Applications of Pulsed Intense Relativistic Electron Beam to Aquatic Conservation

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ABSTRACT

In this study, we propose aquatic conservations by using a pulsed intense relativistic electron beam (PIREB). Treatments of introduced species and toxics azo dyes by irradiating PIREB are investigated in this report. Zooplankton contained in water have been inactivated by irradiation of PIREB. A treatment chamber is filled with a solution of 3-wt% salt in water containing Artemia larvae as zooplankton samples, and is irradiated using the PIREB (2 MeV, 0.4 kA, 140 ns). We found that up to 24 % of the Artemia are inactivated by firing 10 shots of PIREB irradiation. It is found that pH changes did not affect to inactivate the Artemia larvae during the time scale of PIREB irradiation. The reaction of congo red, a well-known toxic azo dye, occurred after irradiation by PIREB. An aquation of congo red was irradiated by PIREB (2 MeV, 0.36 kA, 140 ns). After PIREB irradiation, the solution was measured by electrospray ionization-mass spectrometry and liquid chromatography/mass spectrometry. It was found that congo red underwent a reaction (77 % conversion after five shots of PIREB irradiation) and the hydroxylated compounds of the dye were observed as reaction products.

Keywords

pulsed intense relativistic electron beam (PIREB), ballast water, pulsed power, zooplankton, ocean ecosystem, azo dyes, congo red

1. Introduction

A pulsed intense relativistic electron beam (PIREB) has been applied as a technology for environmental cleanup. For example, multi-shot PIREB irradiation reportedly decreased the NOx concentration in a chamber, treated the volatile organic compounds contained in soil [1]. PIREBs have great potential for various treatment effects because they not only provide electrons with high kinetic energy but also generate radicals and X-ray emission. The safety of water supplies and aquatic conservation are pressing problems. Therefore, it is important to develop technologies for the decomposition of the pollutants in water; various

water cleanup techniques have received much attention [2].

In comparison with the treatment method using a DC electron beam, the PIREB method has the advantage of offering brief treatments because the beam current is on the order of kA with short pulse duration.

In this study, we propose the aquatic conservation by using PIREB irradiation. Treatments of introduced species and toxics azo dyes by irradiating PIREB are investigated in this report.

2. Inactivation of Zooplankton by Irradiation with Pulsed Intense Relativistic Electron Beam

Ships such as cargo ships use ballast water to stabilize their hulls during navigation. The ballast water is carried around the world and is dumped at a port of call, causing an undesirable propagation of microbes, bacilli and eggs and larvae of marine organisms and the growth of marine plankton in ocean ecosystems. To conserve the ocean environment, a convention was adopted by the International Maritime Organization in 2004 [3]. It specifies that ships must manage their ballast water by using devices such as a ballast water treatment device, not later than 2016 [3].

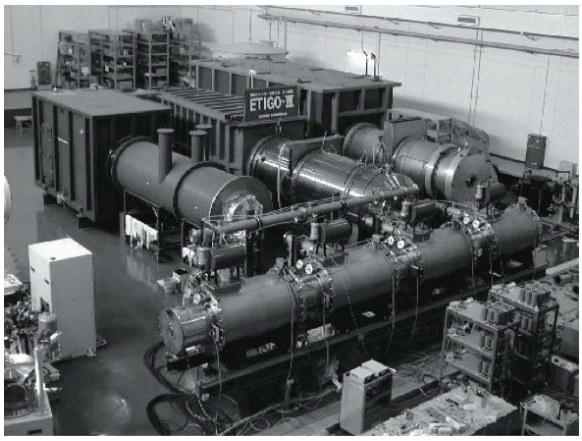

Fig.1 PIREB generator ETIGO-III at Extreme Energy-Density Research Institute, Nagaoka University of Technology

In this study, we propose a new method of treatment, which uses irradiation by PIREB [4]. In this method, chemicals and/or additives are unnecessary for treatment. The purpose of this paper is to investigate the properties of PIREB injection into ballast water and the effects of irradiation by the PIREB on zooplankton

The PIREB with a kinetic energy of up to 2 MeV is generated using a field-emission foilless electron-beam diode, in which a hollow cathode and a ring anode are set at the first acceleration cell of the pulsed power generator ETIGO-III [5] as shown in Fig.1. The diode gap is vacuumed to 0.02 Pa.

