Development of a Functional Mortar for Restraining Attached Algae Growth

S. Park¹, J-H. Kim¹, H. Kang¹, S. Y. Choi² and Y. M. Lim¹*

¹ Department of Civil and Environmental Engineering, Yonsei University, Seoul, Korea
² Department of Materials Science and Engineering, Yonsei University, Seoul, Korea

ABSTRACT: One of the problems that are involved in the maintenance of concrete or mortar in aquatic habitat is proliferation of algae on the surface of them. Their growth may decrease durability of structures by bio-deterioration. In this study, we developed a functional mortar for restraining bio-deterioration by using heavy metal ions, especially Cu²⁺. The mortar contains soluble glass made of Cu ions, which can dissolve in water slowly. Mortars prepared with different content of glass (0, 2, 5, 10, 15 %) were placed in culture medium with algae and incubated over a month period. Water chemistry, chlorophyll-a (Chl-a), and a suite of extracellular enzyme activities were monitored. We used two types of water, freshwater and seawater, to assess applicability to both systems. Overall, mortar with Cu glass exhibited lower Chl-a content, suggesting that the material did exhibit anti-algal functions. In contrast, DOC concentration increased, which appear to be originated from debris of dead algae. Cu glass also decreased phosphatase activity, which is involved in the regeneration of inorganic phosphorus (P) from organic moiety. This suggests that algal growth may be inhibited in the long-term, as P is often limited nutrient for algal production. In contrast, little impacts were observed for β-glucosidase and N-acetylglucosaminidase activities, suggesting that carbon and nitrogen mineralization may not be influenced by the beads.

1 INTRODUCTION

Proliferation of algae on the surface of concrete and mortar structure is of concern, because it reduces physical stability as well as aesthetic value. It has been widely acknowledged that photosynthetic organism colonized on the surface of concrete structure accelerates weathering by releasing various organic acids and by other physical mechanism (Ortega-Calvo et al., 1995). As such, various functional concretes and mortars have been suggested. For example, Hiroshi et al. (2001) proposed a painting material containing ferrous sulfate (FeSO₄) to inhibit algal propagation on concrete surfaces. To function properly, concrete or mortar should release anti-algal chemicals slowly and steadily to ensure the long-term effects as well as little impacts on ecosystems. In addition, detailed mechanism for anti-algal function should be understood.

In the present study, we employed a new approach using glass beads containing anti-algal property. We prepared mortar specimen containing glass beads with copper compound, which was designed to be released and function as an inhibitory chemical against algae. The specimen was exposed to freshwater or seawater with a large amount of algae, and changes in algal biomass as chlorophyll-a (Chl-a) content and other biological property such as extracellular enzyme activities were monitored.

Extracellular enzymes are mainly produced by algae and microorganisms. Once released from microbes or algae, extracellular enzymes degrade large organic matter into small carbon or
inorganic nutrients. They, in turn, are assimilated by microbes and algae to maintain nutrient cycle and energy flow. It has been reported that such enzymatic process is a rate limiting step in overall material cycles. Particularly, phosphatase has drawn much attention in aquatic ecosystems since it releases inorganic phosphorus from organic moiety, which is often a limiting nutrient for algal growth. As such, lowering of phosphatase is needed to secure the long-term inhibition of algal propagation.

The objectives of this study were to monitor changes in algal biomass in water that are contacted with mortar with different concentration of copper-containing glass beads and to determine changes in extracellular enzyme activities in water.

2 MATERIALS AND METHODS

2.1 Mortar composition

Each mortar specimen measures 50 mm x 50 mm x 50 mm, which was prepared by mixing Portland cement (85g), dried sand (208.33g), and water (41.225g) to cure for 2 days. The glass-beads were composed of 15Cu2O • 15Na2O • 5B2O3 • 65P2O5 of which size ranged between 250-425 µm. This allows rapid dissolution when they are exposed to water. Mortar specimen with five concentrations of glass-beads were prepared; 0, 2, 5, 10, 15%.

2.2 Incubation

Freshwater was collected from Hongje stream in Seoul, while seawater sample was collected from Jebudo in Gyeonggi Province. Water samples were filtered to remove any suspended materials and 1 L of water sample was placed in a 2 L container. Mortar specimen with different glass-bead concentration was placed in each container and incubated for 37 days. The experiment setting was exposed to 12/12-hour day/night cycle at 20 °C to ensure optimal conditions for photosynthesis. Three replicate settings were prepared for each concentration. Water samples were collected at days of 0 (just before the placement of mortar), 5, 10 and 37. Algal biomass and enzyme activities were determined for all concentrations of mortar at day 5, but only control, 2% and 5% settings were determined at all sampling dates.

2.3 Chlorophyll-a

Chl-a concentration was measured by a standard method. In short, 100 mL of water was filtered (GF/C 45 nm) and the filtered paper was ground with 10 mL of acetone solution (9:1). This, then, was maintained at 4 °C in dark condition for 24 hours. Extract was centrifuged and absorbance of supernatant was determined at wavelengths of 663 nm, 645 nm, 750 nm, and 630 nm to calculate the concentration of Chl-a.

2.4 Extracellular enzymes

β-glucosidase, N-acetylglucosaminidase, and phosphatase activities were determined using methylumbelliferyl (MUF) compounds as a model substrate. MUF-β-glucopyranoside (400 µM), MUF-acetylglucosamine (400 µM) and MUF-phosphate (800 µM) solutions were used for substrates for β-glucosidase, N-acetylglucosaminidase, and phosphatase, respectively. Five mL of each substrate solution was added with 1 mL of water sample and incubated for 60 minutes,
after which fluorescence was determined by a fluorometer (FLUOstar OPTIMA; BMG Labtech).

