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Porosity-dependent absorption capacity of red tide algae by ceramic absorbers

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***Cochlodinium* red tides occur over a wide area in South Korea, from the south coast to the east coast, and last from August until October. The damage to fisheries caused by these red tides amounts to tens of billions per year. Chemical spray, sedimentation, and red clay spray methods can prevent red tides, but the most practical method, the red clay spray method, also has a negative effect on marine ecosystems. Therefore, to protect marine life from a *Cochlodinium* red tide without affecting the marine ecosystem, six ceramic absorbers were applied to a pontoon system, a type of cage fish farm, to compare their absorbing capacity for red tide algae that is dependent on the porosity of the ceramic absorber. This experiment was performed to determine which ceramic absorber can effectively prevent red tide penetration. Previous studies have shown that most fish die when exposed to 8.0×10^3 cells/mL of *Cochlodinium polykrikoides* for 8 hrs. From the results of this experiment, the concentration of red tide algae that passed through ceramic absorber D (average porosity 60.3%), was 0.14×10^3 cells/mL. For ceramic absorber L (average porosity of 57.3%) it was 0.18×10^3 cells/mL. These two values were the highest red tide absorption rates recorded in this study. Even when the average porosity was as low as 34.6%, such as in ceramic absorber K that had a small particle size, a high absorption efficiency of 0.18×10^3 cells/mL was observed.**

Key words: Ceramic absorber, *Chattonella* red tide algae, Porosity.

Introduction

The coastal area near the South Sea of Korea boasts of beautiful natural scenery and excellent water quality. Because of that, the rias coast (estuary) is well developed for leisure and has been designated as a national maritime park for a long time. In addition, because of the proper inland water inflow, the nutrient salt supply, and the mild climate, fish production is very active in some of the enclosed bays. However, the Yeochun Petrochemical Complex, which started its operation in 1969, and the completion of the Gwangyang Steel Works in 1987 caused many changes to the nearby Gohheung coast and to the marine environments of Yeojaman Bay and Deukryang Bay. Also affected were the marine environments of Yeosu Bay, Gamak Bay, and Namhae Yeonagyeok, including Gwangyang Bay [1].

In the 1970s, about 10 cases of red tide occurred intermittently each year in some enclosed bays. In the 1980s, the occurrence of red tides began to increase rapidly, with more than 30 cases recorded annually. Since 1990, the number and duration of red tide seas have increased. The organisms that cause red tides vary from diatoms to monocotyledons. The financial loss from damage to fisheries was less than 2 billion Won in the 1980s but increased to several billion Won annually in the 1990s [2]. In particular, the economic loss from the *Cochlodinium* red tide that started on August 29 and continued until to October 21, 1995, was high. This event occurred in a wide area, from the south coast to the east coast, and the total economic loss by fisheries amounted to 76.4 billion Won. Chemical spray, ultrasound waves, ozone treatment, sea surface recovery, red clay (loess) spray, and sedimentation, as well as other methods, are the current countermeasures against red tides, but none of them has been used on an industrial scale. Only the clay spray method is somewhat practical in that secondary pollution is less likely to occur [3]. However, the effects of the clay spray method on red tides have not been proven yet at elevated temperature. Since red tides are concentrated in the summer when the water temperature is high, the impact of this method on the marine ecosystem is worrisome. Therefore, the effects of red clay spray have been investigated with various methods. Studies have been performed on water quality; on shellfish such as oysters, mussels, and scallops. They have also been performed on the marine sedimentation environment; and on benthic animals living among rocks and sand, and at the bottom of the river and the sea. These include coral, sea urchin, and shrimp. When red clay is sprayed on red tide organisms in water, some of the organisms are decomposed in the water and some are transferred to the sediment layer by the red clay particles and then decomposed. Organic matter decomposition occurs actively, and approximately 20 to 60% of the organic matter produced in a water

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system is decomposed in the surface layer of sediment. Through this process, chemical elements or molecules of seawater with physical and chemical properties similar to those of the ocean move through the biosphere, the hydrosphere, and the geosphere. The sedimentary layers are also likely to become anaerobic. Thus, approximately 50% of the organic matter deposited on the surface will be decomposed by anaerobic bacteria, which can be sulfate reducing bacteria. These can result in hydrogen sulfide as a final product, which is harmful to the marine environment [4].