Figure 2 shows a side view of the treatment chamber for PIREB irradiation. The chamber was made of a polypropylene pipe with an inner diameter of 110 mm, a length of 86 mm, and a capacity of 0.8 L, where an end flange of the chamber was floated from the ground. The chamber was separated from the vacuum part of the electron-beam diode by an air bulkhead and was filled with a 3-wt% salt solution as ballast water. The salt solution was made from distilled water and common salt. Artemia larvae were added to the salt solution as zooplankton.

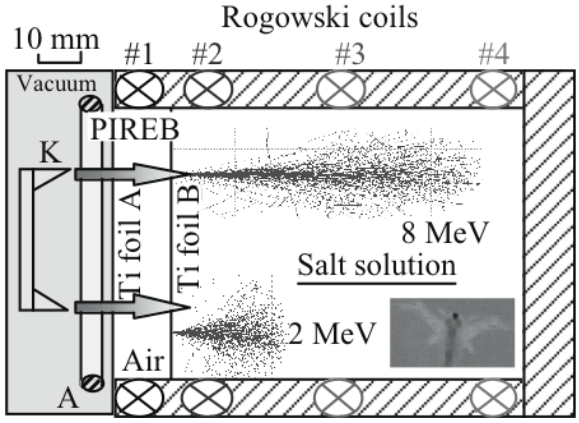

Fig.2 Side view of treatment chamber. Calculated electron trajectories are also indicated

Figure 2 also shows the measurement setup for the PIREB. The irradiated and injected PIREB current in the salt solution was measured with Rogowski coils placed at the inlet (#1), front (#2), middle (#3), and end (#4) of the treatment chamber. Rogowski coil #1 was placed at the front of titanium foil B and the coils #2, #3, and #4 were placed behind titanium foil B at a

distance of 5 mm, 35 mm, and 77 mm, respectively. The zooplanktons, Artemia larvae, were observed using a stereoscopic microscope. We assumed that the Artemia larvae that stop moving in one minute were inactivated because of irradiation.

Electron trajectories in the solution simulated using the CASINO [6] are also shown in Fig.2. The maximum penetration depth of 8 MeV electrons was found to reach 70 mm. Although the depth was reduced to 17 mm for 2 MeV electrons, the electrons spread over 30 mm. This indicates that the 2 MeV PIREB is suitable for treatment over a large area.

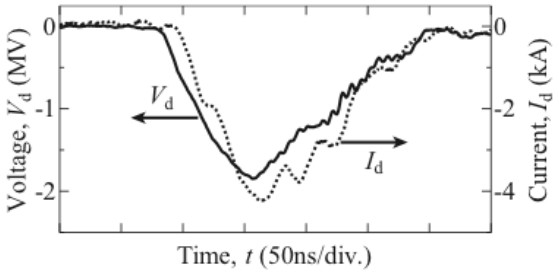

Fig.3 Typical voltage and current waveforms at diode

Figure 3 shows the typical time evolution of the electron-beam diode voltage V_d and current I_d. Results show that the V_d and Id corresponding to the acceleration voltage and the beam current of the PIREB reach -2 MV and -4 kA within 70 ns.

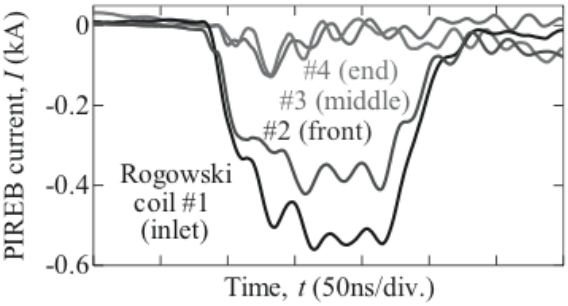

Fig.4 PIREB current in treatment chamber at various positions

Figure 4 shows the typical time evolution of the PIREB current in the treatment chamber at each depth. The results indicate that a PIREB with a current of -0.55 kA was irradiated into the chamber. We also estimated that the current injected by the PIREB into the solution was more than -0.4 kA. Because the PIREB deposits energy within the solution, the current decreased drastically at the middle and end of the chamber.