2.5 Compressive strength of Mortar

To determine applicability of mortar with glass beads, compressive strength with the same size of cubic specimens was tested using Instron (UTM). The standard testing method is adopted for these tests and the 28 days compressive strength was measured.

3 RESULTS AND DISCUSSION

3.1 Chlorophyll-a

At the end of 5-day’s incubation, concentrations of Chl-a decreased substantially both in freshwater and seawater placed with glass-bead mortar (Fig. 1). This result indicates that the mortar proposed in this study did exhibit anti-algal functions. In freshwater system, the presence of mortar itself decreased Chl-a substantially (Fig. 1-(A)), suggesting chemicals in mortar itself is highly toxic to freshwater algae. It is speculated that freshwater algae are highly sensitive to pH changes by mortar. In contrast, such decrease was not observed in seawater (Fig. 1-(B)), probably due to higher resistance of seawater algae to higher pH as they are exposed to alkaline pH in natural conditions.

Copper is known to inhibit both seawater and freshwater algae at as low concentration as 1 ppb (Nielsen et al., 1971). Copper can be incorporated into algal cell to influence physiology as well as inhibition of sulfide residues of key enzymes. Additionally, it has been reported that copper can interfere with biosynthesis of pigments and phospholipids, resulting in lower photosynthetic rates (Barón et al., 1995).

![Figure 1. Chlorophyll-a concentrations in freshwater (A) and seawater (B) before incubation (Day 0) and after 5 days of incubation with concretes with different concentrations of glass beads. Mean ± S.E. (n = 3)](image)

3.2 Extracellular enzymes

No distinctive changes were found in β-glucosidase activities by glass-bead containing mortar in freshwater (Fig. 2-(A), while the activities decreased slightly by glass-bead containing mortar.
in seawater (Fig. 2-(B)). However, no differences were discernible in relation to the concentrations of glass-beads. β-glucosidase is involved in organic carbon (i.e., cellulose) decomposition, and this result suggests that impacts on carbon cycling would be minimal by the mortar. Another possibility is that algal biomass would die off and provide ample amount of organic carbon to systems, which may mask-off inhibitory role of glass-beads on β-glucosidase activity.

![Figure 2](image_url)

Figure 2. β-glucosidase activities in freshwater (A) and seawater (B) before incubation (Day 0) and after 5 days of incubation with concretes with different concentrations of glass beads. Mean ± S.E. (n = 3)

Similarly, N-acetylglucosaminidase activities did not change by the presence of glass-beads (Fig. 3). This enzyme is involved in chitin decomposition and hence reflects influences on nitrogen and partially carbon cycles. The results suggest that nitrogen cycle would not be strongly affected by glass-bead in the systems. It is interesting to note that mere presence of mortar decreased dramatically N-acetylglucosaminidase, indicating that certain components in mortar or environmental changes by it could impede nitrogen cycle in the long-term. Further studies are warranted to reveal mechanism for such intense inhibition.

![Figure 3](image_url)

Figure 3. N-acetylglucosaminidase activities in freshwater (A) and seawater (B) before incubation (Day 0) and after 5 days of incubation with concretes with different concentrations of glass beads. Mean ± S.E. (n = 3)

Unlike β-glucosidase or N-acetylglucosamindase activities, mortar with glass-beads did decrease phosphatase activities in both systems (Fig. 4). A stronger inhibition was found in seawater system compared with a freshwater ecosystem. This result is in accordance with Wang.
et al. (1995), who reported inhibition of alkaline phosphatase by copper in marine algae. This result has an implication that glass-bead with copper would not only inhibit directly algal propagation (as expressed in Chl-a content), but also may hinder its proliferation by impeding phosphorus cycle. Since phosphorus is often the most common limiting factor for algal production in aquatic ecosystems, decreases in phosphatase would induce slower P release and lower algal production.

![Graph](image1.png)

**Figure 4.** Phosphatase activities in freshwater (A) and seawater (B) before incubation (Day 0) and after 5 days of incubation with concretes with different concentrations of glass beads. Mean ± S.E. (n = 3)

When data for 37 days’ incubation were all considered, some parameters exhibited different patterns from those at 5 day. For example, substantial decreases in Chl-a at day 5 disappeared in freshwater ecosystem, while such inhibition lasted in seawater system (Table 1). Particularly, 5% mortar in seawater maintained strong inhibitory effects on algal biomass over 37 days. Similarly, lowered phosphatase activities by glass-beads recovered to the level of control in freshwater system (Table 1). In contrast, β-glucosidase and N-acetylglucosaminidase activities decreased in the longer-term compared with those at day 5. A mortar proposed in this study would maintain function properly in seawater system, while long-term consequence may differ in freshwater system.

<table>
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<th>Parameters</th>
<th>Days</th>
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<td></td>
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<td>10</td>
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<td>Chl-a</td>
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<td>79.8 (42.9)</td>
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<td></td>
<td>5%</td>
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</table>

### 3.3 Physical compressive strength of mortar

Compressive strength of mortar specimen ranged between 27.64 to 28.91 MPa, and no significant differences were found among different containment of glass beads. This result indicates that functional mortar proposed in this study has the same physical compressive strength as control mortar without glass beads. So, it can be concluded that the compressive...
strength of the mortar with small portion of glass beads (less than 1.5% of volume fraction) is not affected by the inclusions.

3.4 Conclusions

Overall results of this study suggest that mortar with copper glass-beads would exhibit anti-algal property. Particularly, it would be more effective for seawater than freshwater systems. In addition to direct effects on algal proliferation, copper has a potential as an inhibitory material against phosphatase, which plays a key role in P cycle and algal production. Further study should focus on the longer-term consequence of functional mortar proposed in this study, probably by exposing them under field conditions.

References