Therefore, in this study the absorption effect of ceramic absorbers on red tide algae was studied. Six types of ceramic absorbers considered to have little influence on the marine ecosystem, were applied to a pontoon system, a type of cage fish farm. This was done to determine the most appropriate ceramic absorber that can effectively prevent red tide penetration.

Experimental Method

Preparation of raw materials

An experiment was carried out to compare the absorption of red tide algae by six ceramic absorbers with different porosities. The raw material composition and the porosity of the ceramic absorbers used in this experiment are listed in Table 1. The morphologies of the absorbers are shown in Fig. 1.

The red tide algae used in this study were *Chattonella* sp., similar to the *Cochlodinium polykrikoides* red tide algae that most frequently occur along the southern coast. *Chattonella* red tide algae belonging to the class Raphidophyceae, are spherical or spindle- shaped, and reach sizes of 50-130 μm. They mainly appear along the southern coast of Korea (Jinhae Bay) in the summer and their cellular images are shown in Fig. 2. Two different algae; *Chattonella marina* (Figs. 2(a) and Fig. 2(b)) and *Chattonella* sp. (Figs. 2(c) and Fig. 2(d)) are shown in the figures in a culture. Fig. 2(a) and Fig. 2(c) illustrate the morphology of algae without an algaecidal substance, which remain harmful to fish. Fig. 2(b) and Fig. 2(d) illustrate the morphology of algae with an algeacidal substance, which can no longer harm fish because they have been destroyed by the algaecide. The reason for the selection of *Chattonella* red tide algae is that it has not been possible to culture *Cochlodinium polykrikoides* red tide algae artificially in a laboratory yet. Therefore, the algae that were closest in appearance and size were selected and tested.

Table 1. Composition and porosity of the tested ceramic absorbers.

Symbol	Raw material composition	Porosity
D	Clay + EAF (electric arc furnace) dust	60.3%
L	Shale	57.3%
C	Clay + fly ash	37.9%
Y	Dredged soil + fly ash	34.9%
K	Clay + stone dust + spent white clay	34.6%
G	Volcanic stone	30.6%

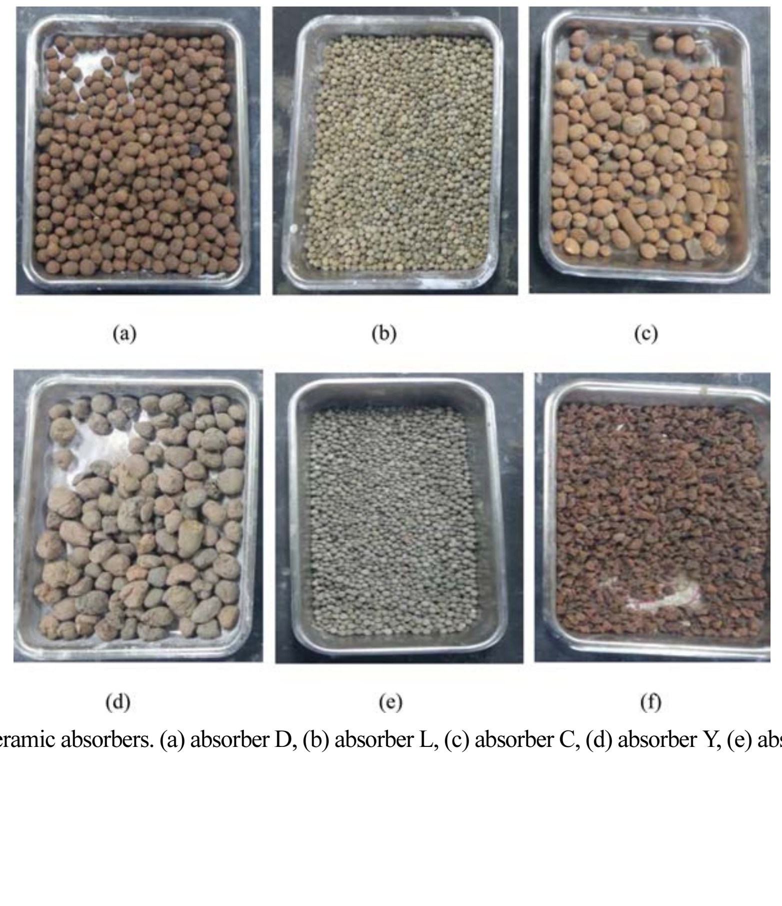

Fig. 1. Morphology of the ceramic absorbers. (a) absorber D, (b) absorber L, (c) absorber C, (d) absorber Y, (e) absorber K, and (f) absorber G.