The inactivation ratio is defined as (Number of inactivated Artemia / Total number of Artemia). 10 and 65 minutes correspond to the minimum time required for irradiation by using one and 10 shots of PIREB irradiation, respectively. Few Artemia larvae were inactivated without PIREB irradiation.

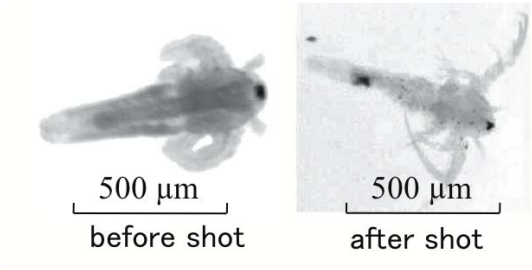

Fig.5 Example of Artemia larvae before irradiation (left) and after irradiation (right)

Figure 5 shows the example of the Artemia larvae before and after PIREB irradiations. The Artemia larvae move their legs actively and swim in the solution before irradiation, whereas the inactivated Artemia turn pale and stop moving after irradiation.

No increase in the inactivation ratio was found with one shot of PIREB irradiation compared to that without PIREB irradiation during 10 min. On the other hand, with 10 shots of PIREB irradiation, the inactivation ratio was in the range of 11-24 %. This indicates that the zooplanktons are successfully treated using PIREB irradiations.

The changes of pH of the solution are considered as one of the reasons for the inactivation mechanism. The Artemia larvae are incubated in salt water with pH of 5.5~5.9. After the irradiation of PIREB, pH of the solution was changed from 5.5~5.9 to 6.8~7.0. For this reason, we investigate the inactivation effect by the pH change to understand the mechanism.

Tables 1 and 2 show the inactivation ratios of the

Artemia larvae without PIREB irradiation in the solution at each time, respectively.

Table 1 Inactivation ratio of Artemia and pH of solution at each state of Artemia during 1 day

pH of solution			Inactivation
Incubation	Throw-in	1 day	Ratio
5.5	7.0	7.1	18 %
5.5	7.0	7.4	17 %
5.5	7.0	7.3	23 %

Table 2 Inactivation ratio of Artemia and pH of solution at each state of Artemia during 10 minutes

pH of solution			Inactivation
Incubation	Throw-in	10 min	Ratio
5.6	6.9	7.0	0 %
5.6	6.9	7.0	0 %
5.6	6.9	7.0	0 %

After the incubation, the Artemia larvae were thrown into the salt water of adjusted pH. We left the Artemia larvae unattended during 1 day or 10 minutes. Although, the Artemia larvae were inactivated after 1 day as shown in Table 1, the Artemia larvae did not be inactivated during 10 minutes as shown in Table 2. For this reason, pH changes did not affect to inactivate the Artemia larvae during the time scale of PIREB irradiation.

3. Reaction of Congo Red in Water after Irradiation by Pulsed Intense Relativistic Electron Beam

We demonstrated the degradation of congo red, a well-known toxic azo dye, by the PIREB treatment. Azo dyes are widely used in various products and leak out with industrial wastewater into the environment. Therefore, the development of a treatment technique for the removal or decomposition of azo dyes is very important.

Figure 6 shows the experimental setup. The electrons emitted from the cathode are accelerated by the applied voltage in the diode gap. The ring anode generates an electron beam with a hollow shape. Because the applied voltage is 2 MV in the diode gap in a vacuum (0.02 Pa), PIREB can be extracted to the outside of the diode. PIREB travels through air space after passing through a Ti foil and irradiates 45 mL of a congo red aquation (0.10 mM) in a reactor containing Ti foil. The reactor was spatially isolated from the diode. To generate PIREB, we used the first acceleration cell of the pulsed power generator ETIGO-III, which is an electron induction accelerator.

