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STUDIES ON THE ELECTROLYTIC TREATMENT OF MARINE SEDIMENT

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CARBONACEOUS BIOCHEMICAL OXYGEN DEMAND AND NITRIFICATION OXYGEN DEMAND OF THE EFFLUENTS OF *Penaeus monodon* CULTURE PONDS

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Studies on the electrolytic treatment of marine sediment

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Abstract

Study on the electrolytic treatment of marine sediment was conducted in Tsukuba University, Japan. It is found that the electrolytic treatment of marine sediment suspensions based on oxidant formation at the electrodes was able to reduce both organic carbon and Vibrio. As with results for electro-oxidation in water, *Vibrio* destruction was much faster than organic matter reduction. The rate of reduction for organic carbon in sediment was much slower compared to that in water. Oxidant formation (measured as total residual oxidant or TRO) rate was much faster than the sediment organic carbon oxidation rate, and there is a tendency for excess TRO accumulation especially if there is little or no organic matter present in the water. From the results of *Vibrio*, two rates of *Vibrio* destruction were observed. The initial destruction rate was very high but lasted only for a short time (about 10 minutes) followed by a slower destruction rate. The faster rate of *Vibrio* destruction may be attributed to the death of the microorganisms in sediment regions, which are easily accessible, by TRO. The second phase of slower destruction may be attributed to death of *Vibrio* in less TRO-accessible regions in the sediment.

Introduction

Recently, shrimp culture in many countries including Thailand has been confronted with environmental problems and disease outbreaks. High residual organic carbon in pond bottom sediments is a serious environmental problem because it contains uneaten feed, shrimp feces, exoskeleton and dead plankton. Also, in shrimp ponds where the cultivations have been aborted due to disease like vibriosis, residual amount of pathogens like *Vibrio* may also remain in the sediment. Therefore, the "cleaning" of such sediments may be necessary in order to ensure that the next cultivation will not encounter problems associated with dirty (high organic matter content) pond bottoms and potential pathogens. Electrolytic treatment by electro-oxidation has been considered an alternative strategy for removing both organic matter and pathogens such as *Vibrio* in sediment. The process is based on the electrolytic formation of oxidants from chloride and bromide ions in the water, which acts as oxidizing and disinfecting agents for organic matter and pathogens, respectively. The process can also have some potential for rehabilitation of sediments from abandoned (due to disease) shrimp ponds. The purpose of this study is to conduct a preliminary study to evaluate the removal of organic matter and *Vibrio* from marine sediment. Although the marine sediment used did not come from an actual shrimp farm, the results obtain from this model system may be used as a basis for future study in actual shrimp pond sediment.

Materials and methods

Preparation of marine sediment suspensions

Two types of marine sediments collected from the Tokyo Bay area were used in the experiment: (1) pelletized sediments which were relatively dry and hard, and (2) fresh wet sediments which were relatively wet, soft and clayish. These sediments used for electrolysis but for investigating *Vibrio* counts during electrolysis, only fresh wet sediment was used.

Sediment suspensions with a concentration of about 20% (w/v) were used for electrolysis. Artificial seawater (Marine Art Company, Japan) solution (30 g/L) with a salinity of about 30 ppt was used to make the sediment suspensions.

Electrolysis reaction system and experiments

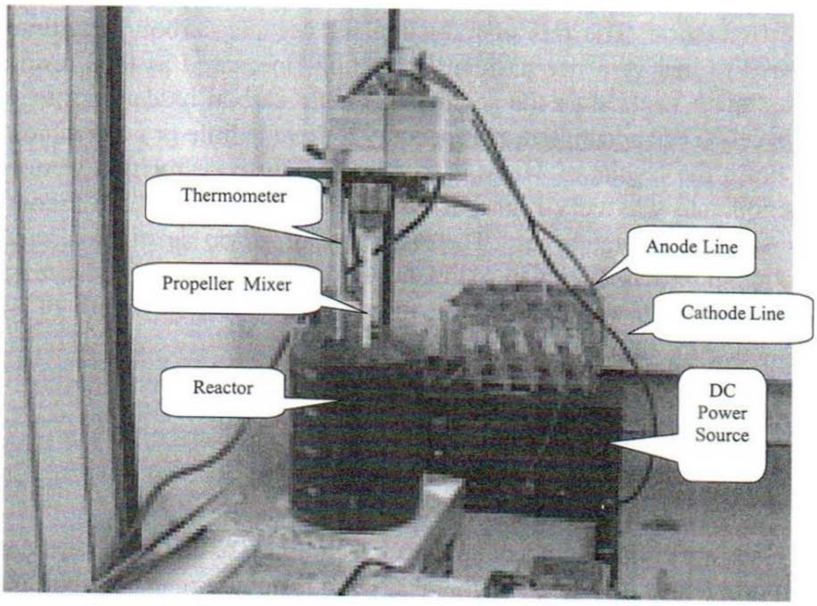

Figure 1 shows a schematic diagram of the experimental set-up.