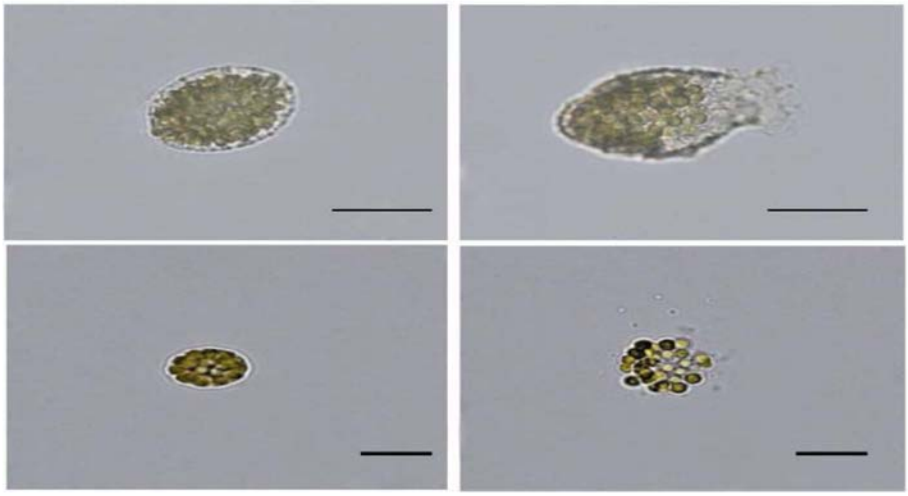

Fig. 2. *Chattonella marina* (above) and *Chattonella* sp. (below) in culture. (left) no algaecide present, and (right) in the presence of algaecide. Scale bar: 50 μm [5].

Experimental method

After washing and drying each ceramic absorber, 1000 mL of a solution containing *Chattonella* red tide algae was deposited in a 1000 mL beaker and 100 g of the ceramic absorber were added. The solution was stirred once every 30 min to prevent the algae from precipitating. Samples were collected periodically to record the reduction in red tide algae concentration using an optical microscope. The correlation between the structure of the ceramic absorber and the absorption efficiency was studied by examining porosity and by SEM analyses.

Results and Discussion

This study was carried out to compare the absorption capacity of six types of ceramic absorbers on red tide algae. The main variable parameter across the absorbers was porosity. First, the porosity of each ceramic absorber was checked to identify the correlation between the absorption efficiency of the ceramic absorber on the red tide algae. Fig. 3(b) shows that ceramic absorber L had mostly pores of about 80 μm and 110 μm. Fig. 3(c) indicates that, unlike the other ceramic absorbers, ceramic absorber C had micropores of about 0.5 μm in size and pores of about 110 μm, similar to the other ceramic absorbers. Ceramic absorber K in Fig. 3(e) had mostly pores with sizes 1-10 μm and 110 μm . Ceramic absorbers D, Y, and G showed similar pore distributions, with the majority of their pores being 110 μm as illustrated in Figs. 3(a), 3(d), and 3(f), respectively. Fig. 4 shows the average porosity of each ceramic absorber used in this experiment and listed in Table 1. Ceramic absorber D exhibited the highest average porosity of 60.2577%, followed by ceramic absorber L with average porosity of 57.2756%. Ceramic absorbers C, Y, K, and G exhibited lower porosities of 37.9395%, 34.8772%, 34.6245%, and 30.5762%, respectively.