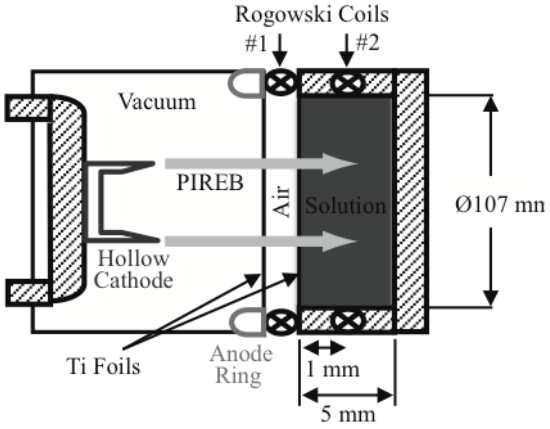

Fig.6 Experimental setup of PIREB irradiation of a reactor containing a congo red solution

Figures 7 and 8 show the typical voltage and beam current waveforms at the electron-beam diode and Rogowski coils, respectively. As shown in Fig.7, the voltage and current corresponding to the extraction voltage and the beam current of PIREB reached -2 MV and -4 kA at the diode, respectively. As shown in Fig.8, PIREB with a peak current of -0.36 kA entered the solution in the reactor.

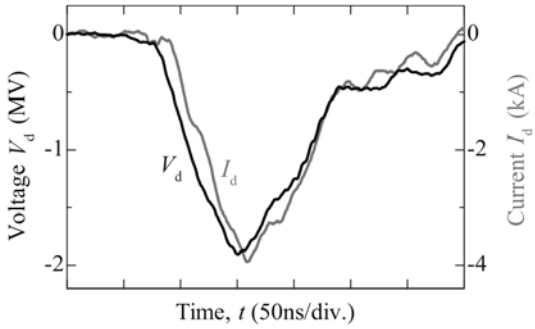

Fig.7 Typical waveforms of voltage and current at the diode

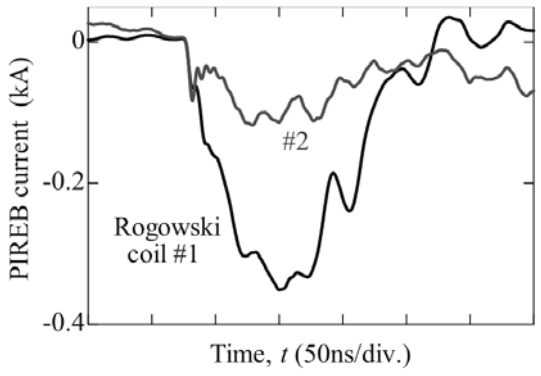

Fig.8 Typical waveforms of PIREB current detected at each Rogowski coil as shown in Fig.6

After PIREB irradiation, the congo red solution changed color from red to dark red. The color of a congo red aquation is well known to deepen with decreasing pH. Therefore, the color change is believed to result from change in pH.

After irradiation, the solution was analyzed by electrospray ionization-mass spectrometry (ESI/MS) and liquid chromatography/mass spectrometry (LC/MS) in order to identify the reaction products and to quantify the amount of congo red, respectively. An LC/MS 2010A mass spectrometer (Shimadzu, Kyoto, Japan) was used for the ESI/MS measurement (negative ion mode). The ESI/MS conditions were as follows: scan range, *m/z* 100-800; heat block temperature, 200℃; interface voltage, 4.5 kV; CDL voltage, 20 V. The solutions (10 μL) were injected into the LC/MS system; the flow rate of the mobile phase (acetonitrile) was 0.20 mL/min. In addition, the LC/MS 2010A instrument was used to quantify the amount of congo red. Amide-80 (Tosoh, Tokyo, Japan: 2.0 x 150 mm i.d.) was used for LC separation. High-performance LC separation was performed at 40℃ using a gradient composed of solution A (6.5 mM ammonium acetate solution adjusted to pH 5.5) and solvent B (acetonitrile). The gradient conditions were as follows: 0-5 min, 100 % solvent B; 5-12 min, a linear decrease from 100 to 25 % B; 12-15 min, hold at 25 % B. The flow rate was 0.20 mL/min. The ESI conditions were the same as those described above. The reaction solutions were diluted 100 times and injected into the LC/MS system. LC/MS acquisition was performed in the selected ion monitoring mode at *m/z* 325.