A beaker with a 2-L working volume was used in the experiments. Mixing at an agitation speed of 500 rpm was provided by a propeller mixer situated at the bottom of the reactor. A DC (direct current) power source with a voltage of 5 volts was used. For electrodes, a sintered platinum metal (5 cm x 8.5 cm) was used as anode and titanium alloy metal (5 cm x 10 cm) was used as the cathode. Electrode spacing was 2.5 cm. The main electrode reaction at the anode is considered to be the conversion of the chloride ions to chlorine, which then reacts with water to form hypochlorous acid and related oxidants. The bromide ion is also considered to interact in the oxidant formation. The main cathode reaction is considered to be hydrogen gas and hydroxide ion formation.

Electrolysis experiments to investigate the removal of sediment organic carbon were conducted on (1) pelletized sediment, and (2) fresh wet sediment. For the evaluation of *Vibrio* removal, electrolysis was done on fresh wet sediment. Time courses were made for the following parameters: sediment organic carbon, total residual oxidant (TRO) concentration in the water, pH, and temperature. A time course for Vibrio count only was made for the run using fresh wet sediment.

Analytical methods

Sediment organic carbon was measured according to the procedure described by Boyd (1995). TRO concentration was determined spectrophotometrically (Sugita et al, 1992). Temperature and pH were measured by a thermometer and pH meter, respectively. The electrical current was measured by an ampere meter.

The total *Vibrio* count was done by the pour plate method on TCBS (Thiosulfate Citrate Bile-salt Sucrose) agar.

Results

Characteristics of pelletized and fresh wet sediment

Since actual marine sediments from a shrimp farm were not available, marine sediments from areas near Tokyo Bay were obtained for use as a model system. As mentioned previously, two types were obtained: pelletized/partially dry and fresh/wet. Table 1 shows the moisture and organic carbon contents of these sediments in comparison with data from shrimp pond sediments from Thailand (Boyd et al, 1994).

Table 1 Some characteristics of obtained marine sediments in comparison with shrimp pond sediments from Thailand

Sediment type	*Moisture (%)*	*Organic Carbon (%) (mean value)*	*pH (mean value)*
Pelletized/semi-dry	17	0.8	8.4[b]
Fresh/wet	47	7.5	7.7[b]
Shrimp pond sediment from Thailand (Boyd et al, 1994)	-	0.65 to 1.10[a]	7.5[c]

[a] based on the conversion, %organic carbon = 0.58 x %organic matter
[b] 20% suspension
[c] 1:1 mixture

In terms of organic carbon content, the pelletized sediment content was in the range of actual shrimp pond bottom from Thailand, but had a higher pH. The fresh wet sediment had a much higher organic carbon content of 7.5%. In addition, the color of the supernatant (on standing) was yellow after electrolysis. It was learned that the sampling site was near a pulp and paper mill factory where the effluent is orange to brown in color due to lignins.