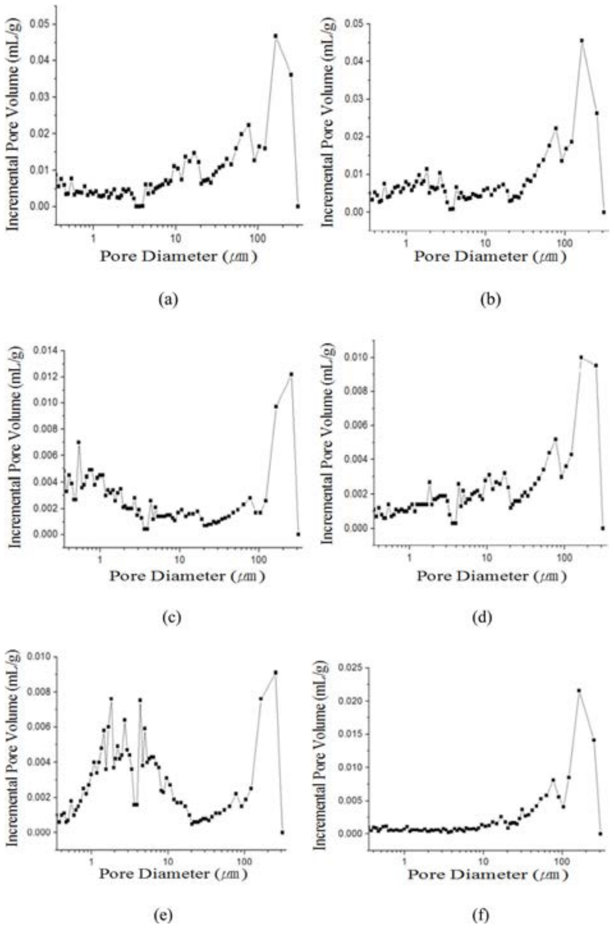

Fig. 3. Pore size distribution of the ceramic absorbers. (a) absorber D, (b) absorber L, (c) absorber C, (d) absorber Y, (e) absorber K and (f) absorber G.

Fig. 5 shows the cell concentration of red tide algae in the solutions over time. Overall, it was found that the initial concentration of red tide algae reduced when any ceramic absorber was in contact with the *Chattonella* red tide algae. The reduction was continuous over time. The

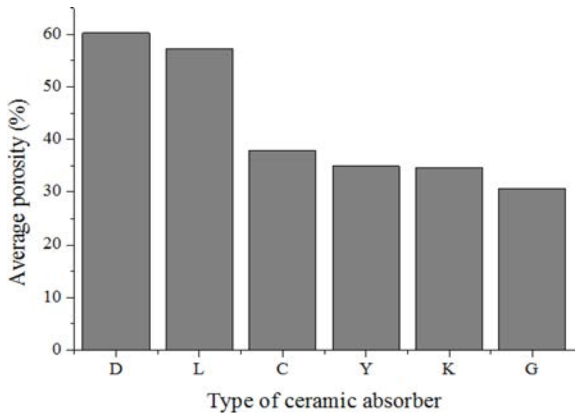

Fig. 4. Average porosity of the six ceramic absorbers.

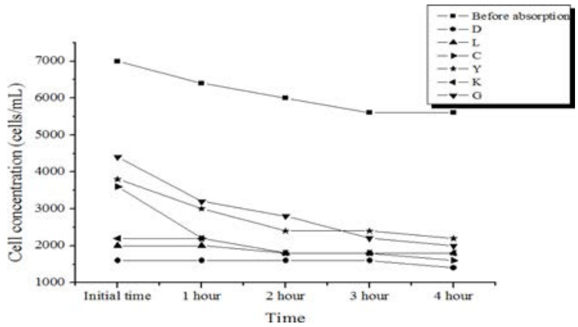

Fig. 5. Cell concentration of red tide algae over time.