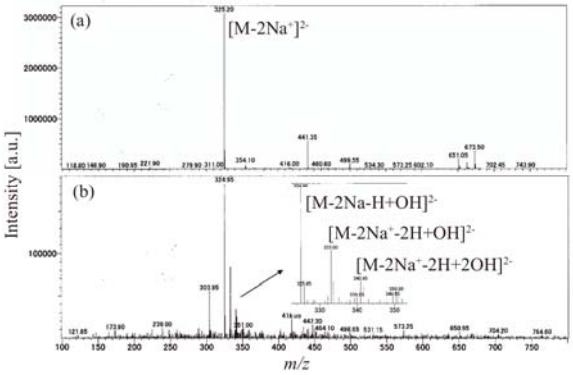

Fig.9 Mass spectrum of congo red solution before (a) and after (b) PIREB irradiation (five shots)

Figure 9 shows the ESI mass spectra of the solutions before and after PIREB irradiation (five shots). The ion peaks assignable to the hydroxylated compounds of congo red (the divalent ion of the monosubstituted compound, *m/z* 333; the divalent ion of the disubstituted compound, *m/z* 340) were observed by ESI/MS. The ion peaks corresponding to the products were not observed by ESI/MS in the positive ion mode. The hydroxylated compounds of congo red have reportedly been formed by gamma-ray irradiation [7]. Radiation-induced oxidative or reductive species such as OH radicals or aqueous electrons degraded congo red in the aqueous solution.

It is also well known that hydroxyl radicals are formed by the radiolysis of water [8]. Therefore, a similar reaction is believed to have occurred in the PIREB reaction. In addition, the absorption spectra of the congo red solution were measured before and after PIREB irradiation after adjusting the pH value to 6. The adjustment of pH was required because the color of the congo red solution changes with pH.

The peak at 500 nm was decreased by PIREB irradiation as shown in Fig.10. This result indicates that the π-electron conjugated system of congo red was broken by the attack of the reaction species formed by PIREB irradiation on the azo group of

congo red.

That is, it is possible that the products, which consist of the broken azo group and cannot be detected by ESI/MS, resulted from PIREB irradiation. The LC/MS results indicated congo red conversion rates of 45 % after one shot of PIREB irradiation and 77 % after five shots.

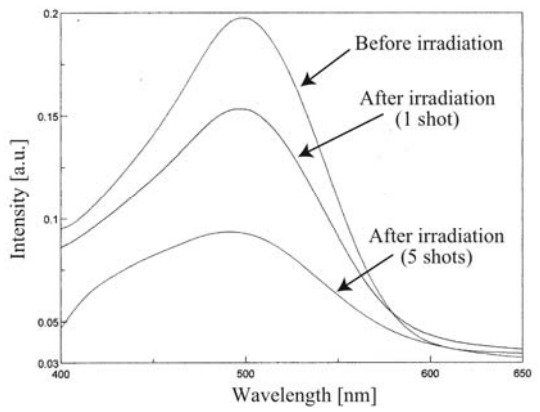

Fig.10 Changes in the UV spectra of congo red aquation after PIREB irradiation

4. Conclusions

In conclusion, we have demonstrated that the inactivation ratio of zooplankton can reach 24 % by firing 10 shots of PIREB irradiation. Increasing the inactivation ratio and elucidating the mechanism of the inactivation are the subjects of our future study. It is found that pH changes did not affect to inactivate the Artemia larvae during the time scale of PIREB irradiation.

A combined electron beam and biological treatment was previously used to purify dyeing wastewater [9]. In this report, we found that congo red was reacted by PIREB irradiation. PIREB irradiation is expected to be applied to the decomposition of azo dyes other than congo red and other environmental pollutants in water. However, there is no evidence that PIREB irradiation decreased the toxicity of the congo red solution. It is necessary to explore any change in the toxicity of the solution after PIREB irradiation in order to apply the technique to the decomposition of pollutants in water. In addition, downsizing of the PIREB irradiation equipment and reducing the initial cost of the equipment are important problems for the widespread application of PIREB as an environmental technology.

References

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