Experiments with pelletized sediment

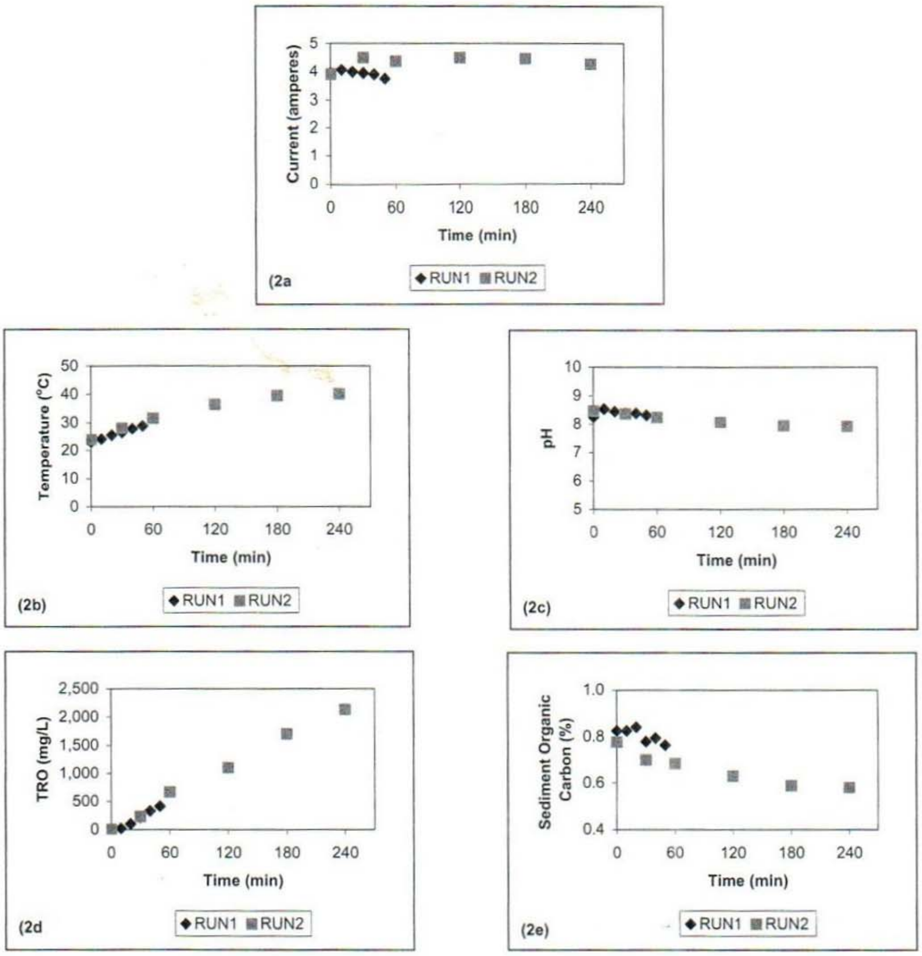

Fig. 2 Time courses for current, temperature, pH, TRO and sediment organic carbon during electrolysis of pelletized sediment

Figure 2 shows the time courses for current, temperature, pH, TRO, and organic carbon content during the electrolysis of pelletized sediment (runs 1 and 2). In run 2, the electrolysis time was extended to 4 hours when the results in run 1 showed no significant changes in sediment organic carbon after about 1 hour of electrolysis. The mean current for both runs was about 4 amperes. The average temperature rise at this current was about 0.12 $^{\circ}$C/min for the first 100 minutes after which it gradually stabilized. Although the pH had a tendency to decrease very slightly as electrolysis progresses, overall, the pH change can be considered negligible with an average value of about 8. The decrease in sediment organic carbon content was slow with an average removal rate of 0.003% per minute. Even if the decrease in organic carbon was slow, both runs showed that the TRO increased after 10 minutes of electrolysis. The 10 minutes lag time when TRO was not detected was an indication that the TRO was consumed during the oxidation of organic matter in the water. The TRO concentration shot up to a very high value of about 2,000 mg/L after 4 hours of electrolysis. The results of the sediment organic carbon and TRO profiles indicated that the rate of organic matter reduction in pelletized sediment was much slower than the rate of TRO production.

