from 11.74×10^6/mL to 0.028×10^6/mL. The kill efficiency was 99.89%, in which 27 kinds of organism weren't tested with the kill efficiency of 100%, only *Nitzschia closterium* and *Amphiprora sp* were about 96.7%. Having been monitored 48hrs, even if 64hrs, the organism contents were basically same as that after 24hrs, no longer organism regenerated or new propagated.

The salinity, pH and conductivity are basic constant after the injection of hydroxyl radicals. The salinity changes from 31.351 to 31.349, pH is from 7.13 to 7.12, and the conductivity is from 47.3 to 47.58.

3.2. Killing the Bacterium and Vibrio

The experimental results of killing bacterium and vibrioin in the enclosure are shown in table 2. The contents of bacterium and vibrio are 4.6×10^4/mL and 3.1×10^4/mL respectively. After 24h of OH· solution injected, the bacterium and vibrio weren't tested with the kill efficiency of 100%. Same results were taken after 64h to be monitored.

Table 2. Data for Killing Bacterium and Vibrio

Species	Content (cell/mL)	Content after 24h (cell/mL)	Kill efficiency
Bacterium	46000	---	100
Vibrio	31000	---	100

Note: OH· ratio concentration was 0.68mg/L,
---, not be tested.

3.3. Effect of OH· on Chlorophyll-a

With the strong oxidation and dissociation effects, the hydroxyl radical can make the ocean micro-alga be oxidized and decolored to fail to the photosynthesis resulting in the death of red tide organisms. The effect of OH· on the content of chlorophyll-a is shown in Fig. 2, which is monitored in line with YSI-6600-M Environmental Monitoring System. When the ratio concentration of OH· was 0.68mg/L, about 90% chlorophyll-a was decomposed after 10 minutes. The content of chlorophyll-a was not to be tested after 20 minutes, which had the same experimental result after 64hrs.

3.4. Effect of OH· on Dissolved Oxygen (DO) of Seawater

The effect of OH· on DO of seawater is shown in Fig. 3, which is monitored in line with YSI-6600-M Environmental Monitoring System. When the ratio concentration of OH· was 0.68mg/L, the saturation of DO was increased to 75% after 5minutes, to 85% after 10 minutes, and to 100% after 20minutes. Also DO was tested by Iodimetry method. After, 10 minutes spraying the dissolved OH·, DO was increased from 7.47 mg/L to 13.24mg/L, having 77.24% increased. The reasons of DO increase are that the residual OH· and the organism bodies were dissociated into O_2 and dissolved into seawater. Therefore the hydroxyl radical is possible to renovate the polluted seawater as same as killing the red tide organisms.

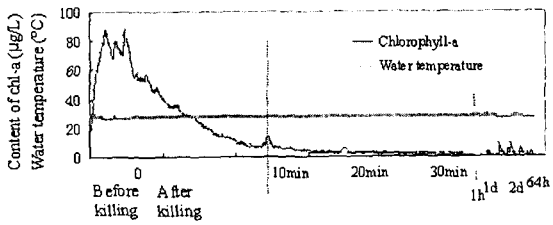

Fig. 2. Effect of OH· on Chlorophyll-a

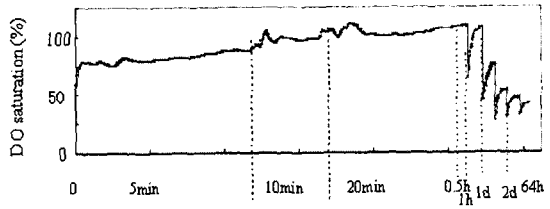

Fig. 3. Effect of OH· on DO of seawater

IV. CONCLUSIONS

1) The Strong dielectric barrier discharge in microgap is more effective method in producing larger numbers of OH radicals.
2) The ratio concentration of OH· is 0.68mg/L for killing the red tide organisms.
3) The kill efficiency of red tide organisms reached 99.98%, in which the kill efficiency of bacterium and vibrio are 100%.
4) *Gonyaulax cysts* and *Prei. Cysts* are killed 100%, which is difficult to be killed using common medicament.
5) Chlorophyll-a is decreased the lowest limit of test after 20 minutes to loss the effect of photosynthesis.
6) The saturation of DO is increased to 100%. The polluted seawater is improved and renovated as same as killing the red tide organisms,
7) The treatment of red tide using OH· radicals is a kind of advanced oxidation technology, which realizes Zero Emission and Zero Pollution in the process of the production of OH· radicals and killing the red tide organisms.

Table 1. Data for Killing the Red Tide Organisms in Sea Enclosure

No.	Species of Organism	Original Content (cell/mL)	Content after 24h (cell/mL)	Kill efficiency (%)	Content after 48h (cell/mL)	Kill efficiency (%)
1	*Chaetoceros lorenzianus*	2835000	14000	99.5	4000	99.9
2	*Ch.curvisetus*	2646000	-----	100	-----	100.0
3	*Ch.decipiens*	223000	-----	100	-----	100.0
4	*Ch.terres*	63300	-----	100	-----	100.0
5	*Ch.didymus*	22000	-----	100	-----	100.0
6	*Ch. sp.*	14000	-----	100	-----	100.0
7	*Ch.affinis*	314600	-----	100	-----	100.0
8	*Nitzschia sp.*	5786000	-----	100	-----	99.9
9	*Nitzschia closterium*	60600	2000	96.7	-----	100.0
10	*Asterionella japonica*	601300	4000	99.3	-----	100.0
11	*Amphiprora sp.*	262000	8000	96.9	2000	99.2
12	*Thalassiosira sp.*	153300	-----	100	-----	100.0
13	*Skeletonema costatum*	680000	-----	100	-----	100.0
14	*Streptotheca thamesis*	8000	-----	100	-----	100.0
15	*Eucampia zoodianus*	4000	-----	100	-----	100.0
16	*Biddulphia sinensis*	4000	-----	100	-----	100.0
17	*Rhiz.stolterfothii*	2000	-----	100	-----	100.0
18	*Hemiaulus sinensis*	4000	-----	100	-----	100.0
19	*Scrippsiella trochiodea*	2000	-----	100	-----	100.0
20	*Peridinium pellucidum*	3000	-----	100	-----	100.0
21	*Peri. pallidum*	2000	-----	100	-----	100.0
22	*Peri. Bipes*	4000	-----	100	-----	100.0
23	*Peri. spp.*	3000	-----	100	-----	100.0
24	*Peri. quiquecorne*	9300	-----	100	4000	57.0
25	*Gonyaulax polygramme*	11300	-----	100	-----	100.0
26	*Prorocentrum tristinum*	2000	-----	100	-----	100.0
27	*Gyrodinium sp.*	9300	-----	100	-----	100.0
28	*dinoflagellates*	11300	-----	100	-----	100.0
29	*Gonyaulax cysts*	2000	-----	100	-----	100.0
30	*Prei. cysts*	2000	-----	100	-----	100.0
31	*Alexandrium sp.*	2000	-----	100	-----	100.0
	Total	11740000	28000	99.89	14000	99.9

Note: OH^- ratio concentration was 0.68mg/L; -----, not be tested.

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