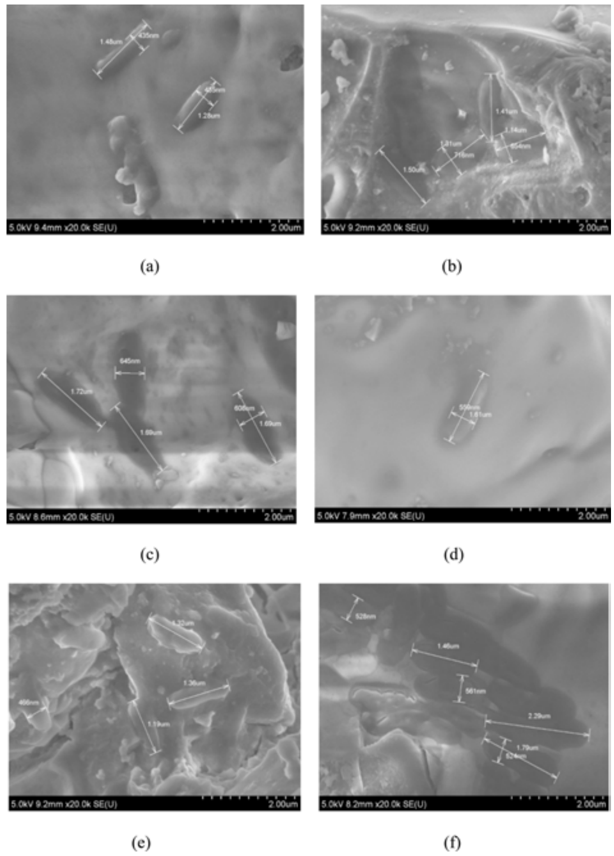

Fig. 6. SEM micrographs of the *Chattonella* cells on ceramic absorbers (a) absorber D, (b) absorber L, (c) absorber C, (d) absorber Y, (e) absorber K, and (f) absorber G.

initial time was defined as the instant immediately following the placement of 1000 mL of a solution containing *Chattonella* red tide algae in a beaker and the addition of a ceramic absorber. Ceramic absorber D demonstrated the lowest rate of change. Concentration dropped from 1,600 cells/mL to 1,400 cells / mL after 4 hrs. This was attributed to the fact that it had the highest average porosity of 60.3%. When this ceramic absorber was added initially, it settled and the *Chattonella* red tide algae were absorbed on it, thus it became saturated. Likewise, ceramic absorber L had a high average porosity of 57.3% and demonstrated a low rate of change from 2,000 cells/mL to 1,800 cells/mL after 4 hrs. For ceramic absorbers C, Y, and G, even if there was only a slight difference in cell concentration, it always decreased over time. However, ceramic absorber K yielded slightly different results. In Table 1, ceramic absorber K was shown to exhibit a low average porosity of 34.6%, but the rate of change in red tide algae ranged from 2,200 cells/mL to 1,800 cells/mL, a relatively low rate of change comparable to absorbers D and L. The reason is that ceramic absorber K seems to benefit from its grain size. As shown in Fig. 1(b), ceramic absorber K has a smaller grain size than the other ceramic absorbers. Therefore, it is presumed that the relatively low average porosity of 34.6% does not adversely affect algae reduction efficiency.

SEM analysis was performed to identify the absorbed strains (*Chattonella* cells); the results are shown in Fig. 6.

Fig. 6(a-f) illustrates the adherence of the *Chattonella* red tide algae on each ceramic absorber. SEM analysis results demonstrated that the *Chattonella* red tide algae were absorbed onto each ceramic absorber. Usually, *Chattonella* red tide algae vary in size from 50 to 130 μm and the *Chattonella* red tide algae used in this study had an average size of 20 μm. However, they were reduced to about 1-2 μm in the course of drying for SEM analysis. Fig. 6 shows that the rougher the surface of the ceramic absorber, the better the short-term absorption efficiency. As can be seen in Fig. 6, the surface roughness decreased in the order G → L → K and the short-term absorption efficiency decreased proportionally. After 4 h, however, the long-term absorption rate converged to a constant value regardless of the absorbent type.

Conclusions

In this study, six types of ceramic absorbers were applied to a pontoon system, a type of cage fish farm, to compare the absorption capability of ceramic absorbers with different porosities on red tide algae.

This experiment was performed to test if ceramic absorbers can effectively prevent red tide penetration. The experiment was also conducted with various porosities to identify correlations between porosity and pore distribution with absorption rate.

Previous studies have shown that when exposed to 8,000 cells/mL of *Cochlodinium polykrikoides* for 8 hrs, most fish die. Although the mortality rate may vary depending on the fish species; it has been reported that blue fish such as tuna have a much higher mortality rate than white fish, when exposed to this type of red tide [6].

The experimental results show that all six ceramic absorbers have red tide algae absorbing capacity and are applicable to pontoon systems. Among the ones tested, ceramic absorbers D, L, and K had the highest absorption efficiencies and are considered to be the most suitable. In this experiment, measurements were made for 4 hrs. The long-term absorption rate tends to converge to a certain value so the porosity of a ceramic absorber is considered to affect only the short-term absorption rate. Future research will examine whether the ceramic absorber maintains absorption efficiency in the long term.

Acknowledgments

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