Experiments with fresh wet sediment

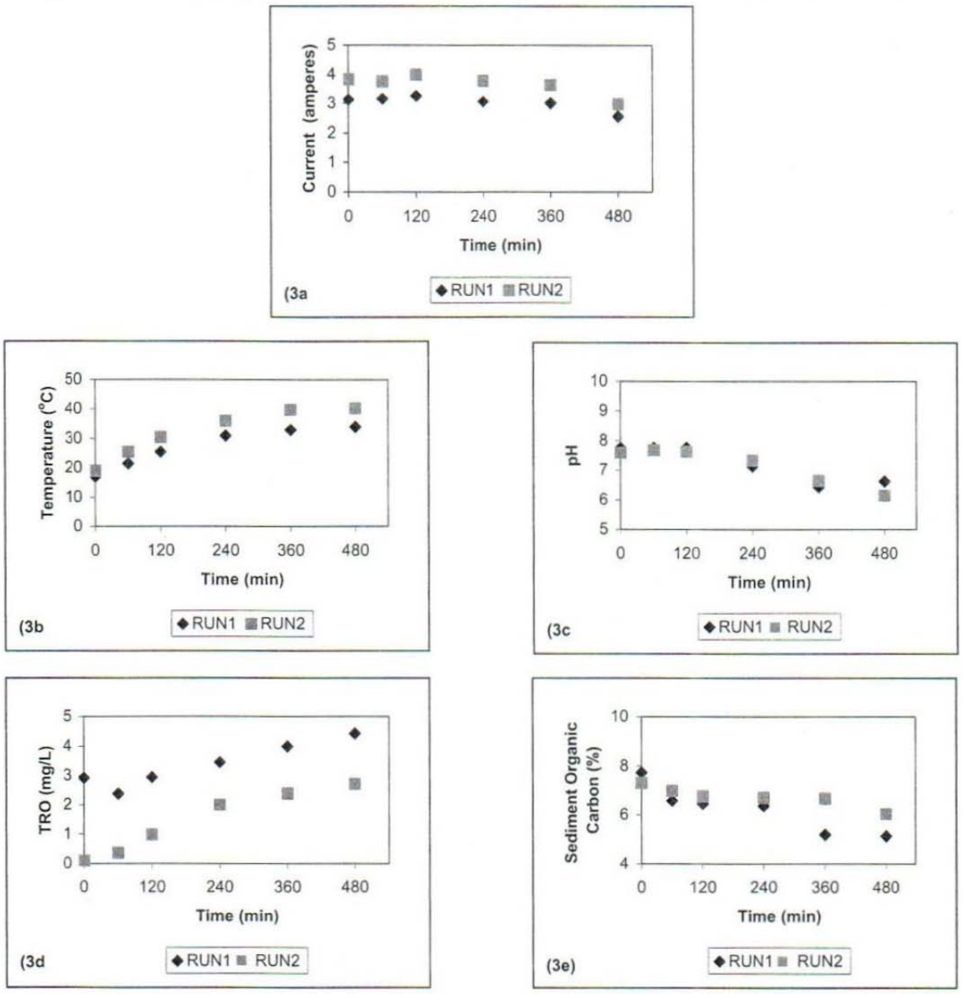

Fig. 3 Time courses for current, temperature, pH, TRO and sediment organic carbon during electrolysis of fresh wet sediment

Figure 3 shows the time courses for current, temperature, pH, TRO, and organic carbon content during the electrolysis of fresh wet sediments (runs 1 and 2). In both runs, the electrolysis time was run up to 8 hours. The average current was initially about 3.5 amperes during the first 3 hours, and but then gradually decreased to about 3 amperes thereafter. The pH was initially constant at about 8 during the first 3 hours, but then gradually declined toward the acidic range of pH 6 thereafter. This is a very different trend compared to pelletized sediment and this may be related to the difference in the type of chemical constituents present in the sediments. Compared to results from pelletized sediment, very small concentrations of TRO were detected in the water, indicating a good reaction of the TRO with large amounts of organic matter in both water and sediment. However, the rate of organic carbon removal in the sediment was also slow, indicating that most of the organic matter reacting with the TRO might be in the water. The average rate of organic carbon in the fresh wet sediment was about 0.046% per minute. The result of the sediment organic carbon and TRO profiles indicated that the rate of organic matter reduction in fresh wet sediment was as much as the rate of TRO production, however, much of TRO seemed to be consumed by organic matter oxidation in the water.

Vibrio profile during electrolysis of fresh wet sediment

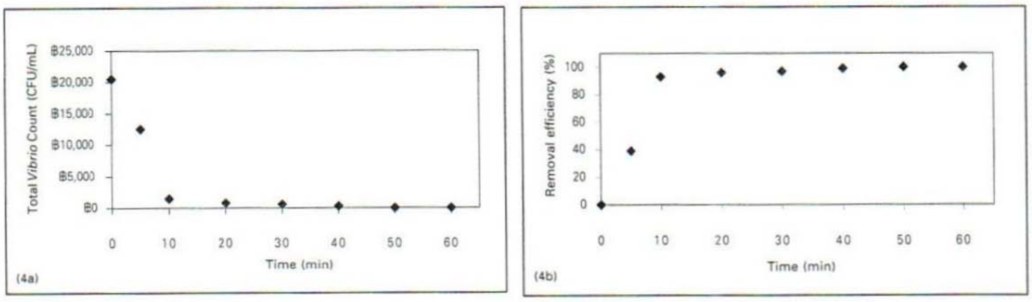

Fig. 4 Time course for Total Vibrio Count and removal efficiency during electrolysis of fresh wet sediment

Figure 4 shows the time course for Total Vibrio Count during the electrolysis of fresh wet sediment that the electrolysis time was run up to 60 minutes. Total *Vibrio* Count in suspension was about 20,500 CFU/mL at initial time and decreased very rapidly during the first 10 minutes but then gradually decreased after that until 50 minutes. It means that large population of *Vibrio* was killed during the first 10 minutes and at 10 minutes Total *Vibrio* Count in suspension was quite low (1,500 CFU/mL), but still remained and gradually decreased until 50 minutes. At 50 minutes, Total *Vibrio* Count in suspension was zero and remained undetected thereafter.

Discussion

Electrolytic treatment of marine sediment suspensions based on oxidant formation at the electrodes was able to reduce both organic carbon and *Vibrio*. As with results for electro-oxidation in water, *Vibrio* destruction was much faster than organic matter reduction. However, the rate of reduction for organic carbon in sediment was much slower compared to that in water.

Oxidant formation (measured as TRO) rate was much faster than the sediment organic carbon oxidation rate, and there is a tendency for excess TRO accumulation especially if there is little or no organic matter present in the water.

Other effects of electro-oxidation of marine sediment include a slight increase temperature. The rate of temperature increase was only about 0.1 $^{\circ}$C/min at the average operating current of 3 amperes in this experiment. The pH was also within acceptable limits, and its change may be related to the nature of chemical constituents present in the sediment. In this experiment, pH of fresh wet sediment tended to go to the acidic range while that of pelletized sediment pH was maintained in the slightly alkaline range.

From the *Vibrio* profiles in Fig 4, two rates of *Vibrio* destruction were observed. The initial destruction rate was very high but lasted only for a short time (about 10 minutes) followed by a slower destruction rate. Normally, it is more difficult to disinfect microorganisms containing particulate solids because there are some areas in the sediment matrix that are difficult to be penetrated by the disinfection agent and therefore provides protection to the microorganism. This may have also occurred for the case of electrolytic disinfection of sediments. The faster rate of *Vibrio* destruction may be attributed to the death of the microorganisms in sediment regions, which are easily accessible, by TRO. The second phase of slower destruction may be attributed to death of *Vibrio* in less TRO-accessible regions in the sediment.

Conclusion

From these experiments, we can conclude that electrolysis via electro-oxidation process can remove organic carbon and decrease the number of Vibrio in sediments at the same time. A more detailed investigation on the optimization of electrolysis using actual marine sediment from shrimp farm is necessary if the process will be applied to actual shrimp cultivation.

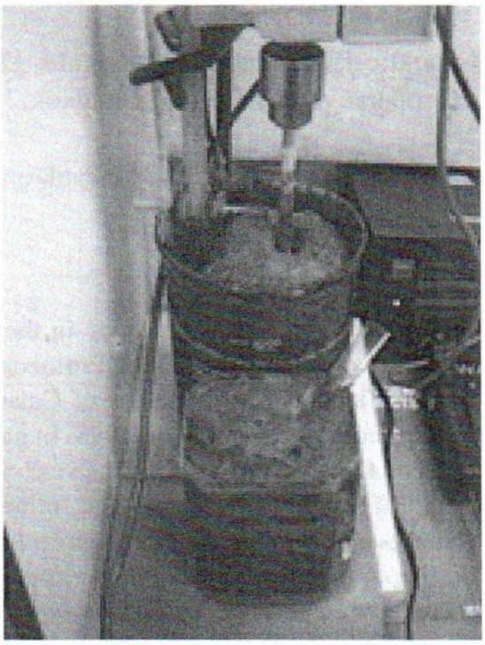

Fig. 5 Fine bubble formed at the surface in during electrolysis 10

During experiments, the formation of a lot of fine bubbles at the surface of water is a great problem (Figure 5). It is recommended that if the electrolytic treatment will be applied in shrimp farms, a skimmer should be used to remove the scum.

References

Boyd, C. E., P. Munsiri, and B. F. Hajek. 1994. Composition of sediment from intensive shrimp ponds in Thailand. World Aquaculture 25(3):53-55.

Boyd, C. E. 1995. Bottom Soils, Sediment, and Pond Aquaculture. Chapman and Hall, New York.

Matsumura, M., N. Whangchai, V. P. Migo, H. K. Young, C. G. Alfafara, and N. Nomura. 2001. Effects of algae die-off on shrimp cultivation in ponds using ozonation. Proceedings of the JSPS-NRCT International Symposium on Sustainable Shrimp Aquaculture and Health Management Diseases and Environment. Tokyo University of Fisheries, Japan.

Sugita, H., K. Hayashi, T. Asai, T. Mitsua, K. Amanuma, C. Maruyama, and Y. Degucha. 1992. Spectrophotometric Method for Determination of Total Residual Oxidants in Seawater. Suisanzoshoku. pp. 45-49 (in Japanese with English abstract).